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A possible explanation to the structure change of isotactic polypropylene occurring at about 135°C

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Abstract

The in situ Fourier transform infrared spectroscopic study of isotactic polypropylene (iPP) shows that a structure change occurs at about 135°C. Some experimental results suggest that this structure change may result from the disordering of helical sequences in the non-crystalline region, which can be further confirmed by the in situ infrared observation of chloride polypropylene (Cl-PP). If the iPP sample is drawn, the transition temperature is elevated. According to the change of infrared absorbance with temperature between 135 and 155°C, the various regularity bands of iPP can be rearranged in terms of the order degree from high to low: 940, 1220, 1167, 1303, 1330, 841, 998, 900, 808, 1100 and 973 cm^{-1}. This sequence is identical with our recent observation based on the melting of iPP crystals. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fourier transform infrared spectroscopy; Isotactic polypropylene; Non-crystalline region

1. Introduction

The mid-infrared spectrum of isotactic polypropylene (iPP) has been well studied during the past 40 years [1–6]. In 1988, Hanna et al. [7] measured the peak absorbance as a function of temperature for various regularity bands. It has been found that the absorbance of a regularity band decreases linearly with increasing temperature to about 135°C, beyond which the intensity decreases much more rapidly. This fact indicates that a structure change occurs for iPP sample at about 135°C. Combined with the experimental data of IR, Raman, NMR and the coefficient of linear expansion, the authors [7] pointed out that this structure change is athermal and therefore is not attributable to premelting. However, they did not give the origin of the structure change occurring at 135°C. In this paper, the infrared spectra of iPP and chloride polypropylene have been carefully investigated, and a possible mechanism to interpret the structure change at 135°C is proposed.

2. Experimental

The isotacticity of the iPP used in this study was 94.5%, and the melt flow index was 3.0 g/10 min. In order to erase the previous thermal history, the iPP film was melted at 210°C for 10 min. Then, the sample was (a) crystallized at 130°C for half an hour and then quickly cooled to 0°C; (b) crystallized at 145°C for 27 h and then quickly cooled to 0°C; (c) crystallized at 110°C for 5 min and then quickly cooled to 0°C; (d) quenched from the melt to the liquid nitrogen. An iPP film directly quenched from the melt was drawn on an Instron 4465 tensile machine at 5.0 mm min^{-1} cross-head speed at room temperature (20°C). The drawn film had draw ratio of 8×.

The chloride polypropylene (Cl-PP) sample was analyzed by PE Series 200 GPC and M_n (M_w/M_n) determined as 22,000 (5.4) on the basis of a calibration with narrow polystyrene standards. The amount of chloride in Cl-PP was 35%.

IR spectra of iPP and Cl-PP were recorded at a resolution of 4.0 cm^{-1} using a Bruker Equinox-55 FTIR spectrometer equipped with a variable temperature cell. The samples were heated from 20 to 210°C at 5°C min^{-1}. In the meantime, the IR spectra were recorded at the rate of 1 spectrum per 10 s so that the relationship of the intensity with temperature can be obtained. Here, the IR intensity of regularity bands refers to the peak area. For 1167 cm^{-1} band, the curve-fitting procedures were adopted. On the other hand, due to the severe overlap of various bands in the wavenumber of 2800–3000 cm^{-1}, peak absorbance (instead of

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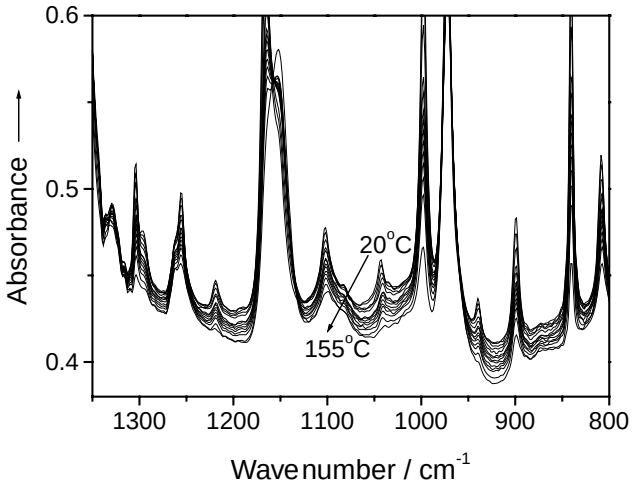

