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Morphological studies on syndiotactic polypropylene prepared by *ansa*-metallocenes

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Propylene was homopolymerized with the *ansa*-metallocene Ph_2C(fluorenyl)(cyclopentadienyl)$ZrCl_2$/methylaluminoxane catalyst to a highly syndiotactic polymer using a constant set of parameters. The properties of the pure syndiotactic polypropylene (sPP) such as molecular weight, chain microstructure and melting point were investigated, and the morphologies of uniaxially oriented films were studied by transmission electron microscopy. The oriented sPP films have a lamellar structure and a single-crystal-like texture from typical preparation conditions. In comparison with the X-ray diffraction pattern reported by De Rosa and Corradini, the electron diffraction pattern shows more detail but leads to the same structure (cell III structure).

(Keywords: syndiotactic polypropylene; electron microscopy; structure)

INTRODUCTION

The preparations of isotactic polypropylene (iPP) and syndiotactic polypropylene (sPP) have generally been known since the work of Natta *et al.*[1], but the physical properties of sPP have been less well investigated than those of the isotactic configuration. Compared to iPP, sPP has enjoyed no such commercial success. New catalyst systems, the highly active homogeneous Ziegler–Natta polymerization catalysts consisting of a group IV metallocene and methylaluminoxane are now of growing interest. The first example of these catalysts, the system Cp_2ZrCl_2/MAO[2–4] (Cp = cyclopentadienyl), polymerized ethylene with an extremely high activity to polyethylene but was not able to polymerize prochiral alkenes such as propylene in a stereospecific way. This disadvantage can be overcome using bridged metallocenes like $Ph_2C(fluo)(Cp)ZrCl_2$[5] (fluo = fluorenyl), which polymerizes propylene to highly syndiotactic polypropylene in sufficient quantities.

Previous investigators of the solid-state structure have proposed the existence of polymorphism in sPP. Drawn fibre samples have been analysed by Corradini *et al.*[6], solution-grown crystals have been studied by Marchetti and Martuscelli[7], and melt-grown single crystals have been investigated by Lotz *et al.*[8]. New investigations show that these different experimental observations have led to different models of chain packing[9]. Depending on the preparation method, three models for the orthorhombic packing of sPP in the helical conformation can be proposed: the *C*-centred cell I structure with space group $C222_1$; a modification of cell II with antichiral packing along the *a*-axis and space group *Pcaa*; and a modification of cell III with antichiral packing along the *a* and *b* axes and space group *Ibca* (*Figure 1*)[6–8]. A knowledge of the current catalyst technology and of the physical parameters influencing crystal structure could be helpful in making sPP a widely useful thermoplastic, semicrystalline polymer.

EXPERIMENTAL

All polymerization operations were performed under an argon atmosphere with standard Schlenk techniques, as used by one of the authors (W.K.) in previous experiments[3,4,10]. Toluene was refluxed and freshly distilled under argon from an Na/K alloy. Polymerization grade propylene was deoxygenated and dried by passage through columns of BASF R3-11 catalyst and 1 nm molecular sieves. The metallocene used was obtained from Hoechst AG. The polymerizations were carried out in a 1 l glass autoclave equipped with an external jacket for temperature control, a magnetic stirrer and several valves for argon and monomer inlet. Toluene (200 ml) and MAO (250 mg) were added to the autoclave. The mixture was stirred at 303 K and saturated with the gaseous monomer at an absolute pressure of 2×10^5 Pa. Meanwhile, MAO (50 mg) was dissolved in 5 ml of a solution of the metallocene in

