Origin of Oriented Recrystallization of Carbon-Coated Preoriented Ultrathin Polymer Films

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ABSTRACT: The origin of oriented recrystallization behavior of vacuum carbon evaporated preoriented polymer thin films was studied by means of transmission electron microscopy and electron diffraction with elaborately designed experimental setups. Through the recrystallization of HDPE in the iPP/HDPE-C sandwich layers with its original chain orientation being preserved by the coated carbon other than epitaxially crystallized on the highly oriented iPP substrate as usually happened without carbon coating, the graphoepitaxial crystallization of the polymer melts on their surface carbon replicas is ruled out of the origin of the oriented recrystallization. Through the different melt recrystallization behavior of melt-drawn 1-iPB thin films on and with vacuum evaporated carbon layers, the strong fixing effect of vacuum evaporated carbon layers on the polymer films has been recognized. This is further confirmed by the dissolution test of the vacuum carbon deposited HDPE thin films. The exact mechanism of the fixing effect of vacuum evaporated carbon layers on the thin polymer films is not quite clear yet. The recognition of the fixing effect is, however, sufficient to explain the oriented recrystallization phenomenon of the carbon coated preoriented thin polymer films. Namely, the vacuum evaporated carbon layer on the polymer thin film has prevented the surface extended macromolecular stems of the crystals from melting or at least from a complete relaxing during high-temperature annealing, and the surface fixing confined crystallization has induced the oriented recrystallization of the thin polymer molten layer.

Introduction

Polymer materials can be processed into oriented structures through shearing their supercooled melts or high degree tensile deformation of their nonoriented solids. The highly oriented polymer materials exhibit unparalleled mechanical and physical properties compared with their isotropic species. For example, the stiffness and strength of highly oriented crystalline polymers[1−3] and the electrical conductivity of doped and aligned conjugated macromolecules[4] can increase to a factor of 100 compared with their nonoriented counterparts. Among many others, further examples of different performance of oriented polymeric materials are the exceptional anisotropic mechanical and physical properties, such as mechanical strength, electrical and thermal conductivity, thermal expansion, and so on.[1] These lead the highly oriented polymer materials to be an exciting research topic for the past few decades.

It is well-known that the well-aligned chains of oriented polymeric materials will be completely relaxed when they are heated to a temperature above their melting points and rearranged in a random way when they are cooled again. In other words, the preferred orientation will be eliminated through a melt recrystallization process. In our recent studies on the recrystallization behavior of carbon coated highly oriented polymer thin films,[5,6] it was found that a thin vacuum evaporated carbon layer on the top surface of the highly oriented polymer films can preserve the high orientation of them. The observed phenomenon may be of great importance for many applications, such as to produce micrometer-size structured polymer films with periodic or well-defined oriented and nonoriented structures through selective carbon coating with the help of microstructured masks and subsequent melt recrystallization.[7] The origin of it is, however, still not quite clear. One of the most acceptable mechanisms of the oriented recrystallization behavior may rest on the graphoepitaxy, i.e., the vacuum evaporated thin carbon layer forms a conformal coating of the ordered semicrystalline polymer surface, and subsequently turn to act as a graphoepitaxial template that induces the oriented regrowth of the polymer melts. But the graphoepitaxial overgrowth cannot well explain the changes of morphology from original shish crystals to lamellar crystals, chain conformation from the 3/1 helical chains to 11/3 helical chains, and the chain packing model from the hexagonal unit cell to a tetragonal one of the isotactic poly(1-butene) caused by recrystallization. Taking this into account, there must be some thing else that controls the oriented recrystallization process. Therefore, a detailed study on the mechanism of the oriented recrystallization behavior of the carbon coated preoriented polymer thin films is necessary.

The purpose of this paper is to present some detailed experimental results regarding the origin of the oriented regrowth of the carbon coated preoriented thin polymer films.

Experimental Section

The polymers used in this work were isotactic polypropylene (iPP), Novolene 1050FP, and high-density polyethylene (HDPE), Lupolen 6021DX, both from BASF AG Ludwigshafen, Germany. The isotactic poly(1-butene) (1-iPB) material, having a melting temperature of ∼130 °C, was purchased from Polymer Laboratories.

