Spontaneous Crystallization Process of the Planar Zigzag Form at 0 °C from the Melt for Syndiotactic Polypropylene

Yasumasa Ohira and Fumitaka Horii*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Takahiko Nakaoki

Faculty of Science and Technology, Ryukoku University, Otsu, Shiga, 520-2194, Japan

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ABSTRACT: The spontaneous crystallization process of the planar zigzag form (form III) of syndiotactic polypropylene has been investigated at 0 °C for samples quenched from the melt by real-time wide-angle X-ray diffractometry and high-resolution solid-state ^{13}C NMR spectroscopy. The X-ray diffraction profile just after quenched from the melt is in good accord with that of the melt, indicating that the sample is in the noncrystalline state. With increasing crystallization time, broad diffraction peaks assignable to form III are found to evidently appear for the diffraction profile obtained after the subtraction of the noncrystalline contribution. The spontaneous crystallization of form III is also confirmed by high-resolution solid-state ^{13}C NMR spectroscopy; for example, the CH_3(I) line assigned to the *tt* conformation really increased in intensity with increasing crystallization time in concomitancy with the decrease of the CH_3(II) line ascribed to the *tg* conformation. The line shape analysis of these CH_3 lines reveals that the degree of crystallinity rapidly increases up to about 0.10 in 5 h, but this value is still as low as 0.13 even after 4500 h. The additional crystallization of form I with the *ttgg* conformation is also found to be highly hindered for the sample kept at 0 °C for a longer period when it is annealed at room temperature, although this form is readily produced for the sample held at 0 °C for a shorter period. On the basis of these results, a structural model for the crystallization of form III at 0 °C is proposed by considering the possible formation of aggregates composed of the segmental chains with the trans-rich conformations in the noncrystalline region.

Introduction

Recent detailed studies of the polymorphism of syndiotactic polypropylene (sPP) have revealed that four different crystal modifications are formed under different crystallization conditions or by appropriate treatments. Of these, three forms referred to as form I, II, and IV are composed of helical chains in the different unit cells as normally expected for vinyl polymers with side groups; $(ttgg)_n$[1−23] for forms I and II and $(ttggtttttgg)_n$[25,26] for form IV. In fact, conformational energy calculations also indicate that the most stable conformation is $(ttgg)_n$ for sPP.[24] In contrast, the planar zigzag form, which is referred to as form III, is known to be also experimentally produced by cold drawing for sPP films quenched at 0 °C from the melt.[2,3,23,26−29] Since this form undergoes the crystal transformation at about 50 °C,[3,26] its crystallization was believed to proceed in the higher energy state induced by some procedure such as drawing.

Very recently, however, we found for the first time that form III is allowed to be spontaneously crystallized at 0 °C without use of any drawing.[30] In this case the sPP films were quenched at 0 °C from the melt and then crystallized for appropriate periods. The spontaneous crystallization of form III at 0 °C was really confirmed by CP/MAS ^{13}C NMR and wide-angle X-ray diffraction methods on the basis of previous results[26−29] obtained for cold-drawn sPP samples. However, since these measurements were performed at room temperature, form I was additionally crystallized possibly in the heating process from 0 °C to room temperature. Moreover, some change in crystallinity and morphology may be also induced for form III crystals as a result of annealing at room temperature.

In this study, therefore, we investigate the crystallization process of form III at 0 °C for the quenched sPP films by real-time wide-angle X-ray diffractometry and high-resolution solid-state ^{13}C NMR spectroscopy. The latter method is found to be also very powerful in characterizing the conformation and dynamics for sPP as for other semicrystalline polymers such as polyethylene,[31,32] poly(vinyl alcohol),[33,34] liquid crystalline polymers,[35,36] and cellulose.[37,38] Another real-time FT-IR study of the crystallization process of form III will be also published somewhere,[39] and a separate investigation of the crystal transformation from spontaneously crystallized form III to form II is now in progress.

