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Crystallization of isotactic polypropylene from mesomorphic phase: a constant heating rate study

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Abstract. We have studied crystallization behaviour of isotactic polypropylene (iPP) from mesomorphic phase in structural point of view. Time-resolved wide-angle X-ray diffraction (WAXD) measurements during a heating process have been performed using a synchrotron radiation (SR) X-ray beam line at SPring-8, Japan. The heating process was so programmed to reproduce a thermal trace of differential scanning calorimetry (DSC) with a constant heating rate (10 °C/min) in order to compare the structural change with thermal behaviour. SR-WAXD sensitively detected the crystallization behaviour and we have obtained fractions of alpha-crystal, mesomorphic phase and amorphous phase as a function of temperature by analysing the data. The results showed that the crystallization from mesomorphic phase proceeds in between 60 and 120 °C (meso-alpha transition). During this process, the crystallization from amorphous hardly takes place. The crystalline fraction shows almost constant in between 120 and 140 °C; meanwhile, the mesomorphic fraction still decreases above 120 °C. The crystalline fraction starts to decrease above 140 °C and the most extensively decreases at around 165 °C (melting point). We have also determined the energy level of the mesomorphic phase (meta-stable state) relative to that of alpha-crystal (stable state), considering the balance among the fractions of alpha-crystal, mesomorphic phase and amorphous.

1. Introduction

From a standpoint of thermal process, crystallization of bulk polymer is classified into mainly two categories; one is cooling from molten state and another is heating from "pre-quenched state". In both processes usually growth of spherulites in micrometer scale are observed, though the latter process yields more or less higher nucleus density than the former one. In those polymers "pre-quenched state" is mostly equivalent to "glassy state". However, this is not the case for isotactic polypropylene (iPP). In the heating process of pre-quenched iPP, the growth of spherulites is never observed and the macroscopic appearance is almost transparent up to the melting temperature T_m. The absence of the spherulites and the transparency not necessarily imply that the pre-quenched iPP does not crystallize. The pre-quenched iPP indeed crystallizes in the heating process [1], but the higher order structure is quite different from one that is crystallized from molten state [2]. The specific behaviour of the crystallization of iPP from the pre-quenched state is considered to be due to the presence of mesomorphic phase. IPP has three well-established polymorphisms; such as alpha (monoclinic), beta

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1

(hexagonal) and gamma (orthorhombic) forms [3], however, the mesomorphic phase does not correspond to any polymorphisms. The structure of mesomorphic phase of iPP shows intermediate one between the crystal and amorphous [4]. The mesomorphic phase of iPP is obtained by rapidly quenching molten iPP into low temperature, empirically 0 °C. The mesomorphic iPP lasts stably at room temperature (RT) without transforming into crystal although the nominal glass transition temperature T_g is below RT [5]. Formation of the mesomorphic phase of iPP is exothermic process as was demonstrated by a high-speed differential scanning calorimetry [6, 7]. Considering these characteristics, the mesomorphic phase of iPP is considered a meta-stable state whose energy level is very low comparable to that of crystal.

Differential scanning calorimetry (DSC) is usually a versatile method to examine various transitions among states in polymer materials. However, this method is a rather insensitive to investigate the transition of iPP from mesomorphic phase to crystal, since the majority of the exotherm was completed during the formation of the mesomorphic phase and the remaining exothermic enthalpy is considered to be small as was mentioned in the preceding paragraph. To make the matter more complex, other transitions such as mesomorphic to amorphous and/or amorphous to crystal may co-occur during heating, whose enthalpy are larger than that of the mesomorphic to crystal. Alternatively, the transition should be investigated in structural point of view. In this respect, wide-angle X-ray diffraction (WAXD) measurement is a sensitive method to detect the structural change whether or not the transition is accompanied by exo- or endotherm. Recent developments of high-intensity synchrotron radiation (SR) source and sensitive time-resolved detector system enable in-situ WAXD measurements in the similar thermal trace of DSC measurement. In this study, such a SR-WAXD technique has been applied to investigate crystallization of iPP from mesomorphic phase. Fractions of alpha-crystal, mesomorphic phase and amorphous phase as a function of temperature have been obtained by a component analysis of WAXD profile. The derivative of the crystalline fraction as a function of temperature clearly shows crystallization behaviour of iPP from mesomorphic phase, which backs up the above-mentioned disadvantage of DSC method.

