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A near-infrared study of thermally induced structural changes in polyethylene crystal

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Abstract

Thermally induced structural changes of polyethylene (PE) have been studied by means of near-infrared (NIR) spectroscopy in the course of heating up to the melting temperature. NIR bands characteristic of the regular orthorhombic phase, the conformationally disordered hexagonal phase, and the amorphous phase have been successfully identified. It has been found that for the unoriented PE sample, the disordering process of orthorhombic lattice starts above room temperature and that it mostly occurs above 100 °C for the uniaxially oriented PE sample. In the latter case, the enhancement of crystallinity has clearly been detected just below T_m due to the reorganization of crystalline lattice. For the geometrically constrained ultradrawn PE sample, the phase transition from orthorhombic to hexagonal phase has been detected immediately below the melting point. The NIR bands characteristic of the hexagonal phase have been confirmed definitely. Usefulness of NIR spectroscopy has been demonstrated successfully in such a study of thermally induced phase transition behavior of PE samples with appreciable thickness, for which mid-IR spectroscopy is difficult to apply because of the intensity saturation of various key bands.

Keywords: Polyethylene; Near-infrared (NIR); Phase transition

1. Introduction

The structural rearrangement process in semicrystalline polymers on annealing has been a subject of essential importance. Its importance arises not only from fundamental polymer science standpoint but also from industrial point of view. Changes in the aggregation state of the crystalline and amorphous phases during heating are closely related to industrially important properties such as mechanical strength, fatigue life, thermal behavior and appearance. Therefore, a number of investigations were carried out on this matter for more than two decades [1–3]. Among the structural changes occurring upon heating, a phase transition within the crystallite of a polymer has been of particular interest.

When polyethylene (PE) is crystallized from the melt state under elevated pressure, it crystallizes into an orthorhombic phase through an intermediate phase with a hexagonal 'rotator' structure [4–6]. This transition process is known to reversibly occur even under atmospheric pressure in constrained highly drawn PE when it is annealed to the temperature close to T_m [7,8]. The phase transition behavior of PE has been studied mainly by means of X-ray diffraction [9–17]. Differential scanning calorimetry (DSC) [17–22], X-ray imaging [9,18,23,24], and transmission electron microscopy (TEM) [10,13,17,22]. Raman scattering [10,16,18,21,23,25–31] and infrared spectroscopy [9,18,31–38] have also been utilized to explore the phase transition of PE. In vibrational spectra, the bands originating from the monomer sequences in crystalline phase, amorphous phase, and intermediate phase are separately observable. This feature is one of the advantages of vibrational spectroscopy. In addition, polarized vibrational spectroscopy studies enable one to explore the orientation of chain segments with different geometric isomers.

In the research of PE, mid-infrared (MIR) is a very useful technique. However, the transmission measurement of mid-

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IR is limited to a thin sample due to high-absorption coefficient. This limitation requires remarkable sample preparation techniques and skills especially when one studies phase transition behavior of PE under physical tension [18]. Although measurements by Raman spectroscopy generally do not require complexity in sample preparation and measurements, its usefulness is sometimes reduced due to its unsatisfactory S/N and background luminescence that overlaps with Raman signals of interest. Near-infrared (NIR) spectroscopy has advantages over MIR and Raman spectroscopy in the above-mentioned experimental difficulties. Although NIR spectroscopy has been utilized for polymer analysis for more than two decades [31], remarkable progress has been made in the last half decade mainly due to the advances in NIR instrumentation and spectral analysis methods such as chemometrics and two-dimensional (2D) correlation spectroscopy [39]. NIR has been utilized to characterize PE so far. For example, the density of PE has been determined by NIR with multivariate data analysis [40–42]. However, thermally induced structural changes occurring in one of the most fundamental polymer, PE has not been fully studied by NIR yet. Especially, identification of the bands that originate from regular all-*trans* sequence present in orthorhombic phases, those from disordered random sequence of the *trans* and *gauche* rotational isomers in amorphous domains and those due to hexagonal phases have not been reported yet in NIR spectroscopy. In this study, we have succeeded for the first time to identify the bands due to the orthorhombic, amorphous and hexagonal phases by measuring the NIR spectra of thermally treated PE samples as well as the polarized NIR spectra of uniaxially oriented PE. Through this study, we will demonstrate NIR's capability to study the phase transition between orthorhombic and hexagonal phases in PE.

