

## Effect of lamellar thickness on the epitaxial crystallization of PE on oriented iPP films

Shouke Yan<sup>1</sup>, Jürgen Petermann<sup>1</sup>, Decai Yang<sup>2</sup>

<sup>1</sup> Institute of Materials Science, Department of Chemical Engineering, University of Dortmund, D-44221 Dortmund, Germany

<sup>2</sup> Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P.R. China

Received: 11 July 1996/Revised version: 30 September 1996/Accepted: 30 September 1996

### SUMMARY

The effects of lamellar thickness on the epitaxial crystallization of polyethylene on the oriented isotactic polypropylene have been studied by means of transmission electron microscopy. The results obtained from the bright field electron microscopy and electron diffraction show that the epitaxial orientation of the PE crystals on the iPP substrate depends not only on the thickness of the oriented iPP lamellae, but also on the lamellar thickness of PE crystals. No epitaxial orientation relationship between PE crystal and iPP substrate can be found, when the PE crystals are thicker than the lamellar thickness of iPP along the matching direction. This suggests, that the epitaxial nucleation of PE in the PE/iPP epitaxial system is controlled not only by the chain-row matching, but also by a secondary nucleation process.

### Introduction

Polymer epitaxy has been well documented in three categories, i.e. hetero-, homo-, and graphoepitaxy. In the field of heteroepitaxy, much attention has been paid to the systems of zigzag chain polymers and helical polymers since the early 1980s (1-6), especially, the polyethylene (PE) and isotactic polypropylene (iPP) system, in which the chain axes of the two polymers oriented ca. 50° apart. This kind of epitaxy has been explained in terms of the parallel alignment of PE chains onto the oblique methyl group rows in the lateral *ac* contact plane of iPP with a 0.5nm intermolecular distance for a chain-row matching (7). It resembles some kind of molecular matching between the substrate and the layer, and for this case, the most perfect epitaxial growth is expected at low crystallization rates (low supercoolings). But in contrast to that expectation, the experimental results for PE/iPP systems show, that epitaxial crystallization of PE on iPP substrates can occur only in a certain layer, and the layer thickness of the epitaxial PE crystals decreases remarkably with the decrease of the crystallization rate (8-10). In particular, no epitaxy occurs, when the PE is isothermally crystallized at temperatures above 126°C from the melt on the iPP substrate. Therefore, the matching between certain lattice planes is suspected to be the sufficient controlling factor for epitaxy of polymers. In a preceding work (11), we have found, that epitaxy in PE/iPP systems is caused by the oriented nucleation of the PE crystals on the oriented iPP substrate and the growth of PE crystals along their fastest growing directions, i.e. their b-axes. However,

the reason, why no epitaxial oriented PE nuclei can be generated at low supercoolings is still not clear. Phillips (12) et al have studied the role of secondary nucleation in epitaxial growth and argued, that until the size of the critical PE nucleus is smaller than the dimension of the iPP substrate crystals along the matching direction, epitaxial crystallization will not occur. By using iPP films with increasing lamellar thicknesses obtained by different annealing conditions and crystallizing the PE melt on those films at different cooling rates, the validity of the Phillips' argument can be directly examined. The purpose of this paper is to present some experimental results about the influence of lamellar thicknesses of both the polymers on the epitaxial crystallization of PE on iPP substrates.

### Experimental

The polymers used in this work were isotactic polypropylene and polyethylene (type Novolene, and Lupolen 6021 DX, both from BASF AG Ludwigshafen, Germany). The oriented iPP substrate films were prepared according to the melt-drawn technique introduced by Petermann and Gohil (13). The temperature for preparing the melt-drawn iPP films was 140°C. The resulting iPP films, about 30–50nm thick, can be mounted onto copper grids and directly used for transmission electron microscopy (TEM) observation. In order to study the influence of the iPP lamellar thickness on the epitaxial crystallization of PE crystals, the iPP films were annealed for 30min at 140, 150 and 155°C, respectively, for obtaining various crystal thicknesses,. Water quenched PE films were used here for a depression of their melting temperature in order to depress the melting temperature of the PE films below the lowest annealing temperature (140°C) of the PP substrate films. By melting the PE crystals in the PE/iPP double layers at 140°C for 15min and then cooling them at different rates to room temperature, the influence of the PE lamellar thickness on its epitaxial behavior has been studied. The heat-treatments of the PE/iPP double layers was carried out in DSC apparatus. A Philips CM200 TEM operated at 200kV was used in this study. Bright-field (BF) micrographs were obtained by defocus of the objective lens.

