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ORIGINAL ARTICLE

A two-dimensional IR correlation spectroscopic study of the conformational changes in syndiotactic polypropylene during crystallization

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The conformational changes of syndiotactic polypropylene (sPP) during melting and isothermal crystallization processes were studied by infrared (IR) and two-dimensional (2D) correlation analysis. The band at $963\,cm^{-1}$ is assigned to the contribution of the amorphous component, and the band at $978\,cm^{-1}$ is assigned to a shorter helical conformational length than the bands at 867 and $812\,cm^{-1}$, which are related to crystalline helical conformation. The difference spectra and 2D correlation spectra analysis of the crystallization process indicated that the changes in these regular bands occur in rapid sequence, which is not easily detected by conventional IR spectroscopy. It was found that the absorption intensity of the band at $963\,cm^{-1}$ increases earlier than that of the band at $978\,cm^{-1}$, as well as of the bands at 867 and $812\,cm^{-1}$. The results suggest that the partial chains among the amorphous component change in conformation first, then the sPP chains adjust their local conformations to form short helical conformations and finally crystallization occurs.
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INTRODUCTION

Much effort has been devoted toward obtaining a comprehensive understanding of the crystallization behaviors of semicrystalline polymers from both theoretical and experimental aspects.[1–11] Several concepts for polymer crystallization have been described in the last century, of which the classical nucleation and growth theory (Hoffman–Lauritzen theory),[1–3] the mesomorphic phase concept[4–6] and the spinodal concept[7–11] are the most important. In recent decades, structural formation during the induction period before crystal growth has attracted increasing interest.[8–21] However, crystallization of polymers from metastable liquids and solutions is extremely complex, and many questions remain. The melting process for polymers, as a reverse process of crystallization, may provide some valuable information on crystallization.

Fourier transform infrared spectroscopy (FTIR), a powerful method that is sensitive to chain conformation, has been applied to study the molecular structure and conformational adjustments of semicrystalline polymers in recent years.[22–27] *In situ* FTIR results for the crystallization processes of isotactic polypropylene have shown that crystallization occurs as soon as the ordered helix length exceeds the critical persistent length.[22] FTIR investigation of the crystallization of syndiotactic polypropylene (sPP) revealed a *trans*-gauche transition at around $0\,°C$, which may be one important factor controlling the

formation of sPP crystals with characteristic conformations at this temperature. It is reported that sPP is in the Form III crystalline state during annealing at $0\,°C$ and in the Form I crystalline state during annealing at temperatures higher than $5\,°C$.[23] However, there is a lack of information on the conformational changes and molecular dynamics of sPP at higher crystallization temperatures.

Traditional infrared (IR) analytical methods may result in the loss of some significant information on conformational changes during the melting and crystallization processes of polymers. In the 1990s, Noda[28–30] proposed generalized two-dimensional IR (2D-IR) correlation spectroscopy. Generalized 2D-IR correlation spectroscopy is an extension of the original 2D-IR correlation spectroscopy, which has the features of simplifying complex spectra, improving the spectral resolution by spreading peaks along the second dimension and identifying the specific order of certain events occurring under the effect of a controlled physical variable.[29] 2D-IR correlation spectroscopy has been used to study the subtle conformational adjustments of polymer chains during melting and crystallization processes in terms of temperature- and time-dependent spectral changes.[31–33] 2D-IR correlation spectroscopy results for the conformational changes during the melting process of polyvinylidene difluoride indicated that three kinds of polyvinylidene difluoride components change asynchronously during melting; that is, the amorphous component

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$> \beta$-polyvinylidene difluoride $> \alpha$-polyvinylidene difluoride.[31] The 2D-IR correlation analysis of isotactic polystyrene during the induction period of isotactic polystyrene cold crystallization indicated that the amorphous phase changes first, followed by the ordering of the phenyl rings of isotactic polystyrene, and that the polymer chains consequently adjust their local conformations to form a short 3_1 helix structure before crystallization of isotactic polystyrene.[20] The above-mentioned results suggest that 2D-IR correlation analysis could be helpful for understanding the melting and crystallization of polymers while considering the adjustment of molecular conformation. However, studies on the melting and crystallization of sPP are still limited in the literature, especially for the conformational changes and molecular dynamics during melting and crystallization processes.

In this study, the structural changes of sPP during melting and crystallization processes were investigated by FTIR and 2D-IR correlation analysis. The results could be helpful for understanding the melting and crystallization processes of semicrystalline polymers from the viewpoint of molecular conformational changes.