Uniaxially oriented thin films of HDPE, 1-iPB, and iPP were prepared according to a technique introduced by Petermann and Gohil.[8] According to this method, a small amount of a 0.5 wt % solution of the polymer (HDPE, 1-iPB, or iPP) in xylene

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was poured and uniformly spread on a preheated glass plate, where the solvent was allowed to evaporate. After evaporation of the solvent, the remaining polymer thin molten layer was then picked up by a motor-driven cylinder with a drawing speed of ~20 cm/s, and highly oriented thin polymer films were collected by glass slides. The obtained highly oriented HDPE, 1-iPB, and iPP films, about 30−50 nm thick, can be directly used for transmission electron microscopy observation. The preparation temperatures for HDPE, iPP, and 1-iPB were 130, 140, and 150 °C, respectively.

For checking the crystallization behavior of HDPE sandwiched between the highly oriented iPP film and the *directly* vacuum coated carbon layer, iPP/HDPE-C sandwich samples were prepared by transferring an oriented thin HDPE film onto the top surface of an oriented thin iPP film at first and then vacuum-evaporating a thin layer of carbon on the exposed surface of the highly oriented HDPE film. The thus prepared sandwich film was heat-treated at 150 °C for 15 min and subsequently quenched to room temperature on air.

To compare the crystallization behavior of the vacuum carbon coated 1-iPB thin films with that of carbon supported ones, some of the highly oriented 1-iPB thin films were *directly* vacuum carbon deposited before suffering any heat treatment, while the rest of them were simply put onto the top surface of *preformed* carbon support films before the heat treatments. Heat treatments of the samples were all carried out in a DSC apparatus, and the samples with the same thermal history were heat-treated simultaneously. Therefore, the melting and crystallization conditions of the 1-iPB crystals are exactly the same.

The experiments for the dissolution test were performed by simply putting the carbon coated HDPE melt-drawn thin films direct into the hot xylene solvent at 125 °C. After being dissolved in the hot solvent for various times, the carbon coated HDPE films were taken out of the solvent, washed with fresh hot solvent at the same temperature, and subsequently dried at ambient conditions.

For transmission electron microscopy observations, a Philips CM200 TEM operated at 200 kV was used in this study. Phase contrast bright-field (BF) micrographs were obtained by defocus of the objective lens.$^{9-11}$ To minimize radiation damage by the electron beam, focusing was carried out on an area, then the specimen film was translated to its adjacent undamaged area, and the image was recorded immediately.

Results

Oriented Recrystallization Phenomenon. The oriented recrystallization phenomenon of the carbon coated preoriented thin polymer films has been briefly described in a previous short communication.^{5} For a better understanding of the readers, a simple example is presented in Figure 1, which shows the BF electron micrographs and their corresponding electron diffraction patterns (insets) of the carbon coated melt-drawn HDPE thin films before and after the heat treatment. The arrows in the pictures represent the drawing direction of the film during preparation. In the defocused phase contrast BF images, the bright lines represent the lower mean inner potential amorphous regions, while the gray areas between the bright lines are the high-density crystalline lamellar regions. From the BF electron micrographs, it can be clearly seen that both the carbon coated original melt-drawn HDPE thin film (Figure 1a) and its melt recrystallized counterpart (Figure 1b) consist of highly oriented edge-on lamellae aligned perpendicular to the drawing direction. This demonstrates a high degree of orientation with the molecular chains aligned along the drawing direction. The electron diffraction results show that while the original melt-drawn HDPE thin films exhibit only a fiber orientation with their molecular chains arranged parallel to the drawing direction and crystallographic *a*- and *b*-axes rotated randomly about the chain direction,^{12} the melt recrystallized carbon coated melt-drawn HDPE films provide us a double orientation with the crystallographic *c*- and *b*-axes oriented in the film plane.^{13} This indicates that even a better orientation is achieved after the melt recrystallization. The doubly reoriented HDPE crystals result from the thin film crystallization habit that the fastest growth direction, *b*-axis for HDPE, grows preferentially in the film plane. It should be pointed out that the oriented recrystallization phenomenon is observed not only for HDPE but also for many other polymers. Furthermore, it is independent of the preparation method of the highly oriented samples. Table 1 summarizes a variety of species which we tested to show the same effect. For a direct comparison, their crystalline structures before and after the heat treatments are listed in Table 1.

