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Epitaxial crystallization in the sPP/nylon-12 semicrystalline polymer system

Shouke Yan and Jürgen Petermann*
Institute of Materials Science, Department of Chemical Engineering, University of Dortmund, 44221 Dortmund, Germany

and Decai Yang
Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China
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The epitaxial crystallization behaviour of syndiotactic polypropylene (sPP) on highly oriented nylon-12 substrates has been investigated by means of transmission electron microscopy. The results obtained from bright field electron microscopy and electron diffraction indicate that sPP crystals grow epitaxially on the oriented nylon-12 substrate with their c-axes ± 37° apart from the chain axis of the nylon-12 substrate. The contact planes of the sPP crystals are the (100) lattice planes. Moreover, the epitaxial crystallization of nylon-12 on highly oriented sPP substrates from a dilute solution in cyclohexanone has also been studied using optical microscopy. The results show that the nylon-12 crystals grow epitaxially on the oriented sPP substrate with the oriented nylon-12 lamellae forming large, anisotropic domains. Copyright © 1996 Elsevier Science Ltd.

(Keywords: nylon-12; syndiotactic polypropylene; epitaxy)

INTRODUCTION

Since the early 1980s, heteroepitaxy between polymers has been reported on numerous occasions, and has been an extremely active subject in polymer science. Among these reports, more attention has been paid to the epitaxial crystallization of isotatic polypropylene (iPP) with some zigzag chain polymers in which the zigzag chains are inclined ± 50° to the iPP chain direction[1–5]. This kind of epitaxial orientation relationship has been explained in terms of the alignment of the zigzag chain segments along methyl group rows in the (010) lattice plane of iPP with a 0.5 nm intermolecular distance for chain–row matching[6] and a 15% disregistry between the matching lattice spaces of the two crystals is considered as an upper limit[1]. Recently, the structure and morphology of syndiotactic polypropylene (sPP) have been extensively documented[7–10]. Also, the epitaxial crystallization of sPP with polyethylene (PE), as well as iPP, has been studied[11–13], and new epitaxial orientation relationships have been observed. The epitaxial relationship between sPP and iPP was explained in terms of the methyl group rows in the (010) lattice plate of iPP crystals, which are inclined at an angle of 50° to the molecular axes, being aligned parallel to the rows of $\{CH_3, CH_2, CH_3\}$ groups in the (100) lattice plane of sPP crystals, which are inclined at 45° to the molecular axes[11]. As a result, the c-axes of the two crystals are about 95° apart. For the sPP/PE system[13], the ± 37° inclination between the c-axes of PE and sPP has been explained in terms of the nearly parallel arrangement of PE chains with the rows of $\{CH_3, CH_2, CH_3\}$ groups in the (100) lattice plane of sPP crystals, which deviates 8° from the PE chain direction. It is actually a parallel alignment of the PE chains along the [021] direction in the (100) lattice plane of the orthorhombic sPP crystals with unit cell parameters $a = 1.45$ nm, $b = 1.12$ nm and $c = 0.74$ nm, for which the inclination of the c-axis of PE is exactly an angle of 37° to the chain direction of sPP. Further studies of the epitaxial crystallization of sPP on other polymeric substrates are necessary and may help us to understand the origin of the occurrence of heteroepitaxy between polymers. The purpose of this paper is to describe some experimental results regarding the epitaxial crystallization behaviour of the sPP/nylon-12 semicrystalline polymer system.