2. Experimental

2.1. Materials

High-density polyethylene Liten MB 62 was the basic material for the present study. The sample was supplied by Chemopetrol Litvínov, Czech Republic. Cold-stretched PE was prepared by drawing the standard dumbbell test piece at 23 °C. The processing conditions for specimen preparation are described elsewhere [43]. The gauge length, width and thickness of the injection-moulded test pieces were 90, 10, and 4 mm, respectively. The obtained draw ratio reached the value of 8.8.

For the preparation of quenched specimen, PE was sandwiched in-between a pair of aluminum foil and melted on a hotplate at 140 °C for 5 min. The melt specimen was quickly cooled in liquid nitrogen. To prepare annealed PE, it was heated to just below its melting temperature, 125 °C and it was kept for 5 min followed by quick cooling in liquid nitrogen.

For the phase transition study, commercially available ultrahigh modulus PE fiber, Dyneema (M_w=ca. 3×10^6 and tensile modulus of ca. 130 GPa, ca. 20 μm in diameter) was used, which was kindly supplied by Toyobo Co. Ltd.

2.2. Measurements

NIR measurements of unoriented and oriented PE samples were performed with a spectral resolution of 4 cm^{-1} by means of a thermo nicolet magna 760 FT-IR/NIR spectrometer. A PbS detector and a CaF_2 beam splitter were used for the measurements in the NIR region. Thirty-two spectra were co-added in each measurement. The spectra were measured for approximate dimensions of ca. $7\times5\times0.5$ mm^3 of the

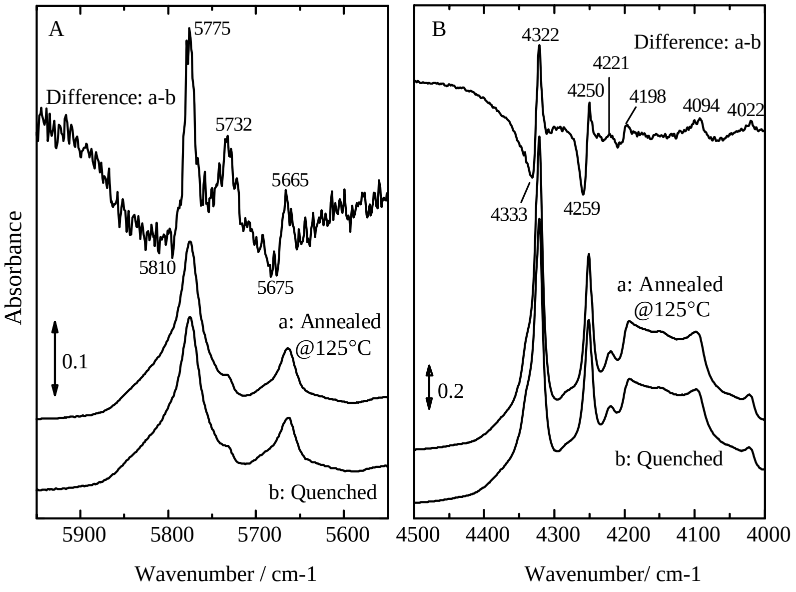

Fig. 1. NIR spectra in the 5950–5600 cm^{-1} (A) and 4500–4000 cm^{-1} regions (B) of unoriented PE after annealing, quenching treatment and their difference spectrum.

