Spontaneous Crystallization of the Planar Zigzag Form of Syndiotactic Polypropylene at 0 °C

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Received January 9, 1998
Revised Manuscript Received February 28, 1998

Introduction. Recently, syndiotactic polypropylene (sPP) with high stereoregularity was synthesized by Ewen et al.[1] Whereas early investigations carried out by using less syndiotactic samples had difficulties in precise characterization, the success of highly stereoregular polymerization made the detailed analysis of the crystal structure possible. A large number of investigations on the molecular chain conformation and molecular packing in crystals have also been reported for sPP. As for the polymorphs, four crystalline forms are known: the planar zigzag,[2−5] $t_2g_2t_6g_2$,[6−8] and two forms with the t_2g_2 conformation.[9−22] Of these, the crystals with the planar zigzag conformation have been believed to be formed only by cold drawing after quenching from the melt into an ice−water mixture.[2−5] Very recently, we have found that the crystallization of the planar zigzag form is spontaneously induced at 0 °C without any mechanical stress, although the growth rate is very slow. In this communication, we report briefly the first results to confirm such spontaneous crystallization of the form at 0 °C, which have been obtained by CP/MAS ^{13}C NMR and wide-angle X-ray scattering methods.

Experimental Section. A highly syndiotactic polypropylene sample with an *rr* fraction of 0.96, provided by Sumitomo Chemical Co. Ltd., was used without further purification. CP/MAS ^{13}C NMR spectra were measured at room temperature on a Bruker MSL 200 spectrometer under a static magnetic field of 4.7 T. Magic angle spinning at 3 kHz was achieved with the double air bearing system. The contact time for the cross polarization process was 1 ms and the pulse delay time was 4 s. ^{13}C chemical shifts were expressed as values relative to tetramethylsilane (Me_4Si) by using the CO carbon line at 176.03 ppm of glycine crystals as an external reference. Wide-angle X-ray diffraction patterns were obtained at room temperature on an automatic RIGAKU diffractometer with Ni-filtered Cu Kα radiation.

Results and Discussion. Figure 1 shows CP/MAS ^{13}C NMR spectra of sPP films quenched in ice−water from the melt at 170 °C, which were measured at room temperature. The times shown in this figure indicate the periods for which each film was kept in ice−water. As shown in Figure 1a, the film taken out immediately after quenching in ice−water gives a spectrum similar to the previously reported one;[23] two resonance lines assignable to the methylene carbons clearly appear at 47.7 and 39.1 ppm. Although the downfield line at 47.7 ppm seems to be composed of multiple components

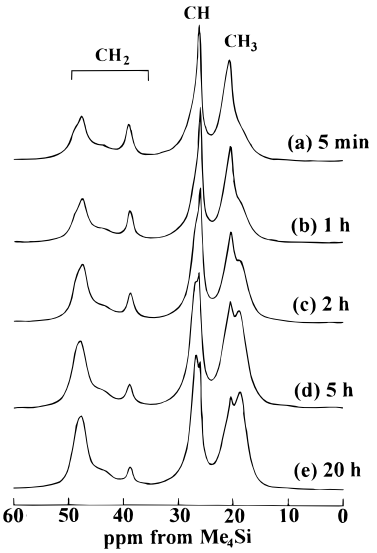

Figure 1. CP/MAS ^{13}C NMR spectra measured at room temperature for sPP films kept in ice−water for different periods after quenching into ice−water from the melt at 170 °C: (a) 5 min; (b) 1 h; (c) 2 h; (d) 5 h; (e) 20 h.

including a noncrystalline one, a line forming a doublet with the upfield line at 39.1 ppm is evidently included in the line at 47.7 ppm.[21,22] Such doublet splitting is induced by the so-called γ-gauche effect[7] for the methylene carbons with different environments in the t_2g_2 helical structure in the crystalline region. The spectral profile begins to change progressively when specimens are soaked in ice−water for a few hours. The signals due to the t_2g_2 conformation are reduced in intensity with increasing time for holding at 0 °C in contrast to new lines at 48.2, 27.0, and 18.8 ppm which increase in intensity. According to the previous reports for the cold drawn sPP samples,[5,21,22] the latter new lines are ascribed to the crystals with the planar zigzag conformation. Moreover, ^{13}C spin−lattice relaxation time (T_{1C}) measurements have confirmed that the lines at 48.2 and 27.0 ppm contain the component with T_{1C} = 30−50 s, which may correspond to the crystalline component, together with the noncrystalline contribution with T_{1C} = 1−5 s and the former fraction increases with the time of holding at 0 °C. It is, therefore, strongly suggested that the crystallization of the planar zigzag form is induced at 0 °C in a period of about 20 h. It is worth noting that, unlike the previous one which employed cold drawing,[2−5] no mechanical stress was applied in this case. It should also be noted that the crystallization of the t_2g_2 form will be additionally favored by the increase in temperature from 0 °C to room temperature after keeping the films at 0 °C. It seems, therefore, that such crystallization has been strongly suppressed by the presence of the crystals with the planar zigzag conformation produced at 0 °C.

