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Stress-induced structure transition of syndiotactic polypropylene via melt spinning

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Abstract

Syndiotactic polypropylene (sPP) fiber was prepared by melt spinning with the taken-up velocity of 200–700 m/min, the conformation and crystallization of which were systematically investigated by a combination of Fourier transform infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). The results indicated that sPP fibers consist of form I crystal with helical conformation at the spinning velocity of 200–300 m/min, and the crystallinity and orientation are improved with the increase of spinning velocity in this range. As the spinning velocity exceeds 300 m/min, sPP fibers contain mainly mesophase with *trans*-planar conformation and the content of form I decreases correspondingly. The crystallization behavior of sPP fiber with spinning velocity is different from that of most other crystalline polymers, i.e., the theory of orientation-induced crystallization is not well conformed to. For sPP, form I comprising of helical conformation is thermodynamically stable, though extensional stress can lead to transition from helical to *trans*-planar conformation, which is not favorable for the crystallization of form I.

Keywords: Syndiotactic polypropylene; Structure transition; Melt spinning

1. Introduction

In the process of melt spinning, the structure variation of polymers, especially the orientation and crystallization along the spinning line, has great influence on the final performances of fibers [1–3]. At present, the theory of stress-induced oriented crystallization in melt spinning has been universally accepted for crystallizable polymers. During the melt-spinning process, the oriented chain segments induced by stress generally decrease the changes of entropy, thus facilitating the nucleation and crystallization processes. On the other hand, the increase of nucleation rate will further result in the increase of crystallization rate. For most linear polymers, the structure formation in melt spinning follows the above-mentioned theory, however, recently some researchers argued that syndiotactic polypropylene (sPP) fiber in melt spinning doesn't follow the mechanism of orientation-induced crystallization [4]. It has been found that the crystallinity of sPP fiber decreases with the increase of spinning velocity. This abnormal behavior might be related with the complicated conformation and crystalline forms of sPP. To clarify these disputations, in-depth investigations on the transition process of conformation and crystallization forms are needed.

Four crystalline and one mesomorphic forms of sPP have been described so far [5–13]. The crystalline forms I and II adopt $(t_2g_2)_n$ helical conformation [14–16], whereas forms III and IV present chains in *trans*-planar and $(t_6g_2t_2g_2)_n$ conformation [17,18], respectively. De Rosa and Auriemma systemically investigated the structure and physical properties of sPP [5], and pointed out that form I is the most stable form and can be obtained under common crystallization conditions, either from melt state or from solution; the metastable helical form II is preferably obtained in oriented fibers by stretching sPP samples of low stereoregularity or removing the tension

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in fibers initially in *trans*-planar form III; form III is obtained by stretching highly stereoregular samples at room temperature; form IV is obtained by exposing stretched fiber of sPP originally in the *trans*-planar form III to organic solvents; besides the four crystalline modifications, a mesomorphic form can be obtained by quenching sPP to 0 °C from the melt. Due to the complicated structures of sPP, numerous investigations have already been reported on the structure transition under different conditions [19–27]. However, the structural formation and transformation in practical processing have been seldom referred to, for instance, during the melt-spinning process. Along the melt-spinning line, polymers are likely to be influenced by a variety of factors, including temperature, stress, strain, spinning velocity, etc. Although there have been some elementary researches on the unusual crystallization behavior of sPP, and the relationship between structure and performance of related fibers has also been touched upon [4,28,29], the structure transition mechanism during melt spinning still keeps not so unambiguous. It is therefore the main aim of the present work is to investigate the correlations between structural variation and melt-spinning parameters and further to elucidate the abnormal crystallization variation of sPP in the melt-spinning process.

2. Experimental

2.1. Materials

Syndiotactic polypropylene was obtained from AtoFina Company with the following basic parameters: weight-averaged molecular weight $M_w = 8.6 \times 10^4$ (GPC), polydispersity $M_w/M_n = 4.1$, melting temperature $T_m = 130\ °C$ (DSC). The chain structure of the sPP sample was analyzed by ^{13}C NMR spectroscopy on a Bruker AM-300 FT-NMR spectrometer, and the syndiotactic pentad was determined to be 80%.