EXPERIMENTAL PROCEDURE
Materials and sample preparation
Syndiotactic polypropylene ($M_w=1.74\times10^5\,\mathrm{g\,mol^{-1}}$, $M_w/M_n=2.32$) in pellet form was purchased from Aldrich (St Louis, MO, USA). The sPP pellets were melt-pressed at $170\,^\circ\mathrm{C}$ for 5 min, followed by slow cooling to room temperature. The obtained thin film was about $100\,\mu\mathrm{m}$ in thickness.

Differential scanning calorimetric measurement
Differential scanning calorimetric (DSC) measurements were carried out on a Perkin-Elmer (Waltham, MA, USA) differential scanning calorimeter (Diamond Series) under a flowing nitrogen atmosphere. The instrument was calibrated using In and Pb as standards. To be consistent with the procedure of the FTIR experiment, the sPP samples ($\sim5\,\mathrm{mg}$) were heated at the rate of $5\,^\circ\mathrm{C\,min^{-1}}$ and cooled at the rate of $15\,^\circ\mathrm{C\,min^{-1}}$.

Wide-angle X-ray diffraction measurement
Wide-angle X-ray diffraction experiments were performed on a Geigerflex D/Max-RB diffractometer (Rigaku, Shibuya-ku, Tokyo, Japan). A rotating anode generator (Cu Kα, $12\,\mathrm{kW}$) was used as the X-ray source.

FTIR and 2D-IR correlation analysis
Time-resolved FTIR measurements were determined using a Bruker Equinox-55 FTIR spectrometer (Ettlingen, Germany) equipped with a hotstage (INSTEC STC200C, Boulder, CO, USA). The sPP thin film ($\sim100\,\mu\mathrm{m}$) was heated to $170\,^\circ\mathrm{C}$ ($40\,^\circ\mathrm{C}$ above the melting point) at a heating rate of $5\,^\circ\mathrm{C\,min^{-1}}$, held for 5 min at $170\,^\circ\mathrm{C}$ and then cooled to $105\,^\circ\mathrm{C}$ at a cooling rate of $15\,^\circ\mathrm{C\,min^{-1}}$ for crystallization. IR spectra were collected at a resolution of $2\,\mathrm{cm^{-1}}$ with 16 co-adding scans during the heating and cooling processes. The IR spectra of the specimen were collected at 2 min intervals during the crystallization process at $105\,^\circ\mathrm{C}$ for 2 h. The IR spectra were preprocessed to eliminate the effects of baseline instability and other possible effects. The wavenumber regions were selected first and processed with a linear baseline correction, followed by offsetting to a zero absorbance value. 2D-IR correlation analysis was carried out by the '2D Shige' software written by Shigeaki Morita (Kwansei Gakuin University, Sanda, Hyogo, Japan). The temperature-averaged reference spectra are shown at the side and top of the 2D correlation maps for reference. In the 2D correlation maps, the unshaded and shaded areas in the contour maps represent positive and negative peaks, respectively.

RESULTS AND DISCUSSION
Melting process of sPP
Figure 1 shows the heating and cooling DSC curves of sPP, which indicate that the melting point (T_m) and the melt crystallization

temperature (T_c) of sPP were at about 133 and $80\,^\circ\mathrm{C}$, respectively. Moreover, the most intense peaks appearing at $2\theta=12.3^\circ$, 15.9°, 20.8° and 24.8° on the wide-angle X-ray diffraction curve of the sample indicate that sPP in the initial sample was in the disordered Form I crystalline state (Figure 2).[34,35]