Experimental Section

Samples. The sPP sample with a racemic triad of 0.96, which was provided by Sumitomo Chemical Co. Ltd., was quenched as follows; a sPP film was melted at 170 °C for 10 min under a N_2 atmosphere. Then, it was rapidly cooled to the freezing point of N_2 and was cut into squares of several millimeters. These quenched samples were quickly set up to each apparatus kept at 0 °C without leaving the sample temperature above 0 °C.

Wide-Angle X-ray Diffraction Measurements. Wide-angle X-ray diffraction patterns were obtained at 0 °C with an automatic Rigaku diffractometer equipped with a home-made variable temperature system, using Ni-filtered Cu Kα radiation. The scanning range of 2θ was 5−35° with a step of 0.02°.

Solid-State ^{13}C NMR Measurements. High-resolution solid-state ^{13}C NMR spectra were recorded at 0 °C on a JEOL JNM-GSX200 spectrometer, equipped with a modified JEOL

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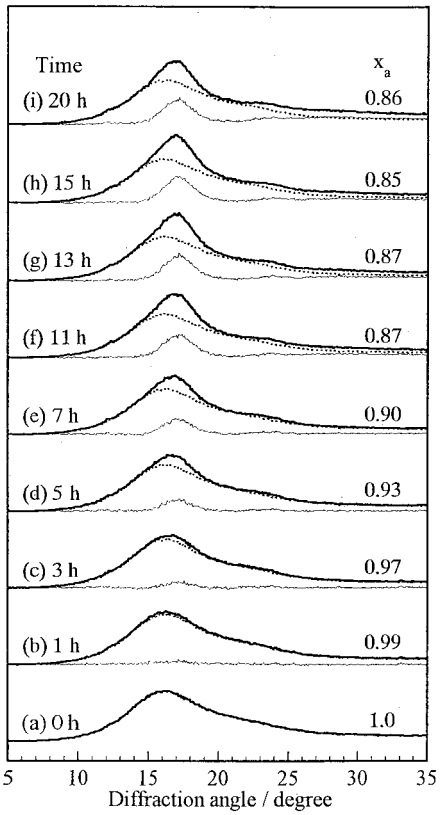

Figure 1. Time change of wide-angle X-ray diffraction profiles measured at 0 °C for the sPP films quenched at 0 °C from the melt.

variable temperature system under a static magnetic field of 4.7 T. The ^{1}H and ^{13}C field strengths $\gamma B_1/2\pi$ were 62.5 kHz. Samples were spun in a zirconia rotor at a rate of 3.0 kHz. CP/MAS ^{13}C NMR spectra were collected with transients of 256, using the following acquisition parameters: the contact time of 1.0 ms for the CP process and the recycle time of 5 s after the acquisition of FID. Dipolar decoupling (DD)/MAS ^{13}C NMR spectra were measured by the $\pi/2$ single pulse sequence with the recycle time of 5 s and transients of 128. ^{13}C chemical shifts were expressed as values relative to tetramethylsilane (Me_4Si) by using the CH_3 line at 17.36 ppm of hexamethylbenzene crystals as an external reference. The sample temperature was calibrated by using the temperature dependence of relative chemical shifts of CH_2 and OH protons of ethylene glycol in a glass ample,[40−42] which was packed with KBr in a MAS rotor. ^{13}C spin−lattice relaxation times (T_{1C}) were measured by using the saturation recovery pulse sequence modified for solid-state measurements.[43,44]

Results and Discussion

Wide-Angle Diffraction Diagrams. Figure 1 shows the time change of the wide-angle X-ray diffraction profile at 0 °C for the sPP sample quenched from the melt to 0 °C without heating it up above this temperature. The observed profiles are drawn as thick solid lines, and numerical values shown at the right side indicate the holding time or the crystallization time at 0 °C. Since the profile just after setting at 0 °C (Figure 1a) is consistent with that for the melt, the sample may be in the noncrystalline state at the initial stage. Each profile shown here seems very broad, but the overall shape is significantly changed with the elapse of time; the main peak position is shifted from about 16° to 17°. To examine whether the change in observed profile is due to the crystallization of form III, subtracted patterns

