ORIGINAL CONTRIBUTION

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Surface induced crystallization of PCL on oriented PE substrates: epitaxy and transcrystallization

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Abstract The crystallization behavior of polycaprolactone (PCL) on the highly oriented polyethylene (PE) substrates was studied by means of optical microscopy (OM), transmission electron microscopy (TEM), and electron diffraction (ED). The results of both OM and TEM observations indicate that PE is a very active nucleation agent for PCL. While a transcrystalline zone of PCL is observed in the boundary area of the PE substrate by optical microscopy, both heteroepitaxy and transcrystallization of PCL on the PE substrates are recognized by TEM observations. It was further found that the transcrystalline zone of PCL in the thin films is composed of two different kinds of crystals, i. e. the edge-on crystalline lamellae at the interface, and the further grown flat-on crystals. In thicker samples, a semi-period lamellar twisting occurs during growth of the transcrystalline crystals.

Introduction

Heterogeneous nucleation is not only a commonly encountered phenomenon of polymer crystallization, but also a fundamentally important research topic for understanding polymer crystallization. Surface induced polymer crystallization, as typical heterogeneous nucleation systems, has received much attention in the past few decades. Transcrystallization [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] and heteroepitaxy [11, 12, 13, 14, 15, 16, 17, 18, 19] of polymers have been of particular interest because of both the unusual crystalline morphologies and the property improvement of the composites. Although both transcrystallization and heteroepitaxy of polymers have been intensively investigated in the past decades,

combined studies of the two aspects are rarely found in the literature.

In the studies of polymer transcrystallization, fibers were generally used as substrates to investigate the nucleation abilities of the substrates, resulting morphologies of the polymers, and the mechanical properties of the polymer/fiber composites. For polymer epitaxial crystallization systems, however, oriented thin polymer ribbons were commonly chosen as substrates to study the above mentioned aspects. As sketched in Fig. 1, when crystallizing a polymer on the boundary of an oriented ultra-thin polymer substrate, which is active in nucleating the polymer and initiating heteroepitaxy of the polymer, a combined study on transcrystallization and heteroepitaxy of a polymer on a polymeric substrate can be performed.
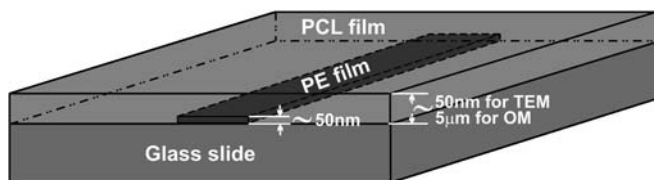
Fig. 1 Sketch showing the experimental procedure used in this work

The purpose of this paper is to present some experimental results relating to the transcrystallization and heteroepitaxy of PCL on highly oriented PE substrates.

Experimental

The polymers used in this work were high-density polyethylene (PE), type Lupolen 6021 DX, produced by BASF AG Ludwigshafen, Germany, and commercial grade polycaprolactone (PCL), with molecular weight $M_w = 65\,000$, polydispersity 1.53, and a melting point of 60 °C. Highly oriented PE films were prepared according to the melt-drawn technique introduced by Petermann and Gohil [20]. Samples for OM and TEM observations were prepared by dipping glass slides, which were partially covered by the oriented PE films, into 2 wt% and 0.1 wt% PCL/chloroform solutions, respectively. After the evaporation of the chloroform, the films obtained for TEM and OM studies are about 50 nm and 5 μm, respectively. The OM samples were directly heat-treated at a temperature of 80 °C (below the melting point of PE but above the PCL melting point) for 10 min and subsequently crystallized isothermally at 55 °C for different times. Samples for TEM observation were at first floated on the surface of distilled water and mounted onto carbon-coated 400 mesh TEM copper grids, and subsequently heat-treated at different temperatures for varying times. For TEM observations, 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 of the polymer samples caused by the electron beam, focusing of the sample was carried out on one region, the specimen film was then translated to its adjacent undamaged area and the image was recorded immediately. For OM observation, a Leitz DM RXP optical microscope equipped with a hot stage was used.

