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Controlling factors for the occurrence of heteroepitaxy of polyethylene on highly oriented isotactic polypropylene

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The controlling factors for the epitaxial crystallization of high-density polyethylene (HDPE) on highly oriented isotactic polypropylene (iPP) substrates have been studied in detail by means of transmission electron microscopy and electron diffraction. The results obtained in this work indicate that the crystallization process must be considered in the investigation of epitaxial growth of polymers on polymeric substrates, because of the unique morphological and crystallization characteristics of polymers. Crystallization rate has an important effect on the epitaxial crystallization of polymers. Higher rates result in the formation of thicker epitaxial layers. Isothermal crystallization temperature is another factor affecting epitaxial growth of polymers. Lower temperatures are favorable to epitaxial crystallization of polymers. There exists a critical epitaxial temperature at given experimental conditions, above which no epitaxial growth occurs at all. The influence of crystal dimensions of both the substrates and the deposited polymers on epitaxial growth confirms that secondary nucleation is an important controlling factor for the occurrence of epitaxial crystallization in polymers. The requirement satisfying the secondary nucleation criterion is that the substrate crystal dimension in the matching direction must be greater than the crystal thickness of the deposited polymer. Once the requirement of the secondary nucleation is satisfied, subsequent epitaxial growth is based on the lamellar growth habit of the deposited polymer itself. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The epitaxial phenomenon was discovered in 1817 when it was recognized by mineralogists that various natural minerals appear in unique shapes[1], and the term 'epitaxy', as in the sense of 'on arrangement', was introduced in 1928[2]. Since then the epitaxial crystallization between low molecular weight materials was studied systematically, and the resulting mutual orientation was explained by a one- or two-dimensional structural analogy between the substrate and the overgrowth materials in the contact planes[3]. Although the structural analogy implies interactions at the molecular scale, such a level of understanding is seldom reached. Therefore, epitaxy is generally defined in terms of pure geometric lattice matching, and 10–15% disregistries are considered to be the upper limit for the occurrence of epitaxial growth.

In the field of polymer heteroepitaxy, much attention has been paid to the systems of zigzag chain polymers with two-fold symmetry and isotactic polypropylene (iPP)[4–9], in which the zigzag chains are inclined ± 50° to the iPP chain direction. This kind of epitaxial orientation relationship has been explained in terms of the parallel alignment of the zigzag chains along methyl group rows in the (010) lattice plane of iPP with a 0.5-nm intermolecular distance for chain-row matching[10]. This explanation resembles some kind of molecular matching between the substrate and the epitaxial layer. However, some experimental results show that the epitaxial growth may also be affected by morphological aspects of the substrates and epitaxial polymers[11]. Very recently, Greso and Phillips[12] proposed the template model, i.e. the role of secondary nucleation, to explain the epitaxial growth of polymers. According to this model, the epitaxial growth of polymeric molecules on polymeric substrates must involve the necessary requirements for the formation of critical secondary nucleation. The major requirement for the formation of secondary nuclei is that the crystal dimension of the substrate in the matching direction must be larger than the critical lamellar thickness of the epitaxially grown crystals. The purpose of this paper is to present some experimental results regarding the controlling factors for the occurrence of epitaxial crystallization of HDPE on highly oriented iPP substrates, which leads to a further understanding of the heteroepitaxial crystallization mechanism in polymers.

EXPERIMENTAL

The polymers used in this work were isotactic polypropylene (iPP) and high-density polyethylene (HDPE), both commercial products. Uniaxially oriented thin films of iPP and HDPE were prepared according to the melt-drawn technique introduced by Petermann and Gohil[13]. According to this method, a small amount of a 0.5% solution of the
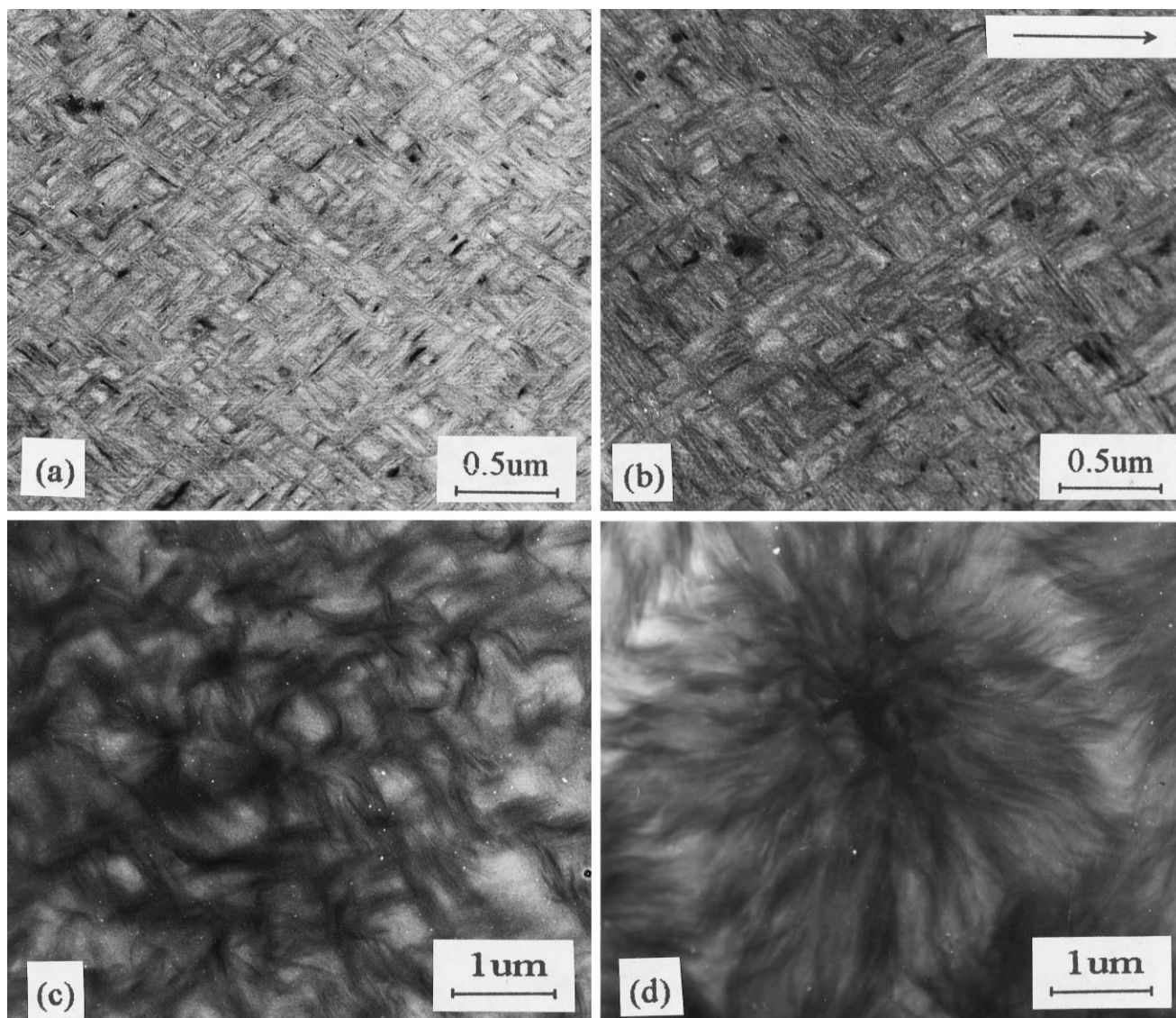
Figure 1 BF electron micrographs of HDPE–iPP multilayered films, heat-treated at 150°C for 10 min and subsequently quenched to room temperature. The arrow indicates the chain direction of iPP. The thicknesses of the HDPE layers are (a) 150, (b) 250, (c) 350, and (d) 500 nm, respectively

