The origin of heteroepitaxy in the system of uniaxially oriented isotactic polypropylene and polyethylene

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The epitaxy of polyethylene (PE) on oriented α and β-form of isotactic polypropylene (PP) at different crystallization temperatures and rates have been investigated. The result shows that the epitaxy of PE on β-form of PP does not differ from that on the α-form of PP. The epitactic alignment of the PE lamellae on the PP films becomes more perfect with higher crystallization rates of PE. The epitaxy of PE on α- or β-form of PP does not occur at crystallization temperatures higher than 123 °C. A nucleation controlled process for the alignment of the PE is proposed.

1. Introduction
The term "epitaxy" is applied to the orientation of one crystalline substance on a different substance. Generally epitaxy involves lattice plane matching. Since the first observations of the epitaxy of PE on the (001) NaCl surface by Willems [1], epitaxial crystallization of various polymers on organic, inorganic and polymeric substrates has been extensively studied. The epitaxial polymerization and crystallization of polymers onto some low molecular weight organic substances was explained by two-dimensional lattice matching [2–4]. In the epitaxial growth of PE and other polymers on ionic crystals, the alignment of the polymer chains is in charged directions, and the orientation is independent of lattice matching [5]. Homoepitaxy, the crystallization of the same material on a substrate, has been observed in polymers quite frequently [6, 7], especially in the case of "shish-kebabs". The epitaxial crystallization between two kinds of zig-zag chain polymers with their molecular chain parallel has been discussed previously [8]. Recent investigations have shown that PE can epitaxially crystallize on α-PP with their chain directions about 50° apart [9, 10]. This kind of epitaxy is explained by the alignment of the zig-zag chain along rows of methyl groups of α-PP with 0.5 nm intermolecular distances for a chain–row match [9]. The purpose of this paper is to present some new experimental results on PE–PP epitaxy and draw conclusions from these results together with other recently published observations on polymer–polymer epitaxy.

2. Experimental procedure
The materials used for the experiments were polypropylene, type Novolene and polyethylene, type Lupolen 6021 DX (HDPE), both from BASF AG Ludwigshafen West Germany. Thin oriented films were prepared according to the method of Petermann and Gohil [11]: a small amount of a 0.5% solution of the polymer (PP or PE) in xylene was poured on a hot glass slide where the solvent was allowed to evaporate. For α-form PP, β-form PP and PE the temperatures on the glass surface were 150, 210 and 130 °C, respectively. The remaining thin polymer film was then picked up on a motor driven cylinder. The resulting thin polymer films were about 50 nm thick and highly oriented in the drawing direction. The films were cut into 3 × 3 mm² pieces, floated onto distilled water and mounted on TEM grids. For multiple films, the PE film was put on top of α- or β-form PP substrates and the layer was subsequently heated to 142 °C (above T_m of PE but below T_m of PP) and cooled at different rates to varying temperatures. The materials were investigated using a Philips EM-400 T electron microscope operated at 100 kV.

3. Results
3.1. Substrate structure of α- and β-form PP
Fig. 1a and b show electron micrographs and diffraction patterns of pure α- and β-form PP. The molecular direction (as indicated by an arrow) is horizontal. It can be seen that both the pure α- and β-form PP have the same morphology.