Results and discussion

Optical microscopy studies

Figure 2a shows an OM micrograph of the PCL crystallized isothermally on a neat glass slide at 50 °C for 24 h. It is clear that the PCL exhibits a spherulitic morphology. The dimension of the spherulites depends remarkably on the crystallization condition and the sample thickness. For example, when the same sample as in Fig. 2a was first crystallized isothermally at 55 °C for 3 days and subsequently quenched to room temperature, different morphologies are observed. As shown in Fig. 2b, except for four big spherulites, there now mainly exists a substantial amount of small spherulites.
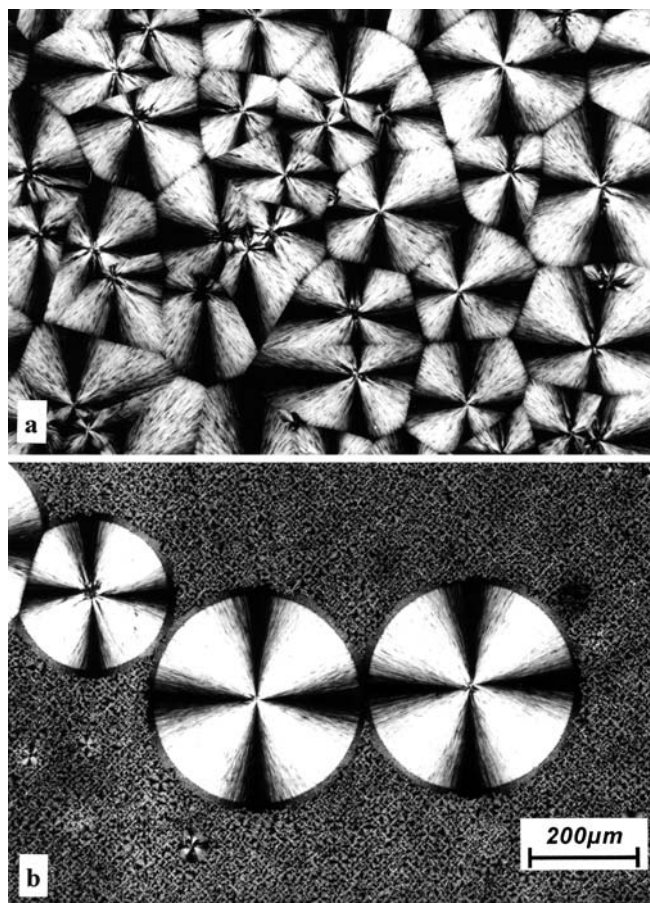

Fig. 2a, b Cross polarized OM micrographs of PCL crystallized isothermally **a** at 50 °C for 24 h; **b** at 55 °C for 3 days and then quenched to room temperature

The big spherulites exhibit stronger birefringence than the small ones. This indicates that both the nucleation and the subsequent crystal growth of PCL at 55 °C are very slow. Therefore, many small spherulites, together with the surrounding layers of the big spherulites (which show the same birefringence as the small spherulites) are formed in the remaining molten PCL after quenching the sample to room temperature.