polymer (iPP or HDPE) in xylene was poured and uniformly spread on a preheated glass slide, where the solvent was allowed to evaporate. After the evaporation of the solvent, the remaining thin polymer film was then picked up by a motor-driven cylinder with a drawing speed of approximately 20 cm/s. The temperatures for preparing the melt-drawn iPP and HDPE films were 140 and 125°C, respectively. The resulting highly oriented films of 30–50 nm in thickness can be directly used for transmission electron microscopy (TEM) observations. The multilayered HDPE–iPP films were prepared as follows. Thin iPP films were floated on the surface of distilled water, and transferred onto the TEM grids, which were subsequently covered by the highly oriented HDPE films. The thickness of the HDPE layer in HDPE–iPP composite system was controlled by putting different numbers of HDPE films on top of the iPP substrate[14]. For TEM observations of the crystallization behavior of HDPE on the boundary of the oriented iPP substrate, the thin HDPE film was transferred onto the surface of a glass slide, which was partially covered by an iPP substrate film[15]. The films were then detached from

the glass slide with the help of a poly(acrylic acid) layer. The heat-treatment of the multilayered HDPE–iPP films was carried out in a thermostatically controlled oven or a d.s.c. apparatus by heating the samples to a temperature above the T_m of the HDPE, but below the T_m of iPP, for 10–15 min, and then cooled at different rates to the desired temperatures. A Philips CM200 TEM operated at 200 kV was used in this study. Bright-field (BF) micrographs were obtained by defocus of the objective lens. In order to minimize radiation damage to the polymer samples caused by the electron beam, focusing of the sample was carried out in one area and imaging in its adjacent undamaged area.

RESULTS

The results of BF electron microscopy and electron diffraction of the melt-drawn iPP and HDPE films indicate that both of them consist of highly oriented crystalline lamellae with their growing direction perpendicular to and c-axes parallel to the drawing direction of the films[13,14,16].
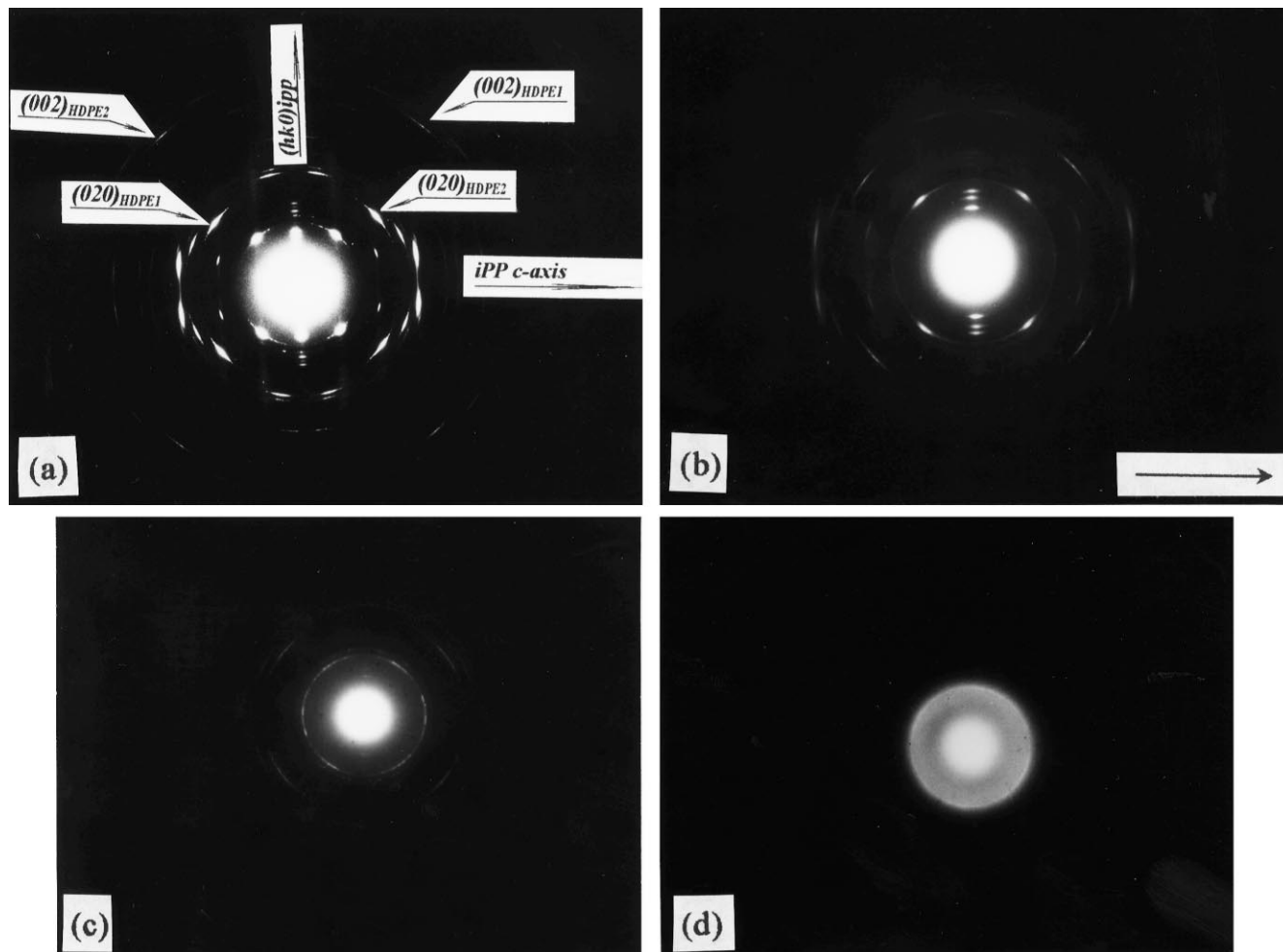
Figure 2 The corresponding electron diffraction patterns of HDPE–iPP multilayered films as in *Figure 1*. The arrow shows the chain direction of iPP

Effects of crystallization rates on epitaxial layer thicknesses of HDPE on oriented iPP substrates

Figure 1 shows the BF electron micrographs of HDPE–iPP multilayered films, which had been heat-treated at 150°C for 10 min and subsequently quenched to room temperature in air. The thicknesses of the HDPE layers on oriented iPP substrates are 150, 250, 350, and 500 nm, respectively. The chain direction of the iPP substrates is horizontal (as indicated by the arrow). It can be seen that when the thickness of the HDPE layer is thinner than 250 nm (*Figure 1a,b*), a cross-hatched lamellar structure arises, with the HDPE lamellae being inclined at $\pm 40°$ with respect to the iPP c-axes. This peculiar arrangement of the HDPE lamellae was explained by epitaxial crystallization of HDPE on oriented iPP substrates[17,18]. When the layer thickness of HDPE is above 350 nm, crystalline aggregates with random orientation or complete spherulites of HDPE are observed (*Figure 1c,d*).