EXPERIMENTAL

The polymers used in this work were syndiotactic polypropylene (sPP), type EOD 93-07, from Fina Oil & Chemical Company and nylon-12, lot 2-1285, from Polyscience Inc. Uniaxially oriented thin films of sPP and nylon-12 were prepared according to a technique introduced by Petermann and Gohil[14]. Accordingly, a small amount of a 0.5 wt% solution of sPP in xylene or nylon-12 in cyclohexanone was poured and spread onto a preheated glass slide where the solvent was allowed to evaporate. After evaporation of the solvent, the remaining thin polymer film was then picked up by a motor-driven cylinder with a drawing speed of around $20\,\mathrm{cm\,s^{-1}}$. The temperatures used for preparing the

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* To whom correspondence should be addressed

melt-drawn films of sPP and nylon-12 were 100°C and 160°C, respectively. The resulting highly oriented films, which were about 50 nm thick, were mounted on copper grids and used directly for observation by transmission electron microscopy (TEM). For the TEM observations of the crystallization behaviour of sPP on the oriented nylon-12 substrate, the thin sPP film was floated on the surface of distilled water and mounted onto the surface of the oriented nylon-12, which was supported by a TEM copper grid. The layered films of sPP/nylon-12 were heated to 150°C for 15 min and quickly cooled to room temperature. For optical microscopy observations, a thin, oriented sPP film was transferred onto the surface of a glass slide and preheated to 80°C. Subsequently, a drop of a 0.1 wt% solution of nylon-12 in cyclohexanone at 80°C was added. After evaporation of the solvent, such samples were used directly for optical microscopy observation. A Philips CM200 TEM operating at 200 kV was used in this study. Bright field (BF) micrographs were obtained by defocusing the objective lens. In order to minimize radiation damage by the electron beam, we focused the beam on one area of the film, then moved the film so that the beam was trained on an adjacent, undamaged area and recorded the image immediately. Optical microscopy experiments were carried out with a Leitz type DMR microscope.

RESULTS AND DISCUSSION

Microstructures of highly oriented sPP and nylon-12 films

The crystal structure of sPP was first investigated by Corradini *et al.*[15] and found to have $C222_1$ space group with the lattice parameters $a = 1.45$ nm, $b = 0.56$ nm and $c = 0.74$ nm. The chain conformation of sPP is $(T_2G_2)_2$. Recently, the structure of sPP was studied carefully and a different chain-packing model with the unit cell constants $a = 1.45$ nm, $b = 1.12$ nm and $c = 0.74$ nm was proposed[7–9]. The space group and chain conformation were, however, the same as those proposed by Corradini *et al. Figure 1* shows a TEM micrograph of the highly oriented sPP film. The arrow in the micrograph indicates the drawing direction of the film. On the BF electron micrograph, small lamellae of sPP, which are aligned perpendicular to the drawing direction of the film, are visible. The corresponding electron diffraction pattern (inserted in *Figure 1*) reveals a high degree of chain axis orientation.

Figure 2a shows the BF electron micrograph of an oriented nylon-12 film. The arrow in the picture represents the drawing direction of the film. It can be seen that the melt-drawn nylon-12 film consists of oriented lamellae, which are aligned perpendicular to the drawing direction. The corresponding electron diffraction pattern is shown in *Figure 2b*. Strong equatorial (100), (010) and (110) reflections, as well as several meridional reflections, can be clearly seen. This diffraction pattern was identified as that of a hexagonal system with the unit cell parameters $a = 0.47$ nm and $c = 3.1$ nm, as given by Northolt *et al.*[16].

TEM observations of sPP epitaxially crystallized on a highly oriented nylon-12 substrate

Figure 3a shows a BF electron micrograph of a sPP/nylon-12 double-layered film, which was heat treated at 150°C for 15 min and then quenched rapidly to room temperature. The molecular direction of the nylon-12 substrate film is indicated by an arrow. It can be seen that after the heat treatment, the sPP recrystallized with all of the sPP lamellae being inclined very accurately at ±53° with respect to the c-axis of the nylon-12 substrate. The average thickness and length of the sPP crystals are about 10 nm and 150 nm, respectively. The corresponding electron diffraction pattern and a sketch of this pattern with the main crystallographic directions indicated are shown in *Figure 3b* and *Figure 4*, respectively. Obviously, there are two sets of sPP reflections, both of them having the ⟨021⟩ directions oriented parallel to the