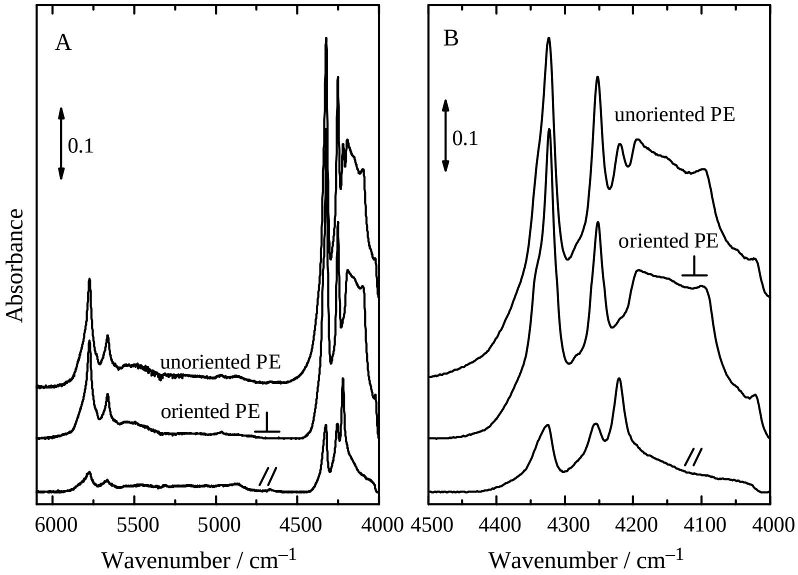

Fig. 2. NIR spectra of uniaxially oriented PE by parallel, perpendicular polarization and no polarizer measurement in the 6050–4000 cm^{-1} (A) and expanded spectra in 4500–4000 cm^{-1} regions (B).

specimens. This sample set was then placed in a heating block. The temperature was controlled by a CHINO UR750 temperature controller. In the temperature-dependent measurements of unoriented specimen, temperature was increased at a constant rate of 2.5 °C/min up to 100 °C and 1 °C/min to the melt. For the measurements of uniaxially oriented PE, temperature was increased at 1.5 °C/min up to 100 °C at 1 °C/min until temperature reached 120 °C, and at 0.2 °C/min to the melt.

2.3. Polarized NIR spectral measurements

Samples for the NIR polarization measurements were obtained from the drawn portions of uniaxially cold-drawn specimens. A KRS-5 wire grid polarizer (JEOL) was placed right in front of the sample holder. Two successive NIR measurements, with parallel and perpendicular polarization of the electric vector with respect to the draw direction of the specimen, were performed at a constant temperature.

2.4. Phase transition study

In the NIR measurement of the ultradrawn PE sample (Dyneema), Nicolet Nexus 8700 spectrometer was employed. An MCT detector and an extended KBr beam splitter were used for the simultaneous measurements through the NIR–MIR region. Thirty-two spectra were co-added at each measurement with a spectral resolution of 4 cm^{-1}. The temperature was increased from room temperature to 130 °C at 2 °C/min followed by 0.4 °C/min to the melt. The sample was fixed tightly around a special sample holder of CaF_2 (three times of winding, ca. 500 μm in thickness), because the phase transition from orthorhombic to hexagonal phases of PE requires the tight constraint of the ultradrawn PE during the measurements [18].

2.5. Curve fitting study

In order to estimate integrated intensities of over wrapped 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

Table 1
Assignments of NIR bands observed for polarized PE sample

Wavenumber (cm^{-1})	Assignments[a]	Phase[b]	Polarization[c]
5810		Amr	NA
5775	$2\nu_{as}(CH_2)$ [40,44]	Orth	⊥
5732		Orth	⊥
5675		Amr	NA
5665	$2\nu_s(CH_2)$ [40,44]	Orth	⊥
4349	$\nu_{as}(CH_2)+\delta(CH_2)$	Hex	⊥
4333		Amr	NA
4322	$\nu_{as}(CH_2)+\delta(CH_2)$ [44]	Orth	⊥
4259		Amr	NA
4256	$\nu_s(CH_2)+\delta(CH_2)$	Hex	⊥
4250	$\nu_s(CH_2)+\delta(CH_2)$ [44]	Orth	⊥
4221	$\nu_{as}(CH_2)+w\ (CH_2)$ [45]	Orth	‖
4198		Orth	⊥
4094		Orth	⊥
4022		Orth	⊥

[a] $\nu_{as}(CH_2)$, CH_2 anti symmetric stretching mode; $\nu_s(CH_2)$, CH_2 symmetric stretching mode; $\delta(CH_2)$, CH_2 scissoring mode; $w(CH_2)$, CH_2 wagging mode.