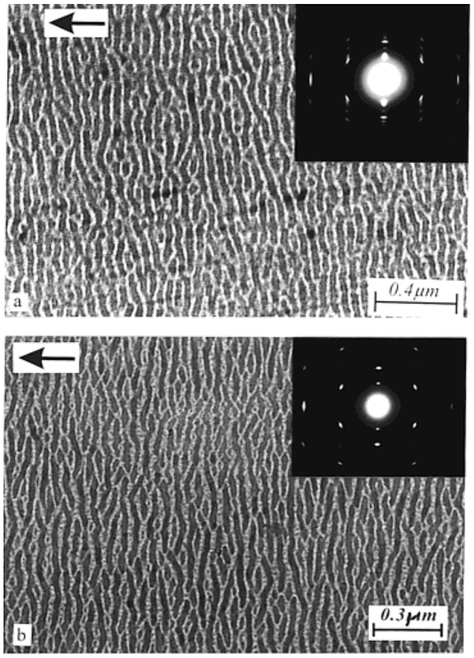

Figure 1. BF electron micrographs and the relating electron diffraction patterns (insets) of a vacuum carbon evaporated melt-drawn HDPE thin film before (a) and after (b) the heat treatment. The heat treatment is performed by heating the sample to 150 °C for 15 min and then cooled with a rate of 1 °C/min to 100 °C for 2 h. The arrows in the pictures indicate the drawing direction of the film during preparation.

Recrystallization of HDPE in iPP/HDPE-C Sandwich Layers. Figure 2 shows the BF electron micrographs and the corresponding electron diffraction pattern of a iPP/HDPE-C sandwich layer with the HDPE embedded in between the highly oriented iPP thin film and the *directly* vacuum evaporated thin carbon layer. The sample was heat-treated at 150 °C, above the melting point of HDPE but below the melting temperature of iPP, for 15 min and then quenched to room temperature on air. In the BF electron micrograph (Figure 2a), the highly oriented iPP lamellae, which are well arranged in the horizontal direction, can be easily identified. Their molecular chain directions are indicated by an arrow. The HDPE crystals cannot be clearly seen in Figure 2a. Nevertheless, with careful observation, also a parallel aligned lamellar structure of HDPE with its crystalline lamellae ca. 20° apart from the chain direction of the iPP substrate can be recognized. In the radiation damaged micrograph (Figure 2b), where the

Table 1. Examples of Materials Exhibiting the Oriented Recrystallization Effect

	structures before and after heat-treatment	
species	before heat-treatment[a]	after heat treatment
polyethylene low and high density	fiber oriented lamellae (M)	double oriented lamellae
	fiber oriented micelle (F)	double oriented lamellae
poly(1-butene)	fiber oriented shish crystals with 3/1 helix (M)	double oriented lamellae with 11/3 helix
isotactic polystyrene	fiber oriented shish crystals (M)	double oriented shish-kebabs
	fiber oriented micelle (F)	double oriented lamellae
syndiotactic polystyrene	fiber oriented lamellae (M)	double oriented lamellae
	fiber oriented micelle (F)	double oriented lamellae
isotactic polypropylene	fiber oriented lamellae (M)	double oriented lamellae

[a] M = melt-drawn samples; F = friction transferred samples.

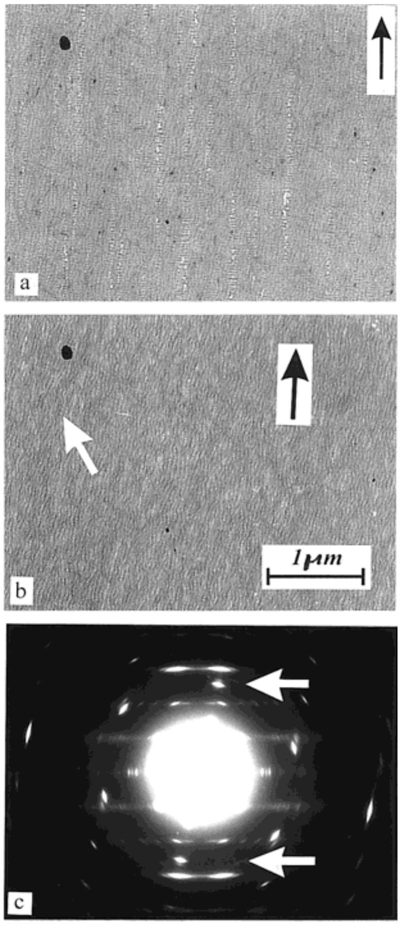

Figure 2. BF electron micrographs (a and b) and the corresponding electron diffraction pattern (c) of the iPP/HDPE-C multilayered sample, which has been heat-treated at 150 °C for 15 min and subsequently quenched to room temperature on air. (b) Radiation damaged image taken in the same area as in (a). The molecular chain direction of the oriented iPP substrate is represented by the black arrow.

