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Single-helix crystal in atactic polypropylene

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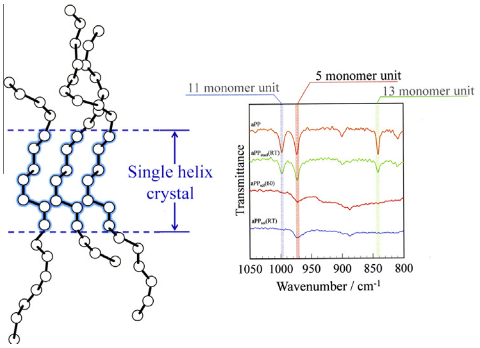
HIGHLIGHTS

- The aPP film with meso pentad =16 % provided the endothermic peak and crystalline X-ray peaks.
- The crystal structure due to α-iPP is formed at local regular sequence.
- 1.2 helical units were constructed for aPP soluble in chloroform.
- In infrared spectrum, only the vibrational mode reflecting the short conformational order less than 5 monomer units was observed.
- It is concluded that a single helix constructs the crystal unit.

GRAPHICAL ABSTRACT



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ABSTRACT

The conformational arrangement of a locally stereoregular sequence of atactic polypropylene (aPP) was investigated via X-ray diffraction, thermal analysis, and infrared spectroscopy. Since the aPP used was an isotactic-rich sample, the X-ray diffraction pattern showed the typical profile of an α-iPP (isotactic polypropylene) crystal, indicating that the crystal is constructed from locally stereoregular sequences. Even for a sample with low stereoregularity (meso pentad = 16%), small peaks due to α-iPP crystals were observed. The melting temperature of aPP was reduced compared with an α-iPP crystal. This corresponds to a shortening of the lamellar thickness. Helical units from chloroform insoluble and soluble fractions having meso pentads of 0.64 and 0.16, respectively, were composed of 3.5 and 1.2 repeating units, respectively. Such short conformational order was also confirmed by infrared spectroscopy. In general, a conformationally sensitive band is observed over a critical regular sequence (n). For the chloroform soluble fraction, a 977 cm^{-1} band for $n = 5$ was observed, but the typical 998 and 841 cm^{-1} bands for $n = 11–12$ and 13–15, respectively, were not observed. This signals that the regular conformation consists of 1–2 repeating units. It is concluded that a short conformational order (about 1–2 helical units) can construct the crystalline unit for aPP.

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1. Introduction

Polypropylene is a representative stereoregular polymer. Isotactic polypropylene (iPP) is one of the earliest stereoregular polymers, synthesized in 1955 using a Ziegler–Natta catalyst [1]. On the other hands, highly syndiotactic polypropylene (sPP) was first polymerized by Kaminsky in 1988 [2]. Stereoregular sequences of these polymers enable the synthesis of stable crystals with high melting points. There are three crystalline modifications (the α, β, and γ-forms) consisting of 3/1 helices for iPP [3–18]. sPP has three conformational structures: trans–trans–gauche–gauche (ttgg) (forms I and II) [19–24], all trans (form III) [25–31], and $t_2g_2t_6g_2$ (form IV) [32,33]. Atactic polyolefin's are generally noncrystalline because of the lack of an extended stereoregular sequence. However, the crystallization of atactic polypropylene (aPP) with a meso pentad of 0.45 and a racemic pentad of 0.20 was recently confirmed by thermal analysis and solid state ^{13}C

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NMR [34]. Local isotactic and syndiotactic sequence have a potential to crystallize to generate a stable structure.

Infrared spectroscopy is a very sensitive means of detecting the conformational structure of polymers. Stereoregularity-sensitive bands vary in intensity with the critical stereoregular sequence number (n) sufficient for production of the vibrational mode. If n is larger than the average length of the helical units present, the corresponding vibrational mode disappears from the spectrum. Kobayashi et al. prepared isotactic polypropylene consisting of hydrated and deuterated monomer units in order to make clear the relationship between the conformationally-sensitive band and n. They showed that the 841 and 998 cm^{-1} bands were observed for sequence lengths shorter than 10, but the other conformationally-sensitive bands disappeared [35]. Kissin et al. also estimated the critical sequence length [36–38]. They concluded that the critical sequence length is 5 for 973 cm^{-1}, 11–12 for 998 cm^{-1}, and 13–15 for 841 cm^{-1}. These results were used to investigate the crystallization process [39].

Atactic polystyrene (aPS) is a representative non-crystalline polymer. In contrast to aPP, the formation of a regular structure is fundamentally impossible for bulk aPS. However, a locally stereoregular conformational arrangement has been confirmed for an aPS/CS_2 gel by infrared spectroscopy [40]. Only vibrational modes indicative of a short critical length in the frequency region of 500–600 cm^{-1} were observed, while the other conformational bands were not observed. Observation of bands in 500–600 cm^{-1} corresponds to the formation of 1–2 repeating units. Since it is not possible for the bulk sample to adopt a regular conformation, it has been suggested that solvent molecules cause formation of the stable conformation.

In this report, the formation of a regular conformation for aPP with an isotactic rich sequence is investigated via X-ray diffraction, thermal analysis, and infrared spectroscopy in order to elucidate the relationship between locally stereoregular sequence length and conformational arrangement.

