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Thermally induced conformational disordering process in high-density polyethylene crystal studied by generalized two-dimensional correlation mid-infrared spectroscopy

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Abstract

Thermally induced conformational changes that occur in high-density polyethylene (HDPE) crystal were studied by mid-infrared (MIR) spectroscopy. Spectral changes of four conformational "defect mode" bands in 1390–1280 cm^{-1} region were observed during the heating up to the melt. The spectra were analyzed by generalized two-dimensional (2D) correlation technique to elucidate correlations in their responses against temperature. Among the conformational defect bands, two bands at 1368 and 1308 cm^{-1} have traditionally been assigned to non-planar conformers of gtg' (*kink*) and *gtg*. However, the present study shows the intensity increment of the band at 1368 cm^{-1} happens at a lower temperature than that of the band at 1308 cm^{-1}. This finding is in favor of the assignment proposed by Cates et al., in which the 1368 cm^{-1} band is assigned to the *gtg* conformation excluding the involvement of *kink*. The spectral correlation among the band at 1368 (*gtg*), 1353 (double-*gauche*, gg'), and 1341 cm^{-1} (end-*gauche*, *eg*) has also been studied by 2D correlation analysis. As a result, it was found that the formation of gg' and *eg* sequences mostly proceeds at a temperature range higher than 115 °C. The formation of *gtg* conformer sequence measured by the band at 1368 cm^{-1} apparently proceeds in two steps: the first at a temperature around 70 °C and the later one occurring at a temperature very close to T_m. The results of this study make correlation relationships clear in the temperature dependency of MIR bands due to conformational disorder sequences.

Keywords: Polyethylene; Mid-infrared (MIR); Conformational defects

1. Introduction

Semicrystalline polymers, such as polyethylene, undergo characteristic transition processes when external physical variables, like temperature and pressure, change [1]. These transitions include the crystallization and melting of ordered molecular chain segments, as well as glass-to-rubber transition and other relaxation processes of the amorphous component. A study under well-controlled temperature is attractive because of the potential for gaining much better thermodynamic understanding of the system. Physical transitions of polymers usually result in the systematic alteration of vibrational spectroscopic features, both intensities and frequencies. By studying such spectral changes, one can often obtain complex structural and morphological information about semicrystalline polymers.

Polyethylene (PE), in particular, has been the polymeric material of extensive studies. A number of studies on PE with respect to its molecular packing, phase transition and the formation of conformational defects have been carried out and summarized [2,3]. The importance of such studies on PE arises not only from scientific merit but also from

