Polymer 50 (2009) 5782–5786

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

In situ FTIR spectroscopic study of the conformational change of syndiotactic polypropylene during the isothermal crystallization

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ARTICLE INFO

Article history:
Received 9 April 2009
Received in revised form
10 September 2009
Accepted 9 October 2009
Available online 14 October 2009

Keywords:
Syndiotactic polypropylene
Crystallization
FTIR

ABSTRACT

The isothermal crystallization of syndiotactic polypropylene (sPP) was investigated by in situ Fourier transform infrared spectroscopy (FTIR) and wide angle X-ray diffraction (WAXD). It was found that the ordered helical structure developed during the induction period of the isothermally crystallization of sPP. Moreover, the normalized intensity profiles of the characteristic FTIR absorption bands of the sPP helical conformation at 1005, 867 and 812 cm^{-1} are not synchronized during the induction period of the sPP crystallization, which suggest that these bands should be corresponding to the helical chain with various persistence lengths. The non-zero value of the initial normalized intensity for the band at 867 cm^{-1} indicates that there are sPP chains in the short helical conformation in the initial amorphous state. However, the helical chains with longer persistence length can only be observed with increasing the annealing time in the induction period as suggested by the intensity changes of the bands at 1005 and 812 cm^{-1}. Particularly, the intensity of the characteristic absorbance band at 1005 cm^{-1} starts to increase at an earlier time than that of 812 cm^{-1}. These observations are discussed in terms of the critical length by Doi theory. It can be estimated that the sPP melt system is stable when the persistence length of helical sequences is less than 16 monomer units. The results could be helpful on the understanding the pathway of polymer chains packing in the early stage of the crystallization of semi crystalline polymers.

1. Introduction

Much effort has been devoted to obtain a comprehensive understanding of the crystallization behaviors of the semi crystalline polymers from both theoretical and experimental aspects [1–11]. Several concepts for polymer crystallization have been depicted in the last century, among which the classical nucleation and growth theory (Hoffman–Lauritzen theory) [1–3], mesomorphic phase concept [4–6], and spinodal concept [7–11] are the most important. More recently, many work focused on the structural formation during the induction period before the crystal growth [8–22]. However, the crystallization of polymers from metastable liquids and solution is extremely complex and many questions are still unclear, especially on the early state.

The structural formation during the induction period of the crystallization of polymers has been attracted considerably interest in the past decades. It was found that the long-period peak emerges in the SAXS spectra before the crystalline peaks appear in the WAXS spectra [23,24]. The kinetics during the induction period of poly(ethylene terephthalate) (PET) was further investigated by means of depolarized light scattering measurements and it was concluded that the spinodal decomposition occurred due to the orientation fluctuations of the polymer segments during this period [11,13]. Phenomenological theory was then proposed that the coupling between density and chain conformation could induce a liquid–liquid binodal within the equilibrium liquid–crystalline solid coexistence region [7]. The studies on the crystallization of poly(ethylene naphthalene) (PEN) also indicated that a SAXS peak at 0.03 $Å^{-1}$ had emerged and grown with time before the primary nucleation occurred during the crystallization [14,15]. More recently, dielectric spectroscopy was used to characterize simultaneously structure development and dynamics by a single

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doi:10.1016/j.polymer.2009.10.017

experiment [12,25]. The results support the existence of precursors of crystallization in the induction period.

Besides the above mentioned techniques, Fourier transform infrared spectroscopy (FTIR), a powerful method sensitive to the chain conformation, has been applied to study the molecular structure and the conformational ordering of semi crystalline polymers in recent years [26–30]. Time resolved FTIR has been used to study the melting and crystallization processes of isotactic polypropylene (iPP). The results show that the helix is stable when the persistence length of helical sequences is less than 12 monomer units in the iPP melt system, whereas crystallization occurs as soon as the helix length exceeds 12 monomer units [26]. The dynamic FTIR investigation of the crystallization of sPP around 0 °C revealed that the extent of the trans–gauche transition will be one of possible important factors to control the formation of the crystals of sPP with characteristic conformations around 0 °C [27]. In situ FTIR investigation of the isothermal crystallization of poly(bisphenol A-co-decane ether) at different temperature also indicated that the intramolecular conformational changes occur before the intermolecular packing process [28]. The molecular dynamics during the expitaxial crystallization of polycarprolactone (PCL) on the oriented polyethylene substrate were studied by in situ FTIR and WAXD. The results indicate the existence of surface-induced anisotropic chain ordering of PCL in its molten state on highly oriented PE substrate [29]. Specifically, the PCL chains first arranged into the similar conformation as that in crystalline phase and then packed into the crystalline lattice during keeping the PCL melt on PE substrate at 59 °C.