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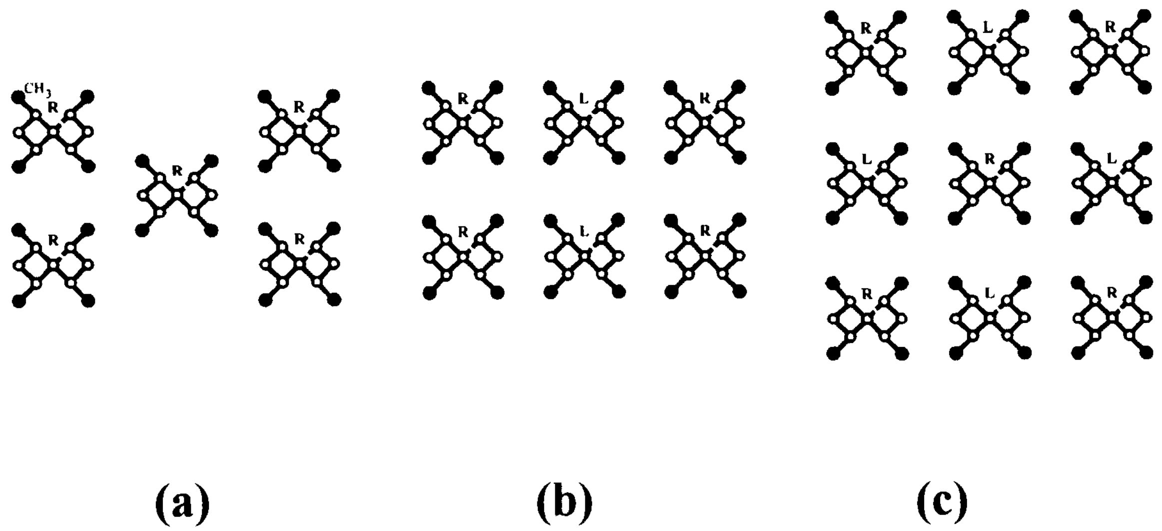

Figure 1 Proposed unit cells for the stable helical form of sPP: (a) *C*-centred cell I; (b) cell II with antichiral packing of chains along the *a* axis; (c) cell III with antichiral packing of chains along the *a* and *b* axes (R, right-handed helices; L, left-handed helices)

toluene (1.25×10^{-6} mol metallocene). After a 15 min preactivation time, this mixture was added via a syringe to the reactor. After 1 h the polymerization was quenched by blowing off the monomer and adding a few drops of ethanol. The obtained polymer was stirred in a 20 vol% ethanolic hydrochloric acid solution overnight, washed with water and ethanol and dried at 333 K to constant weight. The polymerization was performed at least five times using a constant set of parameters[10].

^{13}C n.m.r. measurements were made on a Bruker MSL300 spectrometer operating at 75.47 MHz. The samples were dissolved in 1,2,4-trichlorobenzene/1,1,2,2-tetrachloroethane-d_2 (10:1 v/v). Tactic block lengths n_{syn} were calculated from the integrations of the methyl signals in accordance with the method in the literature[11–13]. The molecular weight distributions were obtained by gel chromatography at 408 K in 1,2,4-trichlorobenzene as solvent using a Waters 150-C. The viscosity average molecular weights M_η were measured in decalin (decahydronaphthalene) at 408 K[14].

The thermal behaviour of sPP was studied using samples of 5 mg. The melting temperatures were determined with a TA/Du Pont DSC 2910 system at a heating rate of 10 K min^{-1}. Wide angle X-ray scattering (WAXS) curves were recorded using a Philips goniometer.

Crystallization was performed from the molten state (443 K) by rapidly cooling the samples in the calorimeter to their crystallization temperatures. Isothermal crystallization below 393 K resulted predominantly in the occurrence of the cell II modification. When we used the isothermal crystallization method and kept the samples above 393 K, no crystallization was observed even after several days. In order to crystallize a reasonable amount of the cell III modification, a method similar to the self-seeding technique[15] of solution crystallization was applied: the samples were cooled from the melt to 388 K, kept at that temperature for a few minutes and subsequently heated to the crystallization temperature (a maximum of 413 K). At the lower temperature the nuclei of the cell III modification were formed and they subsequently grew at the higher temperature, while the growth of the cell II modification was suppressed. Using this procedure, the samples were crystallized

