Heteroepitaxy of Syndiotactic Polypropylene with Polyethylene and Homoepitaxy

M. Schumacher, A. J. Lovinger,*,† P. Agarwal,‡ J. C. Wittmann, and B. Lotz*

Institut Charles Sadron (CRM-EAHP), CNRS and Université Louis Pasteur, 6, rue Boussingault, 67083 Strasbourg, France, and AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

Received April 25, 1994; Revised Manuscript Received July 25, 1994®

ABSTRACT: The epitaxial interactions between syndiotactic polypropylene (sPP) and polyethylene (PE) are analyzed on the basis of electron diffraction patterns of composite bilayers. They rest on the near-parallelism of PE chains with short pseudo *n*-pentane molecular segments of sPP exposed on the (100) plane and inclined by ca. 37° to the helical molecular axis. A related homoepitaxy of sPP, with more limited impact on bulk crystallization, is also described and analyzed on a similar structural basis. It rests on the parallelism of the same *n*-pentane segments for isochiral helices which face each other across the (110) contact plane and results in chain axes mutually rotated by 74°.

Introduction

Polymer-polymer epitaxy is well-documented in a number of systems.[1] The structural relationships between interacting polymers usually reflect molecular features of the crystallographic faces that are in contact, as is best illustrated in binary systems of linear and helical polymers. For example, in polyethylene (PE)-isotactic polypropylene (iPP) epitaxy, the chain axes of the two polymers are oriented ca. 50° apart, which results from the parallel alignment of PE chains onto the oblique pattern of methyl side chains in the lateral *ac* contact face of iPP.[2]

The α phase of iPP provides a further example of polymer-polymer epitaxy leading to the well-known lamellar branching characteristic of this phase.[3] The structural root of this branching has been interpreted as homoepitaxy[4] between two lateral *ac* faces of α iPP consisting of isochiral helices.[5] The crystallographic relationship between the two constituents is best described as a rotation twin,[1,3] with the twin axis oblique to the chain axis direction.

Polymer-polymer epitaxies involving syndiotactic polypropylene (sPP) have already been described and/or analyzed. In a previous study[6] of the sPP crystal structure and morphology, we noted that when a small iPP component is admixed with sPP, it crystallizes in crystallographic registry onto underlying sPP laths. The epitaxial relationship stems from alignment of densely packed rows of CH_3 groups in the *ac* contact face of iPP with the *bc* face of sPP and results in a 95° angle between the chain axes of the two polymers.[6]

More recently, Petermann et al.[7] have reported on an apparent epitaxial relationship between sPP and PE:sPP crystallized on a uniaxially oriented film of PE with its lamellae oriented at an angle of ca. 53° to the PE stretching direction, and the likely sPP contact face was considered to be (100). Details of the epitaxial relationship could not be elucidated any further, mainly because of the fiberlike structure of the PE substrate, which precludes determination of the epitaxially matching PE contact plane.

The present paper is concerned with the structural elucidation of two types of epitaxy involving sPP on its *bc* crystallographic plane, which we investigated by AFM in the companion paper.[8] The first epitaxy is the above-mentioned PE-sPP *hetero*epitaxy: by using a sequence of different epitaxial crystallizations, it has been possible to determine precisely both contact faces and to elucidate the finer details of the PE-sPP relationship. The second is an sPP/sPP *homo*epitaxy which bears strong structural similarities with the α iPP/α iPP one.[4,5] It has only a limited impact on the crystalline morphology but may be present spontaneously and occasionally in bulk crystallized sPP.

Experimental Section

The materials and experimental methods are as described in the preceding paper.[8] The PE used has a molecular weight of 30 000. However, the molecular characteristics are not essential since the PE is vaporized, which creates PE fragments of molecular weight ca. 1300,[10] and since the relationship established is at the unit cell level.