On the grounds of the increasing published results, there is no clear argument on the early stage of the crystallization of semi crystalline polymers. In present work, the isothermal crystallization process of sPP was investigated by in situ FTIR spectroscopy. The results could be helpful on the understanding the pathway of polymer chains packing in the early stage of the crystallization of semi crystalline polymers.

2. Experimental section

2.1. Materials and sample preparation

Syndiotactic polypropylene ($M_w = 1.74 \times 10^5$ g/mol, $M_w/M_n = 2.32$) in pellet form was purchased from Aldrich. The sPP pellets were melt-pressed at 170 °C for 5 min followed by slowly cooled to room temperature. The obtained thin film was about 100 μm in thickness.

Differential scanning calorimetric (DSC) measurements were carried out on a Perkin–Elmer differential scanning calorimeter (Diamond Series) under a flowing nitrogen atmosphere. The instrument was calibrated by using In and Pb as standards. The sPP samples (about 5 mg) were molten at 170 °C for 5 min and then cooled at a cooling rate of 10 °C/min. The DSC measurements shows that the sPP has a melting temperature of 128 °C and the maximum crystallization peak at around 85 °C during cooling.

For FTIR and WAXD experiments, the samples were heated to 170 °C for 5 min, and then cooled to the desired temperature for crystallization.

In situ FTIR measurements were performed on a Bruker Equinox-55 FTIR spectrometer equipped with a hotstage (INSTEC STC200C). IR spectra were collected at a 2 cm^{-1} resolution and 16 co-adding scans with a 2 min interval during the crystallization. The IR spectra were preprocessed to eliminate the effects of baseline instability and other possible effects by OPUS software. The wavenumber regions were selected first and processed a linear baseline correction, followed by offsetting to the zero absorbance value.

WAXD experiments were performed on a Geigerflex D/Max-RB diffractometer. A rotating-anode generator (Cu Kα, 12 kW) was used as the X-ray source. The sample temperature was controlled by a hotstage and nitrogen was used to protect the samples during the measurements.

3. Results and discussion

To fulfill the purpose for monitoring the conformational variations of the sPP chains during the isothermal crystallization process, a suitable temperature for ensuring the nonoccurrence of sPP crystallization should be determined first. On the basis of DSC measurement, we here set the temperature at 112 °C to performance the FTIR and WAXD experiments. From the real-time IR spectra, we found that there was no crystallization occurring immediately after the sample was cooled to 112 °C and that the crystallization rate under this temperature was also suitable for our in situ FTIR measurements. Fig. 1 shows the in situ FTIR spectra collected during the isothermal crystallization of sPP at 112 °C. The conformation sensitive bands of sPP appear in the regions of 1050-795 cm^{-1}. The bands at 812, 867 and 1005 cm^{-1} correspond to the 4_1 helix conformation of sPP chains of sPP form I crystals, while the bands at 977 and 963 cm^{-1} are associated with mesophase or amorphous phase of sPP [31–34]. In Fig. 1, no absorption peak can be observed at 812 and 1005 cm^{-1} on the initial spectrum of sPP, whereas the 867 cm^{-1} peak clear has a non-zero intensity at time = 0, which may be attributed to the ordered conformation in the amorphous phase. Due to that IR spectroscopy are usually more sensitive to chain conformation, the "truly crystalline band" is just found in a few case, such as PE [35]. It may be more accurate to assign the band at 867 cm^{-1} to the helix conformation sensitive band than that of crystalline of sPP. Actually, it has been reported that the band at 867 cm^{-1} of sPP is sensitive to TTGG helix conformation [36]. The results suggest that there are short helix sequences in the initial state of the sample, which not formed ordered three-dimensional structure. That is to say, the length of these helix sequences along the polymer chain's direction is not long enough to induce the intermolecular ordered packing of polymer chains. During the annealing procedure, the short helix may grow to relatively longer helix and new short helix may be formed. However, it is hard to estimate quantitatively the content of the short or long helix. Therefore, in the data processing procedure, we used the normalized intensity (relative to its final intensity after crystallization) to depict the chain conformation changes during the crystallization process.