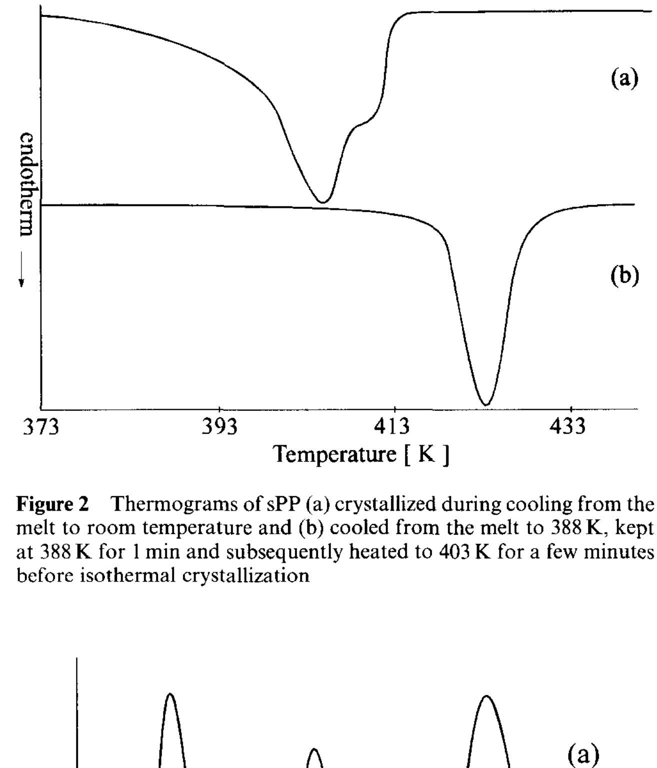

Figure 2 Thermograms of sPP (a) crystallized during cooling from the melt to room temperature and (b) cooled from the melt to 388 K, kept at 388 K for 1 min and subsequently heated to 403 K for a few minutes before isothermal crystallization