Figure 3 shows series OM micrographs of PCL in the boundary area of an oriented PE substrate. The sample was at first heated to 80 °C for 10 min (Fig. 3a) and then cooled to 55 °C for different times (Fig. 3b–f). The PE substrate is located at the lower left corner of the picture. The boundary line of the PE substrate is not difficult to recognize in Fig. 3b–f, while it appears as a bright line in Fig. 3a. The molecular chain direction of the PE substrate is parallel to the boundary line as indicated by an arrow. It should be pointed out that since the sample in Fig 3a was heated to 80 °C, which is far above the melting point of the PCL, no birefringence contribution is expected from the PCL melt. From the fact that no evident difference can be identified between
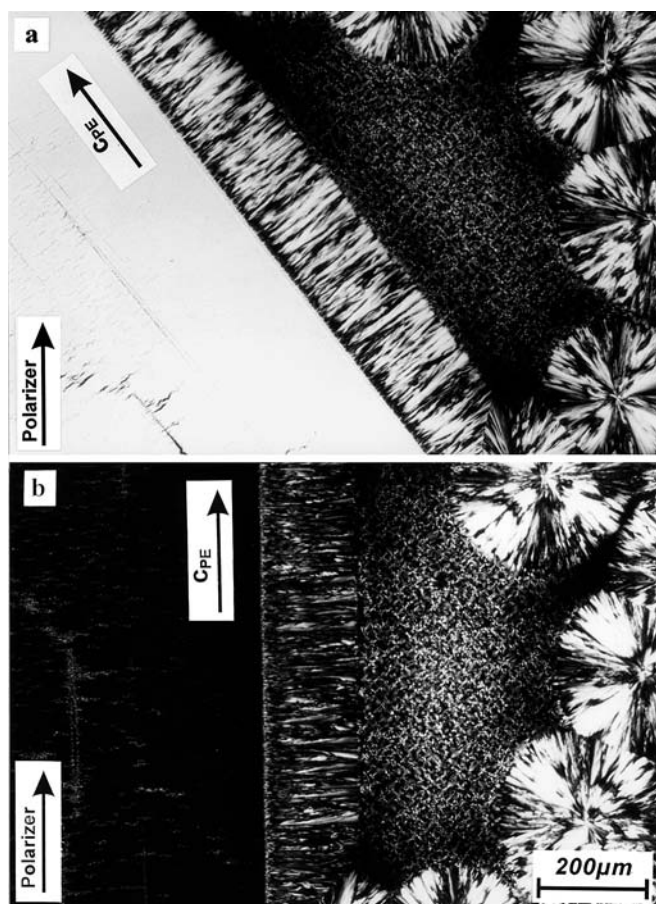
Fig. 3a–f Series of cross polarized OM micrographs showing the PCL crystallized at the boundary area of the oriented PE substrate. The PE substrate is located in the *lower left corner* of the picture. Its molecular chain direction is parallel to the boundary line as indicated by *arrows* labeled with C_{PE}. The sample was heat-treated at 80 °C for 10 min **a** and subsequently cooled to 55 °C for **b** 0, **c** 0.5, **d** 6, **e** 20, and **f** 50 h. The polarization direction of the light is vertical