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industrial importance, because its crystalline structure greatly affects the mechanical properties of this class of materials. Some part of PE remains in the fully disordered or amorphous state, while some other parts of the polymer chains develop localized "defects" within the crystalline structure, which disturb the overall crystallinity of this material [4]. Quantitative estimation and identification of characteristic mid-infrared (MIR) bands due to such disordered domains have been of significant research interest [5–14]. Snyder worked on fully protonated liquid *n*-alkane and pioneered the use of MIR for such research purpose. In the studies, he calculated and tabulated the frequencies for an extensive number of molecular vibrations in alkane systems, including some that are specific to localized "defect" structures. His normal-mode calculations give a very detailed assignment to CH_2 wagging vibrations arising from localized non-planner *gauche* conformers [5]. Following the vibrational analysis and observation, bands at 1368 and 1308 cm^{-1} were assigned to conformational sequences $kink + gtg$, a band at 1352 cm^{-1} to the sequence gg', and one at 1341 cm^{-1} to the *eg* conformation [5–7]. Representations *t* and *g* denote *trans* and *gauche* conformer, respectively. This approach of studying conformational defects in PE crystal attracted many researchers because of several advantages, e.g., no need of probe molecules, reasonably strong intensity of CH_2 wagging bands, and no need of elaborate models for the motion to extract conformational information. This region of an IR spectrum has proved to be an invaluable tool in characterizing the type and extent of disorder not just in *n*-alkanes [15] or PE [16] but also in carboxylic acid [17], phospholipids [18] and surfactants [19,20]. Although intensity changes of the individual bands were studied in the past, the detailed comparison among these "defect mode" bands is not thoroughly studied so far with respect to their temperature dependency. The result of the study will allow us to obtain new insights with respect to their spectral assignments as well as formation mechanism. In order to accentuate the correlation of overlapped bands, we performed 2D correlation analysis. Generalized 2D correlation [21], which is an extension of the original 2D correlation spectroscopy proposed by Noda in 1986 [22–25] has received considerable attention for the past two decades. The generalized 2D method can handle spectral fluctuations as an arbitrary function of time or any other physical variables, such as temperature, pressure, concentration and composition. Its use allows one to probe the specific order of certain spectral events taking place under the influence of a controlling physical variable. Synchronous 2D spectra $\Phi(\nu_1, \nu_2)$ represent the overall similarity of responses measured at two separate spectral variables, ν_1 and ν_2, for a given external variable, such as temperature. Autopeaks at diagonal positions represent the extent of changes of spectral signals induced by the changes of temperature. Cross-peaks at off-diagonal positions represent simultaneous changes of signals at two different spectral variables, suggesting a coupled or related origin of intensity variation, as temperature is varied. If the sign of a cross-peak is positive, the spectral intensities measured at corresponding two spectral variables are either increasing or decreasing together. If negative, on the other hand, one is increasing while the other is decreasing. By convention, negative peaks are denoted by the presence of shading.

Asynchronous 2D IR correlation spectra $\Psi(\nu_1, \nu_2)$ on the other hand, represent the overall dissimilarity of responses measured at two separate spectral variables. Cross-peaks develop only if the spectral intensity varies independently under a common change in temperature. For a sequentially obtained spectral set over the variable, temperature, the sign of a cross-peak becomes positive if the intensity change at ν_1 occurs after ν_2. This sequence is reversed if $\Phi(\nu_1, \nu_2) < 0$. The convention is often employed that cross-peaks are shaded whenever the intensity change at ν_1 occurs after ν_2. In present study of exploring temperature dependency of MIR bands, shaded asynchronous cross-peaks may be interpreted as an indication that spectral intensity change measured at ν_1 occurs at higher temperature compared to that at ν_2.

Through this study, we present temperature dependency of the conformational defect mode bands due to CH_2 wagging mode in HDPE using 2D spectroscopy technique. Particularly, we demonstrate the difference in the formation of conformational defects measured by 1368 and 1308 cm^{-1}, of their spectral assignments have been considered due to same conformer of $kink + gtg$.

2. Experimental

2.1. Materials

Two HDPE samples with different structure and crystallinity were used in this study. Both of the samples 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.

Above samples were all supplied in the form of pellets. In order to prepare a film sample for MIR measurements and also for the sake of adjusting thermal history of the samples, ca. 0.9 g of PE pellet samples were 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 Metler FP800. The spectroscopic studies were completed within one week from the sample preparation.

2.2. Spectral measurements

MIR spectral measurements of PE samples were performed with a spectral resolution of 2 cm^{-1} by means of a Thermo

Table 1

Sample code	Density (g/cm^3)	Crystallinity (%)	Melting point (°C)
HDPE-L	0.953	68.3	128.4
HDPE-H	0.964	74.7	132.4

Nicolet Nexus 870 FT-IR/NIR spectrometer. An MCT detector and an extended KBr beam splitter were used. Total of 32 spectra were co-added in each measurement. The spectra were measured for approximate dimensions of ca. $10 \times 10 \times 0.3$ mm^3 of the specimens. The sample was sandwiched with a pair of CaF_2 plates ($30 \times 15 \times 4$ 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 study

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 MIR spectra as needed. In this process, Lorentzian curve fitting function was adopted and the integrated intensities of individual bands were estimated separately.