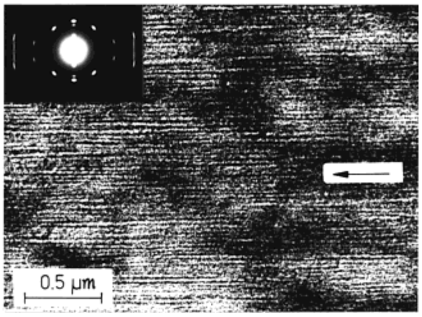

Figure 3. BF electron micrograph and its corresponding electron diffraction pattern (inset) of a melt-drawn oriented 1-iPB thin film. The arrow in the picture indicates the drawing direction of the film during preparation.

morphology of the HDPE becomes more clearly due to the contrast disappearance of iPP substrate, it is seen that the parallel aligned lamellar structure is the predominant morphology of the HDPE. It should be pointed out that a few short HDPE lamellae, as denoted by the white arrows, are aligned 40° apart from the chain direction of the iPP substrate. They are induced by epitaxial crystallization of HDPE on the iPP substrate as well documented in the literature.[14−17] From the BF observation, it may be concluded that the original orientation of the melt-drawn HDPE film is mainly preserved by the vacuum evaporated carbon layer. A few HDPE crystalline lamellae have changed their chain orientation to fit the well-known epitaxial crystallization of HDPE on the iPP substrate. The corresponding electron diffraction pattern (Figure 2c) shows mainly two sets of electron diffractions, which are associated with the uniaxially oriented iPP and HDPE crystals. The electron diffraction contribution of the epitaxially crystallized HDPE part, as indicated by the white arrows, is too weak to be clearly recognized. This clearly demonstrates that in the iPP/HDPE-C sandwiched sample the vacuum evaporated carbon layer has a stronger influence on the oriented nucleation and overgrowth of HDPE than the oriented iPP substrate. Combining the results of BF observation and electron diffraction, it is fair to state that the iPP substrate has a negligible effect on the crystallization of HDPE in the iPP/HDPE-C multilayer with respect to the vacuum coated carbon film.

Recrystallization of 1-iPB on and with Carbon Coating. To clearly illustrate the morphological and crystalline structural changes of the melt recrystallized vacuum carbon evaporated and carbon film supported melt-drawn 1-iPB films, a BF electron micrograph and its corresponding electron diffraction pattern (inset) of the melt-drawn oriented 1-iPB thin films in the as drawn state are presented in Figure 3. The arrow in the picture represents the drawing direction of the film during sample preparation. Unlike the melt-drawn oriented HDPE film as shown in Figure 1a, the melt-drawn 1-iPB films consist of needle crystals with the axes of the long needle crystals aligned in the drawing direction. The corresponding electron diffraction pattern reveals a high degree of fiber orientation with its hexagonal unit cell system.[18,19]

When melt recrystallizing a carbon supported melt-drawn oriented 1-iPB film prepared by simply putting the melt-drawn 1-iPB film onto a *preformed* carbon support film, as expected, the preferred orientation of the melt-drawn 1-iPB film disappears (see Figure 4). Moreover, the crystalline morphologies depend strongly on the recrystallization temperature. When crystallizing

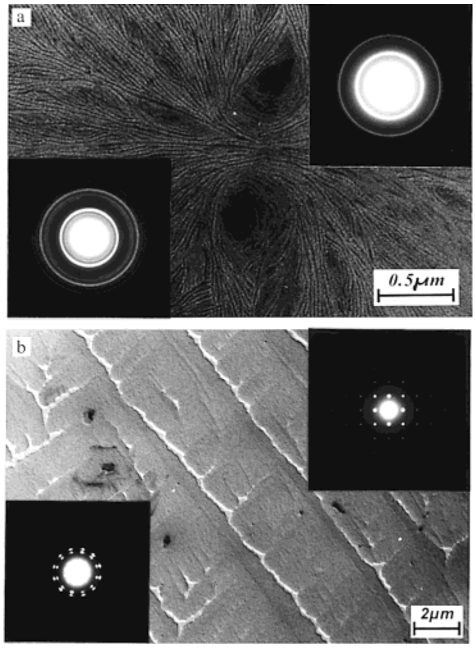

Figure 4. BF electron micrographs and the relating electron diffraction patterns (insets) of the carbon film supported melt-drawn 1-iPB thin films, which were heated to 180 °C for 15 min and subsequently crystallized isothermally at (a) 50 °C for 10 min and (b) 95 °C for 2 h. The electron diffraction patterns inserted in the upper right corners are recorded immediately after the heat treatments, while those inserted in the lower left corners are taken several weeks after the heat treatments.