[b] Amr, amorphous; Orth, orthorhombic; Hex, hexagonal.

[c] NA, not assigned; ⊥, vibrational direction aligned perpendicular to that of incident light; ‖, vibrational direction aligned parallel to that of incident light.

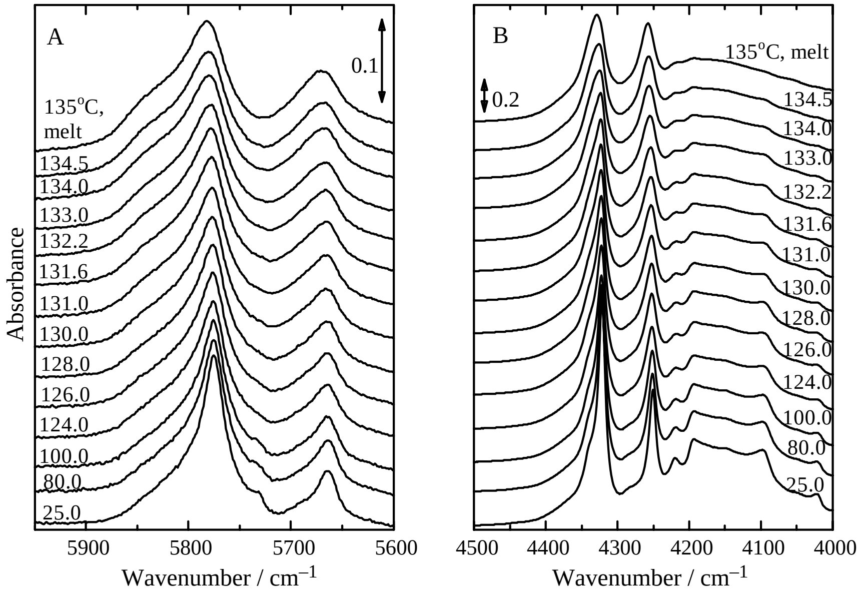

Fig. 3. NIR spectra in the 5950–5600 cm^{-1} region of unoriented PE (A) and 4500–4000 cm^{-1} regions (B) in the temperature range of 25–135 °C.

integrated intensities of individual bands were estimated separately.

3. Results and discussion

3.1. Identification of NIR bands characteristic of phase and amorphous region

In order to identify NIR bands characteristic of regular orthorhombic phase and disordered amorphous region, NIR spectra of unoriented PE were studied after two ways of sample pretreatments, annealing and quenching. The annealing enhances its crystallinity as whole [1]. On the other hand, PE after the quenching treatment has relatively low crystallinity. Hence, the comparison of the two spectra should allow us to identify the bands with respect to the phases of PE. Fig. 1A and B shows the spectra of annealed PE and quenched PE in 5950–5550 and 4500–4000 cm^{-1} regions, respectively. The difference spectrum was obtained by carefully adjusting the subtraction factor so that the baseline becomes as flat as possible throughout the spectral region in the present study.

In the difference spectra between these two samples, bands due to the orthorhombic phase appear upward while those from the amorphous domain appear downward. In this way, the bands at 5775, 5732, 5665, 4322, 4249, 4221, 4198, 4094 and 4022 cm^{-1} are ascribed to the orthorhombic phase while those at 5810, 5675, 4333 and 4259 cm^{-1} are ascribed to the amorphous phase.

Fig. 2A compares the NIR spectrum of unoriented PE samples with the polarized NIR spectra of oriented PE sample at room temperature. Fig. 2B shows the enlargement of the 4500–4000 cm^{-1} region. The $\perp$ and $\parallel$ denote the spectra measured with the incident light whose electric vector was perpendicular and parallel to the orientation direction, respectively. Based on the results of this polarization study as well as that of annealing/quenching study, bands were separated into two groups, NIR bands those originated from crystalline phase or amorphous phase. Table 1 summarizes bands detected by NIR spectroscopy and their assignments [44,45].