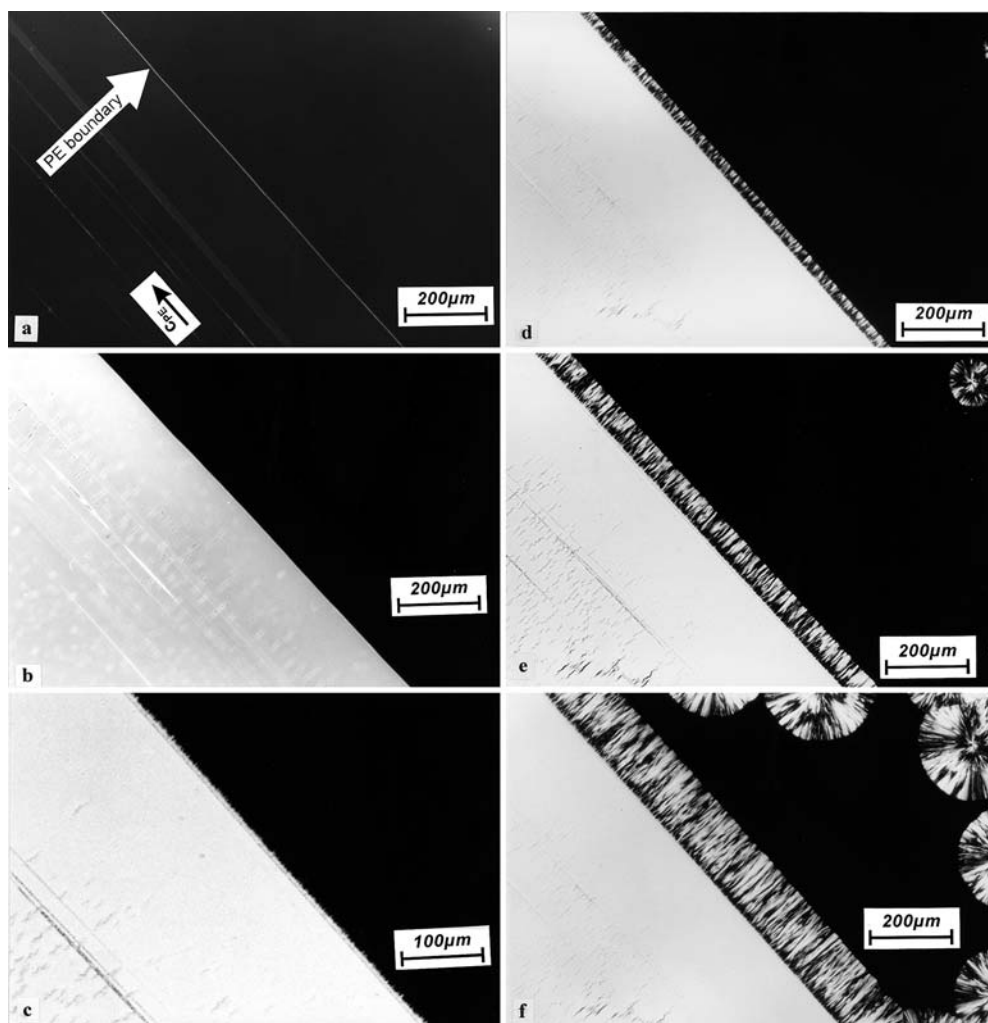
the areas with and without PE substrate, it is concluded that the oriented PE substrate film is too thin to give contrast under polarized light microscope. By cooling the sample down to 55 °C, the responses of the PCL in the areas with and without PE substrate are quite different. As shown in Fig. 3b, while the PCL on the neat glass slide, (upper right corner of the picture) is still in the melt state and exhibits no birefringence, the PCL on the PE substrate (lower left corner of the picture) begins to provide some bright contrast. This clearly demonstrates that the nucleation of PCL is more favorable on the PE substrate than in the bulk of the melt, and the early generated nuclei of PCL provide some birefringence contribution. Keeping the sample at 55 °C, the birefringence of PCL on the PE substrate becomes stronger and stronger. It reaches its maximum brightness 30 min after the sample was cooled down to 55 °C (Fig. 3c). At this moment, even though the PCL on the glass slide far away from the boundary of PE substrate remains unchanged, the crystallization of PCL on the boundary line of the PE substrate has already started.