Fig. 1. IR spectra of iPP at the heating rate of 5°C min^{-1}.

the integrated intensity) was obtained for the conformational band. For all experiments, the scanned wavenumber range was 4000–400 cm^{-1}.

3. Results and discussion

It is well known that the macromolecular chain of semicrystalline iPP has 3_1 helix structure and the intramolecular coupling oscillation of various atomic groups in isotactic sequence gives rise to the IR regularity bands [8]. The bands of 1330, 1303, 1220, 1167, 1100, 998, 940, 900, 841 and 808 cm^{-1} belong to the regularity bands, and they are related to different critical length (n) of isotactic sequences [7,9–15]. The longer the isotactic sequence, the higher the order degree of the correspondent regularity band. Concerning the 973 cm^{-1} band, it has been well reported that this band is not only attributed specifically to the polypropylene head-to-tail sequence of repeating units,

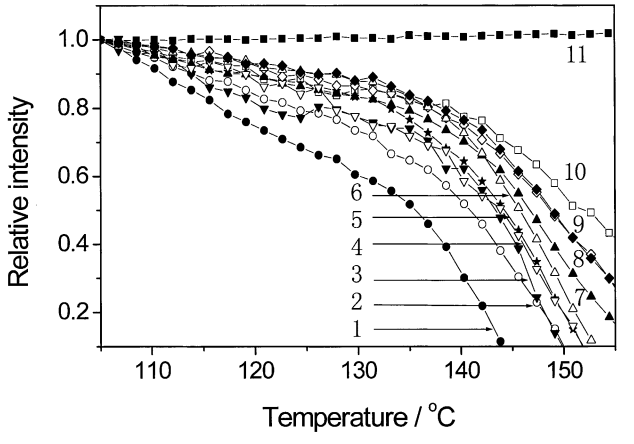

Fig. 2. Temperature dependence of the infrared regularity bands near: (1) 940 cm^{-1}; (2) 1220 cm^{-1}; (3) 1167 cm^{-1}; (4) 1303 cm^{-1}; (5) 1330 cm^{-1}; (6) 841 cm^{-1}; (7) 998 cm^{-1}; (8) 900 cm^{-1}; (9) 808 cm^{-1}; (10) 1100 cm^{-1}; (11) 973 cm^{-1} in iPP at the heating rate of 5°C min^{-1}.

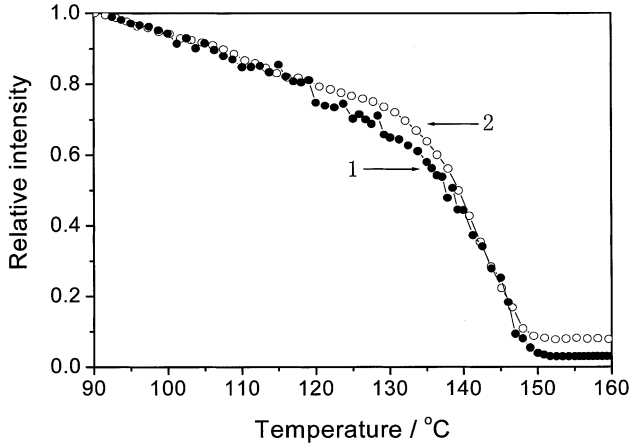

Fig. 3. Temperature dependence of the 998 cm^{-1} band of iPP sample with different thermal history: (1) quenched from the melt to the liquid nitrogen; (2) crystallized at 145°C for 27 h and then quickly cooled to 0°C.

but also associated with the presence of short isotactic helices [10,11,16]. Fig. 1 gives the IR spectra of iPP sample crystallized at 130°C for half an hour, which is measured at various temperatures with the heating rate of 5°C min^{-1}. With increasing the temperature, the intensity of various regularity bands decreases. Fig. 2 is the plot of relative intensity of various regularity bands vs. temperature. It can be found that for all regularity bands there is a linear decrease of absorbance with increasing temperature to about 135°C, beyond which the absorbance decreases much more rapidly. This fact indicates that a structure change occurs in the vicinity of 135°C.