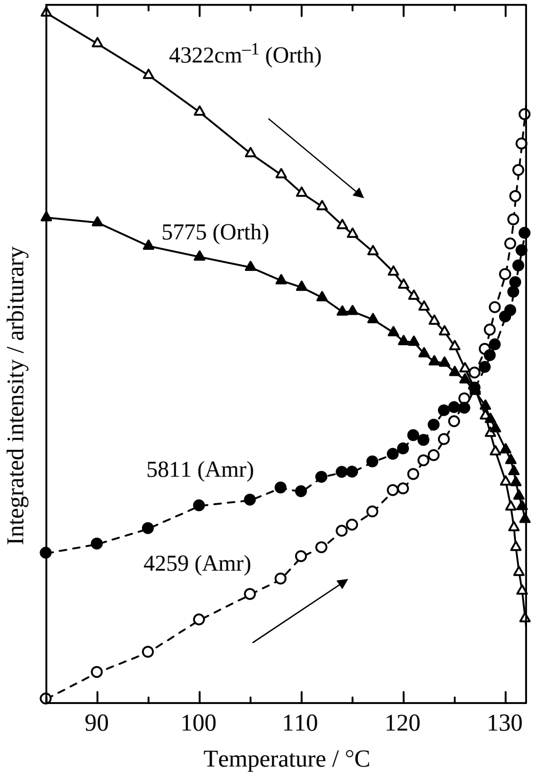

Fig. 4. Temperature dependence of the integrated intensities of NIR bands measured in unoriented PE characteristic of the orthorhombic phases: 4322, 5775 cm^{-1}, amorphous domain: 5811, 4259 cm^{-1} in the temperature range of 85–130 °C.

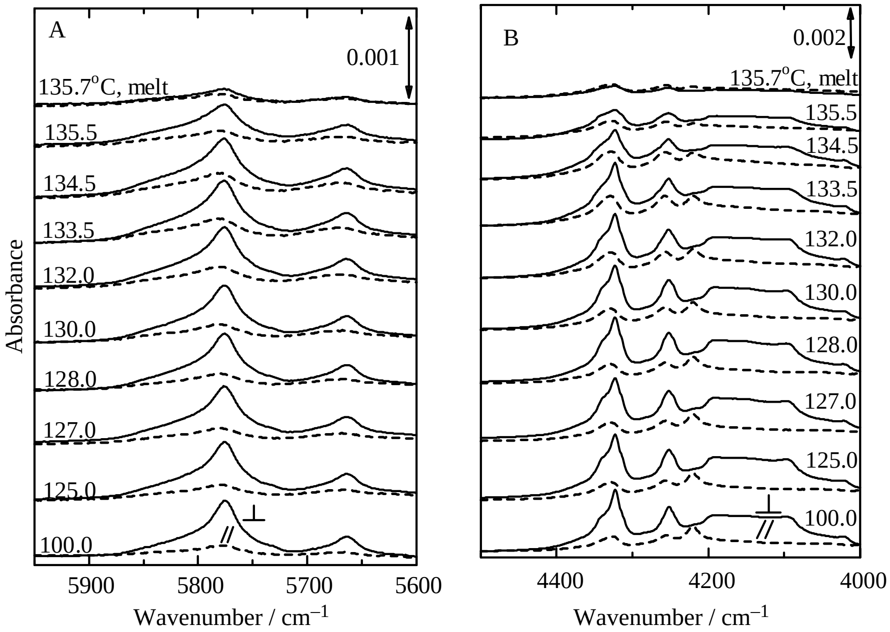

Fig. 5. Temperature dependence of the polarized NIR spectra of uniaxially oriented PE in the 5950–5600 cm^{-1} region (A) and 4500–4000 cm^{-1} regions (B) in the temperature range of 100–135.7 °C by parallell (||, dotted line) and perpendicular polarization ($\perp$, solid line).