This implies that the crystallization of PCL on the PE substrate film has finished within 30 min, and the crystals formed on the boundary of PE substrate start to spread towards the remaining non-crystallized area. This further confirms that the PE surface exhibits very strong nucleation ability towards PCL. Since spherulitic segments from the nuclei densely spaced on the boundary line of PE substrate mutually hinder their lateral growth, the crystallites are allowed to grow only perpendicularly to the boundary line of the PE. As a result, a transcrystalline front has emerged parallel to the PE boundary line, see Fig. 3d. The nucleation of PCL in its bulk is so difficult that only one PCL nucleus in the area without PE substrate is observed after keeping the sample at 55 °C for 6 h. When a transcrystalline zone of 75 μm, from the boundary of PE substrate to the growth front of the PCL, is formed after a period of 20 h crystallization (Fig. 3e), the radius of the biggest spherulites is measured to be 55 μm. Keeping the sample at 55 °C for 2 days (see Fig. 3f), the dimensions of the transcrystalline zone and spherulites reach 140 μm and 120 μm,

respectively. The crystallization of PCL on the glass slide is, however, still not finished due to the very slow growth rate of PCL crystals at 55 °C. When taking the sample out from the hot stage of the microscope, the remaining PCL melt crystallizes rapidly and forms a great number of small spherulites. Figure 4 shows two OM micrographs of PCL crystallized in the boundary area of the PE substrate at 55 °C for 3 days and then quenched to room temperature. The arrows labeled with C_{PE} and polarizer represent the molecular chain direction of the PE substrate and the polarization direction of the light, respectively. Clearly, Fig. 4b is taken from the same area as Fig. 3 as well as Fig. 4a, but with different chain orientation of PE relating to the polarization direction. This is achieved by a 45° rotation of the sample about the light beam. Unambiguously, rotating the sample about the light beam changes the contrast of PCL on PE

Fig. 4a, b Cross polarized OM micrographs of PCL isothermally crystallized on the boundary of the PE substrate at 55 °C for 3 days and subsequently quenched to room temperature. The *arrows* labeled with C_{PE} and *polarizer* indicate the molecular chain direction of the PE substrate and the polarization direction of the light, respectively. Both **a** and **b** are taken with the same sample in the same area but having different chain orientation of PE substrate with respect to the polarization direction

substrate and in the transcrystalline zone. At the beginning, the PE chain direction is 45° apart from the polarization direction, the PCL crystals either on the PE substrate or in the transcrystalline zone exhibit strong birefringence (Fig. 4a). A 45° rotation of the sample results in a parallel alignment of the PE chain direction with respect to the polarization direction. As shown in Fig. 4b, an apparent light extinction arises for the PCL crystals on the PE substrate and in the transcrystallization zone. This is associated to a preferred orientation of PCL crystals on the PE substrate and in the transcrystalline zone.

Observing Figs. 3d–f and 4a carefully, it is found that there exists an extinction band in the PCL transcrystalline zone. The extinction band is about 10 μm in width and stands about 3 μm away from the boundary line of the PE substrate. This demonstrates the occurrence of lamellar twist direct after they are initiated [21, 22]. Since no periodic extinction bands are observed, the semi-periodic lamellar twist cannot be related to the crystallization habit of the PCL itself. Our previous work also demonstrated that spherulites of the pure PCL do not exhibit banded structure [23]. The reason for the formation of the semi-periodic lamellar twist may be caused by the surface stresses created by the congested molecular packing due to high density of the PCL nuclei generated by the PE substrate. Through the one turn twist of the PCL chains about the lamellar axes, the surface stresses are released and a normal crystal growth is realized. Therefore, no further lamellae twist occurs. In order to get detailed structure information about the PCL on and in the vicinity of the PE substrate, TEM investigation was carried out for the thin films.