the carbon supported 1-iPB films at temperatures below 60 °C, a spherulitic structure of the 1-iPB arises with two spherulitic "eyes" on either side of the crystalline nuclei (Figure 4a). The spherulites are composed by closely packed edge-on lamellae grown from the central regions, i.e., the crystalline nuclei, continuously outward by splaying and branching. The corresponding electron diffraction patterns (insets of Figure 4a) show the characteristic concentric reflection rings. All the reflection rings recorded directly after the heat treatment (inset of upper right corner) are accounted for by the tetragonal system, indicating the formation of form II 1-iPB crystals. As already well documented,[20−22] aging the fresh crystallized 1-iPB sample at room temperature, a crystal−crystal phase transition from tetragonal system (form II) to hexagonal system (form I) occurs spontaneously. The complete phase transition takes several weeks. During the solid phase transition, the electron diffraction pattern transforms gradually from its form II into form I (inset of lower left corner), while the morphology keeps unchanged. When recrystallizing the carbon supported melt-drawn 1-iPB at temperatures above 60 °C, instead of spherulitic structure composed by edge-on lamellae, flat-on lath crystals are observed (Figure 4b). The electron diffraction patterns, both before and after the solid phase transition (inserted respectively in upper right and lower left corners of Figure 4b), show sharp and well-defined (*hk*0) reflection spots, implying a flat-on structure of the crystal with the molecular chains oriented parallel to the lamellar thickness direction since the crystals have not been tilted in the electron microscope. These results demonstrate that the packing with molecular chains standing up is the thermodynamically favorable packing model of 1-iPB at lower supercoolings.

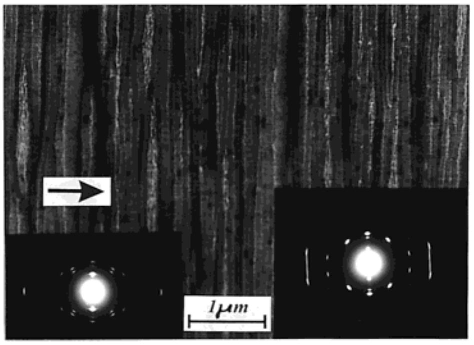

Figure 5. BF electron micrograph and its corresponding electron diffraction patterns (insets) of a carbon coated melt-drawn 1-iPB thin film, which was heated to 180 °C for 15 min and subsequently crystallized isothermally at 95 °C for 2 h. The electron diffraction pattern inserted in the lower left corner is recorded immediately after the heat treatment, while that inserted in the lower right corner is taken several weeks after the heat treatment.

The melt recrystallization behavior of melt-drawn 1-iPB thin films with carbon coating, where the carbon layers are *directly* vacuum evaporated on the surface of the melt-drawn 1-iPB films, is quite different from that of carbon film supported ones. As presented in Figure 5, there are mainly two different morphological features of the melt recrystallized carbon coated 1-iPB thin films as compared with Figure 4. First of all, the molecular chain orientation of the melt-drawn 1-iPB thin films is evidently preserved by the vacuum evaporated thin carbon layer, even though the crystalline morphology has changed from shish crystals into lamellar crystals. Second, the highly oriented edge-on lamellar structure is always the observed morphology in its whole crystallizable temperature range. This apparently indicates that the vacuum coated carbon layer has arrested the formation of the thermodynamically preferred packing of 1-iPB with upright chains. The electron diffraction result obtained from the insets of Figure 5 confirms the molecular chain orientation maintenance of the melt recrystallized carbon coated melt-drawn 1-iPB film, on one hand, and reveals the occurrence of the solid phase transition of the highly oriented 1-iPB edge-on lamellar crystals on the other.

