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Structural Evolution Process of *isotactic* Polypropylene in the Isothermal Crystallization from the Melt

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Abstract. The melt-isothermal crystallization behaviour has been investigated for *isotactic* polypropylene (iPP) by means of time-resolved simultaneous measurements of small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) using synchrotron radiation source in SPring-8. The time-resolved Fourier-transform infrared spectral (FTIR) measurements were also performed to clarify the formation process of helices. The SAXS data were analyzed on the basis of Guinier (isolated domains) and Debye-Bueche (correlated domains) theories and correlation function (stacked lamellae). The results were combined with the FTIR data, allowing us to draw the concrete structural evolution process including the formation of regular helices and their growth, the correlation of higher density domains consisting of these helices, and the increment of correlation between the neighbouring lamellae to build up the stacked lamellar structure of higher crystallinity.

1. Introduction

When a semicrystalline polymer is cooled from the melt it exhibits higher-order structure, which is built up with a complex combination of crystalline, amorphous and intermediate regions. The mechanical properties sensitively depend on this higher-order structure [1]. We need to understand the formation of higher-order structure at molecular level in the crystallization process to develop polymer materials with excellent properties. *isotactic* Polypropylene (iPP) is one of the industrially-important polymers. The crystallization behavior of iPP is quite complex. Although there have been published many reports concerning the structural evolution process of iPP, the details have not yet been clarified enough well [2-4]. In order to establish the structure-property relationship of iPP we need to understand the crystallization phenomenon from the formation of higher order structure to the regular helical chain. The combination of SAXS and WAXD techniques with the vibrational spectroscopy is one of the most useful methods for this purpose. The analysis of infrared bands with
different critical sequence lengths or different number of monomeric units \( (m) \) included in the regular helix is useful to know the growth of regular helical chain [5-7]. The infrared band can be detected for the first time when the regular helical chain length exceeds the \( m \) value. The time-resolved FTIR measurements may tell us the behavior of the infrared bands with the different \( m \) values, from which the regularization process of random coils in the melt can be traced concretely [6, 7]. On the other hand, the analysis of the time-resolved SAXS and WAXD data may give us the information about the formation of stacked lamellar structure and crystal lattice, respectively. The combination of these different information obtained by IR and X-ray measurements should be quite useful to propose the structural evolution process of iPP in the isothermal crystallization phenomenon from the melt, as will be described in the present paper.

2. Experimental
The pure deuterated and hydrogenated iPP sample had the molecular weight \( M_w = 1.6 \times 10^5 \text{ g mol}^{-1} \) and \( M_w/M_n = 3.0 \). In the isothermal crystallization experiment, after keeping the sample in the melt for a while to erase all the thermal histories, the sample was rapidly transferred to \( T_c \) \((127 ^\circ \text{C})\) by using a temperature jump cell. The simultaneous SAXS and WAXD measurements were performed in the BL40B2 beam-line at SPring-8, Japan. The time-resolved FTIR measurements were performed at time interval 3 sec using a Varian FTS7000 spectrometer.

3. Results and Discussion
Figure 1 (a) shows the SAXS profiles detected in the isothermal crystallization process after the temperature jump. Before the appearance of the so-called long period peak, the SAXS profiles change remarkably in the low \( q \) range, where \( q \) is a scattering vector. The following process might be

![Figure 1](image-url)
speculated as a possibility to interpret these SAXS data. The density fluctuation may occur in the melt and some denser regions start to grow to some domains. But these domains are isolated each other. With the passage of time the domains become larger and go to gathering together, and finally a stacked lamellar structure may be formed from these highly-correlated domains. On the basis of these concepts, the SAXS data were analyzed using (i) Guinier plot for an isolated domain \[ \ln[I(q)] = \ln[I(0)] - q^2 R_g^2/3, \]
\[ R_g = \text{the radius of gyration of an isolated domain}, \]
(ii) Debye-Bueche plots for the two-phase structure \[ I(q) = A/(1 + \xi^2 q^2)^2, \]
\[ \xi = \text{correlation length of neighbouring domains} \]
and (iii) the correlation function for a stacked lamellar structure
\[ K(z) = \langle \eta(z') - \langle \eta \rangle \rangle \ [ \langle \eta(z+z') - \langle \eta \rangle \rangle ] = 2 \int_0^\infty (\pi)^{-1} q^2 I(q) \cos(qz) dq. \]

Figure 2. Time dependence of infrared spectra measured for iPP sample at \( T_c = 127 \) °C in the isothermal crystallization process from the melt.

Figure 3. Comparison of infrared band intensity changes with the SAXS (invariant \( Q \)), the domain size (\( R_g \)), correlation length (\( \xi \)) and long period (\( L \)) estimated in the later stage of isothermal crystallization process for iPP sample \( (T_c = 127 \) °C).
Figure 2 shows the time dependence of infrared spectra measured for iPP sample in the isothermal crystallization process at $T_c = 127^\circ$C. The timing of detection of crystallization-sensitive band is different. For example, the band at 998 cm$^{-1}$ started to increase in intensity at around 20 sec after the temperature reached $T_c$. The 841 cm$^{-1}$ band was detected at ca. 30 sec. Another band at 1220 cm$^{-1}$ appeared after ca. 80 seconds. These bands have different critical sequence length $m$ of 10, 14, and longer than 15 monomeric units, respectively.

Figure 3 compares the time dependence of infrared and X-ray data in the isothermal crystallization process of iPP sample at $T_c = 127^\circ$C. After the sample temperature reached the $T_c$ at 0 sec, the amorphous band decreased in intensity and the helical bands at 998, 841 and 1220 cm$^{-1}$ started to appear around 20 sec, 30 sec and 80 sec, respectively. The 998 cm$^{-1}$ band can be detected when the regular helical form is longer than the helix of 10 monomeric units (critical sequence length $m$). Similarly, the band at 841 cm$^{-1}$ for $m = 14$ and the band at 1220 cm$^{-1}$ for $m > 15$. The difference of timing of detection of these bands indicates that the short helices appear after the start of isothermal crystallization and they grow to longer helices with time. In Figure 3, the radius of gyration $R_g$ of isolated domains decreases gradually in parallel to the appearance of these regular helices and their growth. These domains are correlated more strongly and the SAXS profile started to change at around 100 sec. The SAXS data were analyzed by Debye-Bueche equation. At around 100 sec, the $\xi$ value was almost equal to $R_g$ and it started to decrease linearly, during which the regular helical lengths continue to increase. The $\xi$ value starts to deviate from the linear line at about 300 sec, where the peak corresponding to the lamellae started to appear as noticed from the rising up of the invariant $Q$ the degree of crystallinity. At this point the WAXD peaks were also observed clearly. Figure 4 shows the schematic illustration of the structural changes in the isothermal crystallization process deduced from all the experimental data of FTIR, SAXS and WAXD.

![Schematic diagram showing structural evolution process in iPP sample deduced from the combination of FTIR and SAXS/WAXD data (refer to Figure 3).](image)

References