Epitaxial crystallization of sPP was achieved on single crystals of *p*-terphenyl (3Ph) or *p*-quaterphenyl (4Ph), after which the organic aromatic substrate was dissolved with amyl acetate.

To investigate the sPP/PE structural relationship, a thin layer of PE was vaporized on the sPP substrate by thermal cracking at ca. 300 °C in the secondary vacuum of a bell-jar. The composite sPP/PE film was then heated at ca. 100-120 °C to melt the by now low molecular weight PE layer, crystallized by cooling to room temperature, and processed in the usual manner for examination by electron microscopy and electron diffraction. The sPP homoepitaxy was obtained in the thin films after epitaxial crystallization on 3Ph or 4Ph in the form of additional molecular orientations. It is observed more frequently when rapid quenching is used, although its occurrence is not perfectly controlled and depends to some extent on the vagaries of the crystallization procedure.

Results and Discussion

1. sPP/PE Epitaxial Relationship. The selected area electron diffraction pattern of a composite sPP/PE film shown in Figure 1a provides all the necessary clues for the analysis of their epitaxial relationship. The sPP part of this pattern is similar to that analyzed in the preceding paper. We recall that the (100) plane of sPP is exposed. The chain axis is vertical (note the prominent 002 reflection at a spacing of 0.37 nm^{-1}). The strong reflection perpendicular to that axis is indexed as 020 of an orthorhombic cell with *b* parameter 1.12 nm. This sPP structure is based predominantly on a packing of alternating left- and right-handed helices (cell III); cell I, based on packing of isochiral helices and with the *b* parameter halved to 0.56 nm,[11] is

---

* To whom correspondence should be addressed.

† AT&T Bell Laboratories, 600 Mountain Ave., Murray Hill, NJ 07974.

‡ EXXON Chemical International Inc., Hermerslaan 2, B-1831 Machelen, Belgium.

® Abstract published in *Advance ACS Abstracts*, September 1, 1994.