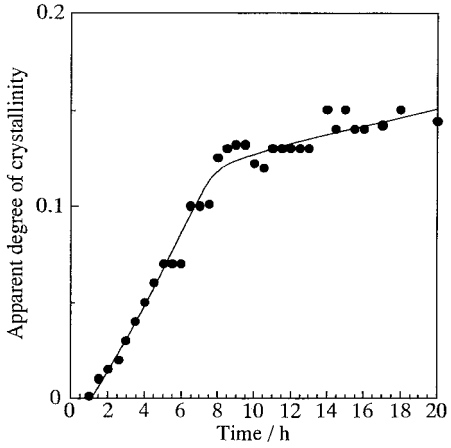

Figure 2. Apparent degree of crystallinity for form III as a function of the crystallization time at 0 °C.

(thin lines) were obtained by subtracting the noncrystalline pattern (dotted line) from each observed profile. Here, the pattern obtained at 0 h was employed as an elementary curve for the noncrystalline component. Each subtraction was conducted by adjusting an intensity factor x_a for the noncrystalline pattern so as to make most part of the baseline for the subtracted pattern horizontal as much as possible. Since the overall integrated intensity for each observed profile stays almost constant, x_a may be regarded as an apparent fraction of the noncrystalline component. As is obviously seen from the patterns (thin lines) thus obtained, two broad peaks appear at $2\theta = \sim 17°$ and 24° with the elapse of time. These peaks were more clearly observed in the same sample measured at room temperature in our previous paper[30] and assigned to the (020)/(110) and (021)/(111) reflections for form III,[28] respectively. It is, therefore, concluded that form III is spontaneously crystallized at 0 °C in several hours. Since the diffraction patterns are very broad, the crystallites produced at 0 °C should be very small, in good accord with the previous result for the cold-drawn sample with several nanometer crystallites.[28] The increase in crystallinity in the heating process to room temperature will be described later. In the previous paper,[30] diffraction peaks ascribed to form I[6−11,19−21] were also evidently recognized for the samples measured at room temperature. Since there exist no diffraction peaks assigned to form I in Figure 1, form I will be additionally crystallized in the heating process to room temperature as discussed somewhat in detail later.

In Figure 2, the apparent degree of crystallinity x_c for form III which is assumed as $x_c = 1 - x_a$ is shown as a function of the crystallization time at 0 °C. With the elapse of time, x_c is remarkably increased until about 8 h, and then the crystallization rate seems to be significantly reduced. Furthermore, the induction period of the crystallization is very short in this system, as is also confirmed by solid-state ^{13}C NMR (in the next section) and FT-IR[39] spectroscopies. From this result, it is found that most of the crystallization of form III occurs within about 8 h, and the level of the crystallinity is as low as about 0.13.

Similar two-step crystallizations are frequently observed when spherulites are formed in a typical growing manner.[45] According to the interpretation for these crystallization processes,[45] the first steep increase in degree of crystallinity is due to the rapid crystal nucleation and growth, while the following reduction in

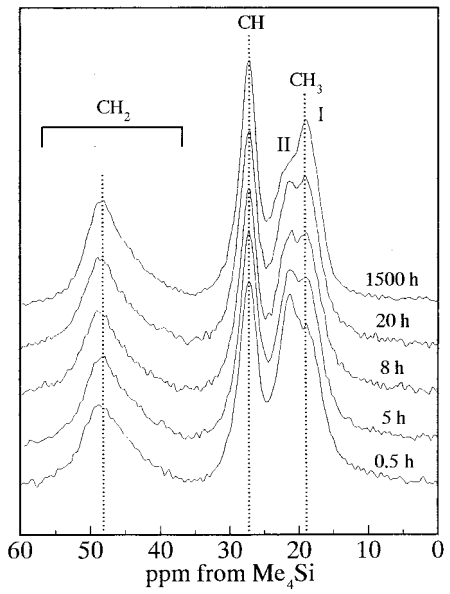

Figure 3. Time change of CP/MAS ^{13}C NMR spectra measured at 0 °C for the sPP films quenched at 0 °C from the melt. Dotted lines indicate the chemical shifts assigned to the respective carbons for the form III crystals.