Figure 3 shows the FTIR spectra of sPP collected *in situ* during the heating process from 40 to $170\,^\circ\mathrm{C}$. The assignments of absorption bands are listed in Table 1.[35–38] In the crystalline phase, the segments predominantly formed 4_1 helices. It is well documented that the bands at 1005, 905, 867 and $812\,\mathrm{cm^{-1}}$ arise from the crystalline phase. The bands located at 978 and $963\,\mathrm{cm^{-1}}$ are associated with the crystalline–amorphous interface. The dependence of the intensity of absorbance bands on temperature is shown in Figure 4. Results indicate that the intensity of IR absorption bands at 1005, 978, 905, 867 and $812\,\mathrm{cm^{-1}}$, which are associated with the helical conformation of sPP chains, decreases with increasing temperature. However, the intensity of the IR absorption band at $963\,\mathrm{cm^{-1}}$, which corresponds to the planar zigzag conformation of sPP chains, increases gradually with increasing temperature. Moreover, the intensity of IR absorption bands at 1005, 978, 905, 867 and $812\,\mathrm{cm^{-1}}$ decreases gradually with increasing sample temperature in the temperature range of 40–$120\,^\circ\mathrm{C}$, which is attributed to the temperature effect of IR spectra. The step in the temperature range of 120–$140\,^\circ\mathrm{C}$ arises from the melting of Form I crystals of sPP, which differs from DSC results (Figure 1). In Figure 1, the wide melting temperature range (90–$140\,^\circ\mathrm{C}$) is generally because of the wider distribution of the lamellar thickness. When the sPP is melted, the regular structure of the chains is destroyed. However, it is determined from the IR results that it is not until $120\,^\circ\mathrm{C}$ that the helix chains begin to collapse. From the combined results above, it can be deduced that, in the early stage of the melting process of sPP, the helix structure does not immediately collapse and a higher temperature is required to destroy the ordered helix structure. By contrast, the intensity of the absorption band at $963\,\mathrm{cm^{-1}}$ increases gradually with increasing temperature, and a step in the temperature range of 120–$140\,^\circ\mathrm{C}$ can be seen. In the melting process of sPP, the ordered crystal structures with sPP helical chains transform into random structures. Therefore, the fraction of the crystalline part in the sample decreases and the fraction of the amorphous component increases
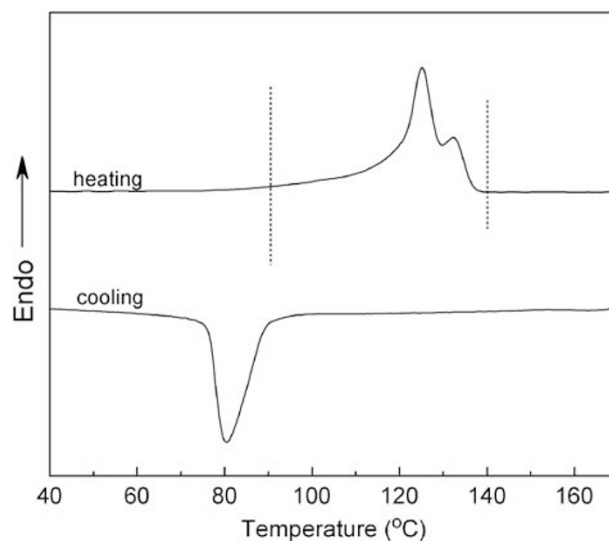

Figure 1 Differential scanning calorimetric heating curve of syndiotactic polypropylene (sPP) at a heating rate of $5\,^\circ\mathrm{C\,min^{-1}}$, and the cooling curve of sPP at a cooling rate of $15\,^\circ\mathrm{C\,min^{-1}}$.
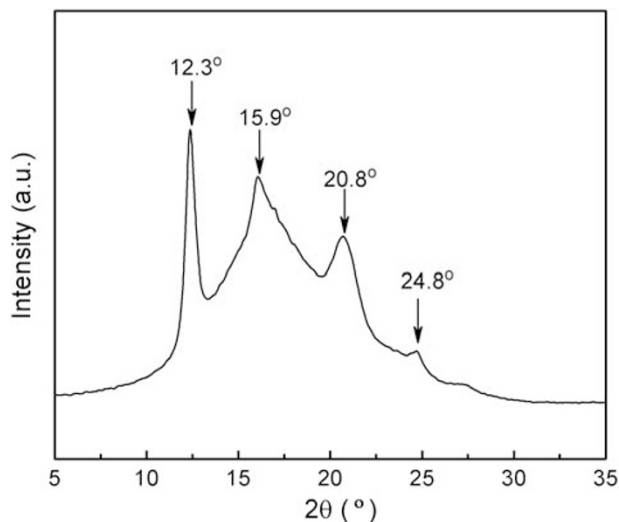
Figure 2 Wide-angle X-ray diffraction intensity profile of syndiotactic polypropylene at room temperature.
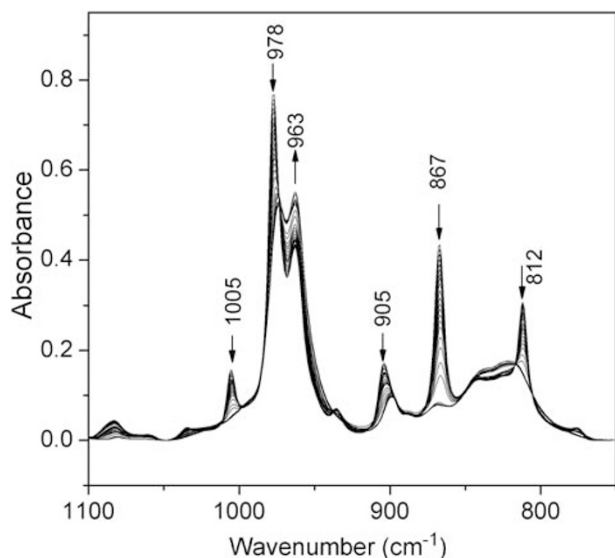

Figure 3 Time-dependent Fourier transform infrared spectra of syndiotactic polypropylene heated at $5\,^{\circ}C\,min^{-1}$ in the wavenumber regions of 1100–750 cm^{-1} from 40 to 170 $^{\circ}C$. Arrows indicate the directions of band intensity changes with increasing temperature.