In order to clarify the origin of this structure change, four samples with different thermal history were prepared: (a) iPP sample was crystallized at 130°C for half an hour, and then quickly cooled to 0°C; (b) iPP sample was crystallized at 145°C for 27 h, and then quickly cooled to 0°C; (c) iPP sample was crystallized at 110°C for 5 min, and then quickly cooled to 0°C; (d) iPP sample was directly quenched from the melt to the liquid nitrogen. Although the thermal history of different samples changes greatly, the transition temperature is almost similar to one another, which displays that the structure change occurring at 135°C does not come from the premelting of crystalline phase. Fig. 3 presents two examples of temperature dependence of the 998 cm^{-1} band for different iPP samples, corresponding to the highest and lowest degree of crystallinity. It can be observed that the sample with low degree of crystallinity gives more remarkable change in the IR intensity, which seems to suggest that the structural change at 135°C may be related to the amorphous region. Hanna et al. [7] adopted another method to study this structure change: the iPP sample was stepwise heated to different temperatures, after equilibrated for a period of time the infrared spectrum was recorded. They observed that the transition temperature is not only independent of the thermal history, but also identical in both cooling and heating processes cycled between 100 and 155°C. Their

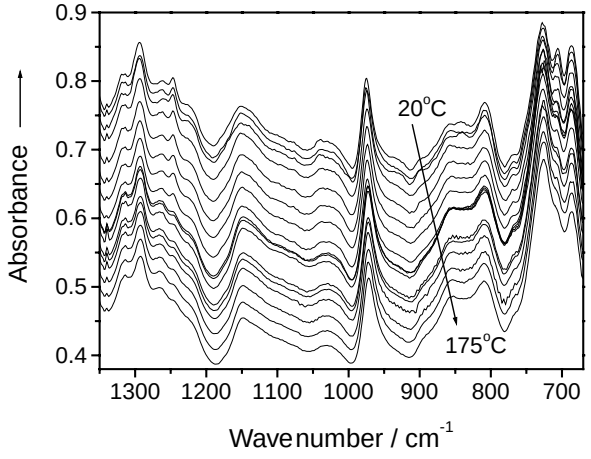

Fig. 4. IR spectra of Cl-PP at the heating rate of 5°C min^{-1}.

observation further confirms that the structure change occurring at 135°C cannot be the result of a premelting phenomenon. Moreover, Hanna et al. [7] also determined the linear dimension of different iPP samples as a function of temperature over the temperature range 60–160°C using rectangular specimens. They found that the coefficient of linear dimension of bulk sample becomes larger when the temperature is higher than 135°C, illustrating the rapid increase in volume and decrease in density above the transition temperature. However, Isasi et al. [17] had reported that the thermal expansion coefficient of the unit cell specific volume for the highly stereoregular polypropylene is constant up to at least 150°C. Our recent WAXD study [18] also indicated that no sudden change for the lattice spacings of iPP crystal cell exists in the vicinity of 135°C. It demonstrates that there is no a sudden change in volume and density for the crystalline region of iPP sample. Consequently, the structure change occurring at 135°C should be related to the non-crystalline region. Many investigations [19,20] have proven that the helical sequences are present not only in the crystalline phase, but also in the smetic phase and amorphous region. Obviously, the structure change of