3.2. Temperature dependence of NIR spectra

3.2.1. Unoriented sample

Fig. 3A and B shows the temperature dependent NIR spectra of the unoriented PE collected during heating up to the melt. Fig. 4 plots the integrated intensities of the bands at 5811, 5775, 4322 and 4259 cm^{-1} as a function of temperature, where the band components were separated by curve fitting method. As temperature increases, intensities of orthorhombic crystalline bands continuously decrease while those of the broad bands characteristic of the melt increase instead. This suggests an occurrence of gradual premelting of the orthorhombic crystalline phase. This phenomenon has also been studied by Raman spectroscopy for melt-crystallized PE and the applicability of the technique for temperature-induced phase structural change is reported [26].

3.2.2. Oriented sample

Fig. 5 depicts the temperature-dependent polarized NIR spectra during the heating measured for the uniaxially oriented PE. The temperature dependence of integrated intensities of some bands observed in oriented PE measured without polarizer is shown in Fig. 6. Note that the behaviors of crystalline bands of the uniaxially oriented PE are quite different from that of the unoriented specimen. The integrated intensities of the amorphous bands increase only above 100 °C, which contrasts with the result for the unoriented specimen that shows the continued disordering process at temperatures above room temperature. In Fig. 7, the dichroic ratio (R) evaluated for orthorhombic crystalline band at 4322 cm^{-1} is plotted against temperature together with the integrated intensity of this band shown in Fig. 6 as a reference. The dichroic ratio R is defined as $R = I_{\parallel}/I_{\perp}$, where $I_{\parallel}$ is the integrated intensity of the parallel component and $I_{\perp}$ is that of the perpendicular component. In the temperature range of 125–130 °C, where annealing effect has been detected as seen in the temporal increment of integrated intensity of the orthorhombic band, R appreciably

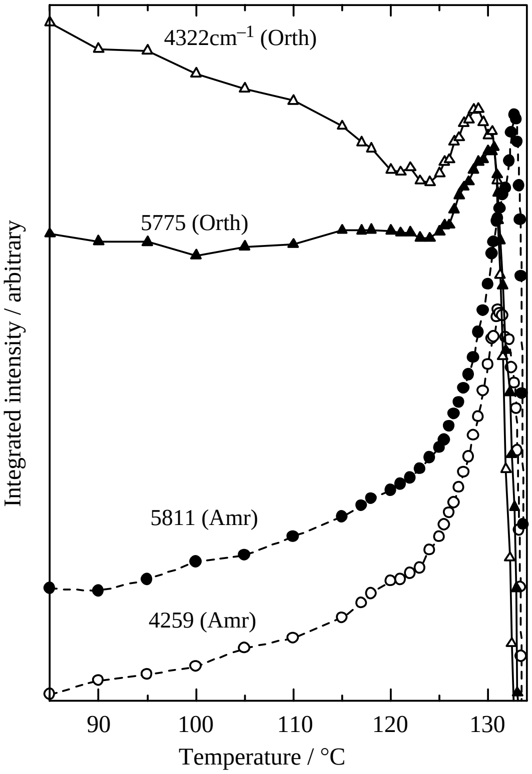

Fig. 6. Temperature dependence of the integrated intensities of polarized NIR bands measured in oriented PE characteristic of the orthorhombic phases: 5775, 4322 cm^{-1}, amorphous domain: 5811, 4259 cm^{-1} in the temperature range of 85–130 °C.