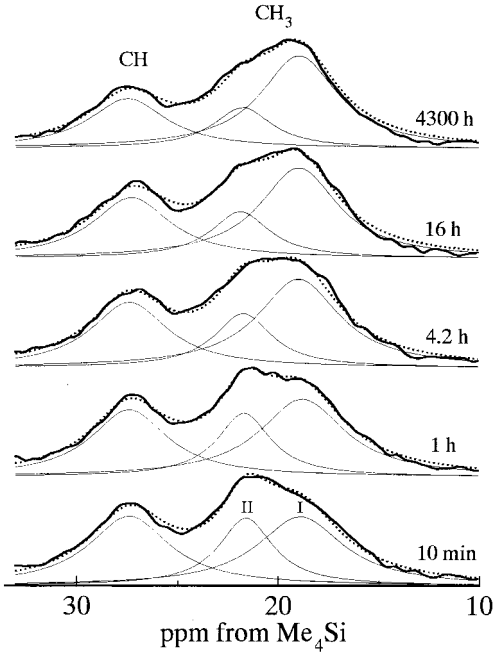

Figure 4. Time change of fully relaxed DD/MAS ^{13}C NMR spectra measured at 0 °C for the sPP films quenched at 0 °C from the melt. The line shape analysis was performed by the least-squares methods by assuming a Lorentzian for each resonance line.

crystallization rate should be ascribed to the collision of the growing spherulites. However, as is clearly understood from Figure 2, it is impossible to interpret the reduction in crystallization rate in terms of the collision of the spherulites in this system, because the degree of crystallinity is extremely low. In fact, the precise degree of crystallinity is also found to be as low as about 0.10 by solid-state ^{13}C NMR measurements as described later. The cause of the prominent decrease in the crystallization rate of form III will be discussed later in detail.

During the crystallization of form III, it is also found that the broad diffraction pattern is not significantly changed in shape as seen in Figure 1. This fact indicates that the increase in crystallite size is not allowed to occur in this system, but the number of crystallites is simply increased with increasing crystallization period.

Analyses of Solid-State ^{13}C NMR Spectra. High-resolution solid-state ^{13}C NMR measurements have been performed for the sample prepared in the same way as for the wide-angle X-ray diffraction measurements. The time change of the CP/MAS ^{13}C NMR spectrum measured at 0 °C for this sample is shown in Figure 3. Here, ^{13}C chemical shift positions corresponding to form III[12,29,30] are also indicated as dotted lines. With increasing crystallization time, the CH_3 resonance line is remarkably changed in shape; the resonance intensity at about 19 ppm increases with increasing time, whereas the intensity at about 22 ppm decreases in the opposite way. Therefore, the increase of the resonance intensity at 19 ppm should be the crystallization process of form III as detected by CP/MAS ^{13}C NMR spectroscopy.

The resonance lines at about 19 and 22 ppm, which are respectively referred to as lines CH_3(I) and CH_3(II) hereafter, have already been assigned to the CH_3 carbons associated with the *tt* and *tg* (or *gt*) conformations for the $CH_2-CH(CH_3)-CH_2$ bond, respectively.[12,23] These assignments are well supported by the results shown in Figure 3; line CH_3(I) is increased in intensity as a result of the crystallization of form III with the planar zigzag conformation, while line CH_3(II) is reduced in intensity by the decrease in the fraction of the noncrystalline component containing the gauche conformations. Here, there is a possibility of exchange between the trans and gauche conformations for the noncrystalline component because 0 °C is somewhat above T_g (about −5 °C) for sPP. However, it was confirmed by the separate examination of the mergence of the CH_3(I) and CH_3(II) lines above T_g that such exchange really occurs at temperatures higher than 10 °C. Accordingly, these lines measured at 0 °C provide exact information about the actual distributions in conformation even in the noncrystalline region.