3.2. Epitaxial crystallization of PE on uniaxially oriented α-PP
The epitaxial crystallization of PE on the α-PP has been investigated in some detail in recent years [9, 10]. It has been found that heating an oriented blend or multiple oriented thin films of α-PP and PE above the melting point of PE and subsequent cooling to room temperature changes the morphology of PE into a cross-hatched structure with the lamellae being about 40° inclined to the molecular direction of PP (Fig. 2). The thickness and length of the lamellae are
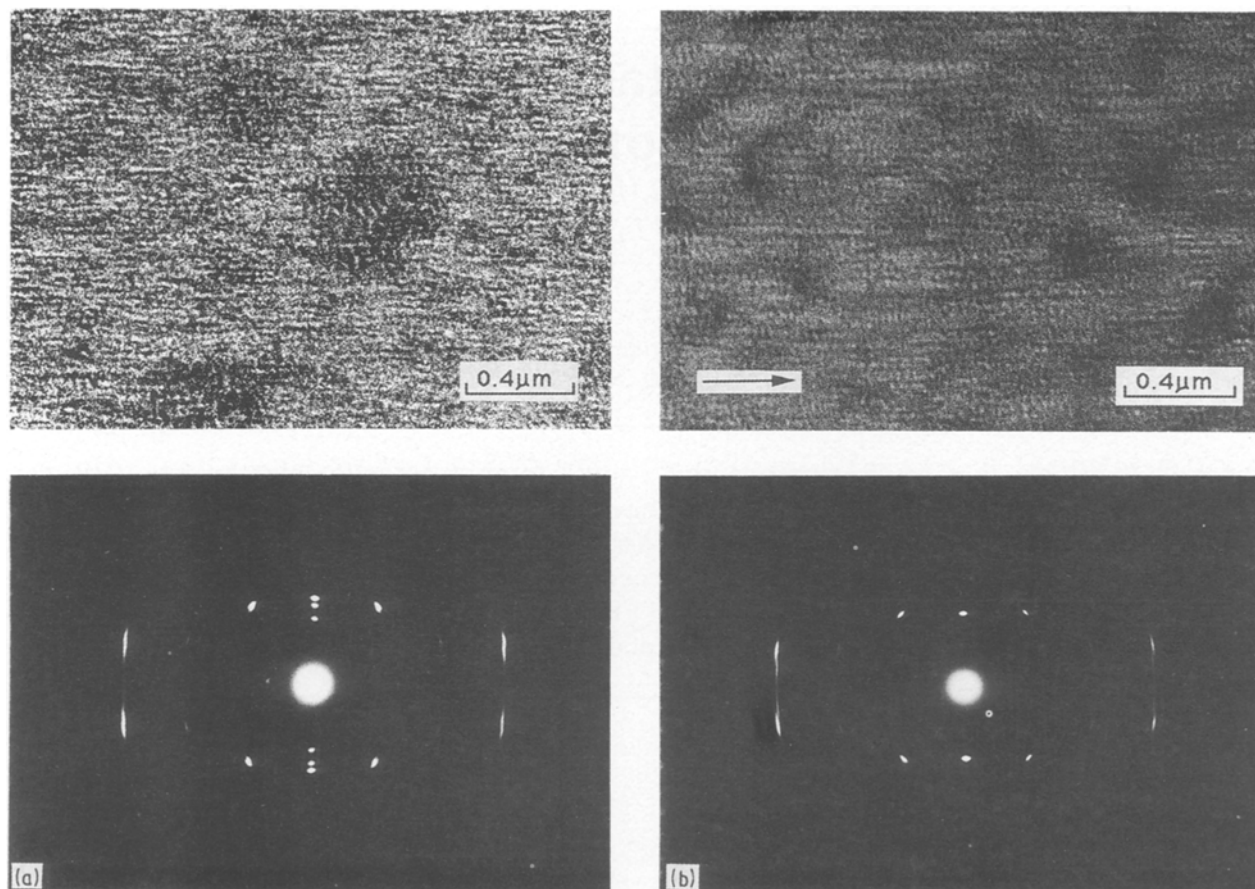
Figure 1 Transmission electron micrographs and electron diffraction patterns of PP substrate films. The molecular directions are indicated by an arrow. (a) α-PP. (b) β-PP.

about 15 and 500 nm, respectively. The peculiar arrangement of the PE lamellae was explained by Wittmann and Lotz with an epitaxy of (100) PE lattice planes parallel to the (010) lattice planes of the α-PP. In Fig. 3, a sketch of the (010) lattice planes in the monoclinic PP crystals is presented. The methyl side groups, which stick out of the plane are shaded. In those planes, inclined 50° to the PP chain direction, rows of the methyl groups can be seen. The inter-row distance is 0.505 nm. The orientation of the PE chains is along the rows, and in the (100) plane of the PE, the chains are 0.495 nm apart.

Generally, epitaxy involves lattice plane matching, and slow crystallization rates should favour epitaxy. The phenomenon in the epitaxy of PP and PE is, however, contrary. After the oriented thin films of α-PP and PE were annealed at 142 °C and sub-sequently cooled with at a rate of 1 °C min^{-1} to 118 °C, no epitaxy was seen (Fig. 4a), but when rapidly quenched into ice-water epitaxy occurs (Fig. 4b). The lamellae are very small, their thickness and length are only 10 and 200 nm, respectively.