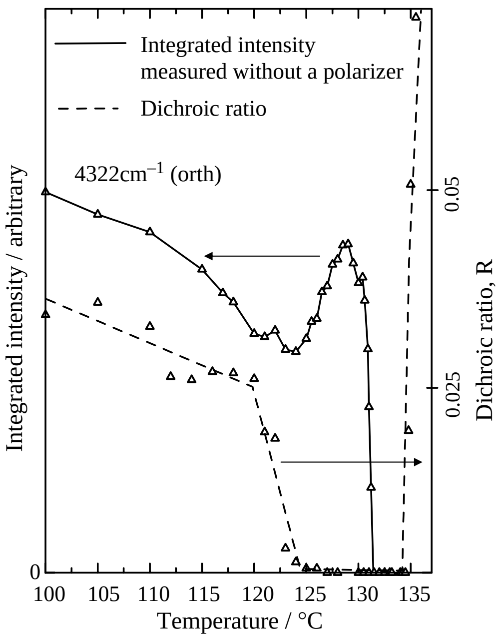

Fig. 7. Temperature dependence of the integrated intensities and the dichroic ratio (R) of NIR band measured in uniaxially oriented PE characteristic of the orthorhombic phase at 4322 cm^{-1} in the temperature range of 100–135.7 °C (solid lines: integrated intensities, dotted lines: R).

decreases to zero. This indicates the melt-re-crystallization. When temperature approaches to the melting temperature, R quickly approaches to 1.0 due to almost loss of chain orientation.

3.2.3. Structural changes in the orthorhombic-to-hexagonal phase transition

By measuring the temperature-dependent NIR spectra of commercially available ultrahigh modulus PE fiber, Dyneema, we have been able to demonstrate the ability of NIR spectroscopy for detecting the phase transition from the orthorhombic to hexagonal phases in PE. An occurrence of the phase change in this geometrically constrained ultra drawn PE below T_m was demonstrated by Tashiro et al. [18,23] by using X-ray imaging plate, DSC, Raman and MIR spectroscopy. In their MIR spectra, remarkable increment of bands at 1466, 1366, 1352 and 1306 cm^{-1} were detected in the temperature range where the occurrence of the phase transition was confirmed by the X-ray diffraction measurement. All of these bands were determined as they originate from hexagonal phase, which consists of conformationally disordered molecular chains [1,2,18,23,46]. In the present experiment, we basically followed the sample preparation technique of Dyneema established by Tashiro et al. [18,23]. The NIR spectra were measured during the heating process at 2 °C/min up to 130 °C followed by 0.4 °C/min to the melt. To confirm the occurrence of the phase transition from orthorhombic to hexagonal in the present experimental set-up, MIR spectra were simultaneously measured with NIR spectra. An FTIR spectrometer was set to scan the frequency region of 7000–800 cm^{-1}.

Fig. 8A presents the temperature-dependent MIR spectral changes in the frequency region of the fundamental CH_2 bending and wagging modes. In the temperature range very close to the melting point, the intensities of the bands at 1466, 1366, 1306 and 1352 cm^{-1} appreciably increase. This demonstrates the occurrence of the orthorhombic-to-hexagonal phase transition. In the NIR spectral region, similar increment in the intensities of bands near 4350 and 4250 cm^{-1} have been found in the temperature range where the phase transition proceeds (Fig. 8B). Since the bands in this region are severely overlapped, the bands were separated by curve fitting. As the result, emergence of two bands at 4349 and 4256 cm^{-1} were confirmed above 148.6 °C. The integrated intensities of NIR