Lastly, combining the structural information by SR-WAXD and DSC measurements, the energy level of mesomorphic phase has been estimated. Although rough estimation of the energy level of mesomorphic phase is possible by assuming the original fraction of mesomorphic phase transforms into the same fraction of alpha-crystal [8, 9], in reality the balance among the fractions of alpha-crystal, mesomorphic phase and amorphous phase as a function of temperature should be taken into consideration for the more precise estimation.

2. Experimental

2.1. Materials and sample preparations
The iPP material has a weight-average molecular weight $M_w = 353000$, a polydispersity of $M_w / M_n = 4.4$, and a degree of isotacticity (a meso pentad value) $mmmm = 0.98$, which was supplied from Idemitsu Unitech Co., Ltd. This isotacticity is higher enough than the critical value (0.68) of isotacticity to form mesomorphic phase [10]. A mesomoprhic phase thin film was obtained by quenching molten iPP to 0 °C by dipping into ice-water. The obtained film was macroscopically transparent and showed two broad peaks in WAXD, which are the characteristics of mesomorphic iPP.

2.2. Measurements
DSC measurements were carried out with a Perkin-Elmer Diamond DSC at a heating rate of 10 °C/min. WAXD measurements were carried out using the beam line BL40B2 in the SR facility, SPring-8, Hyogo, Japan. Wavelength of the incident X-ray was 1.0 Å. The detector used was CMOS flat panel detector from Hamamatsu Photonics K.K. The exposure time was selected to be 0.5 s. A Mettler FP82HT hot stage was used to heat the specimens for WAXD measurements at the same heating rate of the DSC measurement. In both DSC and WAXD measurements, thin films were tightly piled up to the same sample thickness, 0.7 mm, to apply similar thermal conduction within the samples.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC)

Figure 1 shows a DSC curve for a mesomorphic iPP during a heating process. The curve shows a shoulder at around 40 - 50 °C. We assume this shoulder is due to a glass transition like phenomenon of the mesomorphic phase of iPP, though there still is discussion for the origin [11]. It will be discussed elsewhere in this regard. An exothermal shallow peak is observed at around 100 °C. As will be turned out in the WAXD analysis, this exothermal shallow peak is due to the crystallization from the mesomorphic phase. Endotherm starts at around 130 °C and a distinct endothermic peak is observed at around 165 °C. It is unquestionable to assign the distinct endothermic peak to the melting of the crystal.

Integrated areas of these exo- and endothermic peaks do not balance out. This is mainly because that the exothermic enthalpy when the mesomorphic phase transforms into crystal is small, as was mentioned in the introduction. However, it lacks proof to claim these explanations only with the DSC data. This will be discussed in the following section.

3.2. Wide-angle X-ray diffraction (WAXD)

Figure 2 shows in-situ WAXD profiles during a heating process from 30 to 170 °C. Broad peaks appearing at scattering vectors around $q = 10.5$ and 14.9 nm^{-1} for the profiles of low temperatures are characteristics of the mesomorphic iPP. Sharp peaks appearing at $q = 9.7$, 11.5, 12.8 and 15.1 nm^{-1} for the profiles of temperatures between 90 and 160 °C are reflections from alpha-crystal. Single broad peak appearing at $q = 10$ nm^{-1} for the profiles at 170 °C is the so-called amorphous halo.