2.2. Melt-spinning process

The melt-spinning experiments for sPP were carried out on a single-screw melt extruder ($D = 30$ mm, $L/D = 25$) with a spinneret containing one orifice of 0.3 mm diameter. Selecting the spinneret containing only one orifice is to acquire the fiber with uniform structure, for the spinnability of sPP is not as easily controlled as isotactic polypropylene (iPP). The single-screw extruder was set with five temperature zones of 185, 205, 210, 205, and 190 °C, corresponding to the feed, metering, melt-blending, die, and spinneret sections, respectively. The as-spun filaments were collected with a controllable take-up velocity of 200–700 m/min.

2.3. Characterization

DSC measurement was carried out over the temperature range of 20–180 °C using a Perkin–Elmer DSC-7. All operations were performed under nitrogen environment. The prepared sPP fibers were first crushed into fragments before measurement and then heated up from 20 to 180 °C at a rate of 10 °C/min. The thermograms of the first heating run were recorded. The crystallinity of the fibers was calculated based on the DSC data. The fusion heat for 100% crystallinity (form I) of sPP was reported to be $\Delta H^{o}_{m,sPP} = 183$ J/g [30,31], which was taken as the reference for the crystallinity calculation. The crystallinity of the fibers was then calculated according to the formula $X_{c,sPP} = (\Delta H_{m,sPP} - \Delta H_{cc,sPP})/\Delta H^{o}_{m,sPP}$. Here, $\Delta H_{m,sPP}$ is the fusion heat of sPP fiber and $\Delta H_{cc,sPP}$ corresponding to its cool crystallization enthalpy in the process of heating.

XRD data between 6° and 36° were collected on a Rigaku D/MAX-RB X-ray diffractometer with Cu Kα radiation at the generator voltage of 40 kV and current of 50 mA. The fibers were crushed into fragments before measurement.

The infrared spectra of sPP fibers were accumulated by using a Bruker EQUINOX 55 spectrometer with a resolution of 4 cm^{-1} and 32 scans. In order to characterize the orientation of the fibers, the absorptions polarized parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the fiber axis were also measured. An important parameter, dichroic ratio (D), was used to describe the orientation of macromolecular chains in sPP fibers:

$$D = A_{\parallel}/A_{\perp} \tag{1}$$

3. Results and discussion

3.1. Conformation variation of sPP fibers

Infrared spectroscopy is sensitive to the conformational change of molecular chains, especially to that of long chain *n*-alkanes and linear polyolefins. There are several typical IR absorption bands corresponding to the conformation and crystalline form of sPP, which are summarized in Table 1 [22,23,32]. Fig. 1 shows the FTIR spectra of sPP fibers obtained with different spinning velocities. As the spinning velocity is lower than 300 m/min, the bands of the helical conformation, appearing at 810, 977 and 1005 cm^{-1}, are protrudent and well developed, indicating that the helical conformation is the major form. With the increase of spinning velocity, the relative intensities of 830, 963 and 1130 cm^{-1} bands increase, corresponding to increments of the long strands in the *trans*-planar conformation and mesophase, while the helical conformation bands decrease to relatively low intensity (977 cm^{-1}) or disappear (810, 1005 cm^{-1}).

Table 1
FTIR bands sensitive to both conformation and crystal structure of sPP[a]

Wavenumbers (cm^{-1})	Conformation assignment	Morphology assignment
810	Helical	Form I
830	*trans*-Planar	Mesophase
963	*trans*-Planar	Amorphous
977	Helical	Amorphous
1005	Helical	Form I
1130	*trans*-Planar	Mesophase
1153	Conformation insensitive	Amorphous

[a] The assignments were obtained by combinatory consideration of the results of Refs. [22,23,32] and our own experimental data.