Fig. 5 shows electron micrographs of films of α-PP and PE, crystallized at different temperatures with a cooling rate of 10 °C min^{-1}. It can be seen that when the crystallization temperature is 115 °C, the morpho-logy is like that shown in Fig. 2, only the lamellae are much larger and thicker; when the crystallization tem-perature is 121 °C, some very large lamellae look epi-taxially crystallized but others are not epitaxially oriented. The small epitaxial lamellae were formed

from remaining molten PE after taking the sample to room temperature. If the sample was annealed at 121 °C for longer times no small epitaxial lamellae appeared. Crystallization at 123 °C did not give epi-taxy of PE (again, the small epitaxial lamellae result from remaining molten parts of PE at 123 °C and crystallization, when taking the sample to room temperature).

3.3. Epitaxial crystallization of PE on uniaxially oriented β-PP

After the PE and oriented β-form PP films were an-nealed at 142 °C for 10 min, and subsequently cooled to room temperature, the morphology of PE was the same as in the case of epitaxy between α-PP and PE. Fig. 6 shows the phase contrast electron micrograph and the corresponding electron diffraction pattern. From Fig. 6b it can be seen that in the PP films a small amount of α-form remains, but it is less than 10%. When the sample was annealed at 142 °C, then cooled to 120 °C at a rate of 1 °C min^{-1}, the PE does not crystallize epitaxially. Its morphology is very like that shown in Fig. 4a.

Until now several crystal structures have been suggested for β-form PP [12–16]. Keith *et al.* [12] and Addink *et al.* [13] suggested a hexagonal cell. Turner–Jones *et al.* [14] proposed several possible unit cells, which they designated A, B, C, and D. Later the B structure was chosen as the correct unit cell for the β-form crystal by Turner–Jones *et al.* [15] and

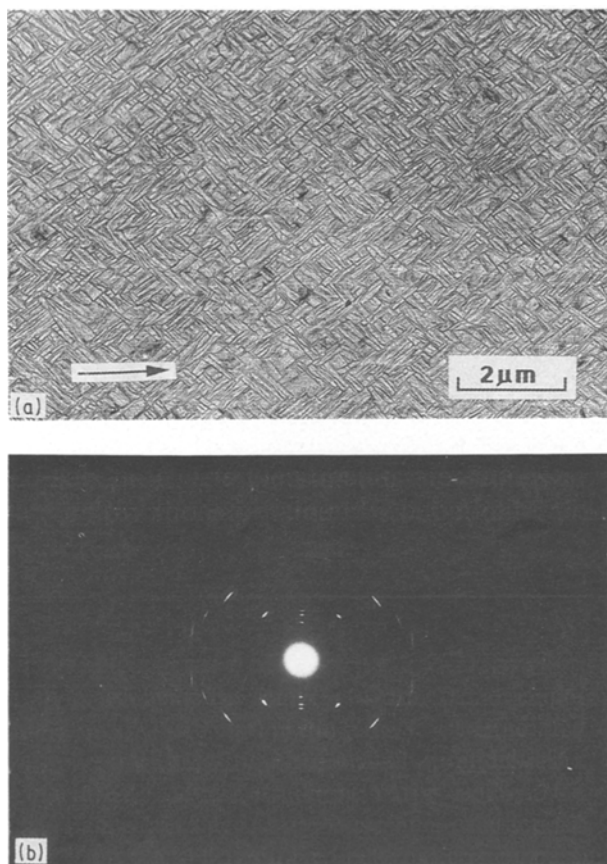*Figure 2* (a) Transmission electron micrograph and electron diffraction pattern of PE and α-form-PP, annealed at 142 °C for 10 min, then cooled to room temperature. The molecular direction is indicated by an arrow.
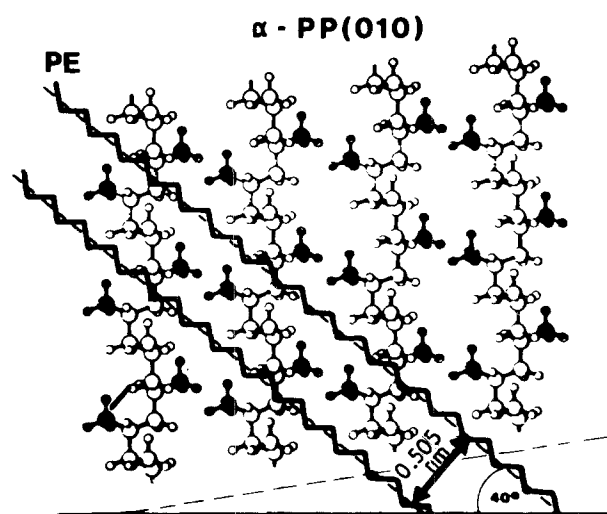
(b) Corresponding electron diffraction pattern.