Transmission electron microscopy studies

Figure 5 shows an electron micrograph and its corresponding electron diffraction pattern of a PCL thin film, which is prepared simply by dipping a glass slide into a 0.1 wt% PCL/chloroform solution. The pure PCL film consists of randomly oriented edge-on lamellae with their molecular chains laying in the film plane (Fig. 5a). This shows as concentric diffraction rings on the electron diffraction pattern (Fig. 5b). The melt-drawn PE thin film, which provides no contrast contribution under the optical microscope, consists of parallel aligned lamellae with fiber orientation, see Fig. 6. Namely, their molecular chain directions oriented along the drawing direction, but the crystallographic a- and b-axes rotate randomly around the crystallographic c-axis.
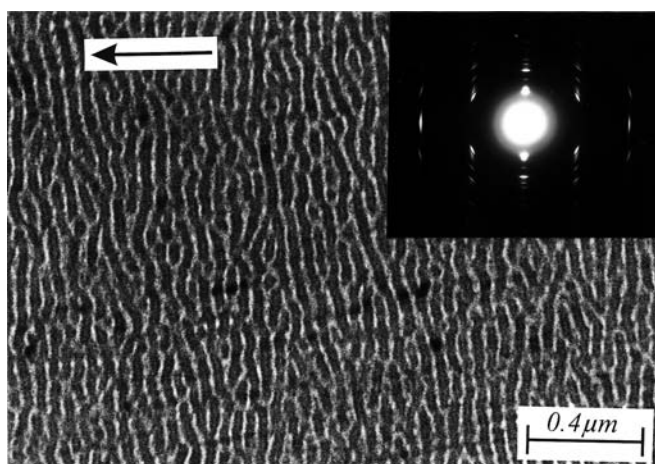
Figure 7 shows the bright field electron micrograph and its corresponding electron diffraction pattern of the PCL/PE double layered film, which was heat-treated at 80 °C for 10 min and subsequently crystallized isothermally at 50 °C for 24 h. The arrow in the picture indi-
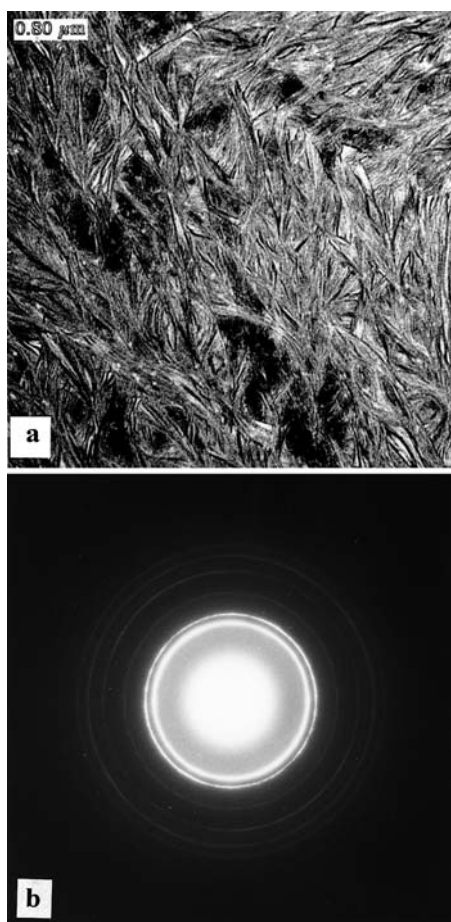
Fig. 5 a BF electron micrograph and b its corresponding electron diffraction pattern of solution cast PCL thin films
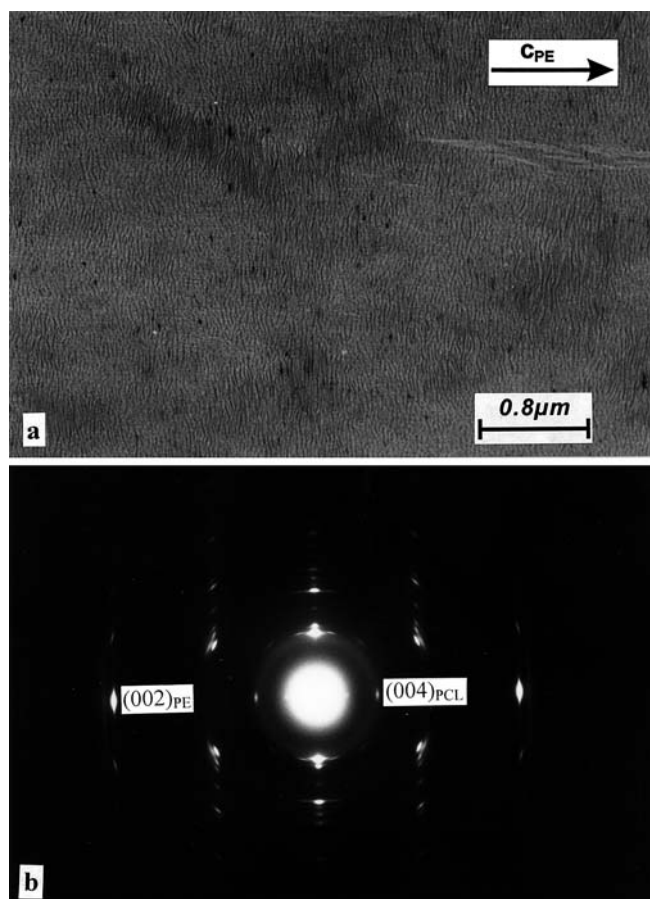
Fig. 7 a BF electron micrograph and b its corresponding electron diffraction pattern of PCL/PE double layered thin films, which was heat-treated at 80 °C for 10 min and subsequently crystallized at 50 °C isothermally for 24 h. The molecular chain direction of the PE substrate is represented by an *arrow*

