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The use of light microscopy for investigations of epitaxial growth of polymers on polymeric substrates

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Summary

In order to study the oriented (epitaxial) crystallization of thermoplastic polymers on oriented polymer substrates, generally the transmission electron microscopy (TEM) is used. With this instrument, the crystallized material can easily be resolved and orientation relationships can be monitored by electron diffraction. Disadvantages are the time consuming sample preparations and difficulties in the in-situ observations of the crystallization events, because of the radiation sensitivity of the polymer crystals. It is demonstrated that these disadvantages of the TEM can be eleminated by the use of different methods of light optical contrasts under specific preparation conditions of the samples and that the optical microscopy being a supplementary method to the TEM for investigations of epitaxial crystallization.

Introduction

Oriented (epitaxial) growth of some semicrystalline polymers onto uniaxially oriented isotactic polypropylene (iPP) (1-4), syndiotactic polypropylene (5) polyamides (6) and polytetrafluorethylene (7) has been found recently. All the investigations were performed by transmission electron microscopy (TEM). But in none of the investigations the crystallization kinetics was studied. For in-situ experiments of the crystallization, the TEM is not useful because the electron irradiation influences the crystallization of polymers. On the other hand, optical microscopy on the epitaxial systems with the use of a heating stage proved to be difficult, because the optical contrasts of layers and substrates are interfering and giving complex images. A new sample preparation method will be presented where the uniaxially oriented substrate iPP films have a thickness of less than 50 nm and therefore do not contribute to the light optical contrast. As the resolution of the optical microscopy is not high enough to image single crystalline lamellae, the light optical investigations can only be interpreted in connection with the TEM results. The supplementary results from TEM and light optical micrographs may contribute for the further understanding of the epitaxial crystallization.

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Experimental

Extremely thin uniaxially oriented iPP films (≈ 30 nm) were prepared according to the method of Petermann and Gohil (8). After preparation they were put on a glass slide as a support in the way that only half part of the glass slide was covered with the iPP-film. Subsequently, a thin solution cast film (≈ 0.5 μm) of HDPE was put over the whole glass slide. The iPP and HDPE used were Novolen 1320H and Lupolen 6021D, respectively, both from the BASF-AG, Ludwigshafen. These samples were put into a heating stage of a POLYVAR (Reichert)-optical microscope and heated for 10 mins to 155°C. At this temperature, the HDPE is in the molten state, while the iPP is still solid. Subsequently, the samples were cooled with about 10°C/min to room temperature (RT) and photographed at RT in polarization and interference contrast modes. Detailed crystallization events at elevated temperatures will be published elsewhere (9). Additionally, the samples where investigated by a confocal laser scanning microscope (Leica CLSM) in reflection mode(*).

Results and Discussion

Fig. 1a is a TEM micrograph of an iPP support film and Fig. 1b shows the cross-hatched lamellar arrangement of HDPE lamellae on the iPP substrate film (TEM micrograph). In both the micrographs the molecular orientation directions of the iPP films are horizontal. The cross-hatched lamellae in Fig. 1b are typical for the epitaxial crystallization of the HDPE on iPP (2,3). But it is not the aim of this note to discuss the phenomenon of polymer/polymer epitaxy. Details of the epitaxial crystallization can be found elsewhere (6). It just shall be men-

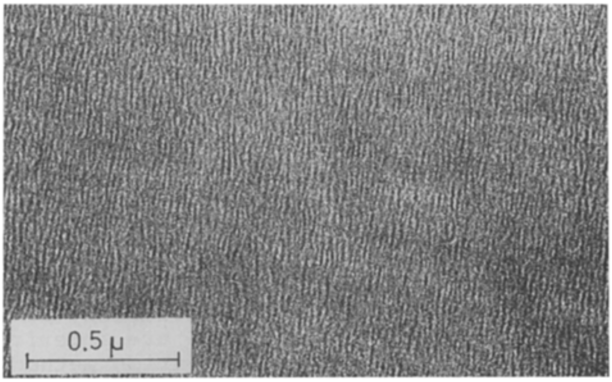

Fig.1a): TEM micrograph of an iPP substrate film. Its molecular direction is horizontal.