Figure 4 Morphologies of α-form-PP and PE annealed at 142 °C for 10 min and (a) subsequently annealed at 118 °C for 1 h. (cooling rate 1 °C min⁻¹) and (b) rapidly quenching into water, a larger magnification is inserted. The molecular directions are indicated by arrows.

Figure 3 Sketch of the (010) plane of the α-PP. The dark methyl groups are sticking out of the plane.

Samuels *et al.* [16]. Even an unequivocal solution has not been possible, it can be seen that it is impossible for β-form PP to have a crystal surface like that shown in Fig. 3 in any suggested crystal structure.

4. Discussion

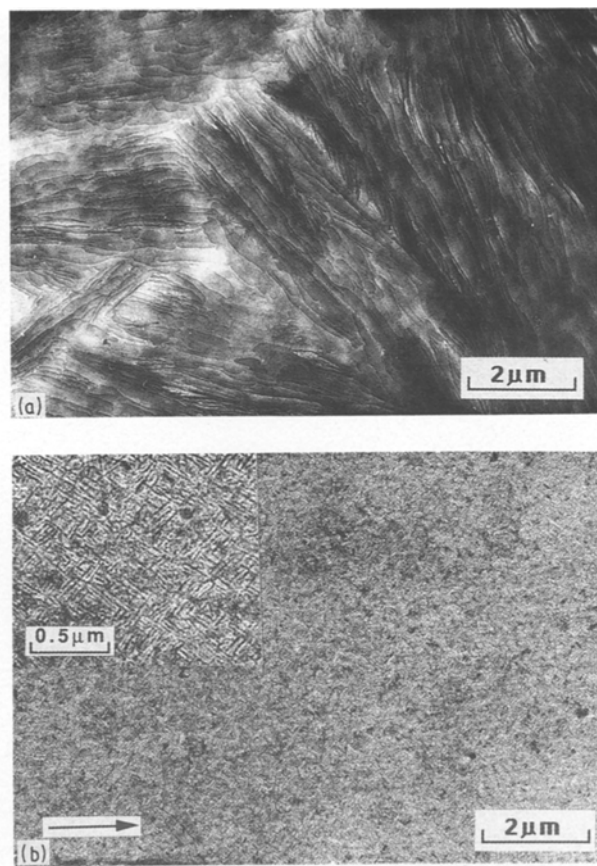It has been found that in epitaxial crystallization between polymers, there are mainly two kinds of situations. One is the epitaxy between two kinds or the same kind of zig-zag chains with their molecular chains parallel, such as the epitaxy of folded chain crystals on extended chain crystal surfaces of the same polymer [17], the lamellar crystals on fibrous substrate of the same polymer as in the case of the shish-kebab [7], and the epitaxy between PE and polycaprolactam [8]. The other kind is the epitaxy between PP and some zig-zag chain polymers with their molecular chain about 50° apart, such as the epitaxy between PP and PE, PP and polyoctenamer [18], PP and nylons [19]. Lotz and Wittmann have used matching of intermolecular spacing with the distance between the rows of methyl side groups in the (010) PP lattice planes to explain the epitaxy between α-PP and some zig-zag chain polymers [19]. These orientation relationships fit the observed diffraction patterns. Some experimental results cannot, however, be explained straightforwardly by this model.