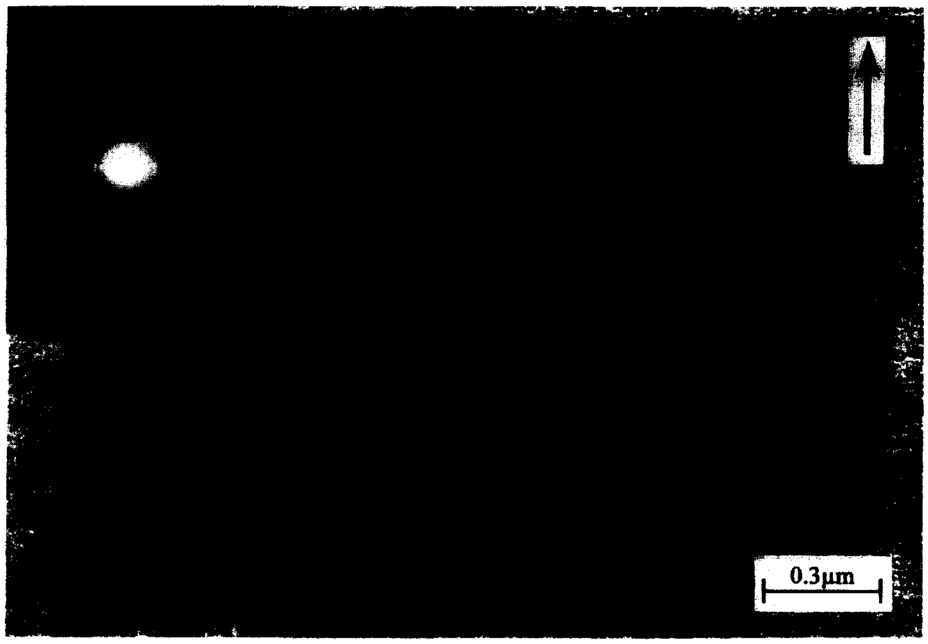

Figure 1 TEM micrograph of an oriented sPP film. The arrow indicates the drawing direction

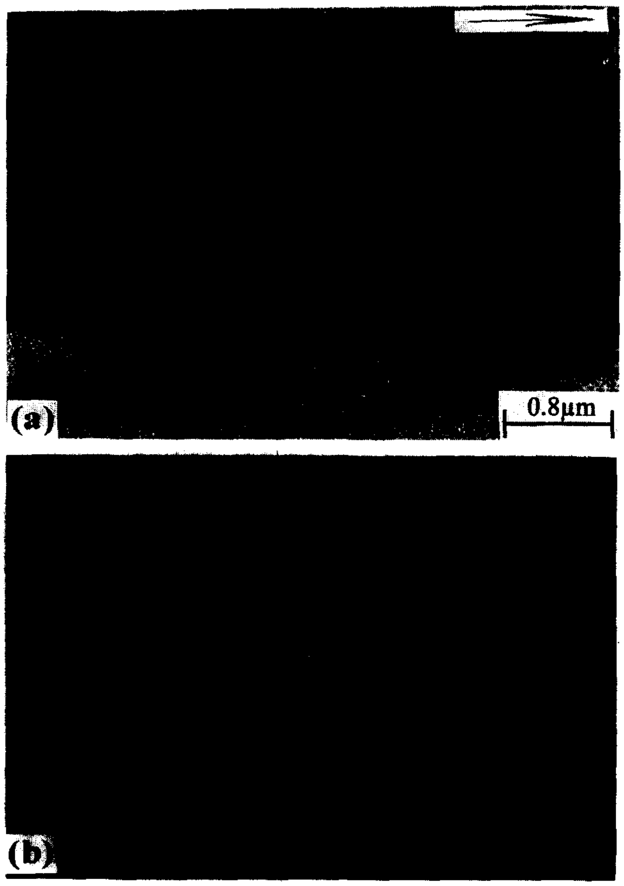

Figure 2 (a) A BF electron micrograph and (b) the corresponding electron diffraction pattern of a highly oriented nylon-12 film. The drawing direction is indicated by an arrow

fibre axis of nylon-12. The molecular directions of the sPP crystals are then in the substrate surface but ±37° apart from the *c*-axis of nylon-12. All of the strong reflections of the sPP can be indexed on the sPP orthorhombic unit cell with only the (020) diffraction spot visible on the equator, confirming that the (100) sPP lattice plane is the contact plane. A sketch of the molecular arrangement at the interface is given in *Figure 5*.