Table 1 Characteristic infrared peak assignments for syndiotactic polypropylene

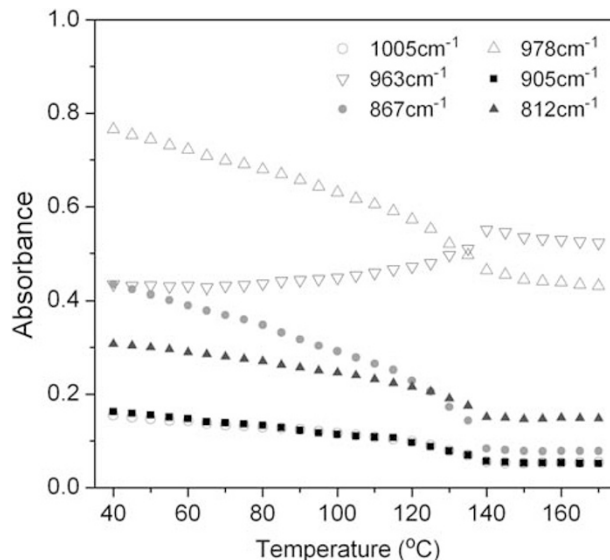| Position (cm^{-1})	Vibrational mode (s)	Morphology
812	$\gamma(CH_2)$	Helical (crystalline)
867	$\gamma(CH_2)$	Helical (crystalline)
905	$\gamma(CH_3)$	Helical (crystalline)
936	$\gamma(CH_3)$, $\nu(C-C)$	Helical (crystalline)
963	$\gamma(CH_3)$, $\nu(C-C)$	Planar zigzag (interfacial)
978	$\gamma(CH_3)$, $\nu(C-C)$	Helical (interfacial)
1005	$\nu(C-CH_3)$, $\gamma(CH_3)$	Helical (crystalline)
1035	$\nu(C-C)$, $\varphi(CH_2)$	Helical (crystalline)
1061	$\nu(C-CH_3)$	Helical (crystalline)
1085	$\nu(C-C)$	Helical (crystalline)

Figure 4 Changes in peak height in infrared bands at 1005, 978, 963, 905, 867 and 812 cm^{-1} as a function of time during the heating process of syndiotactic polypropylene. The heating rate is $5\,^{\circ}C\,min^{-1}$.

simultaneously. Considering the band assignments[39] and intensity changes during the melting process of sPP, it is suggested that the band at 963 cm^{-1} is sensitive to the amorphous component, which is partially composed of the planar zigzag conformational form.

It should be noted that the multiple melting peaks on the DSC curve of sPP, as shown in Figure 1, cannot be revealed by FTIR measurements. This is because the melting of sPP at the first melting peak is followed by instantaneous recrystallization, and the recrystallization rate is too fast to be resolved by the experimental procedure used here. Similar results have been reported in the literature.[40]

Crystallization process of sPP
The isothermal crystallization of sPP was achieved by melting the sample at 170 $^{\circ}C$ for 5 min and then the melted sPP film was cooled at a cooling rate of 15 $^{\circ}C\,min^{-1}$ to 105 $^{\circ}C$ for isothermal crystallization. The temperature for isothermal crystallization was 15 $^{\circ}C$ higher than the initial crystallization temperature of 90 $^{\circ}C$ on the DSC curve of sPP, as shown in Figure 1. Figure 5a shows the spectral changes of the sPP film in the region of 1100–750 cm^{-1} as a function of the isothermal crystallization time. Figure 5b depicts the difference spectra obtained by subtraction of the initial spectrum from the spectra shown in Figure 5a. The results clearly show that the bands associated with the helical conformation of sPP at 1005, 978, 905, 867 and 812 cm^{-1} increase with crystallization time, whereas the band 963 cm^{-1} associated with the planar zigzag conformation of sPP decreases with crystallization time. To identify the specific sequence of these bands during the isothermal crystallization process of sPP, 2D-IR correlation spectroscopy analysis was carried out carefully, which involves both synchronous and asynchronous correlation spectra. The synchronous spectrum represents the intramolecular interactions or correlation of groups corresponding to spectral intensity, whereas the asynchronous spectrum represents sequential or successive changes of spectral intensities measured at different peak positions.