2.4. 2D analysis

To obtain 2D spectra, *2Dshige* 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. MIR spectra

Fig. 1A and B shows, respectively, temperature-dependent MIR spectra in the 1385–1280 cm^{-1} region of HDPE-L and HDPE-H. In the spectra, the intensity of the band at 1378 cm^{-1} assigned to symmetric methyl bending (“umbrella”) vibration decreases as the temperature increase. The intensity and the frequency of this band are known to be sensitive to changes in crystal structure [10]. Hence, its intensity decreases as the increase in temperature that disturbs the orthorhombic crystalline structure. On the other hand, the intensity of the rest of the bands increases with temperature, indicating the formation of conformational defects. 2D correlation analysis has been performed to this methylene wagging mode spectral region to obtain the in-depth understanding on the comparison among the bands due to non-planar conformers.

3.1.1. MIR correlation analysis on CH_2 wagging modes at 1368 and 1308 cm^{-1}

Figs. 2A and 3A show the synchronous 2D MIR correlation spectra $\Phi(\nu_1, \nu_2)$ of HDPE-L and HDPE-H, calculated from the spectra obtained during the heating up, respectively. As shown in figures, positive cross-peaks are detected among the bands at 1368, 1353 and 1308 cm^{-1}. This result confirms the directions of intensity increments of these bands against temperature. The band at 1341 cm^{-1} is, however, not detected on these synchronous spectra. It is likely that relatively strong intensities of the neighborhood bands made it difficult to detect this weak band on the 2D spectra. Figs. 2B and 3B show corresponding asynchronous 2D correlation spectra $\Psi(\nu_1, \nu_2)$ of HDPE-L and HDPE-H, respectively. In the asynchronous 2D spectra, the spectral region of 1370–1280 cm^{-1} against the band at 1368 cm^{-1} develops negative (shaded) cross-peaks. Since corresponding spectral region in the synchronous spectrum (Figs. 2A and 3A) is positive, i.e., $\Phi(\nu_1, \nu_2) > 0$, the change of the band at 1368 cm^{-1} occurs prior to that of the bands in the spectral region 1370–1280 cm^{-1}, including the band at 1308 cm^{-1}. This result is a little bit surprising because the bands at 1368 and 1308 cm^{-1} have been traditionally assigned to both *kink* + *gtg*