The corresponding electron diffraction patterns of HDPE–iPP multilayered films as in *Figure 1* are shown in *Figure 2*. The molecular direction of the iPP substrates is indicated by the arrow. It is quite clear that when the HDPE layer is thinner than 250 nm, it grows epitaxially on the oriented iPP substrate with the c-axes inclined at $\pm 50°$ to the c-axes of iPP (*Figure 2a,b*). The contact planes of the two kinds of crystals are (010) for iPP and (100) for HDPE. When the thickness of the HDPE film is above 350 nm, a

(110) Debye–Scherrer ring, which represents the characteristic HDPE spherulite, is seen (*Figure 2c,d*). This is consistent with the BF observation. The above results indicate that there exists a critical epitaxial layer thickness of HDPE on iPP substrate films, i.e. the epitaxy of HDPE on an iPP substrate can only take place in the interfacial layer. If the thickness of the HDPE layer is thicker than the critical thickness of the epitaxial layer, no epitaxial crystallization occurs. The critical epitaxial layer thickness of HDPE is about 250 nm at the present crystallization conditions.

The BF electron micrographs of HDPE–iPP multilayered films, which were heat-treated at 150°C for 10 min, and then cooled at a rate of 0.5°C/min to room temperature, are represented in *Figure 3*. The molecular direction of the iPP substrate is given by the arrow. The thicknesses of the HDPE layers are 60 and 120 nm, respectively. Unambiguously, low cooling rates result in the formation of larger HDPE lamellae (compared with *Figure 1*). Clearly, when the layer thickness of HDPE is about 60 nm, the HDPE grows epitaxially on the oriented iPP film (*Figure 3a*). When the thickness of the HDPE layer is about 120 nm, two kinds of crystalline morphologies of HDPE, i.e. lamellae grown epitaxially on the iPP substrate and crystalline aggregates with random orientation, were observed (*Figure 3b*). This means that the critical epitaxial layer thickness of HDPE is not more than 120 nm at the cooling
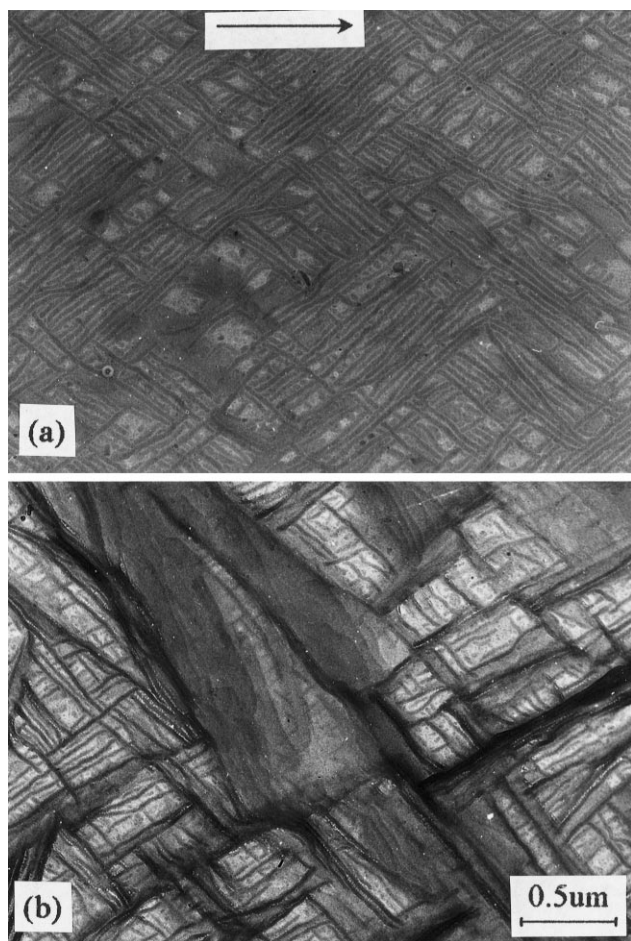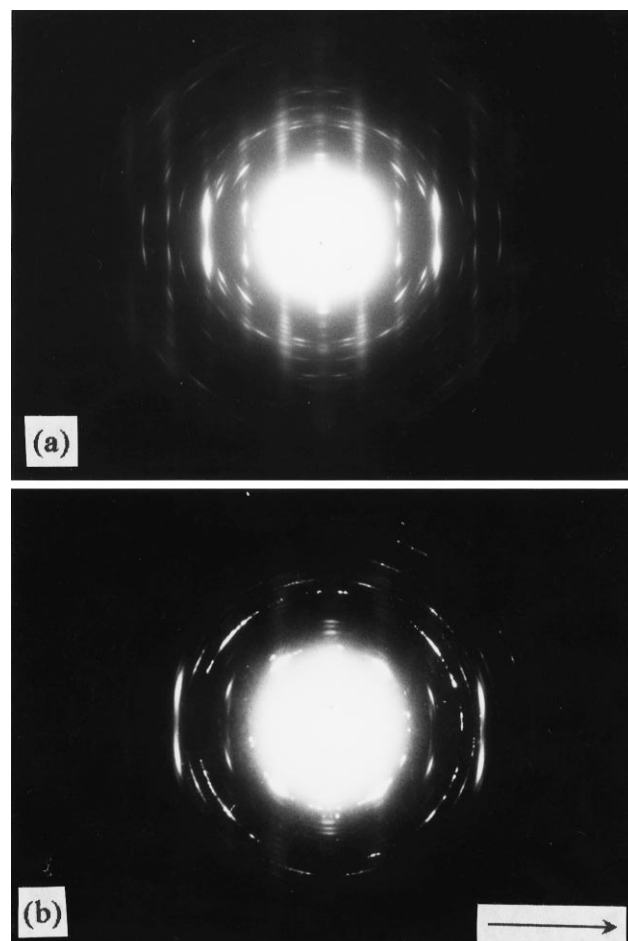
Figure 3 BF electron micrographs of HDPE–iPP multilayered films, heat-treated at 150°C for 10 min and then cooled at a rate of 0.5°C/min to room temperature. The chain direction of iPP is indicated by the arrow. The thicknesses of the HDPE layers are (a) 60 and (b) 120 nm, respectively

Figure 4 The corresponding electron diffraction patterns of HDPE–iPP multilayered films as in *Figure 3*. The arrow indicates the chain direction of iPP

rate of 0.5°C/min. The corresponding electron diffraction patterns of the samples, as in *Figure 3*, are shown in *Figure 4*. When the layer thickness of HDPE is above 120 nm, the $(020)_{HDPE}$ diffraction changes from sharp reflection spots to a discontinuous diffraction ring (*Figure 4b*), which results from crystalline aggregates of HDPE without epitaxial relationships with the iPP substrate. This further confirms the BF results.

The aforementioned results indicate that the epitaxial crystallization of HDPE on the oriented iPP substrates occurs only in a thin interface layer. The critical epitaxial layer thickness of HDPE depends strongly on the crystallization rate. A fast crystallization rate, e.g. quenching the HDPE melt into air at room temperature, results in the formation of a thicker epitaxial layer (*ca.* 250 nm), while a slow crystallization process, e.g. slow cooling at a rate of ~0.5°C/min, results in a thinner epitaxial layer of HDPE (near 120 nm). If the crystallization rate is too slow, e.g. at a cooling rate of 0.1°C/min, no epitaxial growth of HDPE on the oriented iPP substrate takes place (see below).