To determine the degree of crystallinity by using the CH_3(I) and CH_3(II) lines, we have first measured T_{1C} values of these lines at 0 °C by the saturation recovery method modified for solid-state measurements.[43,44] The saturation recovery processes of the CH_3(I) and CH_3(II) lines for the sample crystallized at 0 °C for 1500 h can be well described as single exponentials, resulting in $T_{1C} = 0.66$ and 0.53 s for CH_3(I) and CH_3(II) lines, respectively. These values are much shorter compared to T_{1C} values (30−50 s) obtained for the CH and CH_2 lines, suggesting the enhanced rotation of the CH_3 groups in both crystalline and noncrystalline regions.[12,14]

Figure 4 shows the time change of the DD/MAS ^{13}C NMR spectrum for the sample quenched in the same way as for the samples described above, which was measured at 0 °C by the $\pi/2$ single pulse sequence with a pulse delay time of 5 s. Since the delay time is longer than $5T_{1C}$ for the CH_3 lines, these DD/MAS spectra give fully relaxed resonance lines for the CH_3 carbons. For simplicity, only the CH and CH_3 resonance lines are shown in this figure. It is found that these resonance lines can be well resolved into three Lorentzian curves, which are described as thin lines, by the computer-aided least-squares method. As a result, the total CH_3 line is also satisfactorily resolved into the contributions from the CH_3(I) and CH_3(II) lines. As expected, the intensity

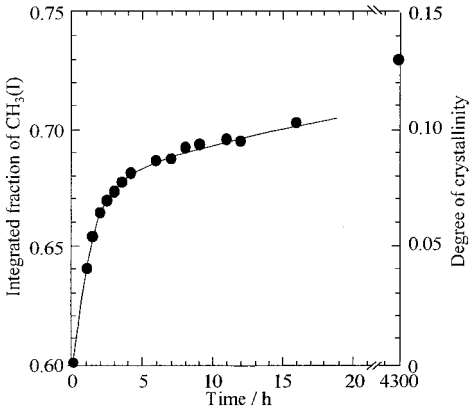

Figure 5. Integrated fraction of the CH_3(I) line or the degree of crystallinity for form III, which was determined by the line shape analysis shown in Figure 4, as a function of the crystallization time.

of the CH_3(I) line is found to be increased with increasing crystallization time.

Figure 5 shows the integrated fraction of the CH_3(I) line against the total CH_3 line shown in Figure 4 as a function of the crystallization time. Since the noncrystalline component may also contain some amount of the *tt* conformation, the integrated fraction of CH_3(I) should not be zero even for the sample just after set at 0 °C. However, this value is unexpectedly as high as 0.60 at $t = 10$ min as is evidently seen in Figure 5. From this value the average trans fraction along the PP chain is estimated to be 0.80. This suggests that the noncrystalline chains are rather locally extended at the initial stage of the crystallization. Almost the same high trans fraction (0.79) was also obtained at about 50 °C for the noncrystalline component by the recent solid-state ^{13}C NMR measurements.[12] Since further detailed studies are in progress on the characterization of the chain conformation of the noncrystalline component at different temperatures, the cause of such a high trans content will be discussed somewhere in near future. Here, we simply determine the degree of crystallinity for this sample as the increment from the initial fraction of CH_3-(I) in the noncrystalline state.

In Figure 5, the degree of crystallinity thus obtained can be read by using the vertical scale at the right side of this figure. With the elapse of the crystallization time, the degree of crystallinity of form III is rapidly increased in initial about 5 h, and then the increase rate becomes much lower. This crystallization process is almost in good accord with that observed by the wide-angle X-ray diffraction measurements shown in Figure 2. However, the real degree of crystallinity is further as low as 0.10 even after 15 h, and this value merely attains to the level of 0.13 after the crystallization at 0 °C for 4300 h.