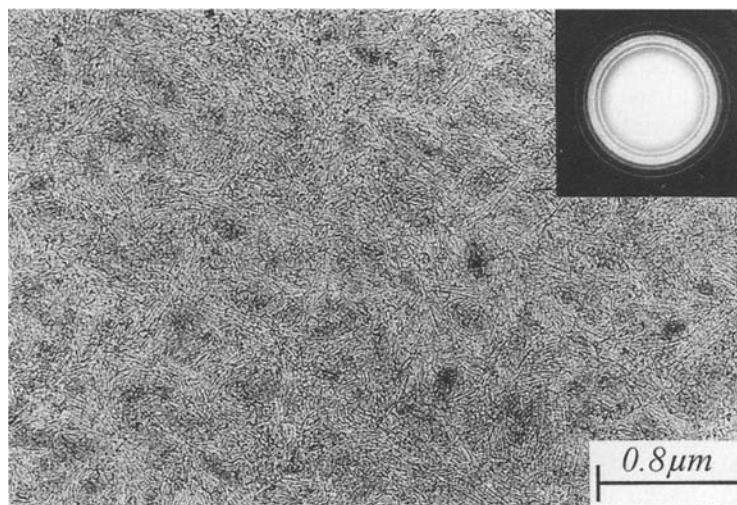


Fig.1 (a) BF electron micrograph and (b) electron diffraction pattern of PE quenched thin films.

## Results and discussion

### *Microstructure of PE quenched films and iPP substrate films*

The BF electron micrograph of a PE quenched thin film exhibits small and randomly oriented lamellae (Fig.1). The Debye-Scherrer rings on the electron diffraction pattern, inserted in Fig.1, show the characteristics of the non oriented morphology. Fig.2 a,b shows the electron micrographs of highly oriented iPP films. The arrow represents the drawing direction of the iPP film. Obviously, the iPP lamellae, which appear as dark lines, are oriented perpendicular to the drawing direction. Furthermore, the thickness of the iPP lamellae depends strongly on the annealing temperature, while the corresponding electron diffraction patterns reveal always the same chain-axis orientation (inset in Fig.2 b).