Figure 6 shows the synchronous and asynchronous correlation spectra of sPP in the region of 1020–800 cm^{-1}, which are calculated from the spectra in Figure 5a. In the synchronous map (Figure 6a),
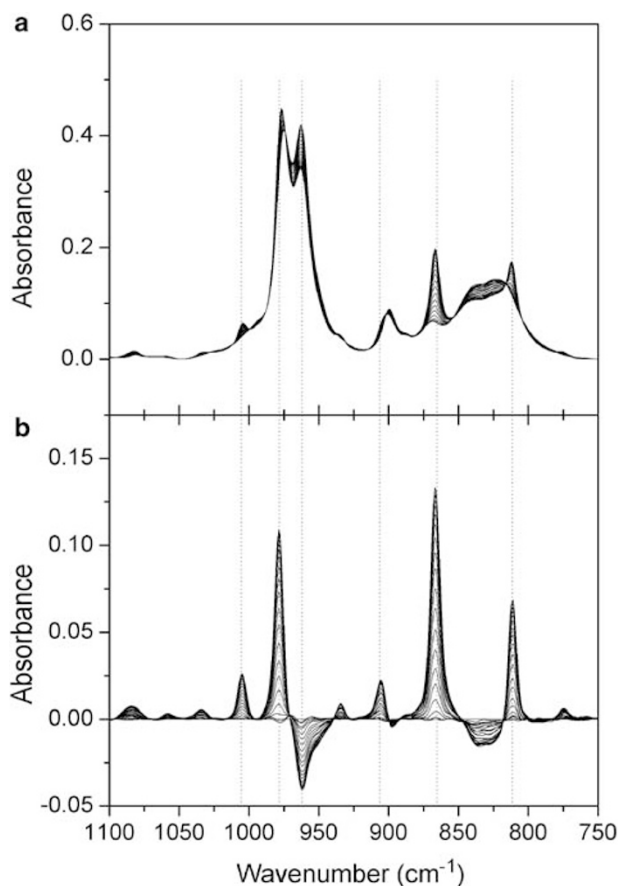
Figure 5 (a) Time-dependent Fourier transform infrared spectra of syndiotactic polypropylene annealed at 105 °C in the wavenumber region of 1100–750 cm^{-1} and (b) difference spectra obtained by the subtraction of initial spectra obtained from the spectra shown in panel a.
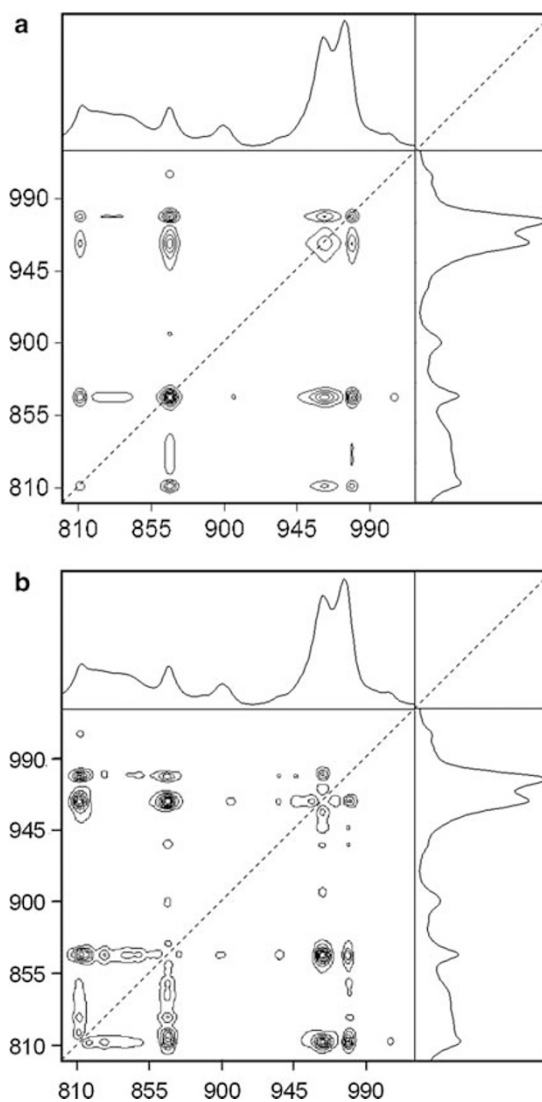

Figure 6 Synchronous (a) and asynchronous (b) two-dimensional (2D) infrared correlation spectra of syndiotactic polypropylene in the wavenumber region of 1020–800 cm^{-1}, calculated from spectra obtained during the isotherm crystallization process at 105 °C. In the 2D correlation maps, the unshaded and shaded areas in contour maps represent positive and negative peaks, respectively.