Dissolution of Carbon Coated HDPE Film. The dissolution of vacuum carbon evaporated PE single crystals had been performed by Bassett and co-workers 40 years ago in their approach to get detachment replicas.[23−25] It was found that by vacuum evaporating a thin layer of carbon on the fold surface of PE single crystals, a 10 °C enhancement of the dissolution temperature in xylene cloud be achieved. They reported that the xylene has no dissolution effect on the carbon coated PE single crystals at temperatures below 85 °C (or 95 °C for the thicker lamellar single crystals). But when dissolving the carbon coated PE single crystals in xylene at temperatures above 105 °C, the PE single crystals will be peeled off the carbon layer completely in several minutes, and one begins to get true replicas. The temperatures ranging from 95 to 105 °C were found to be ideal for dissolving only the single crystal layers which are not in contact with the carbon coating under controlled conditions. It is worth noting that Bassett's work was concerned with the vacuum evaporation of carbon on the lamellar fold surfaces. In present case, the carbon evaporation is conducted on the side surfaces

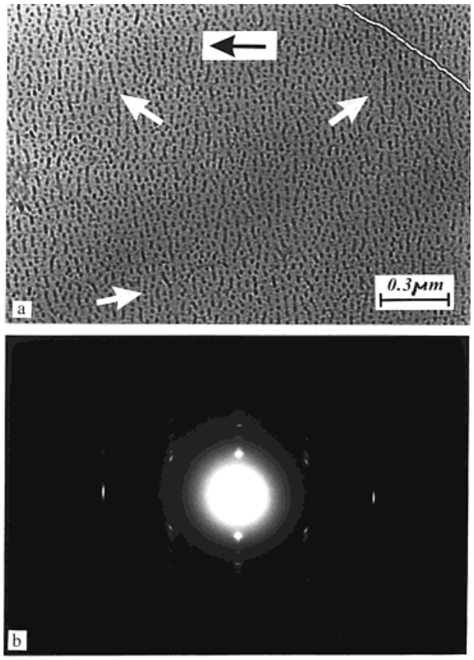

Figure 6. (a) BF electron micrograph and (b) its relating electron diffraction pattern of a carbon coated melt-drawn HDPE thin film, which has been dissolved in xylene at 125 °C for 2 h. The arrow in the micrograph shows the chain direction of HDPE crystals.

of the edge-on lamellae as well as the amorphous interlamellar regions. Therefore, different dissolution behavior may be expected. To check their dissolution behavior, the carbon coated melt-drawn HDPE films were plugged directly into xylene at 125 °C for different times. Figure 6 shows the BF electron micrograph and its corresponding electron diffraction pattern of a carbon coated HDPE film, which has been dissolved in xylene at 125 °C for 2 h. The BF electron micrograph (Figure 6a) shows still a homogeneously dispersed oriented lamellar structure. The oriented lamellae are, however, somewhat discontinuous compared with the original ones (compare with Figure 1a). Some of the lamellae, as denoted by the arrows, even look like dotted lines. This means that a small amount of HDPE has been dissolved away from the vacuum evaporated carbon layer by xylene at 125 °C for 2 h. The electron diffraction pattern (Figure 6b) has a close resemblance with that of the as drawn films (see inset of Figure 1a) and demonstrates that the remaining HDPE crystals on the coated carbon film exhibit still a high degree of fiber orientation. This is different from the melt recrystallized sample (compare with the inset of Figure 1b), where a rearrangement of the HDPE chains into a doubly oriented crystalline structure is accomplished. With increasing dissolution time, an increasing amount of HDPE has been dissolved by the xylene at 125 °C as can be deduced both from the BF electron micrograph and electron diffraction pattern shown in Figure 7. But the remaining HDPE on the vacuum evaporated carbon layer exhibits always the same fiber orientation. It should be pointed out that, unlike in the case of carbon coated PE single crystals, now a complete dissolution of HDPE crystalline lamellae away from the vacuum evaporated carbon layer has never been achieved by dissolving it in xylene at 125 °C within 20 h. Moreover, this is also different from the carbon supported HDPE films, where the HDPE films can be easily detached from the carbon film by the hot xylene solvent within several minutes.

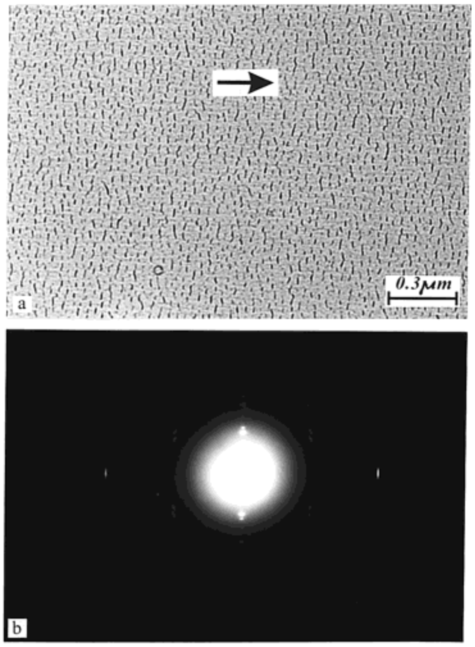

Figure 7. (a) BF electron micrograph and (b) its relating electron diffraction pattern of a carbon coated melt-drawn HDPE thin film, which has been dissolved in xylene at 125 °C for 15 h. The arrow in the micrograph shows the chain direction of HDPE crystals.