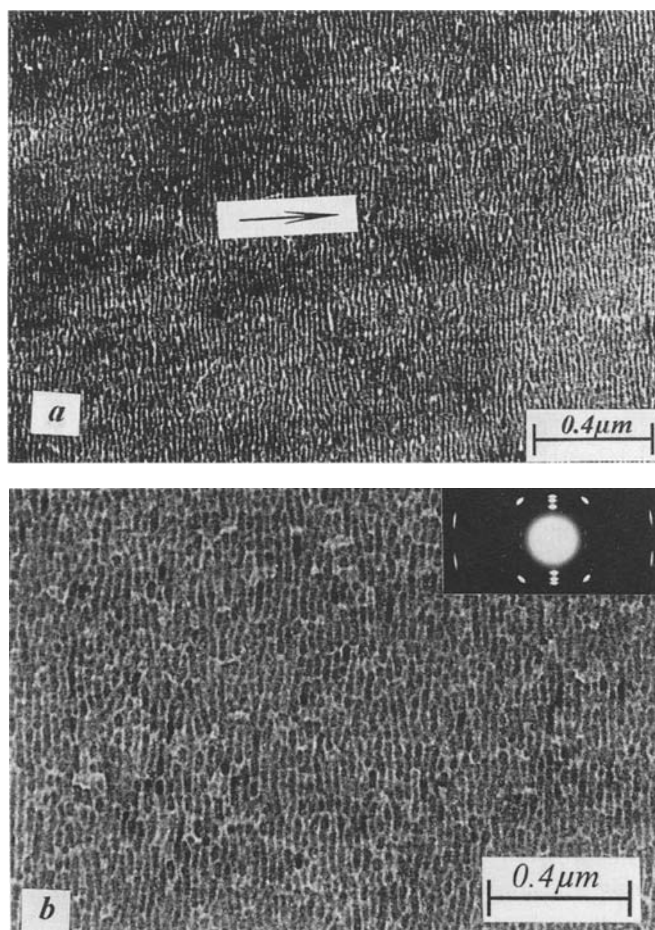


Fig.2 BF micrographs and electron diffraction pattern (inset) of iPP oriented films. The arrow indicates the drawing direction of the film. The films were annealed at (a) 140 and (b) 155°C, respectively.

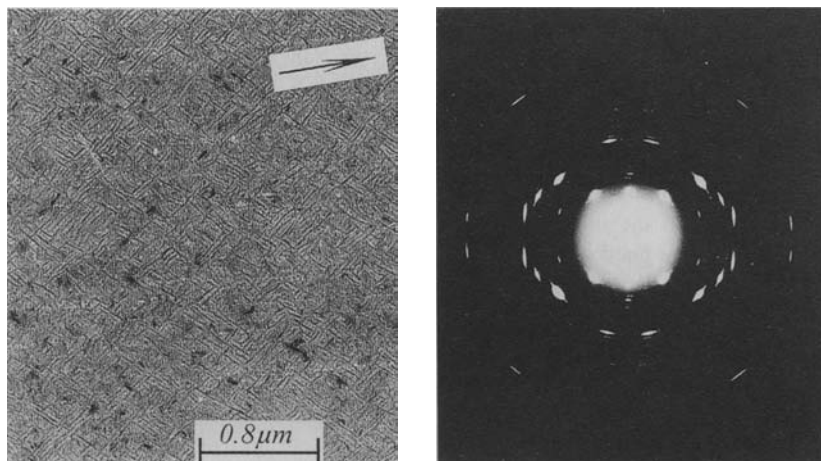


Fig.3 (a) BF electron micrograph and (b) electron diffraction pattern of a PE/iPP double layer, in which the iPP substrate was annealed at 140°C for 30min. The PE/iPP layer was heated to 140°C for 15min and then cooled to room temperature on air. The arrow indicates the molecular direction of iPP crystals.

#### *Crystallization of PE on iPP by air cooling from the melt*

Fig.3a shows a BF micrograph of a PE quenched film, crystallized on the oriented iPP substrate, which was annealed at 140°C for 30min. The PE/iPP double layer was heat-treated at 140°C for 15min and then cooled to room temperature on air. The arrow on the picture exhibits the chain direction of the iPP substrate. Clearly, a cross-hatched lamellar structure of PE crystals arises with their lamellae being inclined at an angle of 40° to the chain-axis of the iPP. The average width and thickness of the PE lamellae are about 150 and 16nm, respectively. This reveals the typical morphology originating from the epitaxial crystallization of PE on the oriented iPP substrate. The corresponding electron diffraction, Fig.3b, confirms, that PE crystallized epitaxially on the iPP substrate with the molecular directions of both the polymers  $\pm 50^\circ$  apart. The same orientation relationships between PE and iPP have been observed when the iPP films, which were annealed at 150 and 155°C, were used as the substrates.

#### *Recrystallization of PE on iPP by cooling from the melt at a rate of 1°C/min*

Fig. 4 shows the BF electron micrograph and the electron diffraction pattern of a PE/iPP double layer, on which the iPP substrate was annealed at 150°C for 30min. The PE/iPP layers were heated to 140°C for 15min and then cooled at a rate of 1°C/min to room-temperature on air. The arrow exhibits the molecular direction of the iPP substrate. It is noticed that, except for the change of the lamellar dimensions, no other morphological differences of PE crystals between Fig.3 and 4 can be found. However, when the iPP substrate, annealed at 140°C for 30min, was used in the PE/iPP double layer, the perfection of the epitaxial orientation of PE crystals is not as good as that in Fig.3a.