*Effects of crystallization temperatures on epitaxial growth of HDPE on oriented iPP substrates*

Figures 5 and 6 show the BF electron micrographs and corresponding electron diffraction patterns of the HDPE–iPP multilayered films, which were heat-treated at 150°C for 10 min and then crystallized isothermally at 124°C for 5 h.

The thicknesses of the HDPE layers are 100 and 120 nm, respectively. The arrow represents the chain direction of the iPP substrate. Clearly, the critical epitaxial layer thickness of HDPE is about 100 nm at this isothermal crystallization condition.
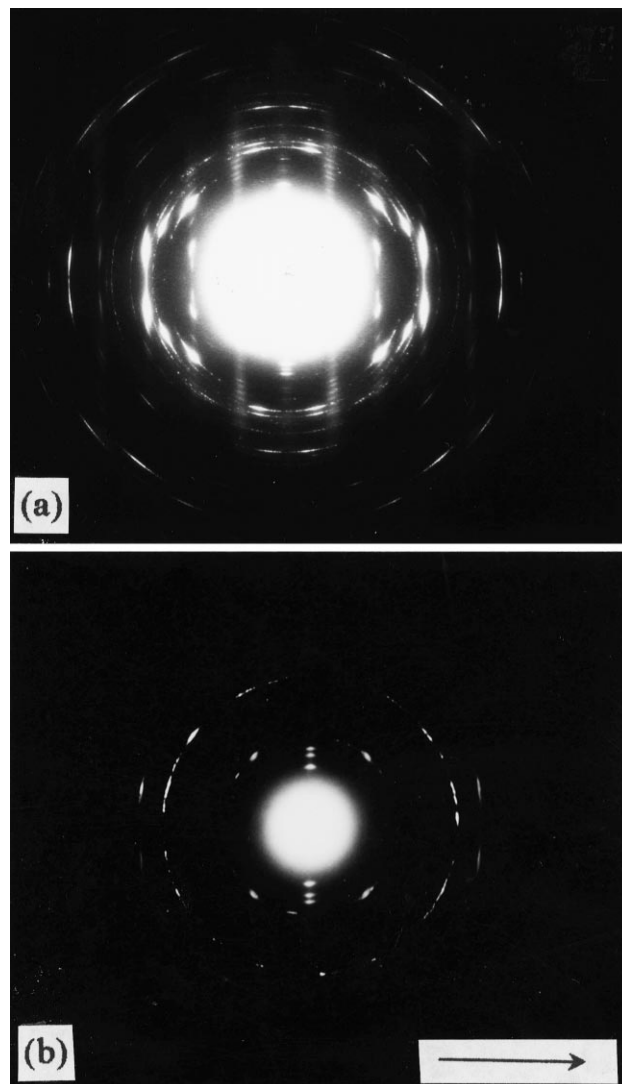
The BF electron micrograph of a HDPE–iPP layered film, which was heat-treated at 150°C for 10 min and then crystallized isothermally at 125°C for 5 h, is shown in *Figure 7*. The thickness of the HDPE layer is 30–50 nm. The molecular direction of the iPP substrate is indicated by the arrow. Two regions with different morphologies of HDPE crystals are observed. In the area with very thin HDPE film (not more than 30 nm), as shown in the lower left area of *Figure 7*, the HDPE crystallizes epitaxially on the oriented iPP substrate with its lamellae inclined at angles of ± 40° to the chain direction of the iPP substrate, while in the region with thicker HDPE film (about 50 nm), as shown in the upper right area of *Figure 7*, no epitaxial relationship between the HDPE and oriented iPP substrate can be recognized. Consequently, the critical epitaxial layer is not more 30 nm when the HDPE is isothermally crystallized on the iPP substrate at 125°C. The corresponding electron diffraction patterns (*Figure 8*) taken in the different areas of *Figure 7* confirm the BF observation. The electron diffraction pattern taken in the thinner area of the HDPE layer (lower left corner of *Figure 7*) reveals an excellent epitaxial relationship between the HDPE and oriented iPP substrate (*Figure 8a*), while the electron
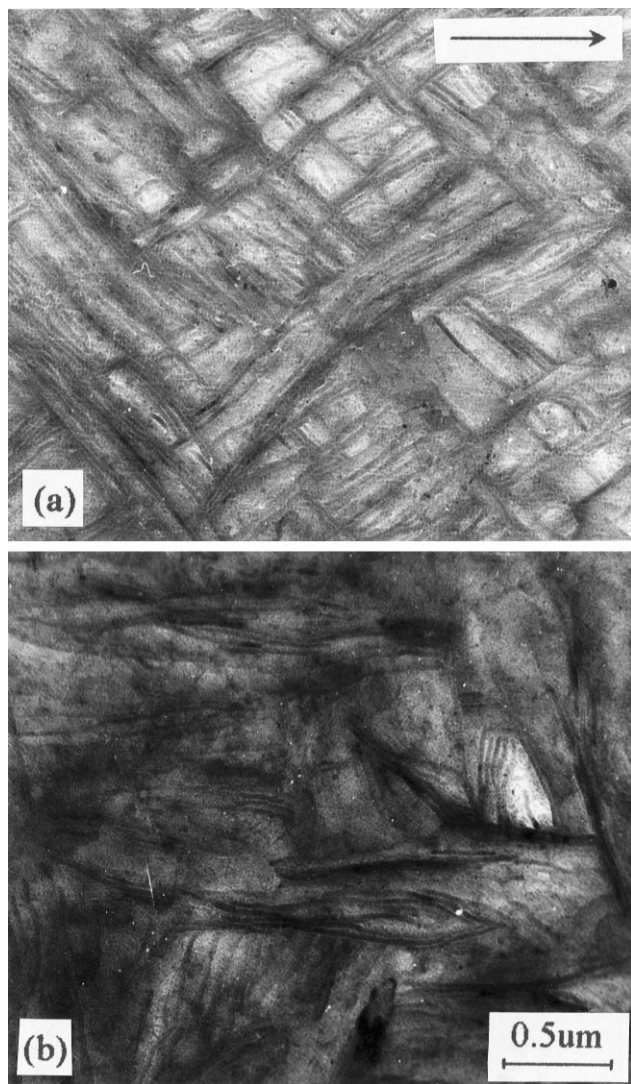
Figure 5 BF electron micrographs of HDPE–iPP multilayered films, heat-treated at 150°C for 10 min and subsequently isothermally crystallized at 124°C for 5 h. The chain direction of iPP is indicated by the arrow. The thicknesses of the HDPE layers are (a) 100 and (b) 120 nm, respectively


Figure 6 The corresponding electron diffraction patterns of HDPE–iPP multilayered films as in *Figure 5*. The arrow indicates the chain direction of iPP

diffraction pattern taken in the thicker area of the HDPE (upper right corner of *Figure 7*) shows several Debye–Scherrer rings relating to the random orientation of the HDPE lamellae.