autopeaks are located at 812, 867, 963 and 978 cm^{-1}; positive cross-peaks are observed at $\Phi(978, 867)$ and $\Phi(978, 812)$ cm^{-1}, whereas negative cross-peaks are observed at $\Phi(978, 963)$, $\Phi(963, 867)$ and $\Phi(963, 812)$ cm^{-1}. Results show that the intensities of crystalline component bands increase with time during isothermal crystallization at 105 °C, whereas that of the amorphous component band decreases with the isothermal crystallization time at 105 °C. The order of IR absorption bands can be clearly separated in the asynchronous correlation map shown in Figure 6b. In the asynchronous map, three positive cross-peaks are located at $\psi(978, 963)$, $\psi(978, 867)$ and $\psi(978, 812)$ cm^{-1}, and two negative cross-peaks are located at $\psi(963, 867)$ and $\psi(963, 812)$ cm^{-1}. Compared with the results of synchronous correlation analysis, the asynchronous spectrum provides additional information about the order of intensity changes of the different IR absorption bands during isothermal crystallization. According to Noda's rules,[29,30] the change in the 963 cm^{-1} band occurs before that of the 978 cm^{-1} band, and the change in the 978 cm^{-1} band precedes that of the 867 and 812 cm^{-1} bands. That is to say, during isothermal crystallization at 105 °C, the amorphous component in the samples initially changes in terms of the molecular chain conformation during isothermal crystallization, after which the polymer chains adjust their local conformations to form crystalline phases during crystallization.

According to the assignments of the IR absorption bands of sPP (Table 1), the bands at 978, 867 and 812 cm^{-1} can be attributed to the

helical conformation sequence within sPP chains. Generally, the structural changes of various groups within polymer chains occur cooperatively during crystallization. However, in the case of the isothermal crystallization of sPP, the different rates of change for helix bands by 2D correlation spectra analysis are unambiguous. As only the Form I crystal could be obtained at this temperature,[34] it is reasonable to assign these different rates of change of regular bands to the contribution of the ordered molecular arrangement along the molecular chain direction. To explain the correlation between crystallinity and IR bands in the spectra of sPP, Guadagno et al.[38] suggested that the band at 978 cm^{-1} is sensitive to both the crystallinity and fraction of the mesophase. Indeed, from the viewpoint of molecular conformation, the so-called mesophase should be the fraction with a less-ordered molecular conformation than the crystalline phase. Therefore, it seems that the difference in the rates of change within the helical bands during the process of formation of the Form I

crystals of sPP should be related to the fraction with a less-ordered molecular conformation. Considering the band assignments and the order of intensity changes, it is reasonable to suppose that the band at $978\,cm^{-1}$ corresponds to a lower-ordered helical sequence than the bands at 867 and $812\,cm^{-1}$. This suggests that, before the close packing of the 4_1 helical chains of sPP, the local molecular conformation is already changed and arranged into some ordered short helical sequences. Strobl and colleagues[4–6,41] proposed a four-state scheme for treating polymer crystallization and suggested that the primary crystallization from the melt produces an imperfect 'native' crystal in the first step, which is subsequently stabilized by structural relaxation processes. However, direct evidence for the occurrence of a mesophase or 'native' crystal between the equilibrated melt and ordered crystallites is absent during the isothermal crystallization of sPP. Moreover, in situ IR and 2D-IR correlation spectroscopy analyses, which are sensitive to intramolecular interactions, can also shed additional light on the polymer crystallization theory, which usually relies heavily on light scattering and morphology data. Therefore, the results mentioned above may be helpful in understanding the crystallization process of semicrystalline polymers from the viewpoint of molecular conformational changes.

CONCLUSION

During the melting process of sPP, the intensity of helical conformational bands decreases and the intensity of the band located at $963\,cm^{-1}$, which is sensitive to the amorphous component, increases with increasing temperature. In the early stage of the melting process of sPP, helical chains do not immediately collapse and thus remain in an ordered helical conformation. Using the analysis of the difference spectra and 2D correlation spectra, it was found that the intensity change of band at $978\,cm^{-1}$ precedes that of bands at 812 and $867\,cm^{-1}$ and lags behind that of the band at $963\,cm^{-1}$ during the crystallization process. It is suggested that the amorphous phase changes first, then the polymer chains adjust their local conformations to form short helical conformations and finally the crystalline phase forms.