Discussion

According to the above obtained experimental results, the origin of oriented recrystallization behavior of the carbon coated preoriented thin polymer films can be discussed. From Table 1, the changes in the morphology, chain conformation, and even crystal structure of the carbon coated thin oriented polymer films after heat treatment help us affirmatively to exclude the possibility of the superheating effect.[25] Considering that the carbon film replicas of the semicrystalline polymer films can record the surface topologies of them, graphoepitaxy, i.e., the vacuum evaporated thin carbon layers with the surface topological structures of semicrystalline polymer films act as a graphoepitaxial templates to induce the oriented overgrowth of the polymer melts, may be easily thought to be the origin of the oriented recrystallization of the carbon coated preoriented polymer films. But this may be actually not the case as can be concluded from the following discussion.

It is well-known that iPP has a conspicuous nucleation effect toward HDPE. Molecular epitaxy will occur whenever a HDPE thin film is crystallized in contact with a highly oriented iPP substrate. As shown in Figure 8, the epitaxial crystallization results in the formation of an unusual crosshatched lamellar structure of HDPE with the chains oriented ±50° apart from the chain direction of the iPP substrate. This unusual mutual orientation reveals the special strong molecular interaction between the HDPE and iPP. Therefore, molecular epitaxy should be more favorable to occur than the graphoepitaxy of HDPE on its amorphous carbon replica, which is just caused by the surface topology. According to the above discussion, the orientation maintenance of the highly oriented HDPE thin film in the iPP/HDPE-C sandwiched sample can hardly be explained simply by graphoepitaxial crystallization of

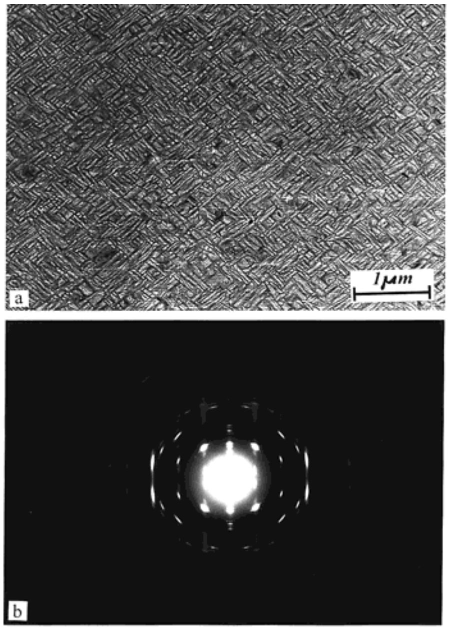

Figure 8. (a) BF electron micrograph and (b) its corresponding electron diffraction pattern illustrate the molecular epitaxy of HDPE on the highly oriented iPP substrate. The HDPE/iPP double-layered sample was heat-treated at 150 °C for 15 min and subsequently quenched to room temperature on air. The chain direction of iPP substrate is horizontal.

the HDPE on its surface carbon replica. Moreover, the epitaxial crystallization of HDPE takes place even in the iPP/HDPE/C multilayered sample with the HDPE sandwiched in the oriented iPP film and *preformed* carbon layer prepared by transferring first a thin HDPE film and then a thin highly oriented iPP film onto the carbon support film. This clearly indicates that the iPP substrate has stronger nucleation ability toward HDPE than carbon support film. Taking this into account, a molecular epitaxial crystallization of HDPE in the iPP/HDPE-C sandwich layers on the oriented iPP side is also expected if the graphoepitaxy is the sole reason for the oriented recrystallization phenomenon. But the experimental results are on the contrary. Therefore, it is forced to the conclusion that the oriented recrystallization of the preoriented thin polymer films is not caused by graphoepitaxial crystallization of the polymers on their vacuum coated carbon replicas.