The result obtained here shows a close resemblance to the epitaxial crystallization of sPP with PE, where the *c*-axes of the two crystals appeared at the same angle apart. From the 0.447 nm interspacing distance between the (021) lattice planes of sPP and the 0.407 nm interspacing distance between the (100) or (010) lattice planes of nylon-12, the epitaxial crystallization of sPP on an oriented nylon-12 substrate can be explained in terms of crystallographic matching between sPP along the [021] direction and nylon-12 along the [100] or [010] direction with an acceptable disregistry of 8.9%.

Optical microscopy study of nylon-12 epitaxially crystallized on a highly oriented sPP substrate from a dilute solution in cyclohexanone

Figure 6 shows an optical micrograph of nylon-12 crystallized on the clean surface of a glass slide from a dilute (0.1 wt%) solution in cyclohexanone at 80°C. It can be seen that the nylon-12 crystals appear in crystalline aggregates, and the crystalline aggregates of nylon-12 grow in a spherulitic morphology.

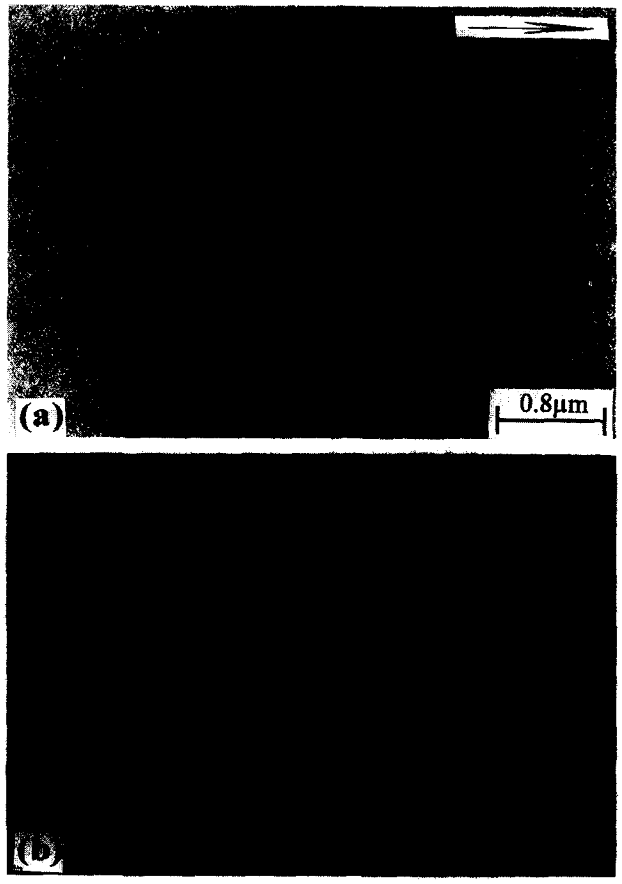

Figure 3 (a) A BF electron micrograph and (b) the corresponding electron diffraction pattern of an sPP/nylon-12 double-layered film which was heat treated at 150°C for 15 min and then quickly cooled to room temperature. The molecular direction of the oriented nylon-12 substrate is indicated by an arrow