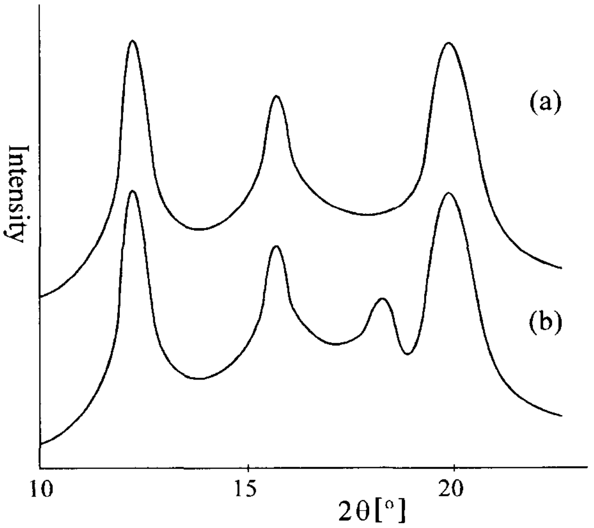

Figure 3 WAXS traces of the sPP samples from (a) *Figure 2a* and (b) *Figure 2b*

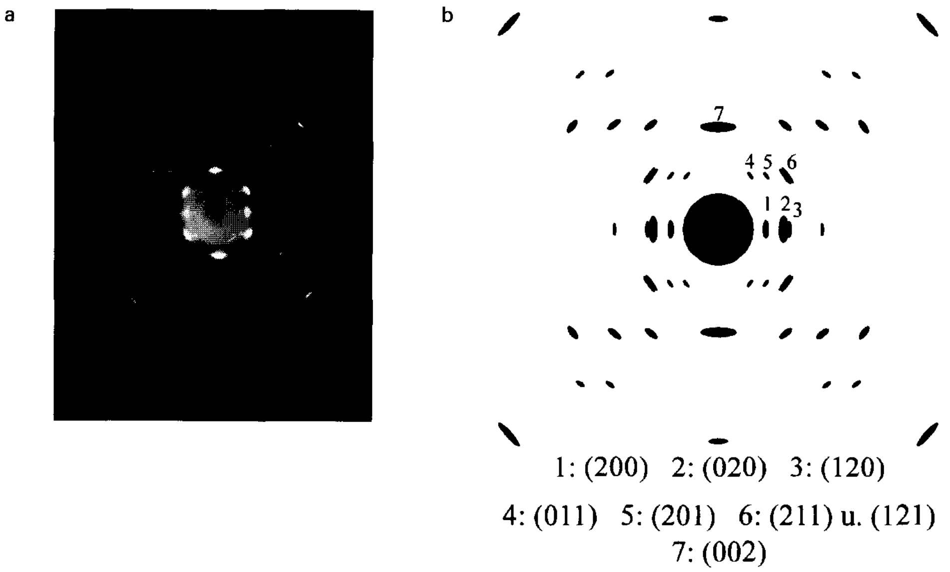

Figure 4 (a) Electron diffraction pattern of oriented sPP and (b) the corresponding sketch

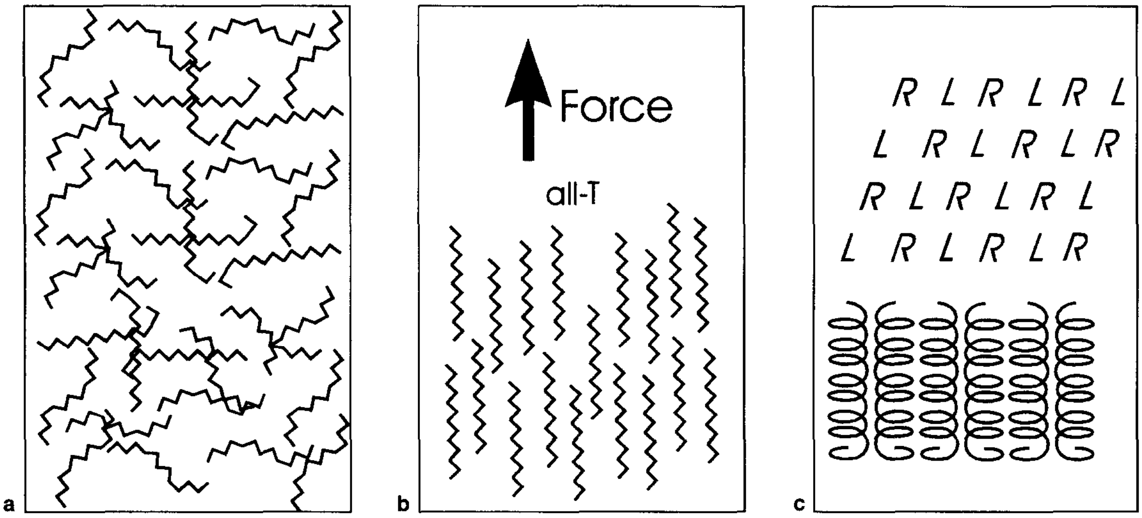

Figure 5 A new model for sPP crystallization kinetics: (a) the melt with a dominant *trans* conformation; (b) the all-*trans* conformation after drawing; (c) the thermodynamically stable cell III phase

predominantly with the cell III modification within a few minutes.

Highly uniaxially oriented films of sPP suitable for transmission electron microscopy (TEM) investigation were prepared by a special melt-drawing technique reported by Petermann and Gohil[16]. A small amount of a 0.5 wt% solution of the polymer in xylene was spread onto the surface of a hot glass slide (385 K), where the solvent was allowed to evaporate. The remaining thin, molten polymer film was picked up with a drawing speed of $10\,\mathrm{cm\,s^{-1}}$. The thicknesses of the resulting oriented solid polymer films were between 20 nm and 100 nm. Some of the films were annealed at a temperature of 403 K for 12 h. All films were directly used for investigation of their structure and morphology in a Philips EM-400T electron microscope operating at 100 kV.