The above results indicate that the isothermal crystallization temperature has an important effect on the epitaxial growth of HDPE on the oriented iPP substrate. The epitaxial layer thickness of HDPE decreases drastically with the increasing crystallization temperature. It reduced from 100 nm, when the HDPE is isothermally crystallized from the melt on the oriented iPP substrate at 124°C, to less than 30 nm, when 125°C was chosen as the crystallization temperature. When the crystallization temperature further increases, e.g. at or above 126°C, there is no epitaxial relationship between the HDPE and the oriented iPP at all. *Figure 9* shows the BF electron micrographs and corresponding electron diffraction patterns of HDPE–iPP layered films heat-treated at 150°C for 10 min and then crystallized isothermally at 126°C for 5 h. The HDPE crystals exhibit mainly large crystalline aggregates with random orientation, even in the very thin area of the HDPE layer, where the underlying highly oriented iPP lamellae can be seen clearly

(*Figure 9a*). The corresponding electron diffraction pattern (*Figure 9b*) documented by several Debye–Scherrer rings, provides evidence supporting the BF observations.

The above results indicate that there exists a critical epitaxial crystallization temperature for the occurrence of epitaxial crystallization of HDPE on oriented iPP substrates, i.e. 125°C. At the critical epitaxial crystallization temperature, the critical epitaxial layer thickness of the HDPE is about 30 nm. Below the critical epitaxial temperature, the critical epitaxial layer thickness of the HDPE is about 100 nm (at 124°C) or larger, according to the crystallization temperature used. If the isothermal crystallization temperature is above the critical epitaxial temperature, e.g. higher than 126°C, no epitaxial crystallization of HDPE on the oriented iPP takes place.

*Effects of iPP lamellar thickness on epitaxial behavior of HDPE on oriented iPP substrates*

Figure 10a–c show the BF electron micrographs of the highly oriented iPP substrate films, which were annealed at 140, 150 and 155°C for 30 min, respectively. The corresponding thicknesses of the iPP lamellae are about 13, 16 and 20 nm. While the lamellar thickness changed
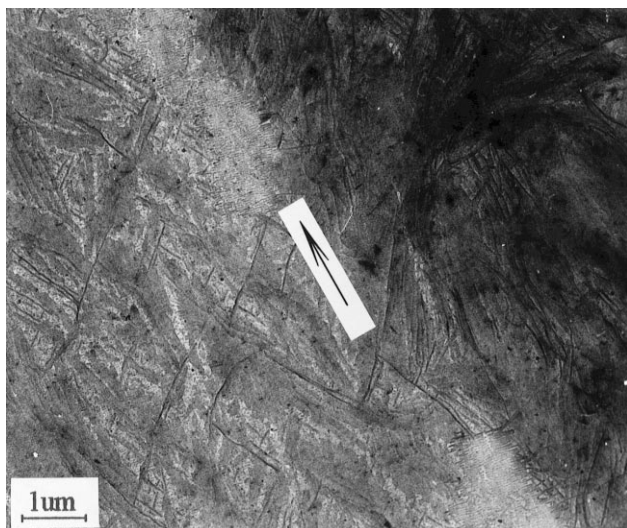
Figure 7 BF electron micrograph of HDPE–iPP double-layered films, which were heat-treated at 150°C for 10 min, and then crystallized isothermally at 125°C for 5 h. The chain direction of the iPP is indicated by the arrow
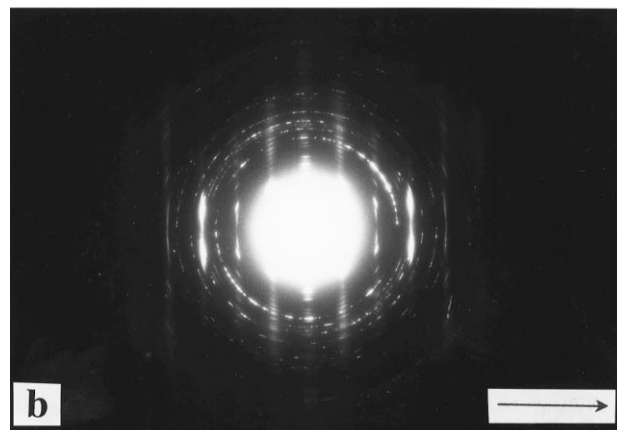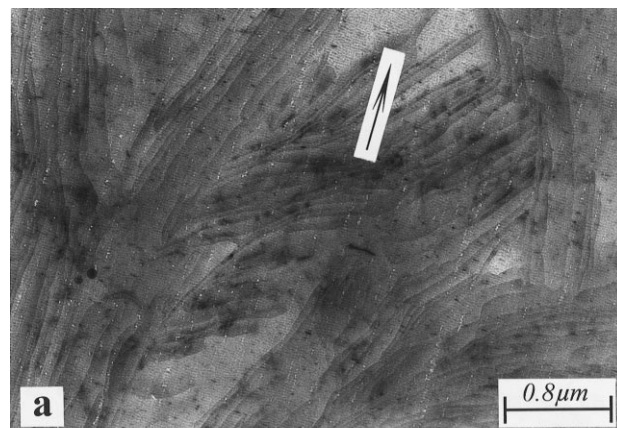
Figure 9 (a) BF electron micrograph and (b) the corresponding electron diffraction pattern of HDPE–iPP double-layered films, which were heat-treated at 150°C for 10 min, and then isothermally crystallized at 126°C for 5 h. The chain direction of the oriented iPP substrate is indicated by the arrow
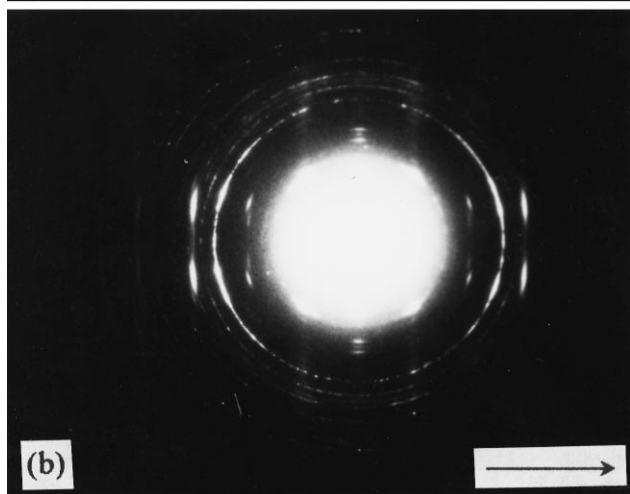

Figure 8 The corresponding electron diffraction patterns of HDPE–iPP double-layered films taken in the area of the lower left corner (a) and the area of the upper right corner (b) of *Figure 7*

remarkably through annealing at the melt-drawn films, the corresponding electron diffraction pattern reveals the high degree orientation of the iPP chain-axes (*Figure 10d*).

The above three kinds of oriented PP films with different lamellar thicknesses were used as the substrate for HDPE. *Figures 11–13* show the BF electron micrographs and corresponding electron diffraction patterns of the HDPE–iPP double layered films, which were heat-treated at 140°C for 15 min and subsequently cooled at a rate of 0.1°C/min to room temperature. The only difference between the samples in *Figures 11–13* is the lamellar thickness of the oriented iPP substrates. When the oriented iPP substrate with thicker lamellar dimensions, e.g. 20 nm, was used, the recrystallized HDPE exhibits an excellent epitaxial relationship with the oriented iPP (*Figure 11*), even if the crystallization rate is very slow. With decreasing lamellar thickness of the oriented iPP substrate, the epitaxial orientation relationship of HDPE with iPP becomes much poorer (*Figure 12*). If the lamellar thickness of the iPP substrate is much smaller, e.g. 13 nm, no epitaxial crystallization of HDPE on the oriented iPP substrate takes place at all (*Figure 13*).