2. Experimental

2.1. Samples

aPP was sourced from Scientific Polymer Products Inc. (weight average molecular weight, approximately 12,000). The aPP was fractionated using chloroform at room temperature and at 60 °C. The chloroform-soluble and -insoluble components are abbreviated aPP_{sol}(RT), aPP_{sol}(60), and $\text{aPP}_{\text{insol}}$(RT). (The fraction of $\text{aPP}_{\text{insol}}$(60) was too small to use). A film was prepared by casting the chloroform solutions of aPP_{sol}(60) and aPP_{sol}(RT) and by swelling with chloroform for the $\text{aPP}_{\text{insol}}$(RT) fraction. The stereoregularity was determined via ^{13}C NMR. The aPP films were dissolved in o-dichlorobenzene and the measurement was carried out at room temperature. The pentad tacticity was calculation from observation of the methylene resonance peak, and a curve-fitting analysis was carried out following a previous report [41], the results of which are listed in Table 1. The diad tacticity calculated using Bernoulli statistics is also shown. The $\text{aPP}_{\text{insol}}$(RT) had a much larger meso fraction than either the aPP_{sol}(RT) or the aPP_{sol}(60). An iPP sample from Showa Denko Co., Ltd. was used as a reference, for which the weight average molecular weight (M_w) and meso triad (mm) were estimated to be 3.9×10^5 and 98.5%, respectively.

Table 1
Pentad and diad tacticities estimated using ^{13}C NMR.

	ppm	aPP	$\text{aPP}_{\text{insol}}$(RT)	aPP_{sol}(60)	aPP_{sol}(RT)
mmmm	23.64	0.24	0.64	0.22	0.16
mmmr	23.39	0.11	0.075	0.090	0.097
rmmr	23.12	0.027	0.021	0.029	0.033
mmrr	22.86	0.14	0.069	0.12	0.13
mmrm + rmrr	22.67	0.13	0.059	0.13	0.13
rmrm	22.49	0.056	0.019	0.055	0.045
rrrr	22.14	0.12	0.033	0.15	0.16
mrrr	22.02	0.10	0.047	0.12	0.15
mrrm	21.83	0.078	0.036	0.076	0.094
m		0.55	0.81	0.51	0.47

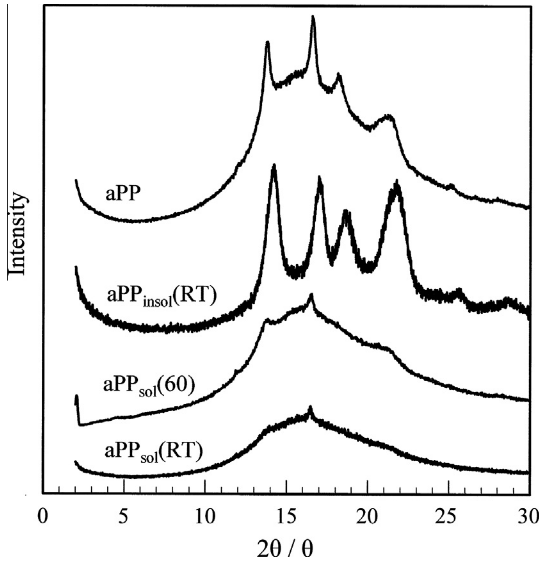

Fig. 1. X-ray diffraction patterns of aPP, $\text{aPP}_{\text{insol}}$(RT), aPP_{sol}(60), and aPP_{sol}(RT). Crystalline peaks due to α-iPP are observed.

2.2. Measurements

Wide-angle X-ray diffraction patterns were obtained on an automatic Rigaku RINT2500 diffractometer with Ni-filtered Cu Kα radiation. Differential scanning calorimetry (DSC) was performed on a Rigaku 8230D instrument. The heating rate was 5 °C/min in the range from room temperature to 200 °C. Fourier transform infrared (FT-IR) spectroscopy was measured using a Jasco FT-IR 660 Plus spectrometer with a DTGS detector. These measurements were carried out at 2 cm^{-1} resolution, and 32 transients were collected for each spectrum at room temperature. KRS-5 was used for the ATR crystal.

3. Results and discussion

3.1. X-ray diffraction analysis of aPP

Fig. 1 shows the X-ray diffraction patterns of the aPP samples. The diffraction pattern is very broad, but sharp peaks due to crystalline particles were also observed. This is direct evidence that crystals are constructed despite a lack of extended stereoregularity. After fractionation, there is a significant difference in the signals of the soluble and insoluble components. The diffraction pattern of $\text{aPP}_{\text{insol}}$(RT) contains sharper peaks than in the original. The diffraction profile is characterized by four sharp peaks at 13.7°, 16.6°, 18.2° and 21.4° which are assumed to be due to the presence of α-iPP crystals. This is because the $\text{aPP}_{\text{insol}}$(RT) fraction has an isotactic-rich sequence; the meso pentad is 0.64, whereas the racemic pentad is only 0.036. The higher probability of the meso sequence allows formation of the α-iPP crystal. On the other hand, the diffraction patterns of aPP_{sol}(60) and aPP_{sol}(RT) were very broad, corresponding to a structure wherein most of the

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