To confirm the formation of the crystals with the planar zigzag conformation, X-ray diffraction measurements have been performed for the same samples as used for CP/MAS ^{13}C NMR measurements, as shown in Figure 2. The film kept in ice−water for 5 min provides somewhat narrow diffraction peaks at 2θ = 12.2, 16.3, 16.9, and 20.6° due to the crystal with the t_2g_2 conformation. The structure is identified with the

S0024-9297(98)00032-1 CCC: $15.00
Published on Web 04/03/1998

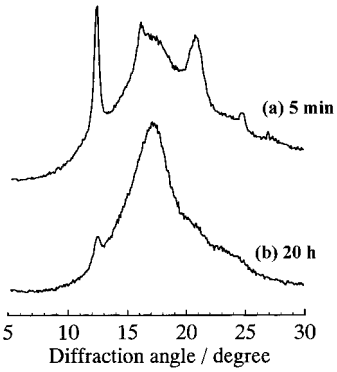

Figure 2. X-ray diffraction profiles of sPP films kept in ice−water for 5 min (a) and 20 h (b) after quenching from the melt at 170 °C. The measurements were carried out at room temperature.

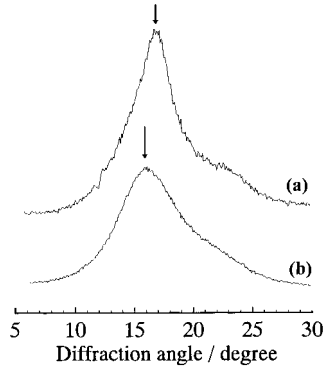

Figure 3. X-ray diffraction profiles for the component grown in ice−water and for amorphous sPP: (a) the scattering profile obtained by subtracting the profile shown in Figure 2a from that shown in Figure 2b; (b) the scattering profile for amorphous sPP in the molten state at 140 °C.

B-pseudo-centered structure by the (020) reflection at $2\theta = 16.3°$.[17] In contrast, the diffraction profile obtained after keeping the film at 0 °C for 20 h becomes simpler as a result of the prominent suppression of the formation of the crystals with the t_2g_2 conformation. To clarify the scattering profile grown in ice−water, the minor diffraction contribution from the crystal with the t_2g_2 conformation has been removed by subtracting the diffraction pattern shown in Figure 2a from that shown in Figure 2b. The diffraction pattern thus obtained is shown in Figure 3a. This pattern provides a simple and broad profile like the pattern obtained for an amorphous sample. However, the peak position and the detailed scattering profile are significantly different from those of the amorphous sample shown in Figure 3b which was measured in the melt at 140 °C. Moreover, the main peak corresponds to the (002) reflection observed for the cold drawn sample having the planar zigzag crystalline form.[4] The broad right-side shoulder is also ascribed to reflections of (020) and (110) types.[4] A separate DSC measurement has also confirmed the appearance of the endothermic peak at about 40 °C for the sample shown in Figure 2b, and this peak can be assigned to the crystal transformation from the planar zigzag form to the t_2g_2 form as previously reported for cold drawn samples.[2−5] From these experimental results, it should be concluded that crystals with the planar zigzag conformation are spontaneously produced at 0 °C in a period of about 20 h without any mechanical stress. The size of the crystallites thus formed seems to be so small that they give rise to the diffuse diffraction pattern shown in Figure 3a. Further experiments to clarify the crystallization mechanism are in progress using CP/MAS ^{13}C NMR, FT-IR, DSC, and wide-angle X-ray diffraction methods.

In summary, we have found for the first time that crystallization of the planar zigzag form is spontaneously induced at 0 °C for syndiotactic polypropylene. Mechanical stress, which was always applied to samples in the conventional method to obtain such crystals, is not essential to induce this type of crystallization. When the temperature of films is increased to room temperature after holding them at 0 °C, crystals with the t_2g_2 conformation are produced in addition but this crystallization is significantly suppressed by the presence of crystals with the planar zigzag conformation formed previously at 0 °C.

Acknowledgment. We thank Drs. Hitoshi Miura and Hiroaki Katayama of Sumitomo Chemical Co. Ltd. for providing the highly syndiotactic polypropylene sample. We are also grateful to Professor David C. Bassett of the University of Reading for critically reading our manuscript. This work was supported in part by the Science Research Promotion Fund of Japan Private School Promotion Foundation.

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MA980032V