In order to discuss the crystallization behaviour quantitatively, component analysis for WAXD profiles was carried out assuming each profile consists of three components such as alpha-crystal, mesomorphic, and amorphous, according to the previously reported method [1]. Dividing the integrated intensity of each component by the integrated intensity of observed (total) intensity for each profile, fractions of alpha-crystal Φ_{cryst}, mesomorphic Φ_{meso} and amorphous Φ_{amorph} as a function of temperature during heating process were obtained, as shown in figure 3. The crystallization from mesomorphic phase proceeds in between 60 and 120 °C (meso-alpha transition); this behaviour is the most conspicuous at around 100 °C. During this process, the crystallization from amorphous hardly takes place. The crystalline fraction shows almost constant in between 120 and 140 °C. The maximum crystalline fraction (crystallinity) at this temperature is in disagreement with the original mesomorphic fraction at RT (figure3), at
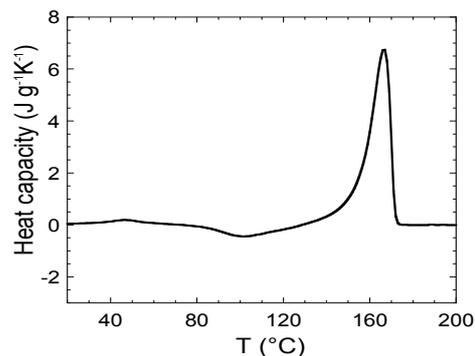
Figure 1. Observed DSC curve for mesomorphic iPP during heating process.
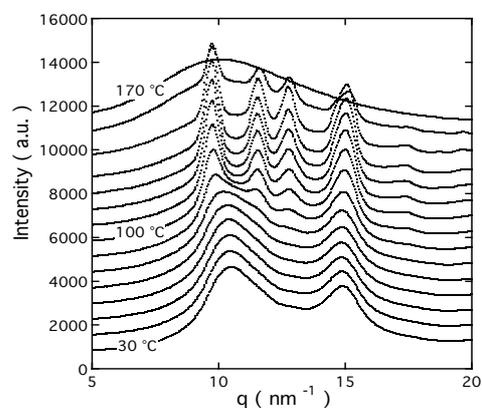
Figure 2. WAXD profiles during heating process from 30 to 170 °C displayed at every 10 °C from bottom to top. The profiles were shifted vertically for clarification.
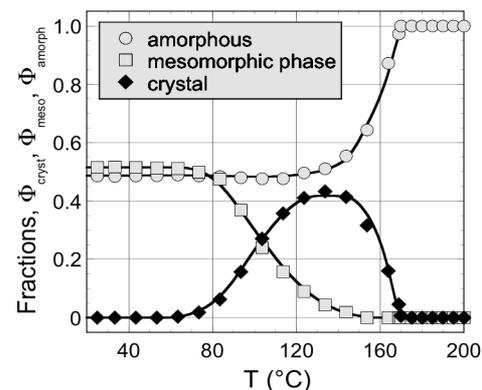
Figure 3. Fractions of alpha-crystal, mesomorphic and amorphous as a function of temperature during heating process.

least in the present experimental condition. A possible reason for this disagreement is that the heating rate of 10 °C/min is not slow enough to let the mesomorphic phase transforms into crystal to the full extent. The crystalline fraction starts to decrease above 140 °C and the most extensively decreases at around 165 °C. Temperature derivative of alpha-crystal fraction $-d\Phi_{cryst}/dT$ more clearly shows crystallization behaviour from mesomorphic phase (figure 4). The integrated areas for the crystallization peak at around 100°C and that for the melting peak at around 165°C are equivalent in principle. With the support of this results, the shallow peak at around 100°C observed in DSC (figure 1) has definitely turned out to be due to the crystallization.

3.3. Energy level of mesomorphic phase
Figure 5 shows schematic diagram of energy levels of alpha-crystal and mesomorphic phase relative to amorphous. Assuming the melting enthalpy of mesomorphic phase (ΔH_{meso}) being x times of that of alpha-crystal (ΔH_{cryst}), namely $\Delta H_{meso} = x \, \Delta H_{cryst}$, the total enthalpy relative to amorphous $\Delta H(T)$ is given by the following equation;

$$\Delta H(T) = \Delta H_{cryst}\Phi_{cryst}(T) + x \, \Delta H_{cryst}\Phi_{meso}(T). \qquad (1)$$

Temperature derivative of $\Delta H(T)$ gives expected value of heat balance. As a reliable value of ΔH_{cryst} was already reported [12], unknown parameter is only x. Figure 6 shows $-d(\Delta H)/dT$ plotted for several values of x. The case when $x = 0.75$ reproduces the experimental DSC well. This value is significantly smaller than the previously reported values (= 0.97 [8] and 0.93 [9]). It is essential to consider the balance among the fractions of alpha-crystal, mesomorphic phase and amorphous phase to obtain the reliable value, otherwise we end up overestimation of the value.

Figure 4. Temperature derivative of alpha-crystal fraction as a function of temperature.
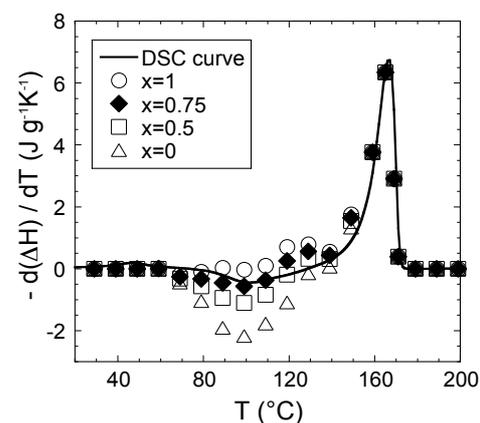
Figure 5. Temperature derivative of total enthalpy as a function of temperature for several numerical parameter x (see text).

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