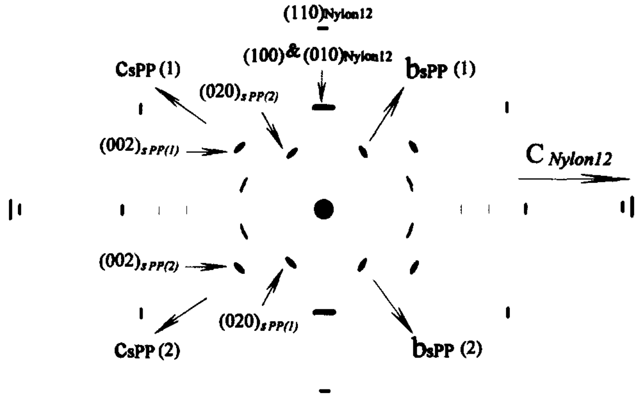

Figure 4 Sketch of the diffraction pattern of the sPP/nylon-12 double-layered film from *Figure 3b*

Figure 7a shows a polarized light micrograph of nylon-12 crystallized on a highly oriented sPP substrate from a 0.1 wt% solution in cyclohexanone at 80°C. The highly oriented sPP substrate film, as described above (see *Figure 1*), is too thin to give any contrast in the optical microscope under the polarized light and interferential conditions used here. The arrow in the picture represents the molecular direction of the oriented sPP substrate. It can be seen that nylon-12 also forms crystalline aggregates on the surface of the oriented sPP film.

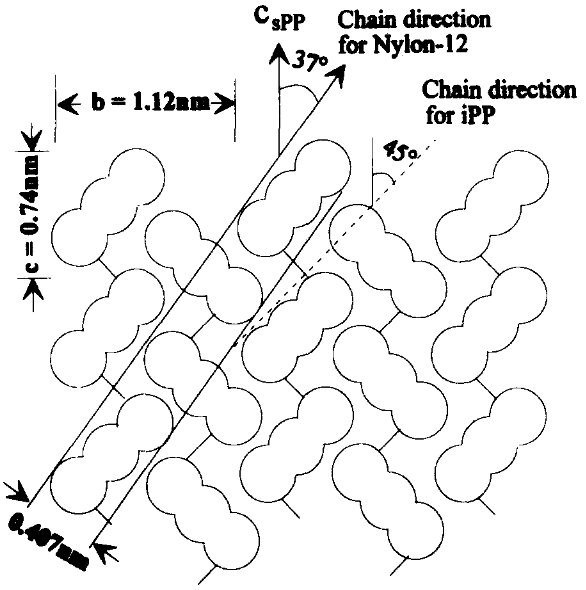

Figure 5 Sketch of the molecular arrangement at the (100) sPP lattice plane

Figure 6 Optical micrograph (polarization contrast) of pure nylon-12 crystallized on the clean surface of a glass slide