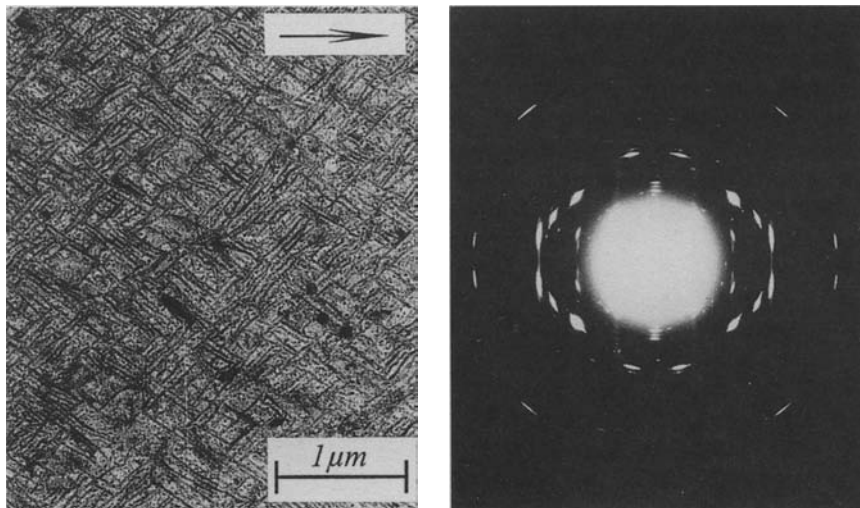


Fig.4 (a) BF image and (b) electron diffraction pattern of PE/iPP double layers, in which the oriented iPP films were annealed at 150°C for 30min. The layers were heat-treated at 140°C for 15min and then cooled at a rate of 1°C/min to room temperature. The molecular direction of the iPP film is shown by an arrow.

#### *Crystallization of PE on iPP by cooling from the melt at a rate of 0.1°C/min*

The micromorphology of the PE/iPP double layer, in which the iPP substrate was annealed at 155°C for 30min, and the layer was heated to 140°C for 15min, then cooled at a rate of 0.1°C/min to room temperature, is shown in Fig.5a. The molecular direction of the iPP substrate is indicated by an arrow. Obviously, the PE lamellae formed at this cooling rate are even larger. But the large PE lamellae have the same orientation arrangement as that shown in Fig.3a. This is also confirmed by the corresponding electron diffraction, Fig.5b. When the iPP film in the PE/iPP layer was annealed only at 150°C, the epitaxial orientation of PE is poorer. Only a rough cross-hatched structure of PE can be seen on the BF image, while on the electron diffraction pattern weak Debye-Scherrer rings with clearly distinct maxima at the positions where the reflection spots appear for the epitaxially crystallized PE, can be observed. Using the iPP substrate, which was annealed at 140°C, the epitaxial orientation is lost completely (Fig. 6a). The

corresponding electron diffraction patterns are in agreement with the BF observation (Fig.6b).

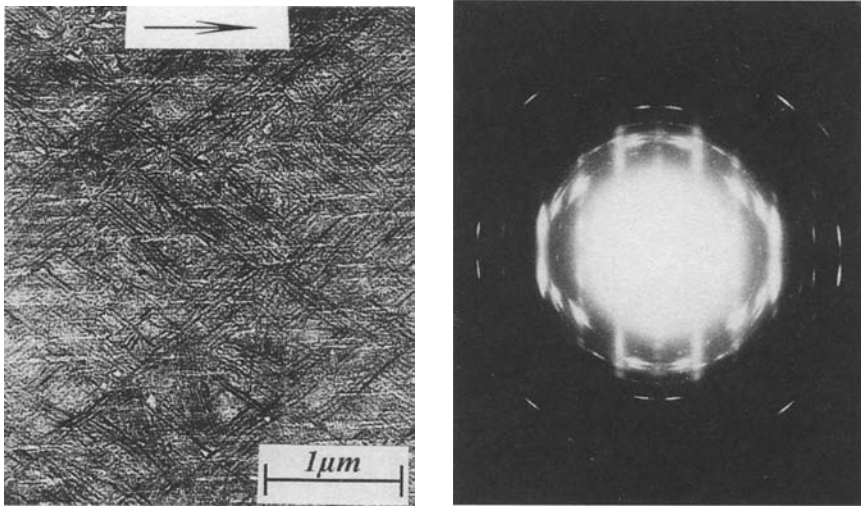


Fig.5 (a) BF electron micrograph and (b) electron diffraction pattern of a PE/iPP layer, in which the iPP substrate was annealed at 155°C for 30min. The layer was heat-treated at 140°C for 15min and then cooled at a rate of 0.1°C/min to room temperature. The molecular direction of the iPP film is indicated by an arrow.