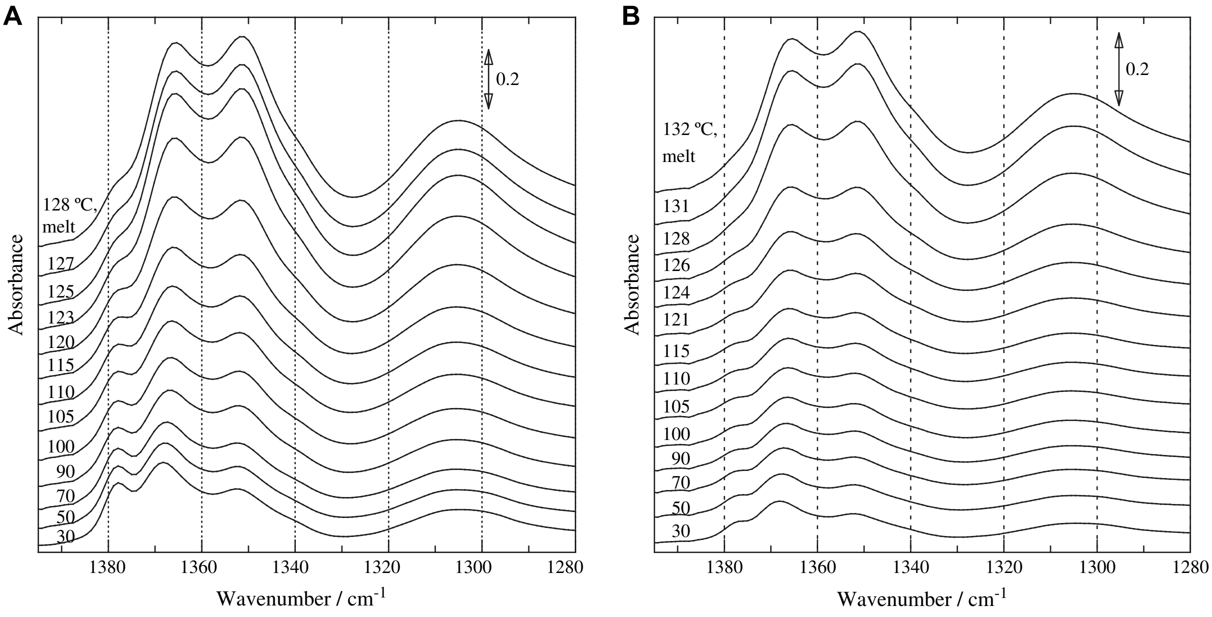

Fig. 1. MIR spectra in 1395–1325 cm^{-1} region of HDPE-L (A) and HDPE-H (B) in the temperature range of ~30 °C to melt.

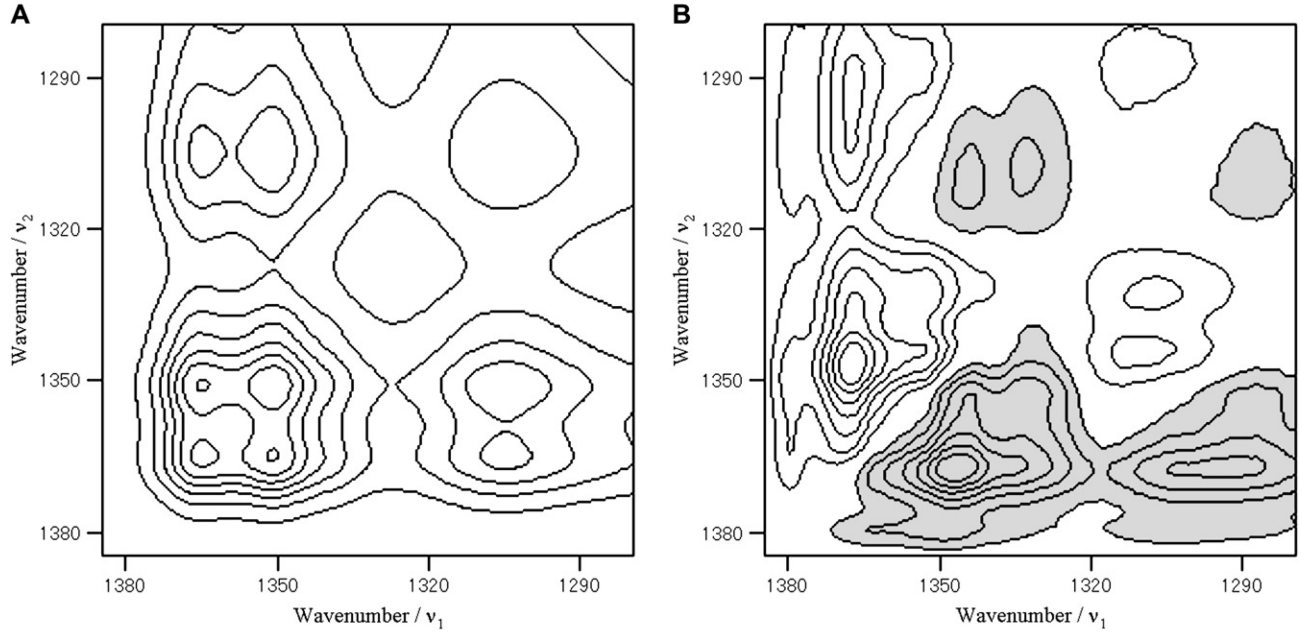

Fig. 2. The contour map representation of the 2D MIR-MIR synchronous (A) and asynchronous (B) correlation spectrum of HDPE-H in 1390–1285 cm^{-1}.