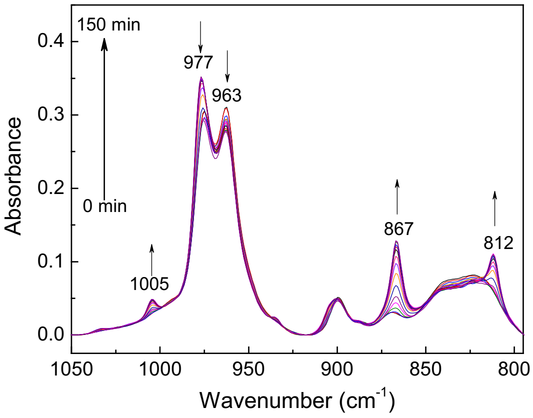

Fig. 1. In situ FTIR spectra of sPP crystallized at 112 °C from molten state in the wavenumber regions of 1050–795 cm^{-1}.

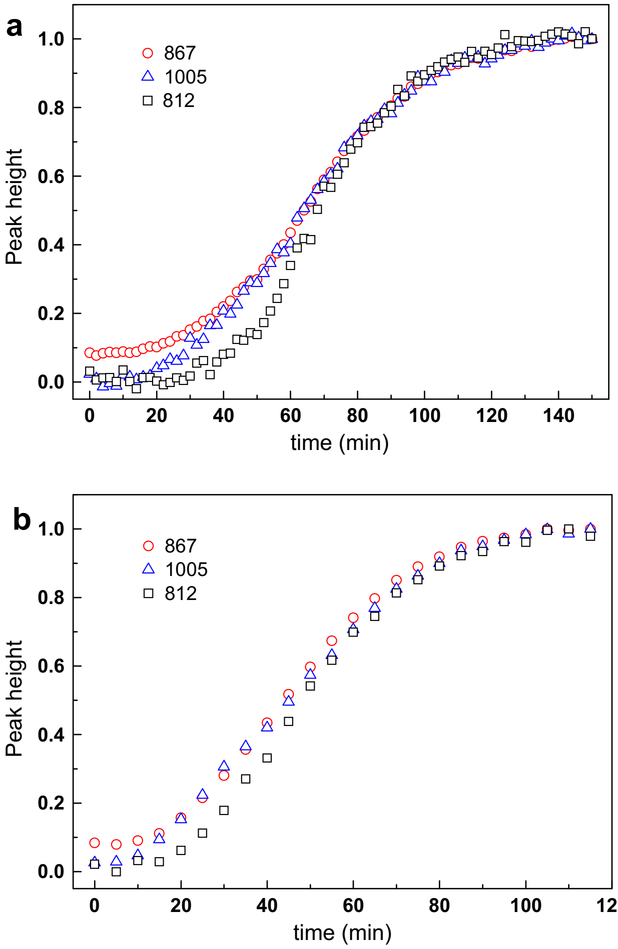

Fig. 2. Peak height of IR bands at 1005, 867, 812 cm^{-1} as a function of annealing time during the isothermal crystallization of sPP at (a) 112 °C and (b) 105 °C.

Fig. 2 shows the peak height as a function of crystallization time. The results demonstrate that the intensities of the bands at 1005, 867, and 812 cm^{-1} increase gradually with the time, which indicates the content of the sPP chain in helical conformation increased in the sample. In the case of annealing the sPP samples at 112 °C (Fig. 2a), the intensities of all the characteristic bands at 1005, 867, 812 cm^{-1} increase very slowly in the first 20 min, then significantly in the following 60 min, and finally slowing down before reaching equilibrium. Moreover, helical conformation bands represent population of a particular conformation in not only the crystalline but also the amorphous regions of the sPP sample. Whatever band has the highest initial normalized intensity would be the band most sensitive to the shortest helical sequence lengths. Obviously, the initial normalized intensity of the peak at 867 cm^{-1} is highest, which would be the band most sensitive to the shortest helical sequence lengths. And the band at 1005 cm^{-1} started to increase intensity earlier than that at 812 cm^{-1}. Similar phenomenon has been found in some literature. For example, it has been reported that in the iPP system, the system becomes unstable and the level of parallel ordering begins to increase when the helical sequence is larger than the critical value (about 12 repeating monomer units) and crystallization occurs [26]. It is known that the sensitive bands, which relate to the intramolecular vibrational coupling within a single chain, only appear when a sequence of the specific conformation repeats regularly along the chains [37]. Therefore, it is estimated that the intensity change of band 1005 cm^{-1} increases faster than that of band 812 cm^{-1} during the crystalline process of bulk sPP is due to that the helical bands change with the helical conformational sequences. The longer of the helical sequences, the lower the corresponding band intensity start to increases, i.e. the band 812 cm^{-1} corresponding more longer helical sequence than the band 1005 cm^{-1}. After 80 min, the curves of different intensity of helical bands are similar. The same trend is observed at different annealing temperature, e.g. 105 °C as shown in Fig. 2b, in which the intensity of the absorption bands of the helix begins to increase at about 15 min, shorter than that at 112 °C. The DSC experiment shows that the maximum crystallization peak is at around 85 °C during cooling. Therefore, the sPP chains need a much longer time to reach their stable conformation before folding into a lamellar crystal at 112 °C than that crystallized at 105 °C.