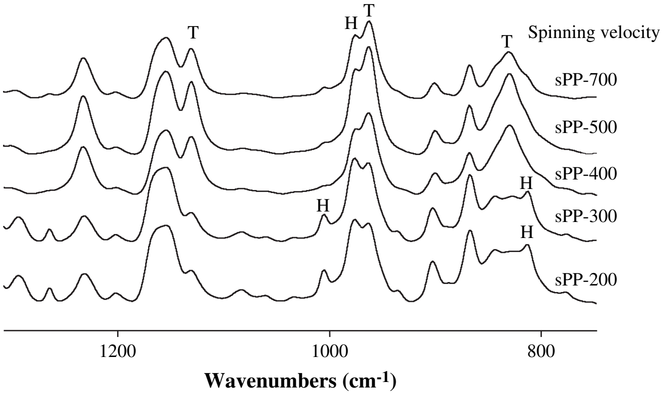

Fig. 1. FTIR spectra of sPP fibers melt spun at different spinning velocities. H: helical conformation; T: *trans*-planar conformation.

In order to further understand the relative change of the chain conformation in sPP fibers at different spinning velocities, the intensity ratio of 963 cm^{-1} (*trans*-planar chain) to 977 cm^{-1} (helical chain) is investigated (Fig. 2). $R_{963/977}$ obtained below 300 m/min is less than 1, indicating relatively higher content of helical conformation in the fibers. With increasing spinning velocity, the content of *trans*-planar conformation increases and thus $R_{963/977}$ exceeds 1. When the spinning velocity is higher than 400 m/min, the *trans*-planar conformation becomes much more prominent, however, further increasing spinning velocity has almost no influence on the conformation transformation. The *trans*-planar conformation (963 cm^{-1}) of sPP-700 fiber even shows slight drop, and contrarily the 810 cm^{-1} band emerges again as a shoulder of 830 cm^{-1}, indicating the slight increase of helical conformation at high spinning velocity. The possible reason is that for sPP-700 fiber, polymer melt stays for much shorter time in the spinning line due to faster spinning velocity and the stable *trans*-planar conformation aggregates have not been formed. Once the sPP-700 fiber is placed at room temperature, unstable *trans*-planar conformation can be transformed into helical conformation. In order to understand the effect of spinning velocity on the content of mesophase of sPP fiber, the absorbance of the mesophase bands at 1130 cm^{-1} was normalized by taking the 1153 cm^{-1} band as the reference (insensitive to the conformation transition). The absorbance ratio of mesophase band is shown below:

$$R = I_{1130}/I_{1153} \tag{2}$$

Fig. 3 shows that the content of mesophase with *trans*-planar conformation increases largely when the spinning velocity is higher than 300 m/min. This result is in well consistent with the conformational changes shown in Fig. 2, indicating that the total relative content of *trans*-planar conformation in sPP fibers is low for sPP-200 and sPP-300, but enhanced abruptly as the spinning velocity exceeds 400 m/min. Therefore, it can be concluded that the processing parameters have great influence on the conformation transition of sPP fibers. The conformation variation induced crystal structure change will be discussed in the following section.

3.2. Crystallization and orientation behaviors of sPP fiber

X-ray diffractograms of sPP fibers are shown in Fig. 4. The results indicate that sPP fibers melt spun at 200 and 300 m/min crystallize in the usual form I with helical conformation, characterized by the most intense peak of 12.3°, corresponding to (200) reflection, mid-intense 16.0° to (010) reflection, 20.8° to (210) reflection, and a weak peak 24.6° to (400) reflection. The absence of the (211) reflection at 18.9° indicates that the disordered modification of form I is obtained in the two sPP fibers. The peak at $2\theta = 16.0°$ for the two fibers is asymmetric accompanied with a shoulder at $2\theta = 17.0°$ (see arrows in Fig. 4), a typical peak of *trans*-planar mesophase, which shows that the two fibers contain a small amount of mesophase with *trans*-planar conformation. The DSC curves of sPP-200 and sPP-300 fibers show weakly endothermic peaks at 40–60 °C (Fig. 5), which result from partial melting and transition of mesophase [33]. With increasing the spinning velocity from