0024-9297/94/2227-6956$04.50/0

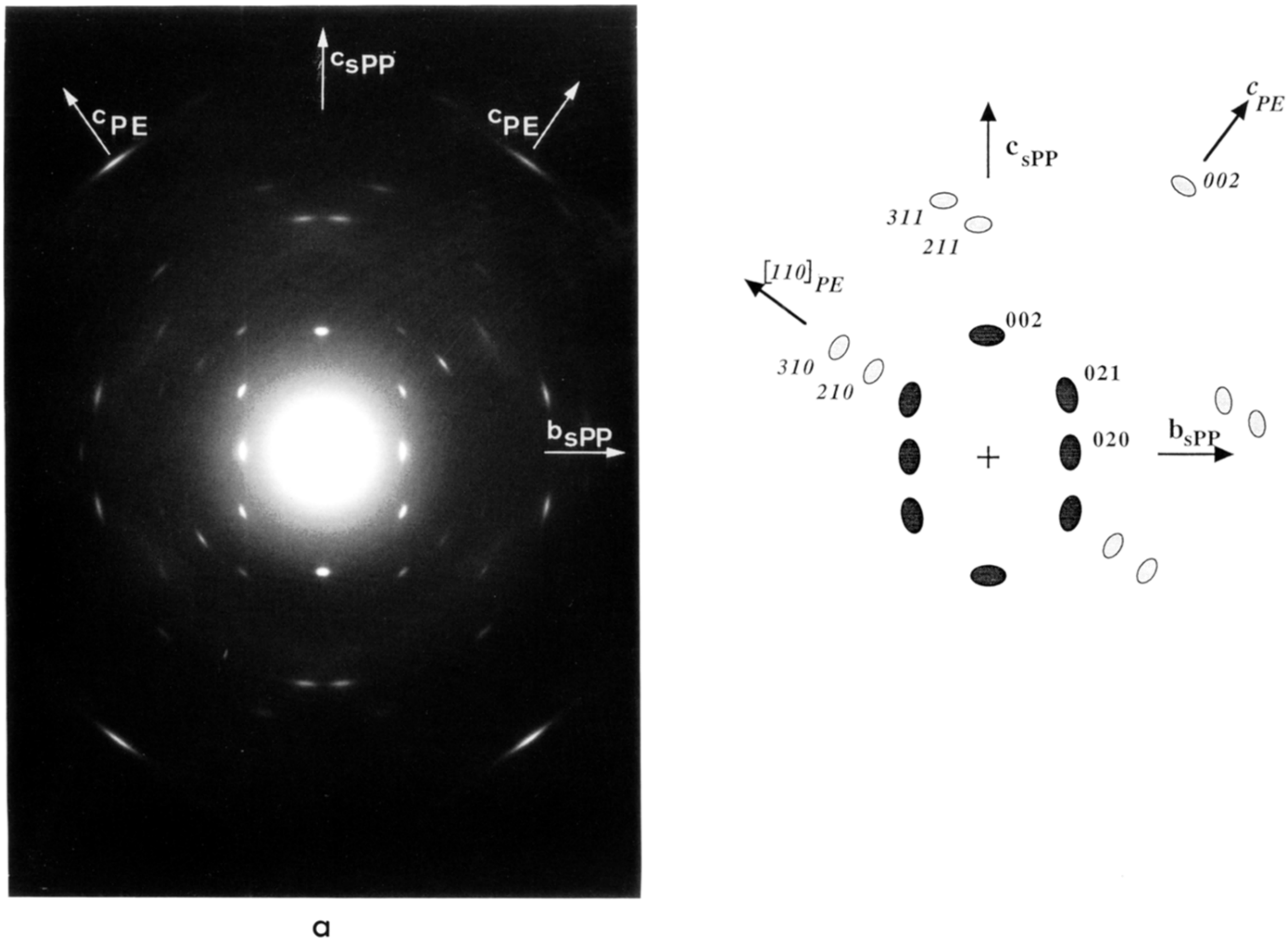

Figure 1. (a) Selected area electron diffraction pattern of a composite sPP/PE thin film. Note the single sPP chain axis orientation (c_{sPP}) and the two PE chain orientations (c_{PE}) at 37° to the sPP one. (b) Schematic indexing of the pattern in (a). For clarity, only one of the PE orientations is shown. Dark spots and roman lettering: sPP. Light spots and italic lettering: PE.

not the main constituent of the present films. The exposed face is as illustrated in the AFM picture of Figure 10c,d in the preceding paper,[8] i.e. a pattern of small stretches of CH_3, CH_2, and CH_3 groups oriented at ±45° to the chain axis, depending on helix chirality.

In addition to the sPP reflections, Figure 1 displays *two* sets of PE reflections (Figure 1b). The most prominent are the exterior pairs of 002 reflections, which indicate that the two PE chain axes are tilted at 37° to the sPP chain axis. The PE contact plane can be determined from reflections appearing normal to the c^* direction: these are the 210 and 310, which are seen to be nearly colinear with the sPP 021 reflection. Since the PE (210) and (310) planes are diffracting, a plane nearly normal to them, i.e. $(\bar{1}10)$, is parallel to the sPP substrate film: a similar situation has already been observed and analyzed for the epitaxial crystallization of PE directly on *p*-terphenyl.[12] The composite electron diffraction pattern of Figure 1 indicates the following crystallographic relationship, keeping in mind that, in PE, the $(\bar{1}10)$ and (110) planes are structurally equivalent:

$$(110)_{PE}//(100)_{sPP} \quad \text{and}$$

$$c_{PE}//[021]_{sPP}$$

This relationship accounts in simple terms for the 53° angle observed by Petermann et al.[7] between sPP lamellae and the PE chain axis, which is equivalent to 37° between chain axes (since sPP chains are nearly normal to lamellar surface). Indeed, the ⟨021⟩ sPP orientation is tilted by

$$\arctan[(b/2_{sPP})/c_{sPP}] = \arctan(0.56/0.74) = 37.1°$$

to the sPP chain axis. Further, a nearly perfect match is achieved between the interchain distances in the $(110)_{PE}$ and the $(021)_{sPP}$ planes: 0.445 and 0.4465 nm, respectively.