[5–7]. Such assignment has widely been used to characterize the chain disorder in a range of systems. The methylene wagging mode of *kink* sequence (*gtg′*) should not appear in MIR spectrum from the selection rule, because this sequence has a local center of symmetry. However, such a band might appear if the amplitude of torsional motion about the central C–C bond of the *gtg′* was sufficiently large. In this case, the inversion center would be in effect. Cates et al. performed spectral simulation works on a MIR spectrum of conformationally disordered PE chain. They concluded that the amplitudes of the C–C torsions are too small to allow *gtg′* wagging mode to appear in MIR at 1368 cm^{-1}. Consequently, the assignment of the band at 1368 cm^{-1} has been determined as *gtg*, excluding the involvement of *kink* sequences [26]. The result of our present 2D analysis is in favor of this proposal in terms of differentiating the assignment of the bands at 1368 and 1308 cm^{-1}. To confirm the result of 2D spectroscopy analysis, the integrated intensity of the bands at 1368 and 1308 cm^{-1} has been plotted in Fig. 4. The integrated intensities were normalized by the mean centering treatment followed by the division by the standard deviation in the temperature range from 60 °C to the melting. As shown in figure, it is evident that the increment in the integrated intensity

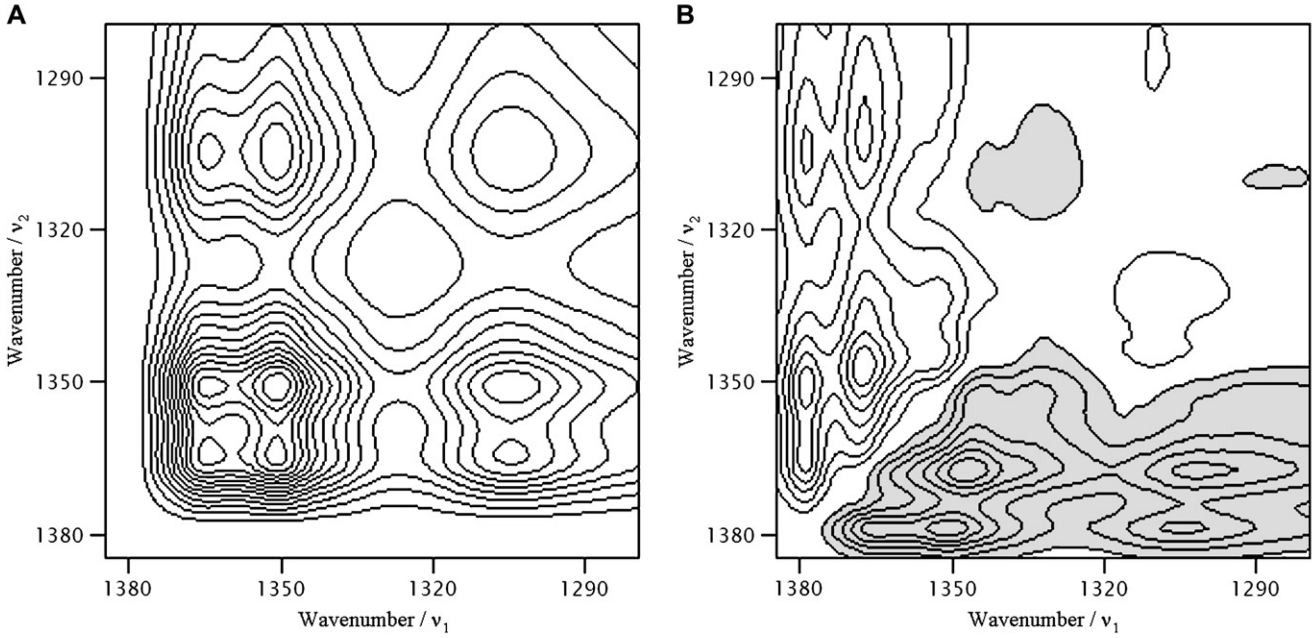

Fig. 3. The contour map representation of the 2D MIR-MIR synchronous (A) and asynchronous (B) correlation spectrum of HDPE-L in 1390–1285 cm^{-1}.