ACKNOWLEDGEMENTS

1 Hoffman, J. D. Regime III crystallization in melt-crystallized polymers: the variable cluster model of chain folding. *Polymer* **24,** 3 (1983).
2 Hoffman, J. D. Theory of the substrate length in polymer crystallization: surface roughening as an inhibitor for substrate completion. *Polymer* **26,** 1763 (1985).
3 Cheng, S. Z. D. & Lotz, B. Enthalpic and entropic origins of nucleation barriers during polymer crystallization: the hoffman-lauritzen theory and beyond. *Polymer* **46,** 8662 (2005).
4 Hauser, G., Schmidtke, J. & Strobl, G. The role of co-units in polymer crystallization and melting: new insights from studies on syndiotactic poly(propene-co-octene). *Macromolecules* **31,** 6250 (1998).
5 Strobl, G. From the melt via mesomorphic and granular crystalline layers to lamellar crystallites: a major route followed in polymer crystallization? *Eur. Phys. J. E.* **3,** 165 (2000).
6 Strobl, G. Crystallization and melting of bulk polymers: new observations, conclusions and a thermodynamic scheme. *Prog. Polym. Sci.* **31,** 398 (2006).
7 Olmsted, P. D., Poon, W. C. K., McLeish, T. C. B., Terrill, N. J. & Ryan, A. J. Spinodal-assisted crystallization in polymer melts. *Phys. Rev. Lett.* **81,** 373 (1998).
8 Gee, R. H., Lacevic, N. & Fried, L. E. Atomistic simulations of spinodal phase separation preceding polymer crystallization. *Nat. Mater.* **5,** 39 (2006).
9 Lacevic, N., Fried, L. E. & Gee, R. H. Heterogeneous directional mobility in the early stages of polymer crystallization. *J. Chem. Phys.* **128,** 014903 (2008).
10 Matsuba, G., Kanaya, T., Saito, M., Kaji, K. & Nishida, K. Further evidence of spinodal decomposition during the induction period of polymer crystallization: time-resolved small-angle X-ray scattering prior to crystallization of poly(ethylene naphthalate). *Phys. Rev. E* **62,** R1497 (2000).
11 Imai, M., Kaji, K., Kanaya, T. & Sakai, Y. Ordering process in the induction period of crystallization of poly(ethylene-terephthalate). *Phys. Rev. B* **52,** 12696 (1995).
12 Imai, M., Kaji, K. & Kanaya, T. Orientation fluctuations of poly(ethylene-terephthalate) during the induction period of crystallization. *Phys. Rev. Lett.* **71,** 4162 (1993).
13 Matsuba, G., Kaji, K., Nishida, K., Kanaya, T. & Imai, M. Conformational change and orientation fluctuations prior to the crystallization of syndiotactic polystyrene. *Macromolecules* **32,** 8932 (1999).
14 Matsuba, G., Kaji, K., Kanaya, T. & Nishida, K. Detailed analysis of the induction period of polymer crystallization by depolarized light scattering. *Phys. Rev. E* **65,** 061801 (2002).
15 Soccio, M., Nogales, A., Lotti, N., Munari, A. & Ezquerra, T. A. Evidence of early stage precursors of polymer crystals by dielectric spectroscopy. *Phys. Rev. Lett.* **98,** 037801 (2007).
16 Fukao, K. & Miyamoto, Y. Dynamical transition and crystallization of polymers. *Phys. Rev. Lett.* **79,** 4613 (1997).
17 Das, N. C., Hikosaka, M., Okada, K., Toda, A. & Inoue, K. Nucleation and size distribution of nucleus during induction period of polyethylene crystallization. *J. Chem. Phys.* **123,** 204906 (2005).
18 Okada, T., Saito, H. & Inoue, T. Time-resolved light-scattering-studies on the early stage of crystallization in isotactic polypropylene. *Macromolecules* **25,** 1908 (1992).
19 Wang, Z. G., Hsiao, B. S., Sirota, E. B., Agarwal, P. & Srinivas, S. Probing the early stages of melt crystallization in polypropylene by simultaneous small- and wide-angle X-ray scattering and laser light scattering. *Macromolecules* **33,** 978 (2000).
20 Zhang, J. M., Duan, Y. X., Shen, D. Y., Yan, S. K., Noda, I. & Ozaki, Y. Structure changes during the induction period of cold crystallization of isotactic polystyrene investigated by infrared and two-dimensional infrared correlation spectroscopy. *Macromolecules* **37,** 3292 (2004).
21 Panine, P., Di Cola, E., Sztucki, A. & Narayanan, T. Early stages of polymer melt crystallization. *Polymer* **49,** 676 (2008).