When analyzing the sPP/PE interactions at the individual molecular level, it is helpful (for reasons of simplicity) to consider first contact faces of the sPP unit cell consisting of isochiral helices and the *b* axis periodicity halved to 0.56 nm,[9,11] although, as indicated above and in the preceding paper, this structure is not the major constituent of our epitaxially crystallized films. This contact face is shown schematically in Figure 2; it is made up of parallel stretches of pseudo *n*-pentane segments 0.445 nm apart and oriented at 45° to the chain axis direction, i.e. only 8° away from the [011] direction (equivalent to [021] in the observed cell with $b = 1.12$ nm). The PE/sPP epitaxy, which may appear mysterious when considering the very different conformations of the molecules, amounts to a straightforward interaction between nearly parallel PE and pseudo PE (short pseudo *n*-pentane) segments (Figure 3a); an additional favorable feature rests in the existence of the 0.445 nm periodicity in the exposed sPP plane, which matches a "natural" interchain distance in the (110) plane of the stable, orthorhombic lattice of PE. Reciprocally, it appears likely that, in the less organized

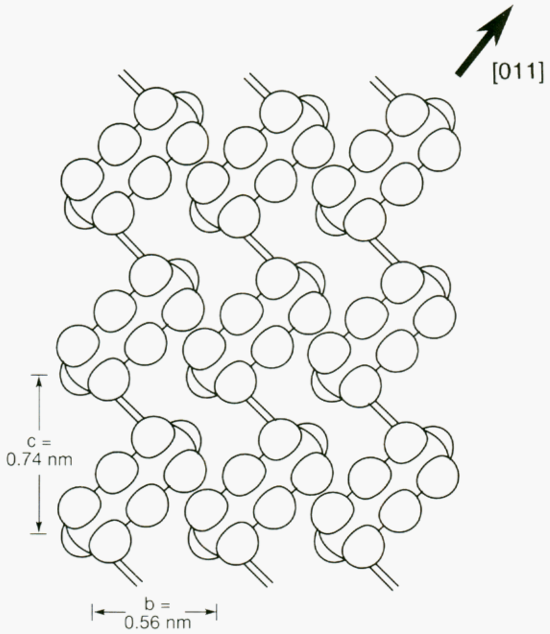

Figure 2. (100) contact fact of sPP for cell I or cell II made of *bc* layers of isochiral (in the present case right-handed) helices. Note the near parallelism of exposed rows of CH_3, CH_2, and CH_3 units with the crystallographic [011] direction.

PE films used by Petermann et al.[7] as substrates, only areas where $(110)_{PE}$ planes were exposed acted as nucleating sites for sPP crystallization. The above scheme is of course valid for cell II (in which any individual *bc* layer is also made of isochiral chains, although successive layers are antichiral) in whatever defect regions it might be present.

Turning now to the sPP cell III made of antichiral helices, it appears that the above structural relationship still applies but is blurred by the existence, in the contact face, of *n*-pentane segments at right angles to each other, as they belong to helices of opposite hand. Figure 3b illustrates a probable epitaxial relationship, which is fully consistent with our diffraction data. The PE chain is almost parallel to the full length of half of the *n*-pentane segments but crosses the other half nearly at right angles. Although possibly less favorable, such a nearly orthogonal orientation is plausible and is actually observed as a stable crystallographic feature in the structure of some fatty acids and of tetradecanamide[13] which are both made of paraffinic segments. Of course, a closer analogy exists in isotactic polypropylene, for which the γ form consists of layers of molecules that alternate in a nearly orthogonal manner.[14]

To summarize, the sPP structure provides a most favorable conformational and crystallographic feature for sPP/PE epitaxy with the existence, in the *bc* plane, of stretches of the helix that mimic a short *n*-pentane molecule. Their orientation at 45° to the helix axis is close to the crystallographic [021] direction. In the sPP/PE epitaxy, the PE chains align parallel to this $[021]_{sPP}$, thus resulting in the previously reported 37° tilt[7] between PE and sPP chain axes. This feature turns out to provide an essential clue in the analysis of sPP homoepitaxy to be described now.