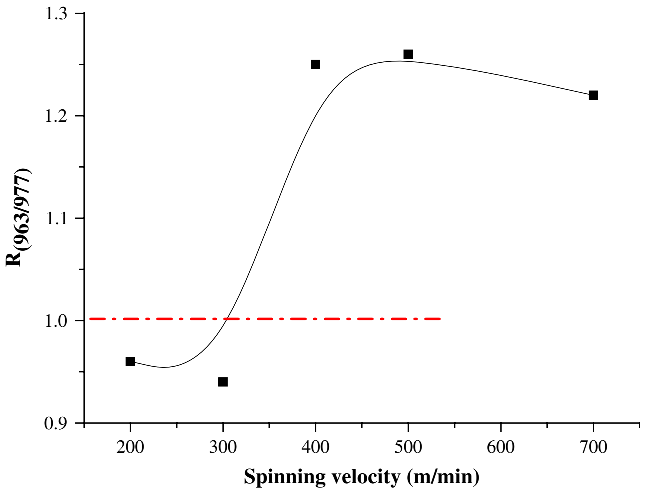

Fig. 2. Intensity ratio of *trans*-planar conformation band (963 cm^{-1}) to helical conformation band (977 cm^{-1}) as a function of the spinning velocity.

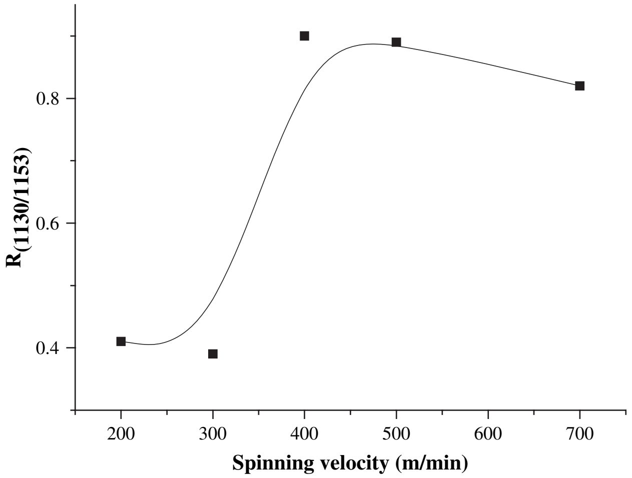

Fig. 3. Relative content of the mesophase (1130 cm^{-1}) in sPP fibers as a function of the spinning velocity.

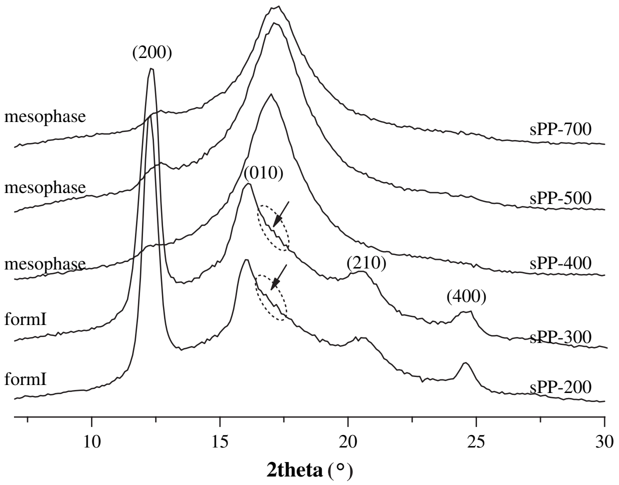

Fig. 4. X-ray diffractograms of sPP fibers melt spun at different spinning velocities.

300 to 700 m/min, the crystallization form of the fibers changes drastically. In Fig. 4, a strong peak of mesophase appears at $2\theta = 17.0°$, while the intensity at 12.3° corresponding to form I or II decreases and the other characteristic peaks of form I disappear. The DSC curves of these fibers also reveal the obvious endothermic peak of mesophase and the cold crystallization peak of form I (Fig. 5). During heating, the rearrangements in the amorphous region, which result from partial melting of mesophase and transition from *trans*-planar to helical conformation, can induce the crystallization of form I at higher temperatures and the exothermic crystallization peak thus emerges. These results prove that sPP fibers are mainly composed of mesophase at higher spinning velocity (400–700 m/min). However, the shoulder at 12.3° implies the minor existence of form I or II with helical conformation, while the absence of typical peak at $2\theta = 16.0°$ for form I verifies the presence of small amount of form II in sPP fibers melt spun at high spinning velocity [32]. Here, it should be pointed out that form III does not form even at high spinning rates (Fig. 4). The transformation of the helical form into the *trans*-planar form (form III or mesophase) depends on the stereoregularity of the sample and stretching stress [26,27], i.e., during stretching, the high stereoregularity of sPP and high stress favor the formation of form III. In the spinning line, sPP can acquire high stress under high spinning velocity. However, the stress on sPP fibers is easy to relax after the sPP fibers are taken-up. Therefore in the present study, form III does not emerge in sPP as-spun fibers even at high spinning velocity, for the stereoregularity of sPP used is relatively low (rrrr = 80%) and the imposed stress is not large enough to keep the stable existence of form III at room temperature.