The above results indicate the effect of the lamellar thickness of oriented iPP substrates on the epitaxial growth of HDPE for a given set of crystallization conditions. It is evident that the iPP substrates with thicker lamellae favor the epitaxial growth of HDPE. On the other hand, the epitaxial crystallization of HDPE on iPP must be affected by the lamellar thickness of HDPE itself, which changes with
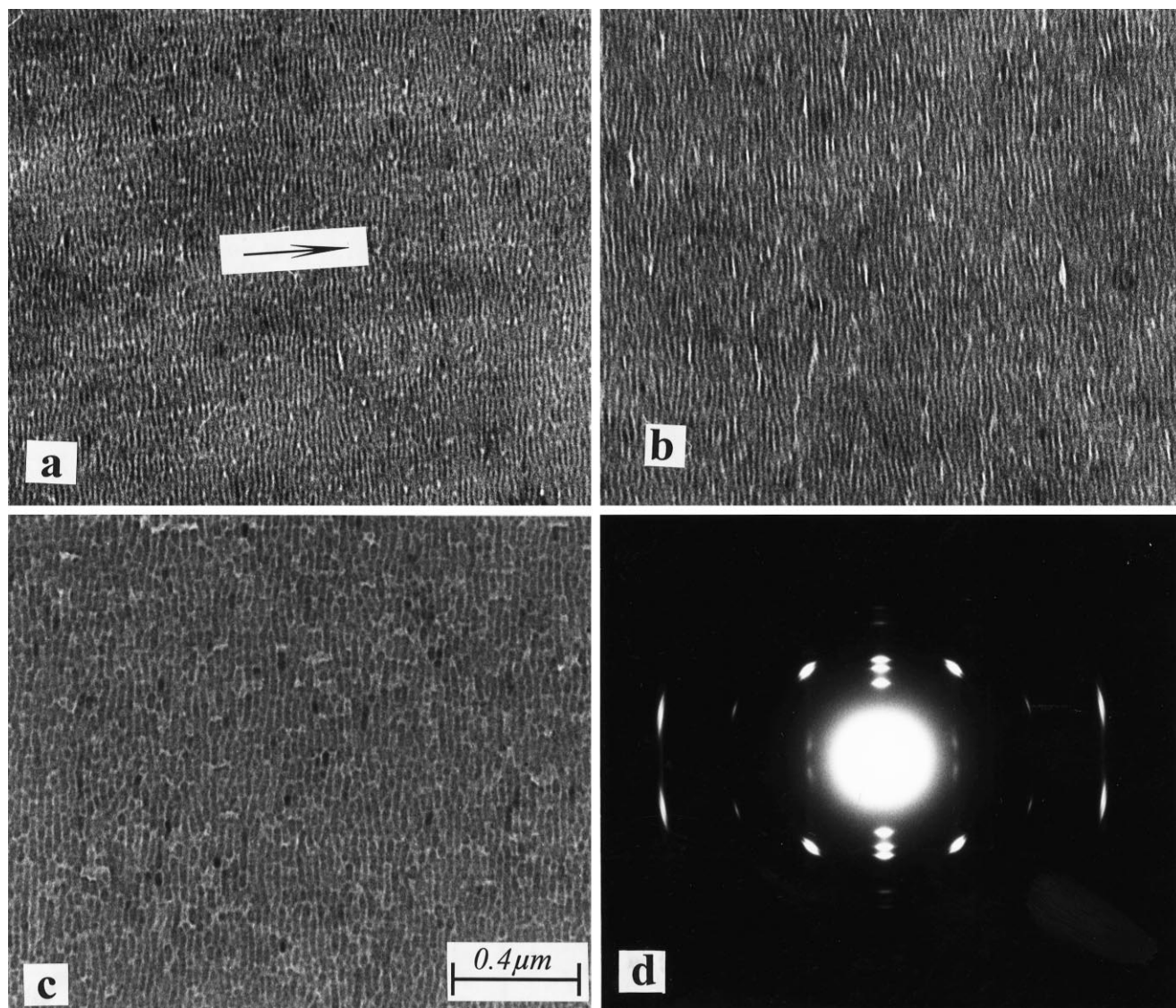
Figure 10 (a–c) BF electron micrographs and (d) electron diffraction pattern of iPP oriented films, which were heat-treated at (a) 140, (b) 150, and (c) 155°C for 30 min, respectively. The arrow represents the chain direction

changing crystallization conditions (such as crystallization temperature and cooling rate)[19]. The epitaxial behavior of HDPE with various lamellar thicknesses with respect to different iPP substrates are listed in *Table 1*. It is clear from *Table 1* that thinner lamellae of HDPE are favorable for the epitaxial growth of the HDPE itself on oriented iPP substrates. Meanwhile, by comparing the lamellar thickness of HDPE and the lamellar dimension of iPP in the matching direction, it is found that epitaxial crystallization of HDPE on iPP substrates takes place only when the lamellar thickness of the HDPE is smaller than the lamellar dimension of iPP in the matching direction.

Epitaxial behavior of HDPE on the boundary of oriented iPP substrates

Observation of the crystallization behavior of HDPE on the sharp boundary between an oriented iPP substrate, which induces epitaxial growth of HDPE, and a glass or mica surface, which does not initiate epitaxy, may help us to further understand the epitaxial crystallization process. *Figure 14a* shows a BF electron micrograph of HDPE crystallized on the boundary of the iPP substrate. The

sample was heated to 150°C for 10 min, and subsequently cooled to room temperature. The dashed line represents the boundary line of the iPP substrate. It is easily recognized that the HDPE supported by the oriented iPP film (designated 'A' in *Figure 14a*) exhibits the typical epitaxial morphology, while the HDPE crystallized on the glass surface (designated 'C' in *Figure 14a*) creates a spherulitic morphology. On the boundary, a special morphology arises in which the HDPE lamellae grow epitaxially across the boundary of the iPP substrate and extend into the area without the iPP substrate (designated 'B' in *Figure 14a*).