Effects of Annealing at Room Temperature. Since the degree of crystallinity of form III is extremely low in this sample as shown in Figure 5, there are possibilities of the increase in crystallinity for form III and other additional crystallizations of different polymorphs when the sample is annealed at room temperature. Figure 6 shows wide-angle X-ray diffraction profiles measured at *room temperature* for the samples that were kept at 0 °C for different periods. Here, those periods are indicated on the right side of this figure. Solid and dotted lines denote main diffraction angles assigned to forms III and I, respectively. For the sample held at 0 °C for 6 min relatively strong diffraction peaks

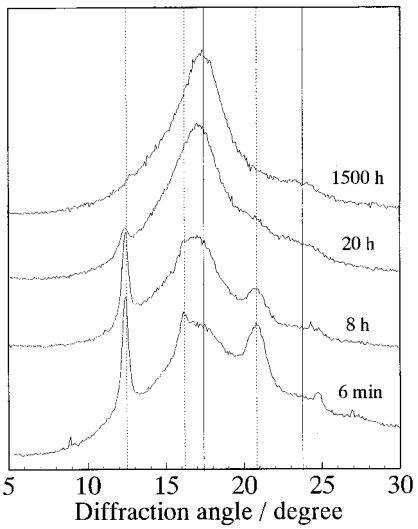

Figure 6. Wide-angle X-ray diffraction profiles measured at room temperature for the sPP films kept at 0 °C for different periods: The solid and dotted lines indicate the diffraction angles assigned to forms III and I, respectively.

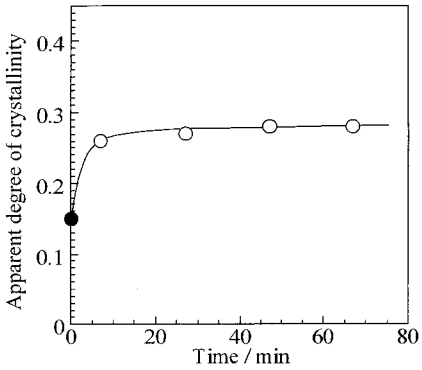

Figure 7. Time change in apparent degree of crystallinity during annealing at room temperature for the sPP films kept at 0 °C for 24 h.

of form I are clearly observed, indicating that form I crystals are additionally produced during the heating and annealing processes at room temperature. However, the diffraction intensity of form I is prominently decreased with increasing holding time at 0 °C. Finally, almost no diffraction peaks of form I are observed for the sample kept at 0 °C for 1500 h. Since the degree of crystallinity stays as low as about 0.12 at 0 °C for this sample, it is not plausible to assume that the crystallites of form III may hinder the additional crystallization of form I. There may be produced segmental aggregates that are composed of the locally extended noncrystalline chains as described above, and the additional crystallization of form I will be hindered by them. These structural entities will not contribute to crystalline wide-angle diffraction patterns but may be assumed to be embryos for the crystallization of form III at room temperature. In fact, the apparent degree of crystallinity of form III obtained by X-ray diffractometry has found to increase from 0.15 to 0.28, as shown in Figure 7, for the sample kept at 0 °C for 24 h, when this sample is annealed at room temperature for about 1 h. In particular, it should be noted that most of the increase in degree of crystallinity is induced within about 10 min. This fact implies that segmental aggregates, which highly restrict the additional crystallization of form I as described above, will preferably promote the further crystallization of form III probably as its embryos. Since

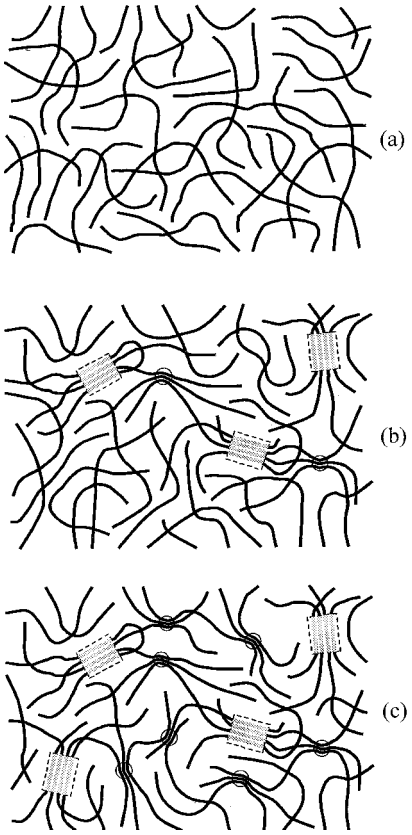

Figure 8. A schematic structural model for the spontaneous crystallization process of form III at 0 °C. Small circles indicate possible aggregates composed of noncrystalline chains with the trans-rich conformations.

the diffraction pattern was not significantly changed in broadness by annealing at room temperature (not shown here), the increase in degree of crystallinity may be mainly due to the increase in number of the crystallites. More detailed annealing experiments including the crystal transformation from form III to form II at somewhat higher temperatures are in progress, and the results will be published somewhere in the near future.