To discuss the IR bands intensity change ratios during the crystalline process, the proper way is to discuss the characteristic time of the change, which can be generally determined by the peak position of the first order derivation of the IR bands intensity profiles as a function of crystallization time and the results are shown in Fig. 3. In Fig. 3, the sequence of helix bands intensity change can be depicted clearly. It shows that the helix band intensity at 1005 cm^{-1} increases earlier than that of 867 cm^{-1} and then than that of 812 cm^{-1}. In other words, band at 1005 cm^{-1} start to increase first. Moreover, there are short sPP helix in the initial amorphous state which can be confirmed by the non-zero peak intensity at 867 cm^{-1}, which is most sensitive to helical conformation.

The isothermal crystallization procedure of sPP at 112 °C was also investigated by in situ WAXD experiments and the results are shown in Fig. 4. It is known that sPP has four crystalline forms [38–43] and one mesomorphic form [31,44,45]. The form I crystal of sPP is stable with the (TTGG)$_n$ helical chain conformation, T and G represent trans and gauche conformation, respectively. The WAXD results indicate that there is no crystallization occurred immediately before the sPP molten sample was isothermally crystallized at 112 °C for 82 min (Fig. 4). Whereas the characteristic diffraction peaks for sPP form I crystal at $2\theta = 12.2$, 15.8, and 20.6° appears on the WAXD curves after 82 min, which indicates the beginning of the sPP crystallization at this moment. Meanwhile, the intensity of these peaks increases with crystallization time after 82 min.

Considering both of the FTIR and WAXD results, it can be concluded that the content of the sPP chains in helix conformation is increased before the crystallization occurs when the sPP is annealed at 112 °C, which means that the ordered structure may be develop before the occurrence of the crystallization. Similar results

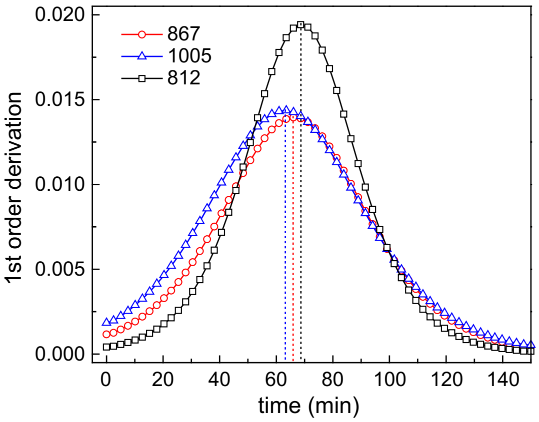

Fig. 3. The first order derivation of the IR bands intensity as a function of crystallization time during the isothermal crystallization of sPP at 112 °C.

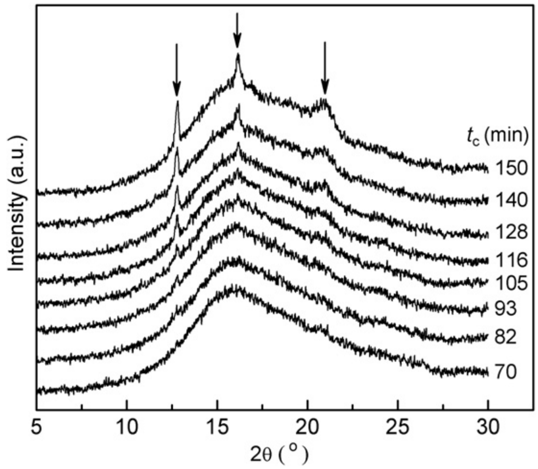

Fig. 4. WAXD intensity profile of sPP annealed at 112 °C for different time. The sample was first heat to 170 °C for 5 min to erase the possible thermal history and then cooled to 112 °C.