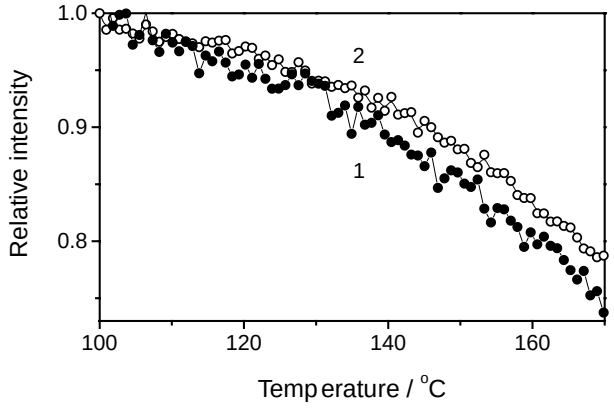

Fig. 5. Temperature dependence of the infrared regularity bands near: (1) 808 cm^{-1}; (2) 973 cm^{-1} in Cl-PP at the heating rate of 5°C min^{-1}.

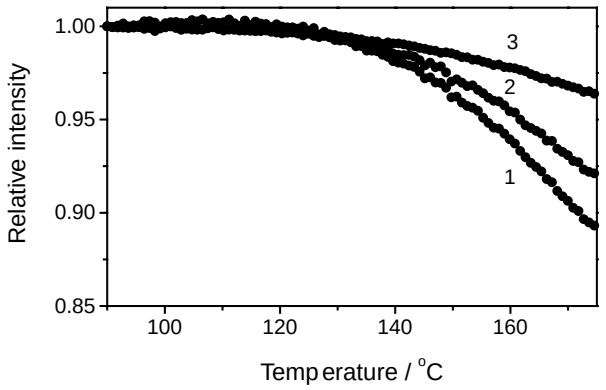

Fig. 6. The variation of conformational bands vs. temperature for Cl-PP at the heating rate of 5°C min^{-1}: (1) $A_{2880\ cm^{-1}}$; (2) $A_{2950\ cm^{-1}}$; (3) $A_{2880\ cm^{-1}}/A_{2930\ cm^{-1}}$.

helical sequences in non-crystalline region must have an important effect on the infrared absorption. Based on the experimental results aforementioned, a possible mechanism to interpret the structure change at 135°C is proposed: when the heating temperature is higher than 135°C, the mobility of helical regularity sequences in non-crystalline region increases dramatically, while the mobility of molecular chains in the crystalline region changes only slightly due to the restraint of crystal lattice; thus, the decrease of infrared absorbance comes from the disordering of helical sequences in non-crystalline region.

Our surmise can be corroborated by the spectroscopic study of chloride polypropylene (Cl-PP). Fig. 4 presents the IR spectra of Cl-PP at the heating rate of 5°C min^{-1}. Since a lot of hydrogen atoms are substituted by chlorine atoms, the Cl-PP is not crystalline. Compared with the spectra shown in Fig. 1, many regularity bands related to longer isotactic sequences disappear and only several bands related to shorter isotactic sequences are present in the IR spectra of chloride polypropylene. Fig. 5 is the plot of relative intensity of regularity band versus temperature for Cl-PP. It is apparent that the intensity of regularity bands decreases much faster as soon as the temperature is higher than about 135°C. Note that the 973 cm^{-1} intensity of Cl-PP decreases quickly when the temperature is higher than 135°C, which is different from that of iPP shown in Fig. 2. For iPP, most part of macromolecules are in 3_1 helix structure and the isotactic sequence is long, while only small part of Cl-PP molecules have helix structure and the isotactic sequence is very short. The variation of conformational bands vs. temperature is given in Fig. 6. The conformational bands near 2880 and 2950 cm^{-1} result from the CH_3 symmetric and asymmetric stretching modes, respectively, and they are related to the *trans* conformer [3,21,22]. Moreover, the $A_{2880\ cm^{-1}}/A_{2930\ cm^{-1}}$ value is sensitive to the physical state of hydrocarbon chains and can be used as an order/disorder parameter [21,22]. Fig. 6 shows that all of $A_{2880\ cm^{-1}}$, $A_{2950\ cm^{-1}}$ and $A_{2880\ cm^{-1}}/A_{2930\ cm^{-1}}$ decrease with increasing temperature, which means that the *gauche*

