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Epitaxial crystallization of syndiotactic polypropylene on uniaxially oriented polyethylene

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The epitaxial crystallization of syndiotactic polypropylene (sPP) on uniaxially oriented polyethylene (PE) has been investigated by electron microscopy and electron diffraction. It is found that the sPP lamellae grow epitaxially on the PE substrate film with the preference in sPP for the *b* axis as the fast growth direction. Instead of 50° as in the system of isotactic polypropylene with PE, the molecular chains of the sPP crystals are $\sim \pm 37°$ inclined to the chain direction of PE.

Keywords: polyethylene; syndiotactic polypropylene; epitaxy; morphology)

Introduction

In recent years many investigations have been devoted to epitaxial crystallization of polymers. Generally, according to the structure relationship, the epitaxy of polymers can be divided into two main categories. One type is the homoepitaxy between similar polymers with their molecular chains parallel to each other, as in the case of shish kebabs[1], where lamellae are growing epitaxially on fibres. The other type is heteroepitaxy between isotactic polypropylene (iPP) and some zigzag chain polymers, such as polyethylene (PE), polyoctenamer and nylons, with their chain directions $\sim 50°$ apart[2–11]. The latter has been explained by Lotz and Wittmann[5] in terms of the alignment of the zigzag chains along methyl group rows of α-iPP with 0.5 nm intermolecular distances for a chain–row match. Recently, an epitaxial relationship between iPP and syndiotactic polystyrene (sPS) was reported with the chain direction $\pm 40°$ apart[12]. In this work a new epitaxial relationship between syndiotactic polypropylene (sPP) and PE has been confirmed with their chain directions $\sim 37°$ apart. This new orientation relationship may help for the further understanding of the mechanisms of epitaxial crystallization in polymers.

Experimental

The high density PE used in the experiment was Lupolene DX (BASF AG Ludwigshafen, Germany). The sPP was kindly supplied by the FINA Corp. The melting temperature of sPP is $\sim 129°C$. Uniaxially oriented thin films of PE were prepared according to the technique reported by Petermann and Gohil[13]. A small amount of a 0.5 wt% solution of the polymer in xylene was poured and spread on a preheated glass slide (125–130°C). After evaporating the solvent the remaining polymer film was picked up with a drawing speed of $\sim 20\ cm\ s^{-1}$. The resulting films of PE were ~50 nm thick and were directly used for TEM investigations. Thin films of sPP were solution-cast from a 0.1 wt% solution in xylene on the surface of glycerin at a temperature of $\sim 80°C$. Heat treatments of double layered films of sPP and PE were carried out in a differential scanning calorimeter at a temperature above the melting temperature (T_m) of sPP (129°C) and below T_m of PE (132°C). For the epitaxial crystallization of sPP on PE films from solution, sPP was dissolved in a 0.1 wt% solution in xylene at 120°C. Subsequently, the solution was cooled down to 55°C, and the PE film, which was preheated at the same temperature in pure xylene, was immersed and held for a specified time. Electron microscopy and electron diffraction on the films were performed using a Philips EM-400T electron microscope operated at 100 kV.

Results and discussion

Figure 1a shows an electron micrograph of a PE substrate film. The film consists of oriented lamellae and needle crystals, i.e. shish-kebab morphology. The electron diffraction indicates a high degree of chain axis orientation as well as a single crystal like texture in which the *a* axis is preferentially oriented perpendicular to the film plane and the *c* axis is oriented along the drawing direction. The crystal structure of sPP was investigated by Corradini *et al.*[14] as the $C222_1$ space group with lattice constants $a = 14.5$ Å, $b = 5.6$ Å and $c = 7.4$ Å. It was proved that the molecular chain has a $(t_2g_2)_2$ conformation which corresponds to an s(2/1)2 symmetry. *Figure 1b* shows an electron micrograph of the solution-cast film of sPP. The film has a lamellar morphology with random growth directions. The electron diffraction pattern inset in *Figure 1b* exhibits strong reflections of the (2 0 0) and (0 1 0) planes in the sPP crystals.