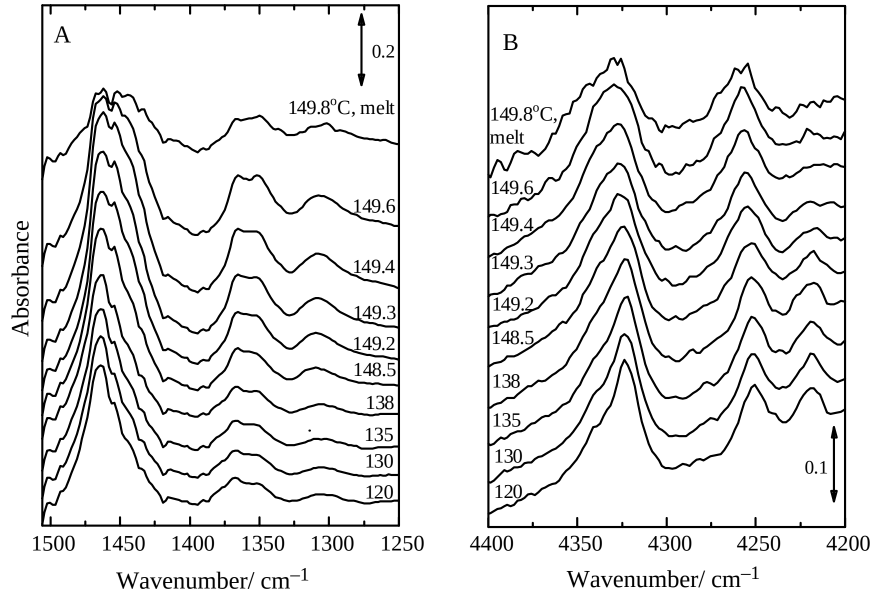

Fig. 8. NIR spectra in the 5950–5600 cm^{-1} (A) and 4500–4000 cm^{-1} regions (B) of chain-extended ultradrawn PE, Dyneema in the temperature range of 120–149.8 °C.

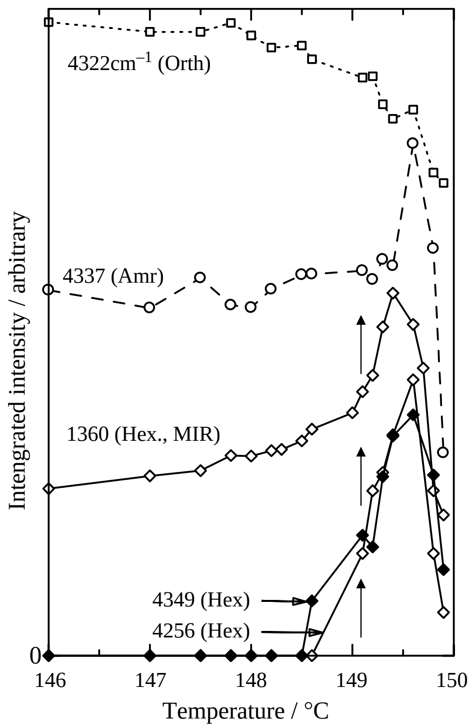

Fig. 9. Temperature dependence of the integrated intensities and of NIR bands for orthorhombic (4322 cm^{-1}), amorphous (4337 cm^{-1}) and hexagonal (4349, 5256 and 1360 cm^{-1} in MIR region for reference) bands measured for constrained chain-extended ultradrawn PE, Dyneema in the temperature range of 146–149.8 °C.

bands are plotted in Fig. 9. As the temperature increases in the phase transition temperature detected in the MIR spectral experiment, the new bands at 4349 and 4256 cm^{-1} emerge and their intensity increases transiently, but these bands decrease in intensity in the melt region. In this way, it is concluded that the bands at 4349 and 4256 cm^{-1} originate from the hexagonal phase. The integtared intensity of these hexagonal bands decreased when temperature approached to the melting temperature. Instead, the intensity of the amorphous band at 4337 cm^{-1} increased just below the melting (149.6 °C), indicating the loss of chain orientation. Since this phase transition study was carried out while fixing the specimen around a CaF_2 sample holder, it was impossible to keep recording the spectra after the melt. This explains the intensity decrement of the amorphous band at 4337 cm^{-1} above 149.6 °C. Newly assigned NIR bands due to hexagonal phase as well as known NIR band assignments are summarized in Table 1.

4. Conclusion

In the present study, we have investigated thermally induced structural changes of PE by means of NIR spectroscopy. The present study has demonstrated the potential of NIR spectroscopy in investigating the structural and phase transition behavior of PE crystal by using relatively thick samples. The following conclusions have been reached from the present study.

1. The NIR bands at 4349 and 4256 cm^{-1} have been identified to arise from the hexagonal condis phase by performing the temperature dependent NIR measurement for the uniaxially oriented sample under geometrically constrained condition.
2. NIR spectroscopy has demonstrated the occurrence of disordering process of orthorhombic crystalline lattice in the unoriented PE that continuously undergo above room temperature to the melt. In the uniaxially oriented PE, it was confirmed mostly above 100 °C.
3. The annealing effect that leads to the enhancement of crystallinity just below T_m in PE was confirmed by means of NIR spectroscopy.

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