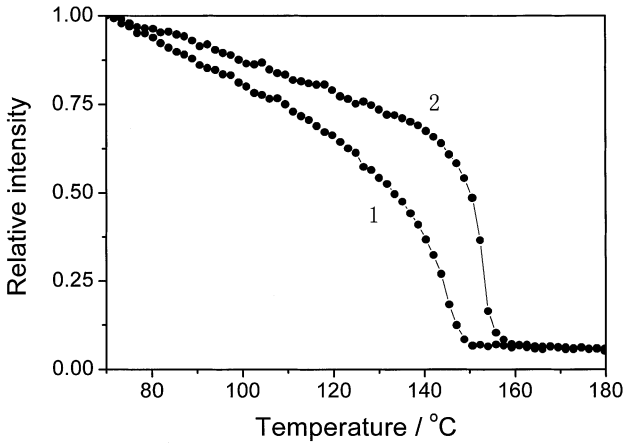

Fig. 7. The absorbance–temperature plot of: (1) undrawn and (2) drawn iPP sample. The draw ratio is 8×.

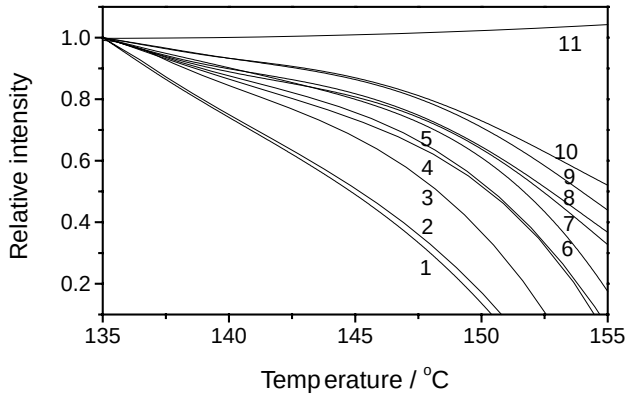

Fig. 8. Temperature dependence of the various regularity bands of iPP sample: (1) 940 cm^{-1}; (2) 1220 cm^{-1}; (3) 1167 cm^{-1}; (4) 1303 cm^{-1}; (5) 1330 cm^{-1}; (6) 841 cm^{-1}; (7) 998 cm^{-1}; (8) 900 cm^{-1}; (9) 808 cm^{-1}; (10) 1100 cm^{-1}; (11) 973 cm^{-1}. The heating rate is 5°C min^{-1} and the intensity at 135°C is set to unit.

conformers increase and the order of iPP sample falls with elevating the temperature. Both the regularity and conformational band observation of Cl-PP exhibits that a disordering process of helical sequences in amorphous state occurs at about 135°C. Therefore, it can be inferred that the structure change of iPP occurring at 135°C results from the disordering of helical sequences in non-crystalline region.

Fig. 7 provides the absorbance–temperature plot of drawn iPP sample. Due to the orientation of helical sequence in non-crystalline phase, the structural transition temperature is enhanced from 135 up to 145°C.

If the IR intensity of various regularity bands in Fig. 2 is normalized and the intensity at 135°C is set to unit, the change of absorbance with temperature is shown in Fig. 8. With increasing the temperature, the intensity of 940 cm^{-1} band decreases most quickly, then the 1220, 1167, 1303, 1330, 841, 998, 900, 808 and 1100 cm^{-1}. During the heating process, the intensity of 973 cm^{-1} band is almost unchanged. It is evident that the longer the helix length of isotactic sequence, the faster the intensity decrease of the correspondent band. Accordingly, the various regularity bands can be arranged according to the order degree from high to low: 940, 1220, 1167, 1303, 1330, 841, 998, 900, 808, 1100 and 973 cm^{-1}. This sequence is identical with our recent observation based on the melting of iPP crystals at higher temperatures [14].

Acknowledgements

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