Figure 2a shows the electron micrograph of the sPP–PE layered film annealed at 130°C for 10 min and then cooled to room temperature. Most of the sPP lamellae exhibit a cross-hatched structure with $\sim \pm 53°$ inclination to the chain direction of PE. *Figure 2b* is the

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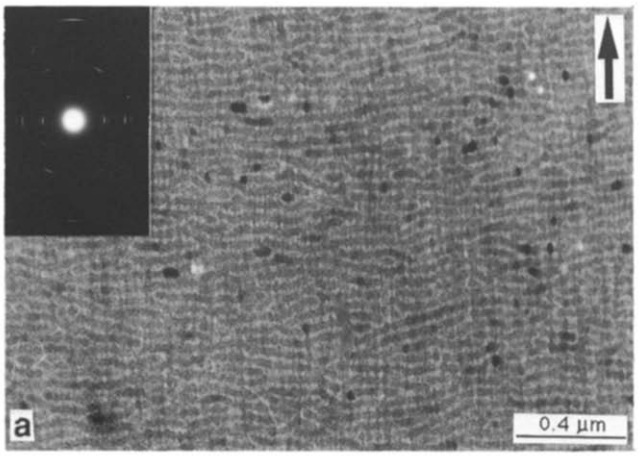


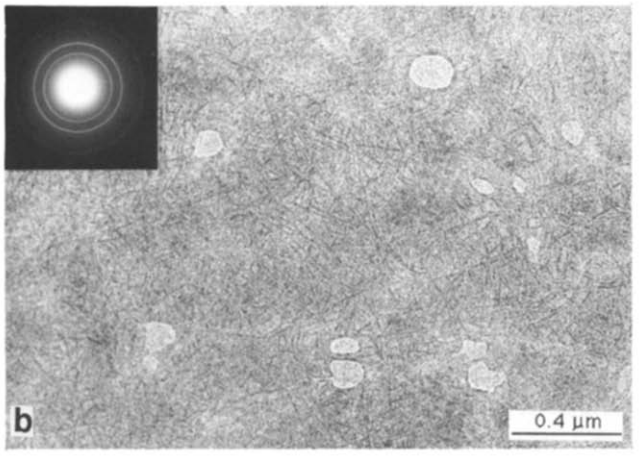
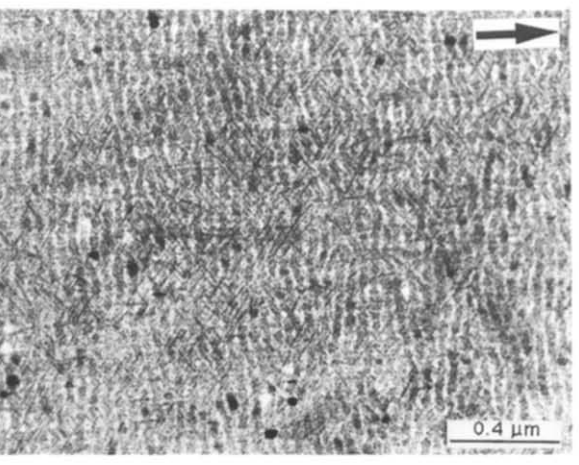


Figure 1 (a) Transmission electron micrograph and electron diffraction pattern (inset) of PE substrate film. The molecular direction is indicated by an arrow. (b) Morphology and electron diffraction pattern (inset) of a solution-cast film of sPP

corresponding electron diffraction pattern and *Figure 2c* is a sketch of this pattern with the main crystallographic directions indicated. The chain directions of the sPP crystals are in the substrate surface but $\pm 37°$ inclined with respect to the molecular direction of the PE substrate film. The strong reflections of (0 1 0) planes and the absence of (2 0 0) reflections of sPP indicates that the *b* axis is oriented in the film plane and the *a* axis is oriented perpendicular to the surface of the film. Obviously, the lamellar growth direction of sPP is along the *b* axis, while the (2 0 0) surface becomes the contact plane to the PE film surface. It should be pointed out that, in addition to the cross-hatched structure of sPP, some of the sPP lamellae can be seen with their growth direction parallel to the chain direction of the PE film (*Figure 2a*). No reflections of these crystals, however, can be observed in the electron diffraction pattern (*Figure 2b*) because they are too few in number. Nearly the same crystalline morphology of sPP crystallized on oriented PE films from dilute solutions of sPP at 55°C for 5 h can be observed (*Figure 3*). The epitaxial relationship between the sPP and the PE crystals is the same as in the layered films, with their molecular chain $\sim \pm 37°$ apart. More complex textures with the sPP perpendicular to the substrate PE films are observed at crystallization temperatures below 50°C and above 60°C.