Table 1 Calculated *d* values of the important reflexes shown in *Figure 4*

hkl	*d* (Å)[a]
200	7.25
011	6.09
020	5.60
120	5.22
201	5.18
211	4.70
121	4.27
002	3.70

[a] 1 Å = 0.1 nm

Table 2 Comparison of our data with those of De Rosa and Corradini[9]

hkl	Observed intensities (and structure factors) of De Rosa and Corradini	Observed intensities of our sample with a single-crystal-like texture
200	Very strong (77)	Weak
020	Strong (53)	Strong

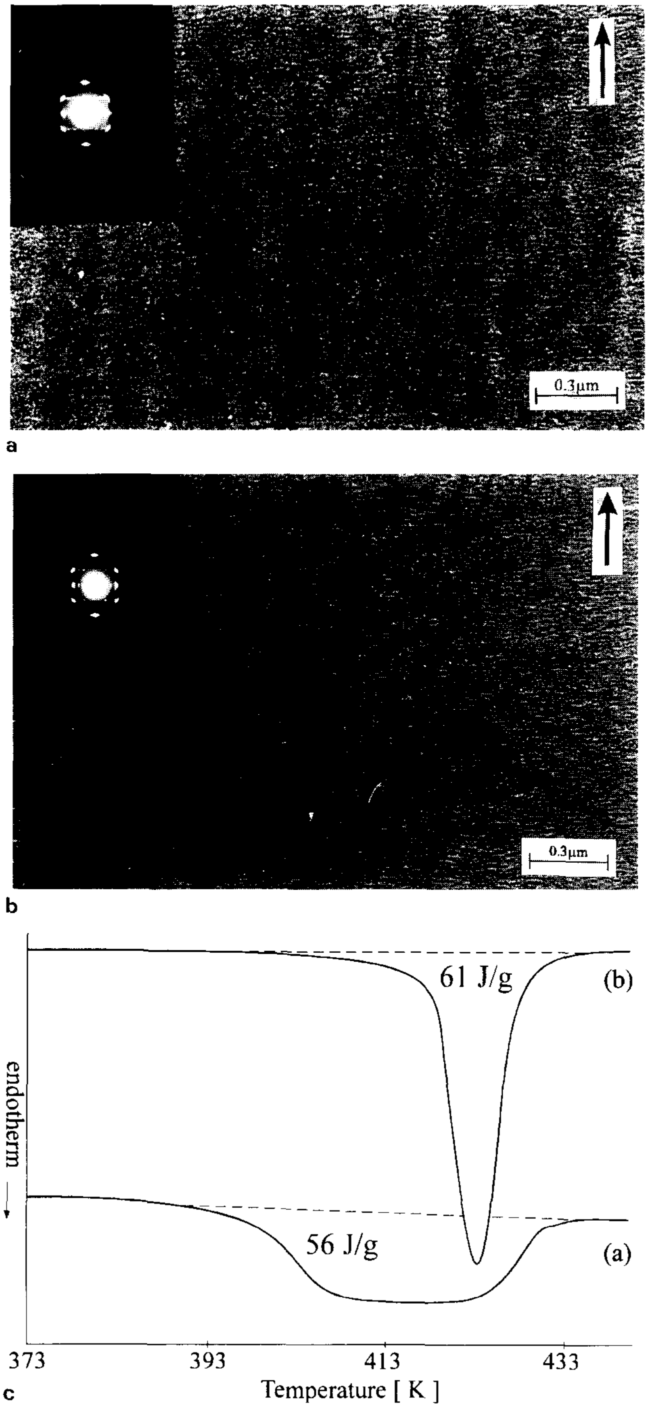

Figure 6 (a, b) Bright field electron micrographs of uniaxially oriented sPP: (a) as drawn; (b) annealed for 12 h at 403 K. The arrow indicates the drawing and crystallographic *c* direction. (c) The corresponding d.s.c. curves.

RESULTS AND DISCUSSION

The crystallization behaviour of sPP has been investigated since the mid-1960s, but such investigations have always been influenced by the poor quality of the material. With the new group of metallocene catalysts, sPP can be obtained relatively pure, so investigations without the influence of isotactic sequences or different molecular weight distributions can be made. The n.m.r. data exhibit for the sPP used a syndiotactic pentad content (rrrr) of more than 95%, with a syndiotactic sequence length n_{syn} of 21.1. The molecular weight distribution M_w/M_n was 2.3.

The double-peak melting behaviour in differential scanning calorimetry (d.s.c.) traces has been discussed in the literature[17,18] as a sign of polymorphism in sPP. The high and low temperature melting peaks may result from two different crystal structures or, in general, from a kinetically favoured low temperature phase and a thermodynamically stable high temperature phase of the same or a different crystal structure[18,19].