A fibre texture of the α-form PP substrate film (Fig. 1a) indicates that only a small fraction of the α-form PP lamellae have the orientation with the (010)-lattice plane as a surface plane. Not every epitaxial PE lamella can be in contact with a PP-lamella having a (010) surface plane or acting as nucleation site. The PE-lamellae are too small for this event and other (*hk*0) planes of PP must therefore lead to the same orientational relationship despite no matching being present.
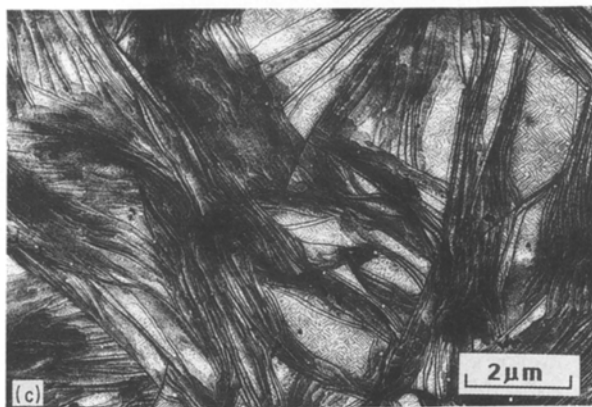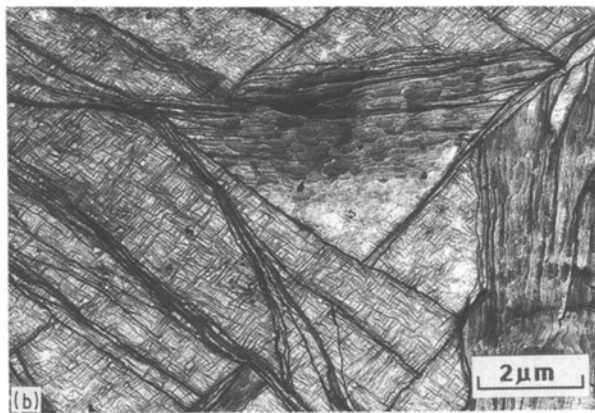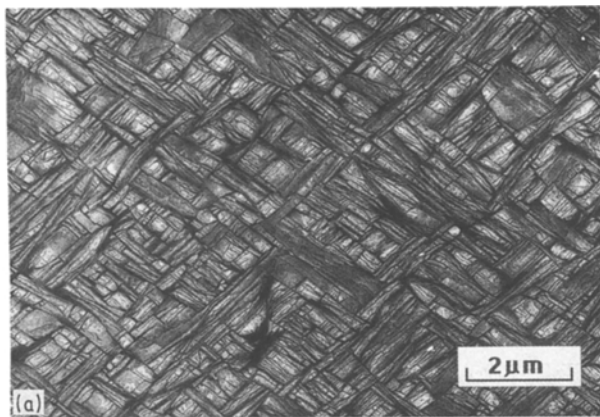
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Figure 6 Phase contrast micrograph and corresponding diffraction pattern of β-form PP and PE, annealed at 142 °C for 10 min, and cooled to room temperature. The molecular direction is indicated by an arrow.

Figure 5 Morphology of α-form PP and PE. Annealed at 142 °C for 10 min, (a) subsequently annealed at 115 °C for 2 h. (b) 121 °C for 2 h (c) 123 °C for 2 h. Cooling rate: 10 °C min⁻¹. The molecular directions of the PP are indicated by arrows or are horizontal.

The matching of the methyl rows of the PP with the (100) intermolecular distances of PE should result in a PE–PP interface having minimum interface energy, hence, according to crystallization theories the observed epitaxy should be better at very low crystallization rates. In fact having low crystallization rates (at 123 °C) no epitaxy is observed (Fig. 5c); having higher crystallization rates (at 115 °C), a not very perfect epitaxial alignment of the PE-lamellae can be seen (Fig. 5a), and a nearly perfect alignment is seen at very high crystallization rates when quenching the samples from the melt into ice water very quickly (Fig. 4b). In a previous paper [20] it was mentioned that the β-form PP and PE does not exhibit epitaxy. This result was due to bad quality β-form PP samples and is revised in this paper, where on good quality β-form