Figure 14b is the corresponding electron diffraction pattern of the boundary area of *Figure 14a*. In *Figure 14b*, all of the reflection spots are indexed as the reflection of the HDPE crystals. Although there are no diffraction spots of the iPP substrate in this area, there exist two sets of epitaxially oriented HDPE diffraction spots. This result is consistent with that of the BF observation, implying that the epitaxially grown crystals of HDPE on oriented iPP substrates can grow out of the boundary of iPP and extend into a pure HDPE area (*Figure 15*). In addition, the
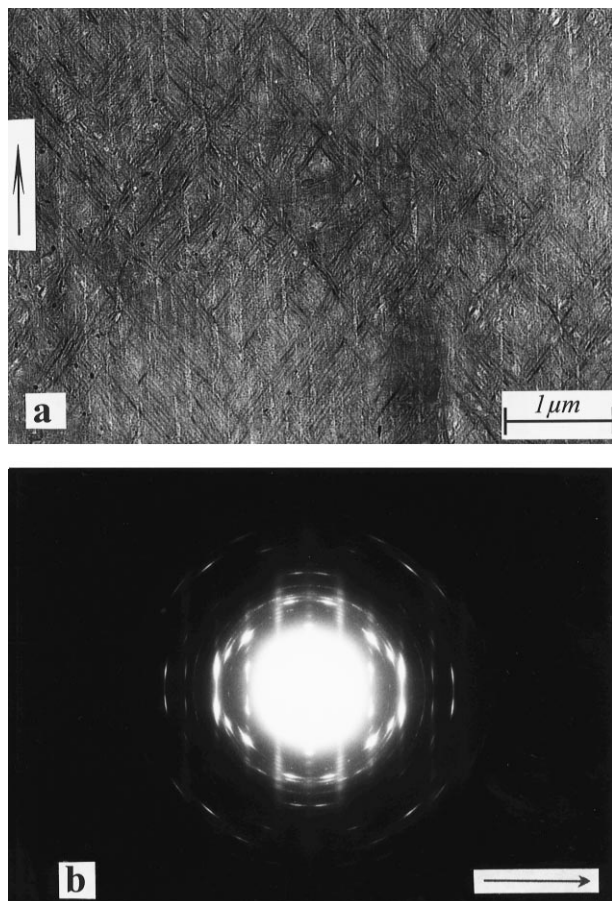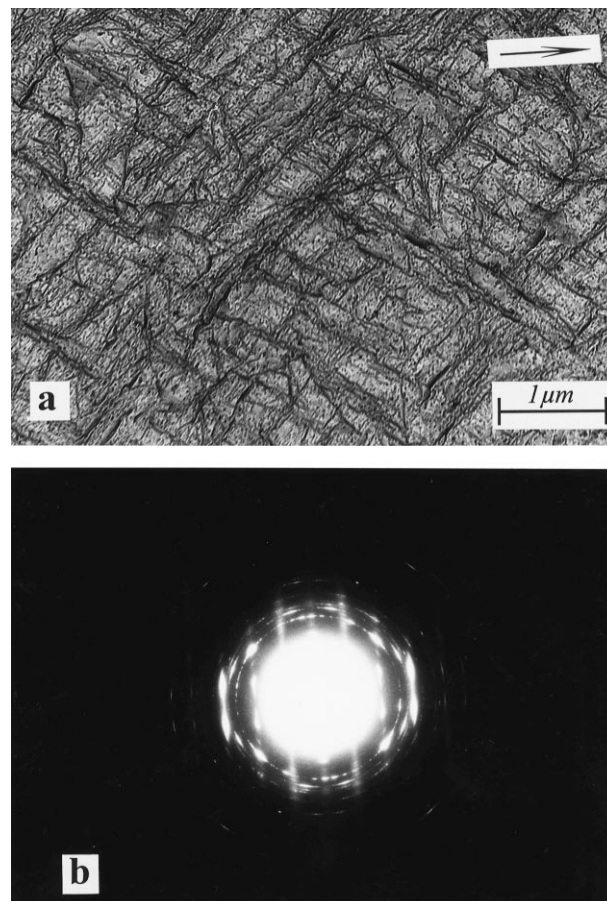
Figure 11 (a) BF electron micrograph and (b) corresponding electron diffraction pattern of HDPE–iPP double-layered films with iPP lamellar thicknesses of about 20 nm, which were heat-treated at 140°C for 15 min and then cooled at a rate of 0.1°C/min to room temperature. The chain direction of iPP is indicated by the arrow

Figure 12 (a) BF electron micrograph and (b) corresponding electron diffraction pattern of HDPE–iPP double-layered films with iPP lamellar thicknesses of about 16 nm, which were heat-treated at 140°C for 15 min and then cooled at a rate of 0.1°C/min to room temperature. The arrow shows the chain direction of iPP

appearance of a weak (110) Debye–Scherrer ring of HDPE in *Figure 14b* reflects a small amount of randomly oriented HDPE crystals in this area.

DISCUSSION

Up to now, most of the research work on heteroepitaxy of polymers has been focused on the epitaxial crystallization of iPP with some zigzag chain polymers, such as polyethylene[10,11,14], polyoctanamer[20], *trans*-1,4-polybutadiene[21] and polyamides [10], in which the zigzag chains are inclined ± 50° to the iPP chain direction. This kind of epitaxy 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[10]. This model resembles some kind of molecular matching and, indeed, it explains excellently the epitaxial orientation relationship between the substrate and the epitaxial crystals. However, the experimental results reported here and some epitaxial phenomena reported previously[11] in HDPE–iPP epitaxial systems indicate that epitaxial growth may also be controlled by morphological aspects. The matching of the methyl rows of the iPP with the (100) intermolecular distance of HDPE should result in a HDPE–iPP interface having minimum interface energy, hence, according to the crystallization theories, the most perfect epitaxial growth is expected at slow crystallization rates (low supercoolings). Nevertheless, the epitaxial

crystallization of HDPE on highly oriented iPP substrates can occur only in a thin interfacial layer, i.e. existing in a critical epitaxial layer, and the critical epitaxial layer thickness of the epitaxial HDPE crystals decreases remarkably with the decreasing crystallization rate. For example, the critical thickness changes from about 250 nm when the sample was quenched to room temperature to about 120 nm at a cooling rate of 0.5°C/min. In particular, no epitaxy takes place when the crystallization rate is slow enough, e.g. at the cooling rate of 0.1°C/min, at the given crystal dimensions of the iPP substrate (see *Table 1*). Of particular interest is the effect of crystallization temperature. Lower isothermal crystallization temperatures are favorable to epitaxial growth of HDPE on oriented iPP substrates. There exists a critical epitaxial temperature of 125°C for the present experimental conditions. If the isothermal crystallization temperature is above the critical temperature, e.g. above 126°C, there is no epitaxial growth of HDPE on the oriented iPP substrate.

Clearly, it is not enough to explain these experimental observations in terms of the chain–row matching model. In fact, the chain–row matching model is a purely geometric structural lattice match in atomic positions, and the morphological aspects caused by crystallization process has not been considered. In the heteroepitaxial systems of polymers, taking their unique morphology and crystallization into account, it is necessary to ensure that the dimensions of the epitaxial critical secondary nucleus

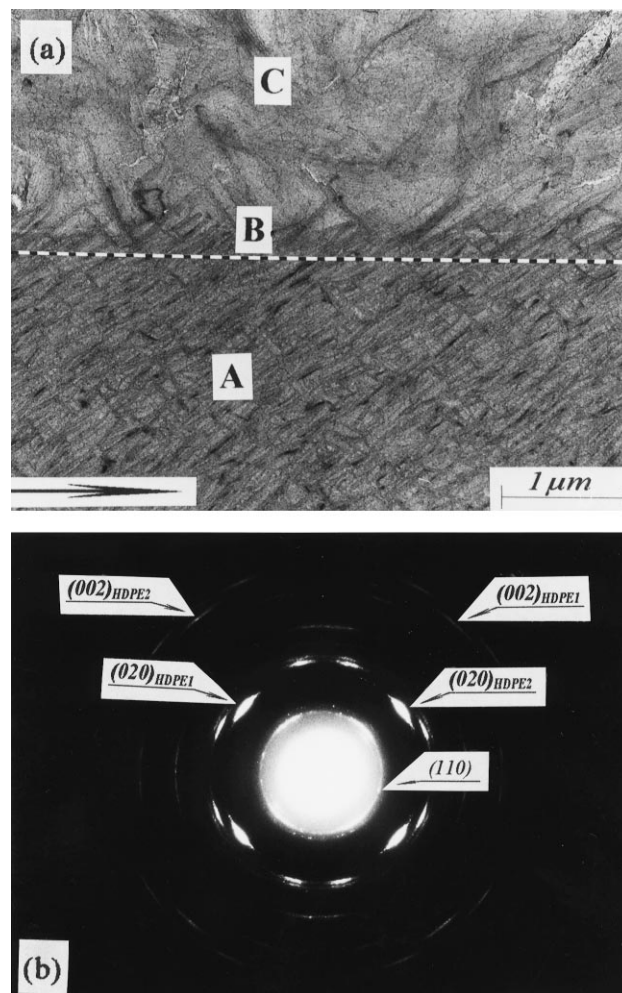**Table 1** Epitaxies of HDPE–iPP with different lamellar thickness