The morphological and structural features of the melt-drawn 1-iPB thin films recrystallized on the *preformed* vacuum evaporated carbon support film clearly indicate that at lower supercoolings the packing of 1-iPB with upright molecular chains is more favorable than that with the molecular chains lying in the film plane. Therefore, the 1-iPB grows in lath crystals with molecular chains oriented parallel to the normal direction of the film plane at elevated crystallization temperatures. The different recrystallization behavior of *directly* vacuum carbon evaporated melt-drawn 1-iPB thin films, i.e., the molecular chains aligned always in the film plane with high degree of orientation at any conditions, may imply that the vacuum evaporated carbon layer has fixed the 1-iPB molecular chains to the film plane. Consequently, the thermodynamically favored packing with upright macromolecular chains cannot be realized in the whole crystallizable temperature range. The dissolution test of the carbon coated HDPE melt-drawn film further confirms that the *directly* vacuum evaporated carbon layer exhibits very strong adhesion with the HDPE thin film. In some place, the linkage between the vacuum evaporated carbon layer and the HDPE film are so tight that the attempt to dissolve the HDPE away from the carbon layer has never been succeeded in xylene at 125 °C within 20 h. This is quite different from that of carbon supported HDPE thin film prepared by placing the melt-drawn HDPE thin film onto the *preformed* carbon films, where the superimposed HDPE film will fall off the carbon support film completely within only several minutes in xylene at 125 °C. The different dissolution behavior leads again to the conclusion that the *directly* vacuum evaporated carbon film exhibits strong fixing effect on the semicrystalline thin polymer film. The fixing effect may associate with one of the following: (i) Some extent of the carbon vapor particles has diffused into the areas between the molecular chains in the amorphous interlamellar regions of the well-ordered polymer thin films. These diffused carbon particles accumulate and form pillars that are connected to and fixed by the evaporated carbon layer. The generated carbon pillars may moor the entangled macromolecular ties in the amorphous area, and the inlayed macromolecular ties in the amorphous area may act as anchors to fixing the extended crystalline macromolecular chains in the coated carbon layer. (ii) One may also suggest that free radicals in the evaporated carbon film have linked it to the surface of the thin polymer film via covalent bonds so that the surface monolayer molecules have been fixed by the vacuum evaporated carbon layer. The exact mechanism of the fixing effect of vacuum evaporated carbon layer on the thin polymer film is not quite clear yet. It is, however, sufficient merely to recognize the surface fixing effect of the vacuum evaporated carbon layer on the polymer surface for explaining the oriented recrystallization phenomenon of the carbon coated preoriented thin polymer films. Namely, the vacuum evaporated carbon layer on the polymer thin film surface has, maybe to some extent, fixed the surface monolayer molecules of the oriented polymer films and prevented the surface layer extended crystalline macromolecular chains from melting or at least from a complete relaxing during high-temperature annealing. The extended or relatively extended macromolecular chains can act as the nucleation sites during the recrystallization process and easily induce the oriented regrowth of the polymer melts. In other words, the oriented recrystallization behavior of the vacuum carbon evaporated preoriented thin semicrystalline polymer films is caused by the surface fixing confined crystallization. Taking the strong fixing effect of vacuum evaporated carbon layer on the surface of thin polymer films into account, the orientation maintenance of the highly oriented HDPE thin film in the iPP/HDPE-C sandwiched sample can easily be understood.

Conclusions

The origin of the oriented recrystallization behavior of the vacuum carbon evaporated preoriented thin polymer films was studied by means of transmission electron microscopy and electron diffraction with elaborately designed experimental setups.

The recrystallization of HDPE in the iPP/HDPE-C sandwich layers with its original chain orientation being preserved by the vacuum evaporated carbon layer other than epitaxially crystallized on the highly oriented iPP substrate demonstrates that the graphoepitaxial crystallization of the polymer melts on their surface carbon replicas is not the true origin of the oriented recrystallization of the carbon coated preoriented thin polymer films.

The different melt recrystallization behavior of melt-drawn 1-iPB thin films on and with vacuum evaporated carbon layer forces us to the conclusion that vacuum evaporated thin carbon layer has a strong fixing effect on the surface monolayer macromolecular chains of the semicrystalline polymer films. This has been further confirmed by the dissolution test of the vacuum carbon deposited HDPE thin films. The recognition of the surface fixing effect of the vacuum evaporated carbon layer on the polymer surface leads to the rational explanation of the oriented recrystallization phenomenon of the carbon coated preoriented thin polymer films. Namely, the vacuum evaporated carbon layer on the polymer thin film surface has fixed the surface monolayer molecules of the well ordered thin polymer films and prevented the extended crystalline macromolecular chains of the oriented crystals from melting or at least a complete relaxing during high-temperature annealing. The extended or relatively extended macromolecular chains act as the nucleation sites during the recrystallization process and induce the oriented regrowth of the polymer melts.

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