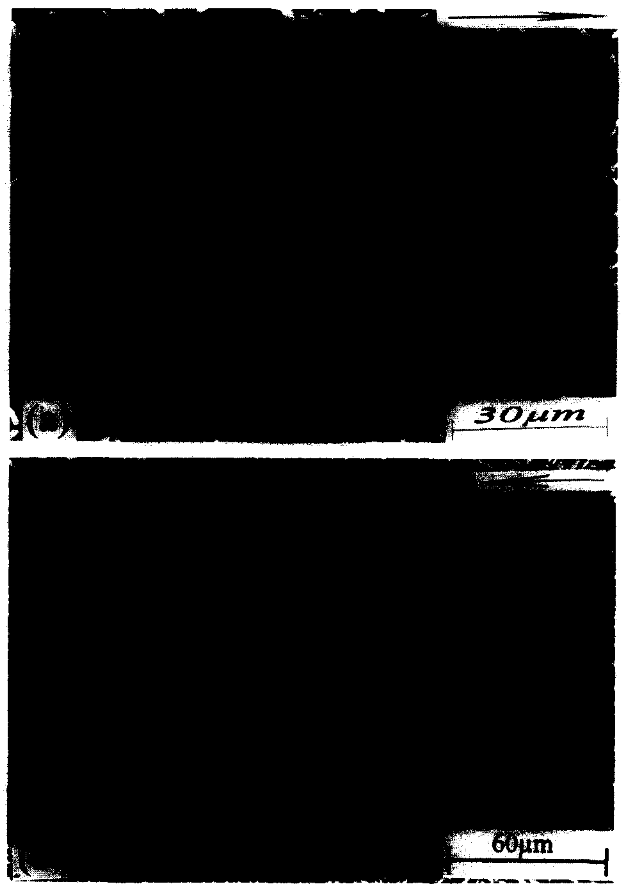

Figure 7 (a) Polarizing and (b) interferential optical micrographs of nylon-12 crystallized on the surface of the oriented sPP substrate. The arrow represents the molecular direction of the sPP substrate

However, unlike on the surface of the glass, where the nylon-12 crystals form spherulites, the nylon-12 crystalline aggregates formed on the surface of the oriented sPP substrate (as shown in *Figure 7a*) exhibit predominantly two directions with each of them being inclined by about ± 53° with respect to the molecular direction of the oriented sPP substrate. The same microstructure can also be imaged with optical interference contrast (as shown in *Figure 7b*). Under the preparative conditions used by us, the nylon-12 aggregates were too thick for TEM investigation. By combining the results obtained from TEM for the sPP/nylon-12 double-layered film, we can explain the morphology observed by optical microscopy in terms of the epitaxial crystallization of nylon-12 on the oriented sPP substrate with a similar orientation relationship as that seen for sPP crystallized on the oriented nylon-12 substrate.

It was noticed that the intensity of the polarized light contrast of the nylon-12 crystalline aggregates on the sPP film depended on the rotation angle of the sPP molecular direction with respect to the polarization direction. As shown in *Figure 8*, when the molecular direction of the sPP substrate is parallel to the polarization direction, the nylon-12 aggregates show strong contrast (*Figure 8a*). With rotation of the sample about the axis of the light beam, at first the intensity of the contrast for one set of nylon-12 aggregates increases, while that for the other set decreases. After about a 10° rotation, the contrast of both of the two sets of nylon-12 aggregates decreases. The contrast becomes very weak when the sample is rotated so that the molecular direction of the oriented sPP is at 45° to the polarization direction, and almost all of the crystalline aggregates of nylon-12 disappear (see *Figure 8b*). When the sample is further rotated, the contrast of the nylon-12 crystals changes once again, and becomes strong when the molecular direction of the sPP is perpendicular to the polarization direction (as shown in *Figure 8c*).

These observations are in accordance with the molecular orientation of the nylon-12 aggregates being within the contact plane and inclined by ± 37° to the molecular direction of the sPP substrate. However, no conclusion can be reached about the chain orientation within the elliptical nylon-12 aggregates. Two arrangements are possible (*Figure 9*), with the nylon-12 chain axes parallel or nearly perpendicular to the long axis of the ellipsoid. Selected area electron diffraction is suitable to solve this problem, but, as mentioned earlier, the aggregates are too thick for TEM investigation.