		Lamellar dimensions of iPP (nm)					
		l	l'	l	l'	l	l'
HDPE–iPP epitaxies		13	20	16	25	20	31
Lamellar thickness of HDPE (nm)	16 (quench to RT)	Good		Good		Good	
	20 (cooling rate 1°C/min)	Poor		Good		Good	
	25 (cooling rate 0.1°C/min)	No		Poor		Good	

Note: l represents the lamellar thickness of iPP; l' represents the lamellar dimension of iPP in the matching direction; $l' = l/\cos 50°$
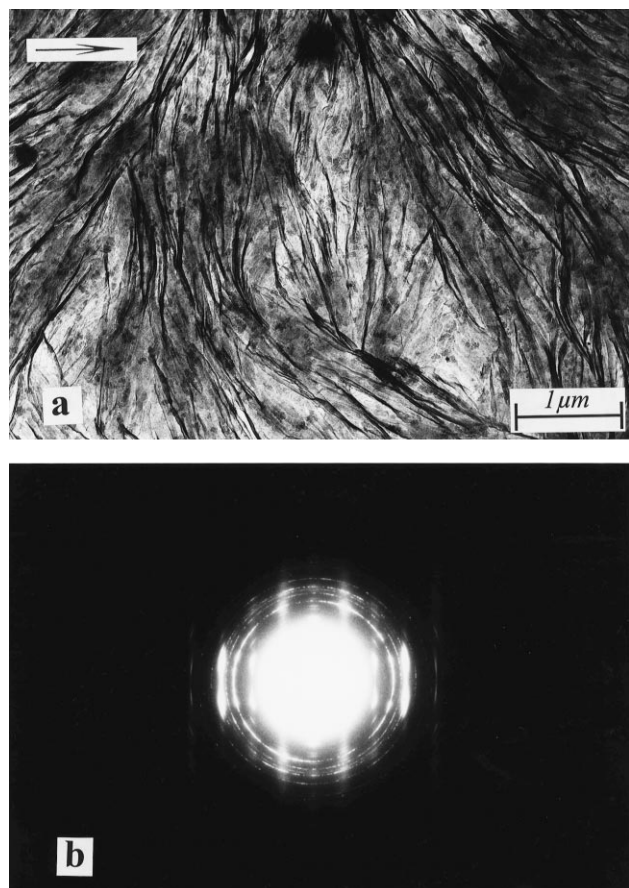
Figure 13 (a) BF electron micrograph and (b) corresponding electron diffraction pattern of HDPE–iPP double-layered films with the iPP lamellar thicknesses of about 13 nm, which were heat-treated at 140°C for 15 min and then cooled at a rate of 0.1°C/min to room temperature. The chain direction of iPP is indicated by the arrow

Figure 14 BF electron micrograph (a) and corresponding electron diffraction pattern (b) of HDPE crystallized on the boundary of the oriented iPP substrate. The iPP substrate is located in the lower part of (a) and its chain direction is indicated by the arrow. The dashed line gives the boundary line of the iPP substrate. The sample was heated to 150°C for 10 min and cooled directly to room temperature

do not exceed the dimensions of the substrate crystal, otherwise the epitaxial crystallization cannot take place. If the dimension of the substrate iPP crystal is large enough, e.g. 31 nm in matching direction (see *Table 1*), excellent epitaxial growth of HDPE on the iPP substrate takes place at any crystallization rate because, in this case, the requirement for secondary nucleation, i.e. the dimension of the substrate crystal in the matching direction is larger than the lamellar thickness of HDPE, can be satisfied. On the other hand, if the lamellar thickness of HDPE formed during the epitaxial crystallization process is much smaller, e.g. 16 nm, it can grow epitaxially on the oriented iPP substrates with various crystal dimensions. Meanwhile, the existence of a critical epitaxial temperature (125°C) is due to HDPE lamellar thickness of 25 nm at 126°C (see *Figure 9a*), which is greater than the dimension of the substrate iPP crystal in the matching direction (~23 nm). In this case, the

requirement for secondary nucleation cannot be satisfied and, therefore, no epitaxy takes place between the HDPE and iPP.

In fact, the heteroepitaxial crystallization of polymers is a surface-induced crystallization process. Therefore, the secondary nucleation must be an important controlling factor for the epitaxial growth of the deposited polymer on the polymeric substrate in addition to the structural lattice matching. Once the necessary requirement of the secondary nucleation is satisfied, subsequent growth of the epitaxial crystals is based on the lamellar growth habits of the material itself, i.e. along their fastest growing directions,
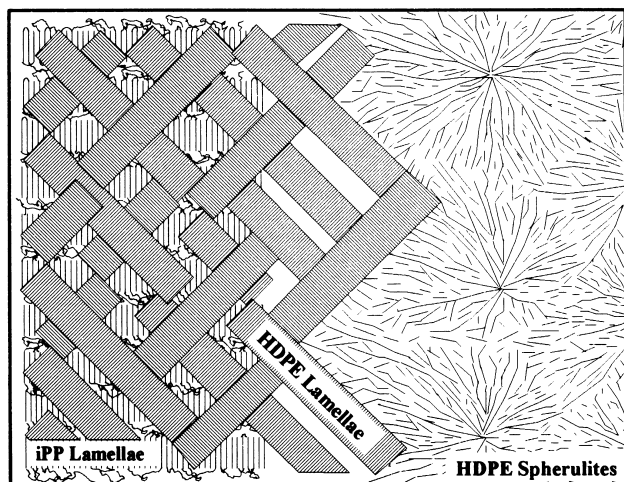
Figure 15 Model of HDPE crystallized on the boundary of the iPP substrate

the *b*-axes for HDPE[15]. The epitaxially grown HDPE lamellae may also grow across the boundary of the iPP substrate into the pure HDPE area while maintaining the epitaxial orientation relationship (see *Figure 14*).

CONCLUSIONS

In summary, crystallization rate is an important effect on the epitaxial crystallization of polymers. Higher rates result in thicker epitaxial layers. The largest epitaxial layer thickness of HDPE on oriented iPP substrates is about 250 nm for the present experimental conditions. Lower isothermal crystallization temperatures are favorable to epitaxy. There exists a critical epitaxial crystallization temperature above which no epitaxial crystallization takes place. For the HDPE–iPP epitaxial system, the critical temperature is about 125°C. In addition to the requirement of structural lattice matching during epitaxial growth, secondary nucleation of critical size is also important for the epitaxial crystallization. The requirement for secondary nucleation is that the substrate crystal dimension in the matching direction must be greater than the lamellar thickness of the deposited polymer. The epitaxial crystals may also grow across the boundary of the substrate.

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