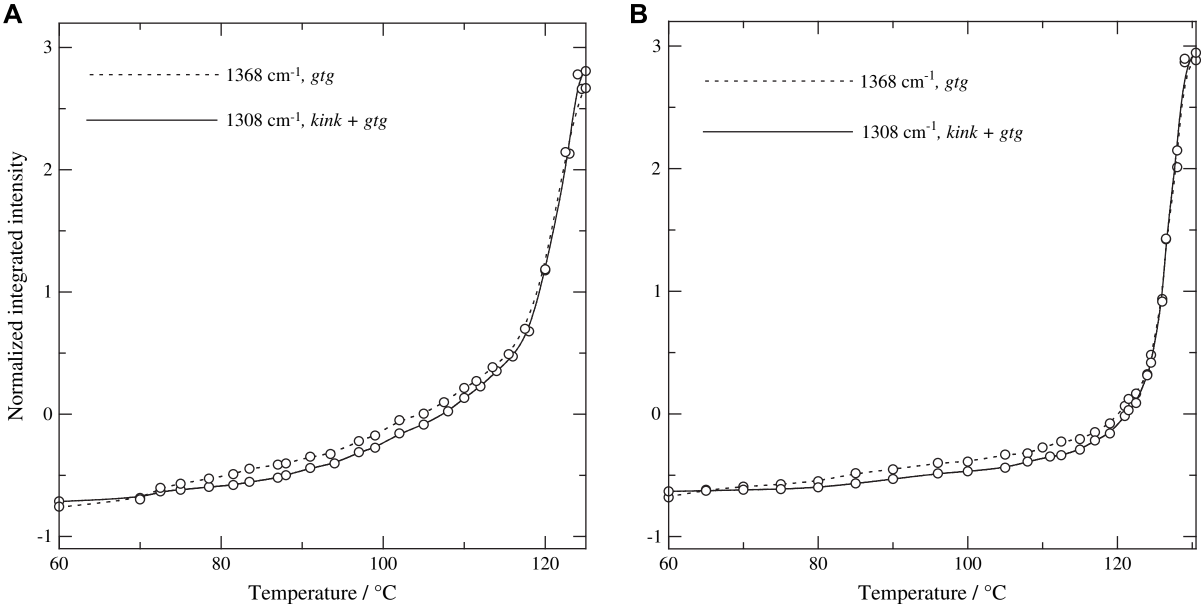

Fig. 4. Temperature dependence of the integrated intensities of the band at 1368 and 1308 cm^{-1} in HDPE-L (A) and HDPE-H (B) in the temperature range of 60 °C to melt.

of 1368 cm^{-1} occurs prior to 1308 cm^{-1} in both types of the HDPE specimens. Although the difference in the crystallinity between HDPE-L and HDPE-H causes difference in the temperature range for the formation of the non-planar conformers, the formation of 1368 cm^{-1} clearly happens for both samples prior to 1308 cm^{-1} against temperature.