Fig. 6 Bright field electron micrograph and its corresponding electron diffraction pattern (*inset*) of melt-drawn PE films. The *arrow* represents the drawing direction of the film during preparation
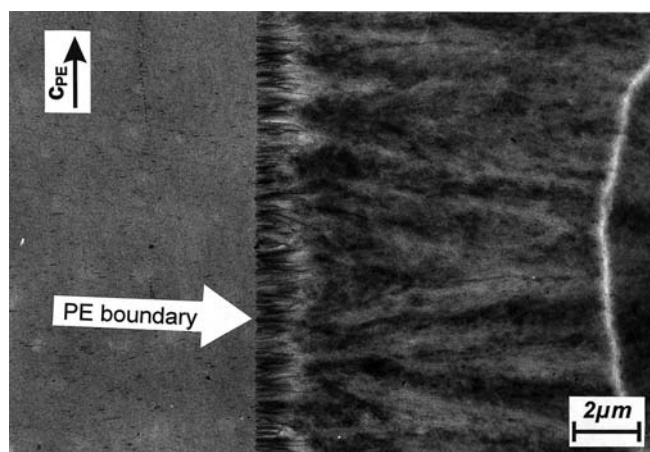
cates the molecular chain direction of the PE substrate. Clearly, a parallel aligned lamellar structure of PCL arises with the PCL lamellae perpendicular to the chain direction of the PE substrate (Fig. 7a). This is associated to an epitaxial crystallization of PCL on the PE substrate [3]. From the electron diffraction results (Fig. 7b), it is concluded that the PCL grows epitaxially on the PE substrate with the molecular chain directions of both polymers parallel. Moreover, it should be pointed out that the stability and intensity of the PCL electron diffraction are much lower than that of the PE crystals. Therefore, the reflection spots in Fig. 7b corresponding to the PCL lamellae are rather weak compared with those from PE.

Similar to the case of thick film for OM observation, a transcrystalline zone is also observed under transmission electron microscope in the boundary area of the thin PE substrate, as shown in Fig. 8a. It is clear that the transcrystalline zone in the thin film system is composed by two different kinds of crystals, i. e. the edge-on
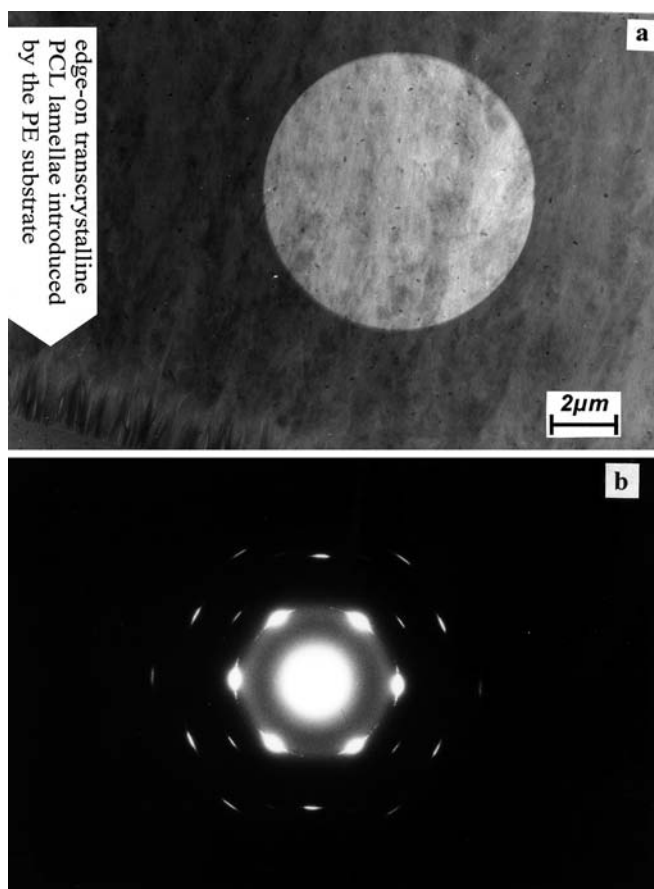
Fig. 8 a BF electron micrograph showing the morphology of PCL/PE double-layered thin films in the boundary area of the PE substrate. A strip of the PE substrate can be seen in the *lower left corner* of the picture. Its molecular chain direction is parallel to the boundary line. The sample was heat-treated at 80 °C for 10 min and subsequently crystallized at 50 °C for 24 h. **b** An electron diffraction pattern taken from the selected area as indicated in the BF electron micrograph