have been reported in other polymer systems, e.g. isotactic and syndiotactic polystyrene (iPS and sPS) [14,20], iPP [26,46,47], poly(bisphenol A-co-decane) [28], PET [11,13], PEN [48], and PCL [29]. In all above mentioned cases, the intramolecular interaction concerning the precursors of the crystal exists during the induction period, which may be associated with the density fluctuation and the rearrangement of chain conformation in the supercooled melt prior to polymer crystallization. Kaji et al. reported that during the induction period of the sPS crystallization, the intensity of the absorption bands of the sPS trans conformations increases (TTTT) on the FTIR spectra, whereas the intensity of the other bands including the gauche conformation bands decreases due to that the gauche conformation convert into trans conformation. The conformation transition leads to the expansion of the sPS chain [14]. The FTIR and FTIR 2D correlation analysis also show the local conformation changes and the formation of the 3_1 helical conformation of the iPS chains during the induction period of crystallization of iPS [20]. In present work, when the sPP molten samples were annealed at 112 °C, the intensity of characteristic bands of the sPP helical conformation increases with annealing time during the first 80 min, which corresponds to the induction period as shown by WAXD experiments. Moreover, the normalized profile at the bands 1005, 867, 812 cm^{-1} are not overlapped each other during this period, which is speculated that the bands of 1005, 867 and 812 cm^{-1} are associated with helical chains with different length. Considering that helical conformation is non-zero even in the initial amorphous state, it is more reasonable to use the raw data rather a subtraction/normalization data to analyze the band sensitivity to different helical sequence lengths. In the beginning of induction period, there are some sPP chains in helical conformation. With increasing annealing time, polymer chains have enough time to develop the $(\text{TTGG})_n$ helical conformation along the chains and form the three-dimensional ordered crystal due to the intermolecular interaction.

Based on Doi-Edwards dynamic theory for the isotropic-to-nematic transition of liquid crystals [49], Imai et al. proposed that the parallel orientation of polymer segments induces a spinodal decomposition type microphase separation prior to crystallization [50–52]. According to this theory, parallel ordering of polymer segments is induced only when their length exceeds a critical value, above which the crystallization occurs. So far, the critical concentration drops as chains extend with conformational change, with a critical length of about 5 alternate T and G conformers in iPS [53], 10 TT sequences in sPS [14] and 12 monomer units in iPP [26]. When the sample is annealed at a temperature above T_g, the critical length at which the isotropic phase becomes unstable is given by following equation [14]:

$$L = \frac{4.19M_0}{bl_0\rho N_A} \tag{1}$$

where L is the persistence length, b the diameter of the polymer segment, ρ the bulk density of polymer, N_A Avogadro's number, and M_0 and l_0 the molecular weight and length of the monomer, respectively. For the sPP melt, accounting for the helical conformation of finally obtained sPP Form I crystal, M_0, b, l_0, and can be taken to be 42 g/mol, 0.56 nm, 0.217 nm, and 0.85 g/cm^3, respectively. With these parameters, the critical length L was found to be 2.83 nm, the level of parallel ordering of helix structure starts to grow, and then crystallization occurs. Since the crystalline sPP has a 4_1 helix conformation and the c axis of the repeat unit is 0.74 nm long, 2.83 nm corresponds to 16 monomer units or 4 consecutive TTGG conformations.

4. Conclusions

In situ FTIR spectroscopy and WAXD experiments were carried out to investigate the isothermal crystallization process of sPP from molten state. The intensity of characteristic absorbance bands of sPP helical conformation at 1005, 867 and 812 cm^{-1} increased with crystallization time before the appearance of the crystal structure of sPP form I crystal structure formed. The FTIR results indicate that the characteristic absorbance band at 867 cm^{-1} has the highest initial normalized intensity, would be the band that is the most sensitive to the shortest helical sequence lengths. The band at 1005 cm^{-1} increases earlier than that of 812 cm^{-1} during the induction period of the sPP crystallization, would be sensitive to shorter helical sequence length than that of 812 cm^{-1}. And the normalized profiles at 1005, 867 and 812 cm^{-1} synchronize each other after holding the sPP melt at 112 °C for 80 min. It is speculated that the ordered structure developed during the induction period of the sPP crystallization. The critical length can tentatively be determined on the basis of Doi's theory. It is calculated that the critical length of helical sequences based on Doi theory is 16 monomer units.

Acknowledgment

We thank Dr. Xuanbo Liu and Prof. Erqiang Chen from Department Polymer Science and Engineering, Peking University for kind help on WAXD experiments. This work was supported by National Natural Science Foundation of China (Grant No. 50821062, 20634050).

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