3.1.2. MIR correlation analysis on CH_2 wagging modes at 1368, 1353 and 1341 cm^{-1}

The result of the sequence analysis based on the 2D asynchronous spectra shown in Figs. 2B and 3B also indicates that intensity increment of bands due to other non-planar conformers, *gg′* conformation at 1353 cm^{-1} and *eg* conformation at 1341 cm^{-1} occurs at a higher temperature range than that of 1368 cm^{-1}. Fig. 5 shows the plot of normalized integrated intensities of the bands. It is shown that the intensity of 1368 cm^{-1} band starts to increase as low as 70 °C prior to that of the other two conformers. However, its intensity increment rate slows down and that of the bands at 1353 and 1341 cm^{-1} exceed above around 115 °C in both HDPE-L and HDPE-H. Fig. 6A and B shows the synchronous and asynchronous 2D MIR correlation spectra of HDPE-H, calculated from the spectra obtained above 115 °C. Observations of $\Phi(1353 \text{ and } 1341, 1368) > 0$ in the synchronous spectrum

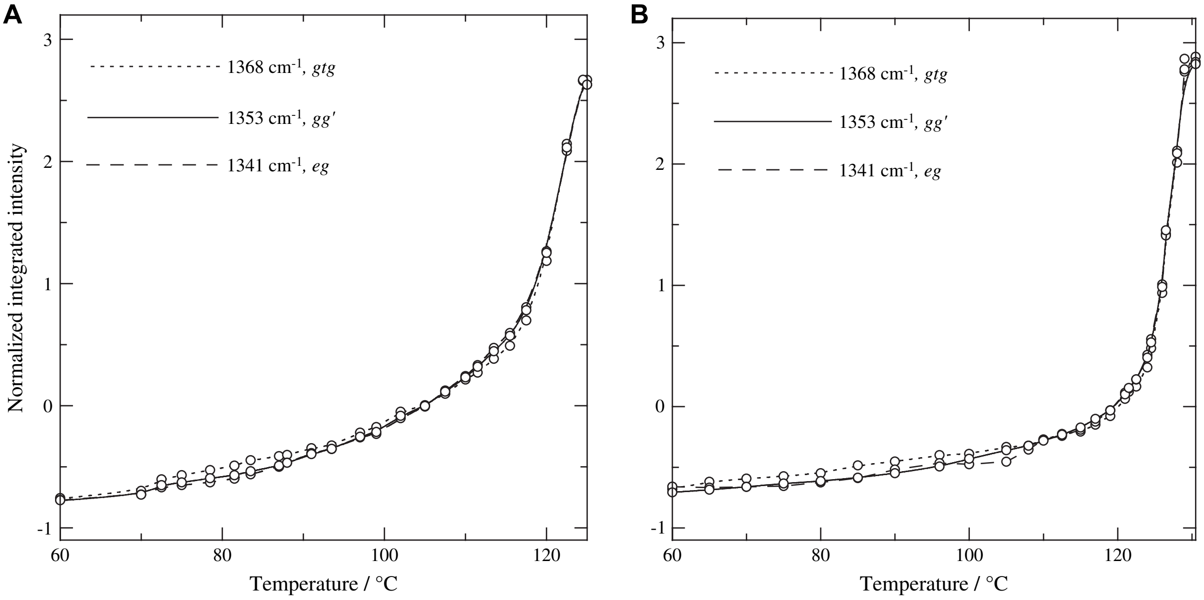

Fig. 5. Temperature dependence of the integrated intensities of the band at 1368, 1353 and 1341 cm^{-1} in HDPE-L (A) and HDPE-H (B) in the temperature range of 60 °C to melt.