The d.s.c. heating trace of a sample cooled from the melt (443 K) in air to room temperature is shown in *Figure 2a*. A melting endotherm at 403 K is observed with an indication of a second melting peak at 410 K. By using the 'self-seeding' procedure and crystallizing at 403 K, only one melting endotherm was obtained at 424 K (*Figure 2b*). Corresponding WAXS investigations resulted in the diffraction peaks of the cell II modification (*Figure 3a*) and the cell III modification (*Figure 3b*), respectively. As the cell III modification is a superstructure of the cell II modification, it can be identified by the extra peak at $2\Theta = 18.9°$ from the 211 reflecting planes[20].

Figure 4a shows the electron diffraction pattern of an oriented sPP film prepared as described above; the corresponding sketch is shown in *Figure 4b*. The electron diffraction pattern exhibits more reflexes in comparison with the X-ray diffraction pattern, but is also consistent with the cell III structure.The *d* values of the 200, 011, 020, 120, 211 and 121 reflexes were calculated and they are consistent with the X-ray data of De Rosa and Corradini (*Table 1*)[9]; the space group was *Ibca*, and the unit cell was orthorhombic with $a = 1.45$ nm, $b = 1.12$ nm and $c = 0.74$ nm. From the electron diffraction pattern, a doubly textured orientation of the crystallites can be evaluated with the *c* and *b* axes in the plane and the *a* axis perpendicular to the plane of the film (single-crystal-like texture) by comparison of the reflection intensities with those of a non-oriented material. The structure factors (theoretical and experimental) of the 200 and 020 reflections predict a higher intensity for the 200 reflection, while in *Figure 4a* a much higher intensity for the 020 reflection is observed (*Table 2*).

In contrast to the cell II crystal structure, the slow-forming cell III structure forms only after very long crystallization times under normal isothermal crystallization conditions. So, after using the melt-drawing technique with its extremely short crystallization times, we find the appearance of the cell III structure surprising. A possible explanation for this result is sketched in *Figure 5*. From recent n.m.r. investigations it is known that a considerably high number of all-*trans* conformations of sPP are found in the amorphous state[21]. Additionally, the elongational deformation of the melt in the preparation conditions of the Petermann and Gohil method favours all-*trans* conformations. In the solid state, all-*trans* conformations appear as metastable chain conformations in cold-drawn sPP samples[22,23]. At elevated temperatures, the all-*trans* conformation transforms into the TTGG helix for reasons of denser packing of the crystalline structure, and the highly ordered cell III structure may be formed readily from elongated all-*trans* chains.

Figure 6a shows a bright field electron micrograph of a uniaxially oriented sPP film prepared as described above.

With phase contrast in underfocus conditions, the darker contrast correlates to the higher density or crystalline areas and the brighter contrast to the lower density or amorphous areas. The film shows a highly oriented crystalline lamellar structure with the growing direction of the lamellae perpendicular to the drawing direction. The thickness of the lamellae averaged at 10 ± 1 nm and the long period was 19 nm.

After heat treating the film at 403 K for 12 h, the lamellae became straighter and significantly thicker (*Figure 6b*). The thickness of the lamellae then came to 12 ± 1 nm with the same long period of 19 nm. The corresponding electron diffraction pattern showed no difference from the pattern for the as-drawn sample. The d.s.c. investigations of these samples confirmed these observations. The melting endotherms of the heat-treated samples became smaller because of the more uniform crystal size distribution and the maximum was at a higher temperature because of the increase in crystal thickness (*Figure 6c*), which was manifested as a higher crystallization enthalpy. The network-like superstructure seen in the bright field micrograph can be attributed to a preparational artefact and may have resulted from impurities in the polymerization procedure.

CONCLUSIONS

The melting behaviour, structure and morphology of sPP were investigated. The formation of the cell III structure was studied for different thermal treatments and crystallization conditions under elongational flow. Annealing the stacked lamellar morphology of the cell III crystal structure resulted in a considerable increase in crystal thickness but no change in long period.

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