Fig. 9 BF electron micrograph showing the morphology of a PCL/PE double-layered thin film in the boundary area of the PE substrate. The molecular chain direction of the PE substrate is vertical as indicated by an *arrow*. The sample was heat-treated at 80 °C for 10 min and subsequently cooled at a rate of 5 °C/min to room temperature

crystalline lamellae, which is in direct contact with the PE boundary, and the further grown flat-on crystals with the molecular chains oriented parallel to the lamellar thickness direction, as concluded from the corresponding diffraction pattern (Fig. 8b). This certifies the occurrence of the lamellar twisting in the transcrystalline zone. The lateral width of the edge-on lamellae is about 2 μm. This is in good accordance with the OM observation. Since the transcrystalline zone formed at present crystallization condition has covered more than one box of the TEM copper grid, it is impossible to get an overall view of the transcrystalline zone. Increasing the supercooling during the crystallization of PCL makes it possible to shoot the whole transcrystalline zone in one TEM negative. Fig. 9 shows a BF electron micrograph with a complete view of the formed transcrystalline zone. The PE substrate is located in the left part of the picture. Its molecular chain direction is

vertical as indicated by an arrow. The sample was heat-treated at 80 °C for 10 min and then cooled at a rate of 5°C/min directly to room temperature. From Fig. 9, it can be recognized that the edge-on PCL lamellae in the transcrystalline zone are evidently not the extension of the epitaxial lamellae. This means that the edge-on transcrystalline PCL lamellae are nucleated by the side face of the PE substrate. Keeping in mind the fact that the melt-drawn PE film exhibits only a fiber orientation, the crystal structure of its side face is actually identical to the top surface. Therefore, the epitaxial interaction plays a very important role in the nucleation process of transcrystallization. On the other hand, the edge-on lamellae are so densely collocated that most of them appear in the form of aggregates. Taking this into account, the surface stresses created by the congested molecular packing, due to the high nucleus density, may take the response of the lamellae twisting. Moreover, the flat-on PCL crystals extend to the end of the transcrystalline zone in the thin films, unlike in the thick sample used for OM observation where the PCL molecular chains try back to the film plane after a semi-periodic lamellar twisting. This may relate to the crystallization habit of the carbon-supported thin polymer films.

Conclusion

Optical microscopy, transmission electron microscopy, and electron diffraction investigations indicate that PE has a very strong heterogeneous nucleation activity towards PCL. While heteroepitaxy is identified in the double-layered films, transcrystallization of PCL on the boundary of the PE substrate is observed. The

transcrystalline zone of PCL in thin films is composed of two different kinds of crystals, i. e. the edge-on crystalline lamellae at the interface, and the further grown flat-on crystals. In thick films, however, a semi-periodic lamellar twisting occurs during the transcrystallization.

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