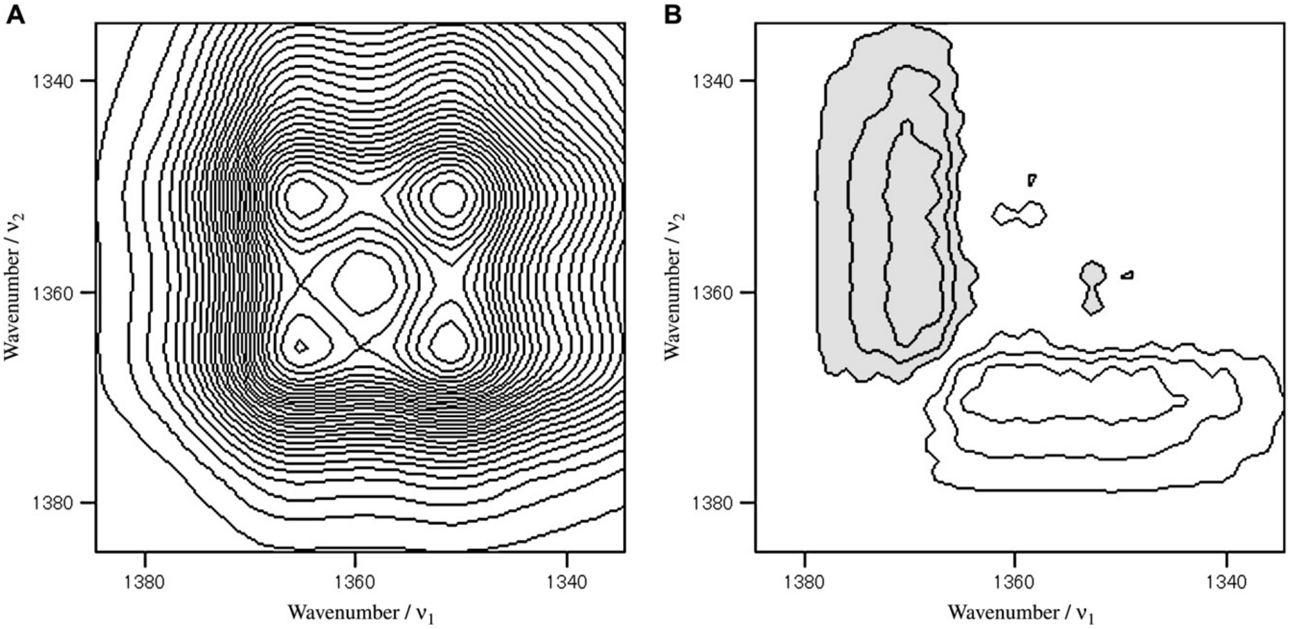

Fig. 6. The contour map representation of the 2D MIR-MIR synchronous (A) and asynchronous (B) correlation spectrum of HDPE-H in 1390–1285 cm^{-1}, calculated from the spectra obtained above 115 °C.

(A) and $\Psi(1353 \text{ and } 1341, 1368) > 0$ in the corresponding asynchronous spectrum (B) indicate that the increment in the intensity of the bands at 1353 and 1341 cm^{-1} occurs prior to that of 1368 cm^{-1} in this temperature region. This result indicates that the formation of conformational defect sequences measured by 1368 cm^{-1} in two steps. The first formation starts around 70 °C and the second step to happen very close to T_m.

Xiao et al. reported the temperature-dependent formation of *eg* sequences in HDPE proceeds mostly at temperature below 84 °C and they diminish at higher temperature [14]. However, *eg* sequences were continuously developed until temperature reaches their T_m in our specimens as shown in Fig. 5A and B.

4. Conclusion

In the present study, we have investigated the intensity change of MIR bands due to non-planner conformers of HDPE during heating up to the melt. The correlation relationship between the defect mode bands was analyzed by 2D correlation spectroscopy technique in order to deliver new insights with their spectral assignments as well as formation mechanism. The following conclusions have been reached.

(1) 2D MIR correlation spectroscopy technique revealed that the increment in the intensity of the band at 1368 cm^{-1} occurs in prior to that of the band at 1308 cm^{-1}. Although both of the bands have been assigned due to *kink* + *gtg* conformers, this result indicates that the bands arise from different conformers. *gtg* conformation is proposed for the band at 1368 cm^{-1}.
(2) The formation of non-planar conformer represented by 1368 cm^{-1} proceeds in two steps when it is compared to the single-step formation of the *gg′* and *eg* conformation. The first step starts around 70 °C, and the second step initiates at a temperature very close to T_m.

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