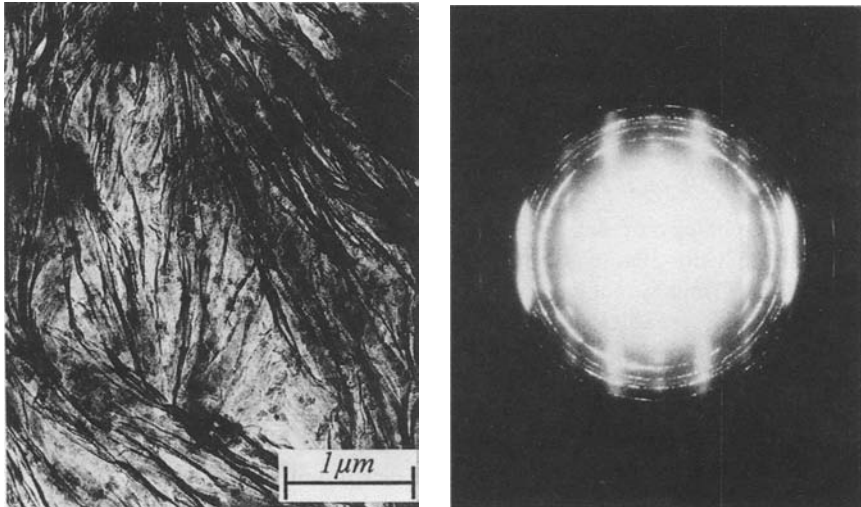


Fig.6 (a) BF electron micrograph and (b) electron diffraction pattern of a PE/iPP film with the iPP being annealed at 140°C for 30min. The arrow represents the molecular direction of the iPP substrate. The thermal history of the sample is the same as that in Fig.5.

In all the experiments mentioned above, the differences are either the crystal dimensions of the iPP substrates or of the PE layers. Therefore, the micromorphological differences in the PE layers must result from the change of the crystal dimensions of iPP as well as PE crystals. When comparing the lamellar thicknesses of the PE crystals and those of the iPP substrate crystals in the epitaxial direction, i.e. the chain-row matching direction (see table 1), we can conclude, that no epitaxial crystallization of PE on iPP substrates occurs until the lamellar thickness of the PE crystals is smaller than that of iPP crystals along the matching direction. This is in accordance with the theoretical prediction of Phillips et al (12).

Table 1 Epitaxial relationships between PE crystals and different iPP substrates

Epitaxial situation between PE and iPP substrates		Lamellar thicknesses of iPP in matching direction ( $l'_{PP}$ ) under different annealing conditions		
		20nm	23nm	30nm
Lamellar thicknesses of the PE ( $l_{PE}$ ) after the different crystallization conditions	16nm	good	good	good
	20nm	poor	good	good
	25nm	no	poor	good

**Note:** The lamellar thickness of iPP matching direction is calculated by dividing along the the actual lamellar thickness  $l_{PP}$  through  $\cos 50^\circ$ , that is,  $l'_{PP} = l_{PP} / \cos 50^\circ$ .

## Conclusion

The experimental results obtained from BF observation and electron diffraction show that the epitaxial crystallization of PE on the iPP substrate occurs only, when the lamellar thickness of the PE crystals is smaller than that of the iPP substrate along the matching direction. This implies that the epitaxial oriented nucleation of PE on the iPP substrate is controlled not only by the chain-row matching, but also a secondary nucleation process.

## Acknowledgment

The financial supports of Max-Planck-Gesellschaft, Germany, as well as the National Key Projects of Fundamental Research, "Macromolecular Condensed State", the State Science and Technology Commission of China are gratefully acknowledged.

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