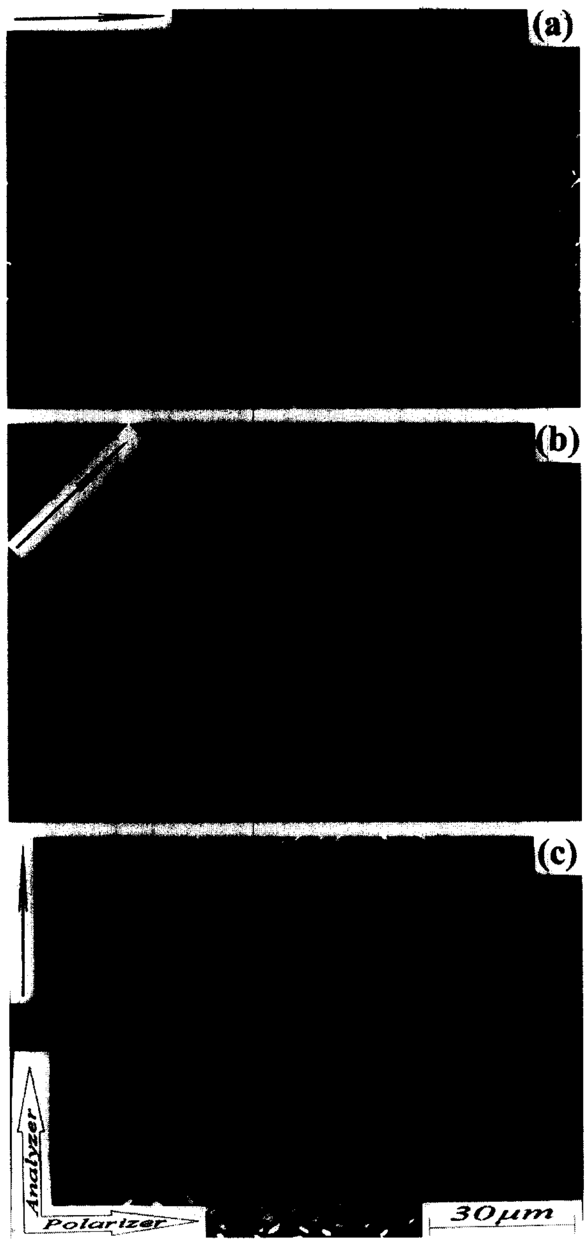

Figure 8 Polarizing optical micrographs of nylon-12 crystallized on the surface of the oriented sPP substrate. The molecular directions of the sPP substrate, which incline at different angles [(a) 0°, (b) 45° and (c) 90°] to the polarization direction, are indicated by the arrows

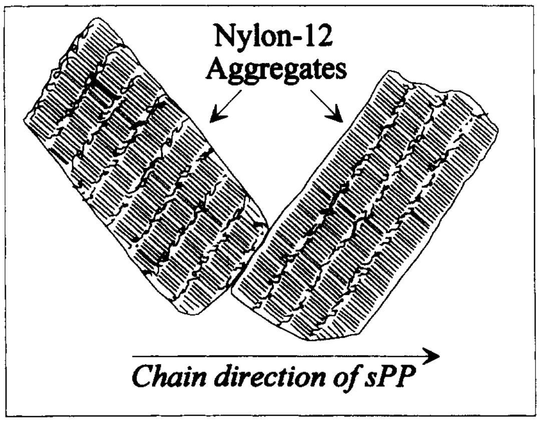

Figure 9 Sketch of the possible lamellar arrangements of nylon-12 on the sPP substrate

CONCLUSIONS

1. The experimental results obtained from BF electron microscopy and electron diffraction show that after melting and recrystallization, sPP crystals grow epitaxially on a highly oriented nylon-12 substrate and form a cross-hatched structure. The epitaxial sPP crystals are oriented, their *c*-axes being ± 37° apart from the fibre axis of the oriented nylon-12 film. The contact plane of sPP is the (100) lattice plane.
2. The optical polarization microscope can also be successfully used for the morphological study of the heteroepitaxy between polymers. By observation of the dependence of the contrast intensity of the crystals on the rotation angle of the sample with respect to the polarization direction, the orientation relationship of the chain axes between nylon-12 crystals and the sPP substrate has been obtained. The results indicate that nylon-12 can also epitaxially crystallize on the oriented sPP substrate from a dilute solution in cyclohexanone with the same orientation relationship as that for sPP/nylon-12 double-layered films.
3. The epitaxial relationship between nylon-12 and sPP can be explained in terms of the 0.447 nm interspacing distance along the [021] direction of the sPP crystals in the (100) lattice plane matching with the 0.407 nm interspacing distance of nylon-12 along the [100] or [010] direction. The mismatch, about 8.9%, is well within the usually accepted range of lattice matches for epitaxy ($\leq 15\%$).

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