22 Zhu, X. Y., Yan, D. Y. & Fang, Y. P. In situ FTIR spectroscopic study of the conformational change of isotactic polypropylene during the crystallization process. *J. Phys. Chem. B* **105,** 12461 (2001).
23 Nakaoki, T., Yamanaka, T., Ohira, Y. & Horii, F. Dynamic FT-IR analysis of the crystallization to the planar zigzag form for syndiotactic polypropylene. *Macromolecules* **33,** 2718 (2000).
24 Jiang, Y., Gu, Q., Li, L., Shen, D. Y., Jin, X. G. & Chan, C. M. Conformational changes in the induction period of crystallization as measured by FT-IR. *Polymer* **44,** 3509 (2003).
25 Yan, C., Li, H. H., Zhang, J. M., Ozaki, Y., Shen, D. Y., Yan, D. D., Shi, A. C. & Yan, S. K. Surface-induced anisotropic chain ordering of polycarprolactone on oriented polyethylene substrate: epitaxy and soft epitaxy. *Macromolecules* **39,** 8041 (2006).
26 Zhu, X. Y., Yan, D. Y., Yao, H. X. & Zhu, P. F. In situ FTIR spectroscopic study of the regularity bands and partial-order melts of isotactic polypropylene. *Macromol. Rapid Commun.* **21,** 354 (2000).
27 Zhu, X. Y., Li, Y. J., Yan, D. Y. & Fang, Y. P. Crystallization behavior of partially melting isotactic polypropylene. *Polymer* **42,** 9217 (2001).
28 Noda, I. Generalized 2-dimensional correlation method applicable to infrared, raman, and other types of spectroscopy. *Appl. Spectrosc.* **47,** 1329 (1993).
29 Noda, I., Dowrey, A. E., Marcott, C., Story, G. M. & Ozaki, Y. Generalized two-dimensional correlation spectroscopy. *Appl. Spectrosc.* **54,** 236A (2000).
30 Noda, I. Determination of two-dimensional correlation spectra using the hilbert transform. *Appl. Spectrosc.* **54,** 994 (2000).
31 Peng, Y. & Wu, P. Y. A two dimensional infrared correlation spectroscopic study on the structure changes of PVDF during the melting process. *Polymer* **45,** 5295 (2004).
32 Zhang, J. M., Tsuji, H., Noda, I. & Ozaki, Y. Weak intermolecular interactions during the melt crystallization of poly(L-lactide) investigated by two-dimensional infrared correlation spectroscopy. *J. Phys. Chem. B* **108,** 11514 (2004).
33 Zhang, J. M., Tsuji, H., Noda, I. & Ozaki, Y. Structural changes and crystallization dynamics of poly(L-lactide) during the cold-crystallization process investigated by infrared and two-dimensional infrared correlation spectroscopy. *Macromolecules* **37,** 6433 (2004).
34 Guadagno, L., D'Aniello, C., Naddeo, C., Vittoria, V. & Meille, S. V. Development of form II crystallinity in oriented syndiotactic polypropylene: role of the trans-planar mesophase. *Macromolecules* **36,** 6756 (2003).
35 Sevegney, M. S., Parthasarthy, G., Kannan, R. M., Thurman, D. W. & Fernandez-Ballester, L. Deformation-induced morphology changes and orientation behavior in syndiotactic polypropylene. *Macromolecules* **36,** 6472 (2003).
36 Sevegney, M. S., Kannan, R. M., Siedle, A. R., Naik, R. & Naik, V. M. Vibrational spectroscopic investigation of stereoregularity effects on syndiotactic polypropylene structure and morphology. *Vib. Spectrosc.* **40,** 246 (2006).
37 Sevegney, M. S., Kannan, R. M., Siedle, A. R. & Percha, P. A. FTIR spectroscopic investigation of thermal effects in semi-syndiotactic polypropylene. *J. Polym. Sci. Pt. B-Polym. Phys.* **43,** 439 (2005).
38 Guadagno, L., D'Arienzo, L. & Vittoria, V. Correlation between crystallinity and some infrared bands in the spectra of syndiotactic polypropylene. *Macromol. Chem. Phys.* **201,** 1465 (2000).
39 Peraldo, M. & Cambini, M. Infra-red spectra of syndiotactic polypropylene. *Spectrochimica Acta* **21,** 1509 (1965).
40 Duan, Y. X., Zhang, J. M., Shen, D. Y. & Yan, S. K. In situ FTIR studies on the cold-crystallization process and multiple melting behavior of isotactic polystyrene. *Macromolecules* **36,** 4874 (2003).
41 Schmidtke, J., Strobl, G. & ThurnAlbrecht, T. A four-state scheme for treating polymer crystallization and melting suggested by calorimetric and small angle X-Ray scattering experiments on syndiotactic polypropylene. *Macromolecules* **30,** 5804 (1997).