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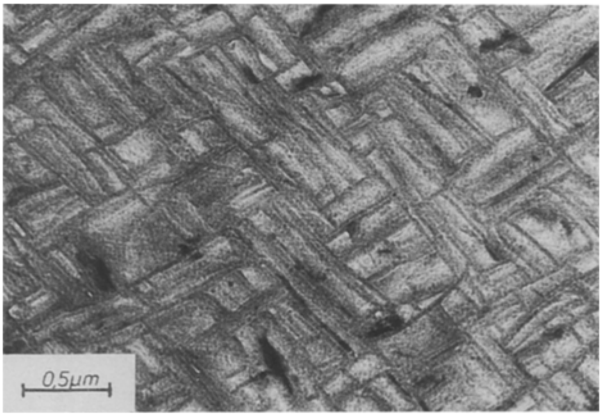

Fig.1b) TEM micrograph of a PE epitaxial layer (cross-hatched ribbons) on an iPP substrate film.

tioned here, that the lateral size of the cross-hatched HDPE lamellae depend strongly on crystallization rates but their orientation direction with respect to the molecular orien-

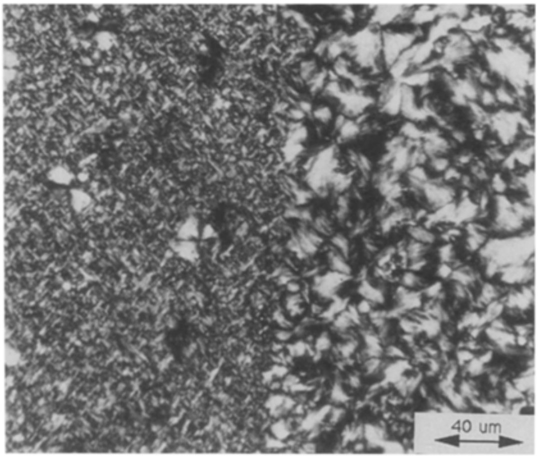

Fig.2: Light optical polarization contrast of HDPE crystallized epitaxially on an iPP film (left side) and on the neat glass surface (right side). The molecular orientation of the substrate iPP film is vertical.

tation of the iPP is always ± 40°. With the distinct molecular orientations of the PE molecules (perpendicular to the lamellae), an optical polarization contrast can be expected. Fig. 2 shows the crystallized HDPE layer on an ultra-thin uniaxially oriented iPP film (left side of the picture) and on the neat glass surface (right side of the picture). A cross-hatched pattern (left) and spherulites (right) can be seen.

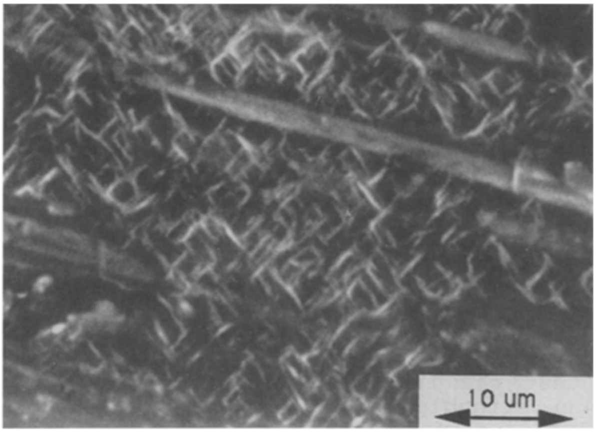

Fig.3: SEM micrograph of epitaxially crystallized HDPE on iPP.

From scanning electron microscopy (SEM) investigations it is evident (Fig. 3), that a topography of the surface of the layered PE reflects the morphology of the HDPE. Hence, an

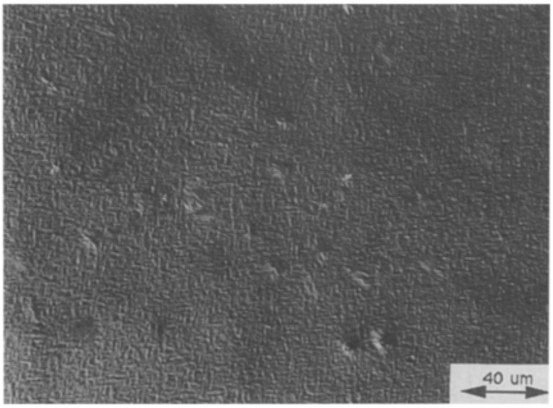

Fig.4: Light optical interference contrast of a HDPE epitaxial layer. The molecular direction of the substrate iPP films is from bottom left to top right side.

interference optical contrast is supposed to occur, too (Fig. 4).