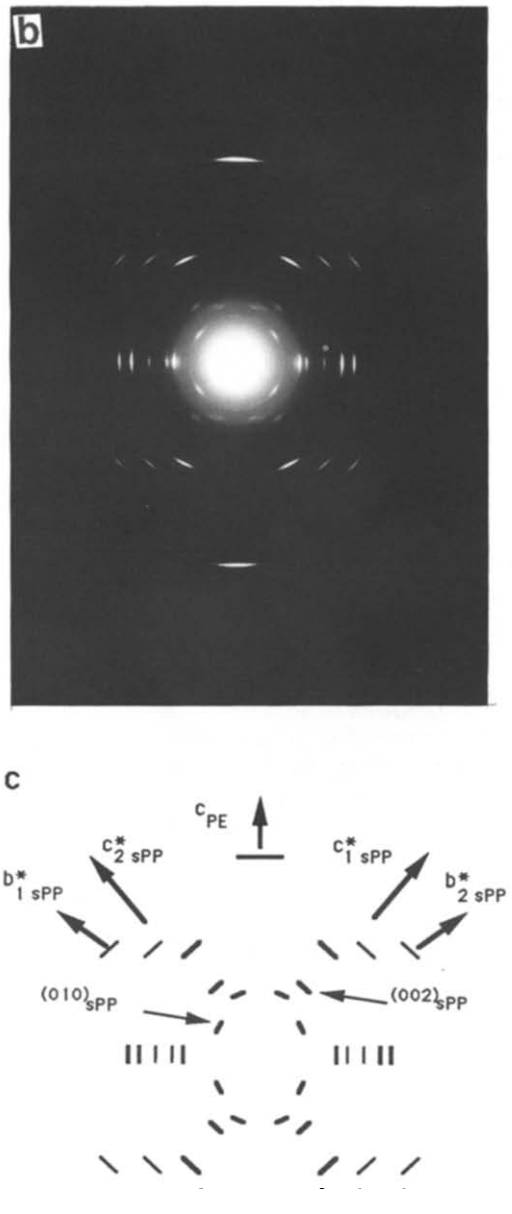


Figure 2 (a) Transmission electron micrograph of layered sPP–PE films annealed at 130°C for 10 min, and cooled to room temperatur The molecular direction of PE is indicated by an arrow corresponding electron diffraction pattern; (c) sketch of the di pattern

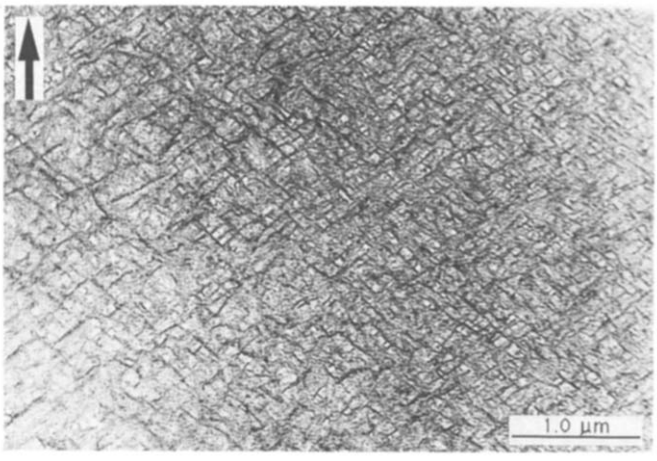


Figure 3 Transmission electron micrograph of sPP crystallized on oriented PE film from a solution of sPP at 55°C for 5 h. The molecular direction is indicated by an arrow

Finally, it should be emphasized that the new orientation relationship between the sPP and PE crystals discussed above can hardly be explained by only a chain–row matching[5]. Further studies of the mechanisms and controlling factors of the epitaxial crystallization in polymers are necessary and the new orientation relationship may help in its understanding.

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