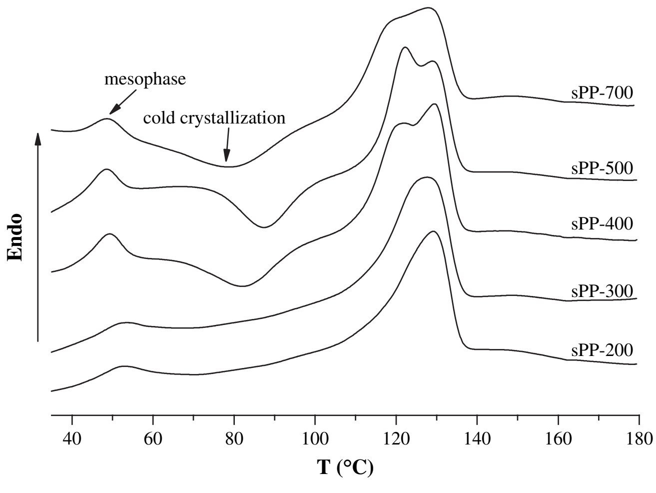

Fig. 5. DSC heating thermograms of sPP fibers melt spun at different spinning velocities.

The crystallization and orientation in melt spinning of crystalline polymers generally depend on three parameters [3]: (1) average axial stress in the melting zone, (2) stress in the crystallization zone, and (3) the crystallization time in spinning line. At constant outflow mass, take-up stress increases with the increase of spinning velocity, which improves the orientation of polymer chain segments. These oriented chain segments improve the nucleation rate and reduce the entropy during the crystallization, thus enhancing the crystallization rate. On the other hand, the high spinning velocity shortens the crystallization time of polymer in spinning line. Therefore, the final crystallinity of fibers at different spinning velocities is the mutual result of crystallization rate and crystallization time. The principle of stress-induced oriented crystallization can be applied to most linear polymers, such as isotactic polypropylene, polyamide, polyester, and so on. In the case of sPP, form I with helical conformation has the tendency to transform into unstable mesophase or form III with *trans*-planar under high stress [22–27], which influences crystallization behavior of sPP during melt spinning. Fig. 6 shows the crystallinity variation of form I and mesophase with spinning velocity. At relatively low spinning velocity (200–300 m/min), the stress in spinning line is lower than σ_{cr} (the critical stress required for transition from helical to *trans*-planar conformation) and form I with helical conformation constitutes the majority of sPP. In this spinning velocity range, the spinning stress is not sufficient to sustain the dominance of *trans*-planar transformation, so the crystallinity of form I increases with increasing the spinning velocity from 200 to 300 m/min. When the spinning velocity reaches 400 m/min, the stress in spinning line increases and becomes larger than σ_{cr}, so the *trans*-planar conformation is dominant in sPP fibers, which is not favorable for the crystallization of form I. As a consequence, the crystallinity of form I decreases and mesophase increases remarkably. Further increasing spinning velocity, *trans*-planar conformation still stands predominant in sPP. However, the mesophase decreases (Fig. 6b), which may be ascribed to less crystallization time in spinning line under faster spinning velocity.