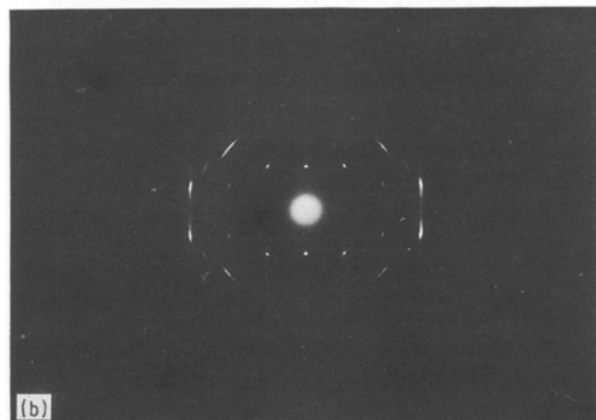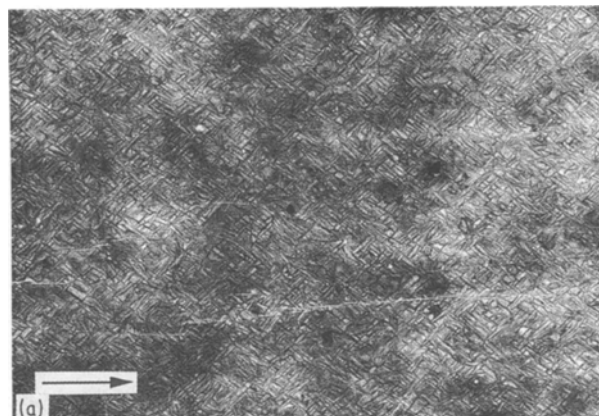PP substrates the epitaxy is demonstrated clearly. Even more surprising, exactly the same chain orientation relationship as in the α-form PP arises, while from matching of methyl rows with the PE-chain direction an inclination angle of 45° is expected.

Other polymers with zig-zag chain conformation of $(CH_2)_n$ segments can also crystallize epitaxially with the α- and β-form of PP, resulting in the same chain orientational relationship (50°) as in the PP–PE system [9, 10]. The mismatching between the methyl rows in the (010) plane of the α-form PP and the interchain distance in the contact plane of the layers are calculated in Table I. The quality of the epitaxy does not strongly depend on a small mismatch but rather on the length of the $(CH_2)_n$ segments and on side groups (syndiotactic polystyrene and β-poly-vinylidenfluoride, both having zig-zag chain conformations, do not exhibit the described epitaxy).

The question remains of by which factors the lattice planes are determined which are in contact with the substrate surface. For all cases in Table I, it can be demonstrated that the contact planes of the layered polymers contain two directions: the molecular chain direction and the fastest growth direction. For PE, fastest growth direction is [010], hence (100) is the contact plane.

In order to obtain the epitaxy as described in this paper, three requirements must be fulfilled.

(i) one of the polymers must be iPP (either α- or β-form),

TABLE I Epitaxial relationships

Polymer	Chemical composition	Epitaxial surface	Intermolecular distance (nm)	Mismatching (α) $\alpha = 100(b - a)/a$ (%)	Epitaxy
PE	CH_2-	(100)	0.495	2.02	+ + +
polyoctenamer	$CH=CH-(CH_2-)_6$	(100)	0.488	3.48	+ + +
poly-ε-caprolactone	$(CH_2-)_5CO-O-$	(100)	0.498	2.02	0
Nylon 6, α	$(CH_2-)_5CO-NH-$	(010)	0.442	14.25	+
Nylon 6.6, α	$(CH_2-)_6NH-CO-(CH_2-)_4CO-NH-$	(010)	0.477	5.89	+
Nylon 11, α	$(CH_2-)_{10}CO-NH-$	(010)	0.477	5.89	+ +
Nylon 12	$(CH_2-)_{11}CO-NH-$	(010)	0.470	7.45	+ +

+ + +: very good epitaxy. + +: good epitaxy. +: poor epitaxy. 0: no epitaxy

$b = 0.505$ nm (interrow distance between the methyl groups in the (010) plane of the α-form PP).

a: the intermolecular distance of PE in the (100) plane.

(ii) the other polymer must contain linear zig-zag segments of $(CH_2)_n$ units with $n > 5$. Using linear paraffin, n must be larger than 40 [21],

(iii) the crystallization rate of the layered polymer must be sufficiently high.

Considering the experimental observations, it is difficult to interpret the results using lattice coincidence models only. It seems likely that a nucleation controlling process is also involved. The nucleation controlling process may result from the interaction between the 3_1 helix of the single PP-chain and linear zig-zag segments of $(CH_2)_n$ in this kind, that above the melting temperature of the layered polymer, adsorbed $(CH_2)_n$ segments at the interface may have preferably an inclination of 50° with respect to the substrate chain direction and rapid quenching this chain orientation relationship is frozen into the crystalline state.

Anyhow, dynamic and static molecular modelling should be carried out in order to find a reliable model for the observed epitaxy.

Acknowledgement

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