2. Homoepitaxy of Syndiotactic Polypropylene. (a) The Epitaxial Relationship. Diffraction patterns of sPP films epitaxially crystallized on 3Ph or 4Ph display infrequently additional reflections which suggest a well-defined sPP homoepitaxy. Figure 4a shows the by now familiar b^*c^* reciprocal plane of the sPP crystal lattice with prominent 002 and 020 reflections (cf. Figure 1b). However, a number of weak additional reflections are observed which have, characteristically, spacings similar to the main orientation ones. They indicate *two additional orientations of sPP, rotated by 74° to the main orientation* (Figure 4b).

The precise angular relationship is very stringent and helps us analyze the composite structure. We note first that no conceivable epitaxial relationship between sPP

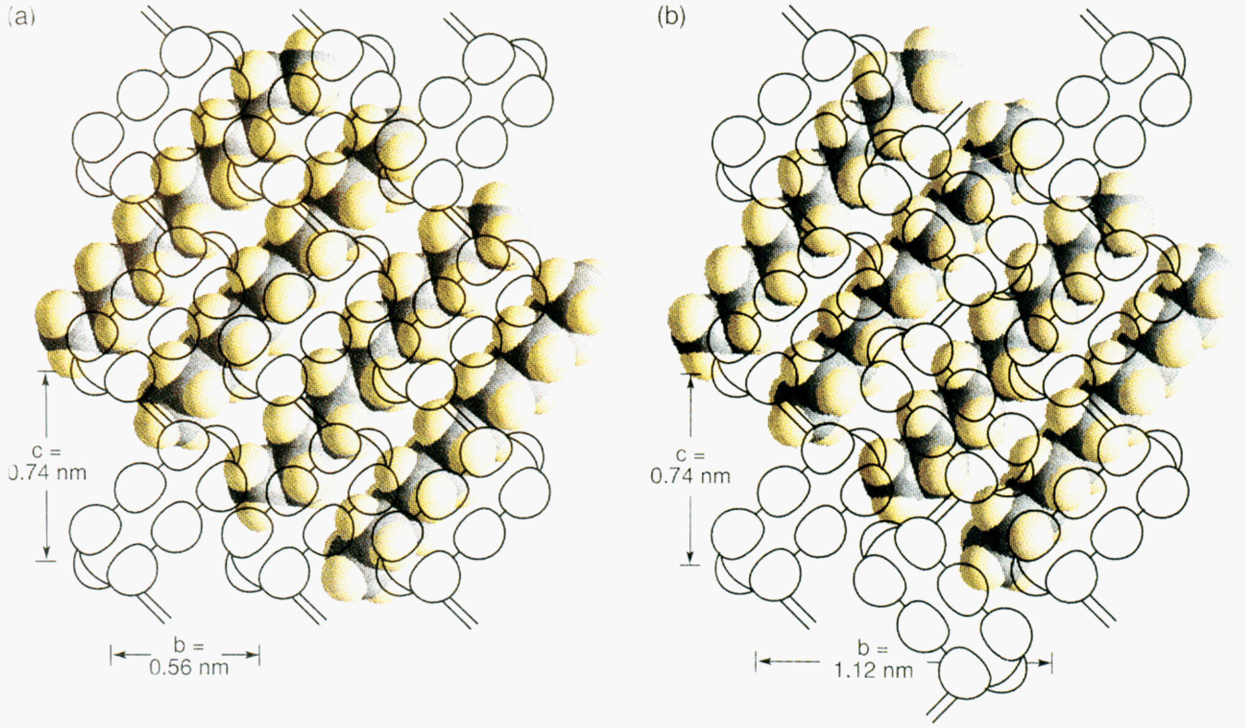