The dichroic ratio of IR spectra provides an access to the degree of orientation for the crystalline form and the conformation in amorphous region during stretching. The 977 and 963 cm^{-1} bands are assigned to the helical and *trans*-planar characteristic bands of amorphous region, respectively. The 811 and 1005 cm^{-1} are assigned to the form I characteristic bands and 1130 cm^{-1} to the mesophase characteristic band. Table 2 shows the orientation of sPP fibers at different spinning velocities by FTIR dichroism. When the spinning velocity is below

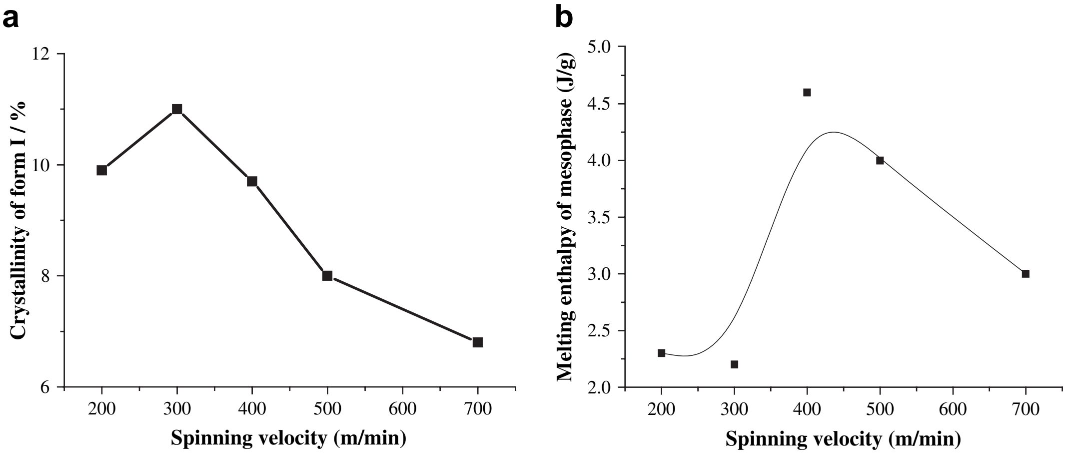

Fig. 6. (a) Crystallinity of sPP fibers melt spun at different spinning velocities; (b) Melting enthalpy of mesophase of sPP fibers melt spun at different spinning velocities.

Table 2
IR dichroic ratio of sPP fibers obtained with different spinning velocities

Sample	Form I		Mesophase	Helical	*trans*-Planar
	811 (cm^{-1})	1005 (cm^{-1})	1130 (cm^{-1})	977 (cm^{-1})	963 (cm^{-1})
sPP-200	0.62	0.66	0.82	1.23	1.02
sPP-300	0.56	0.55	0.97	1.29	1.02
sPP-400	–	–	1.37	1.14	1.09
sPP-500	–	–	1.63	1.27	1.18
sPP-700	–	–	1.46	1.32	1.21

300 m/min, the orientation of form I and helical conformation increases with increasing spinning velocity. Mesophase and *trans*-planar conformation show no obvious evidence of orientation, perhaps because mesophase content is so low that the oriented chain segments easily relax at room temperature. When the spinning velocity is above 300 m/min, mesophase and *trans*-planar conformation become dominant in sPP fibers. The orientation of mesophase, *trans*-planar and helical conformations in amorphous region tends to be evident due to the high spinning velocity.

Based on the above results, it can be concluded that sPP fiber is mainly composed of form I at low spinning velocity and mesophase at high spinning velocity. As the fibers are heated, the mesophase melts and cold crystallization peak emerges. The drawback of instability in practical application demands that the fiber must be annealed at high temperature under tension for the purpose of achieving stable structure and maintaining the tenacity. This part of work is being under investigation in our laboratory.

4. Conclusions

The changes of conformation, crystalline structure and orientation behavior of sPP fibers at different spinning velocities have been investigated. The following main conclusions can be drawn:

(1) At low spinning velocity, sPP fiber exists in the form of form I and helical conformation, and the crystallinity and orientation of form I are improved with the increase of spinning velocity.
(2) With increasing the spinning velocity, the mesophase and *trans*-planar conformation become dominant in sPP fiber. Further increasing the spinning velocity, the content of mesophase is reduced due to the decrease of crystallization time in spinning line. The orientation of mesophase and *trans*-planar and helical conformations in amorphous region increases with increasing spinning velocity.
(3) The crystallinity of stable form I in sPP fiber decreases largely with the increase of spinning velocity, which is different from that of most other crystalline polymers. The increase of the spinning velocity leads to the transition from helical to *trans*-planar conformation, and consequently form I is substituted by mesophase.

Acknowledgement

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