The confocal laser scanning microscopy (CLSM) is a new technique especially sensitive to surface topologies. The laser beam can be focused into different depths of the layered HDPE and the reflected light is monitored. In Fig. 5a the laser beam is focused just below the outer surface of the HDPE film. As in Fig. 2, the HDPE layer is crystallized on the neat glass surface (left side) and on the ultra-thin iPP film (right side). A spherulitic and an epitaxial morphology can clearly be seen. Even better contrast is obtained, when focusing the laser beam about 0.5μm below the top surface of the HDPE layer (Fig. 5b).

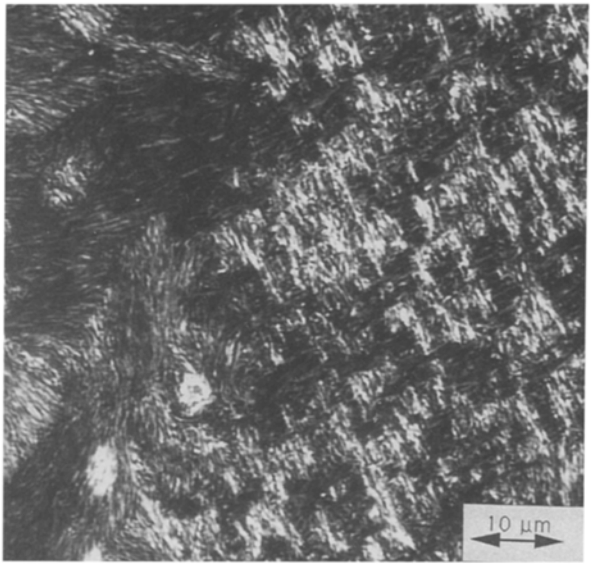

Fig.5a): Confocal Scanning Laser Microscope contrast (focused just below the surface) of HDPE spherulites (left side) and epitaxial morphology (right side).

Obviously, when comparing the epitaxial morphologies obtained by TEM and the other methods, very similar patterns are visible. But while in the TEM micrographs (Fig. 1b) single lamellae are resolved, the lamellar-like pattern in the optical and SEM micrographs cannot result from single lamellae (see magnification scales). Domains of equivalent oriented stacked lamellae would be large enough to be resolved. That indeed the epitaxial oriented lamellae are crystallized in bundles (domains) and not in single independent lamellae can be guessed from the TEM micrograph. The sizes of the bundles are very sensitive to crystallization conditions and because the samples for the TEM pictures and the optical micrographs were prepared under similar but not the same experimental conditions, a perfect coincidence of their sizes is not likely. Nucleation and crystallization studies using the light optical contrasts for in-situ observations with different ultra-thin uniaxially oriented polymer films as substrates are under investigations.

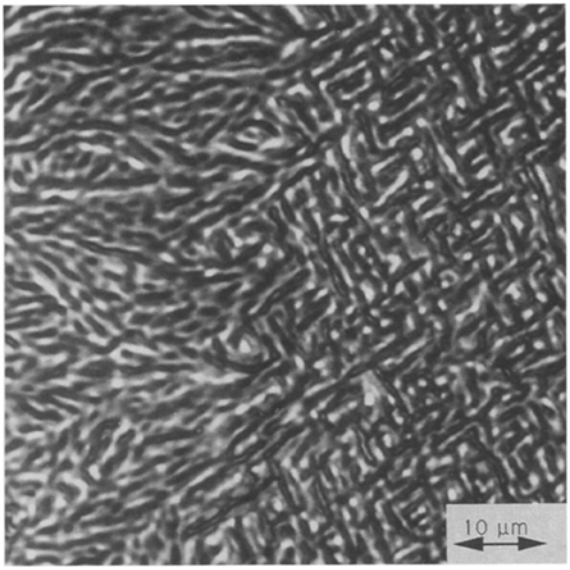

Fig.5b: The same sample as Fig. 5a, but with the laser beam focus about 0.5 μm below the surface.

Acknowledgement

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