Schematic Structural Model for the Crystallization of Form III. On the basis of the results described above, we propose a structural model for the spontaneous crystallization process of form III at 0 °C as shown in Figure 8. The sample just after being quenched at 0 °C from the melt is in the noncrystalline state where the trans−gauche transitions are highly inhibited. Moreover, since the trans content is found to be as high as 0.80, each sPP chain should be locally rather extended as shown in Figure 8a. With the elapse of crystallization time at 0 °C, form III is spontaneously crystallized without any mechanical force such as drawing (Figure 8b). However, about 70% crystallization occurs within about 5 h in this system, and the degree of crystallinity is as low as about 0.13 even after the crystallization for 4500 h. Such a low level crystallinity may be interpreted by assuming that some sort of small-size aggregates composed of the noncrystalline segments will be formed and hinder the further crystallization of form III, as shown in Figure 8c. Although it is very difficult to experimentally observe such aggregates at present, it may be plausible to assume that the locally extended chains with the trans-rich conformations are apt to aggregate with each other. These aggregates must also greatly hinder the additional crystallization of form I when the sample kept at 0 °C for a somewhat longer period is annealed at room temperature, because form I can be really produced for the sample kept at 0 °C for a shorter period. In contrast, form III is allowed to be further crystallized for the sample kept at 0 °C for a long period when it is annealed at room temperature, as described in the previous section. This fact suggests that the aggregates may be embryos for the crystallization of form III at room temperature. However, the crystallization of form III through these embryos may be not induced at 0 °C probably because the conformational change from the gauche to trans will be impossible in the aggregated state. Form III is assumed to be produced at 0 °C simply by the reorientation of individual noncrystalline chains. Further discussion will be made after obtaining more information about the crystallization of forms III and I at different temperatures as well as about the crystal transformation from form III to form II.

Conclusion

Real-time wide-angle X-ray diffraction and high-resolution solid-state ^{13}C NMR measurements have been carried out at 0 °C for syndiotactic polypropylene films quenched from the melt to investigate the spontaneous crystallization process of form III with the planar zigzag conformation, and the following conclusions have been obtained:

The wide-angle diffraction pattern is almost the same as that of the melt for the sample just quenched from the melt, implying the noncrystalline state at the initial stage of crystallization at 0 °C. However, the line shape analysis of the CH_3 resonance line described below indicates that the fraction of the trans conformation is as high as 0.80 in this noncrystalline state, and the resulting chains may be locally rather extended.

With the elapse of crystallization time, the wide-angle diffraction profile is significantly changed in shape. The subtracted diffraction patterns, which are obtained by the subtraction of the noncrystalline contribution from the total, indicate that form III is spontaneously crystallized at 0 °C, but the degree of crystallinity and the crystallite size are at considerably low levels.

In high-resolution solid-state ^{13}C NMR spectra, the CH_3 resonance line is resolved into two lines, CH_3(I) and CH_3(II), that are assigned to the *tt* and *tg* conformations, respectively. The degree of crystallinity determined by this line shape analysis is increased up to about 0.10 in 5 h, but it attains only to about 0.13 even after the crystallization for 4500 h.

Form I with the *ttgg* conformation is found to be additionally produced by annealing at room temperature for the samples kept at 0 °C for shorter periods. In contrast, such an additional crystallization of form I is completely inhibited for the samples held at 0 °C for longer periods, although form III increased in degree of crystallinity by this annealing almost irrespective of the holding time at 0 °C.

A structural model is proposed for the spontaneous crystallization process for form III. In particular, some sort of aggregates that are composed of the noncrystalline chains with the trans-rich conformations should be assumed to interpret the experimental results described above.

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