Figure 3. Schematic representation of PE/sPP epitaxial relationship: (a) isochiral helices (cell I or II); (b) antichiral helices (cell III). The contact planes are $(100)_{sPP}$ and $(110)_{PE}$.

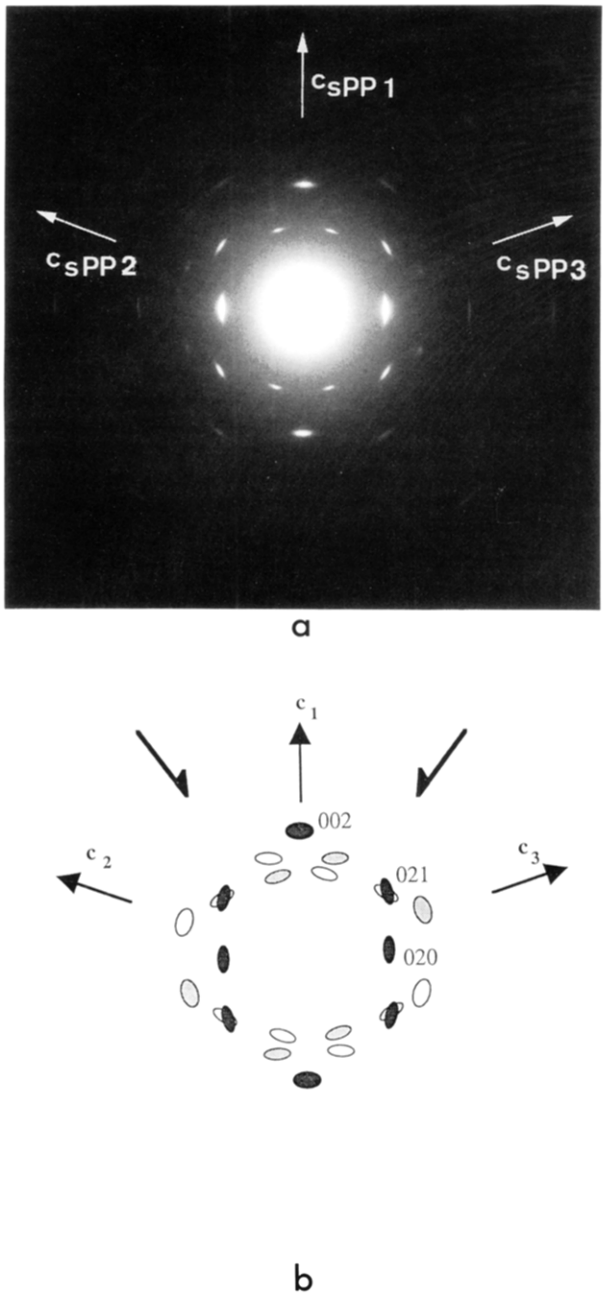

Figure 4. (a) Selected area electron diffraction pattern of a thin sPP film epitaxially crystallized on *p*-terphenyl and displaying three orientations of the sPP chains. (b) Indexing of the pattern in (a). Only reflections corresponding to the main sPP chain orientation (vertical) are indexed. Additional orientations are at ±74° to it. These orientations are generated by two 2_1 rotation twin axes (indicated) at 37° to the major orientation.

and the substrate 3Ph and 4Ph can generate these additional orientations. Their origin must therefore lie in sPP/sPP interactions, the nature of which becomes readily apparent when noting that the tilt (74°) is double that of PE chains in the sPP/PE epitaxy (37°). The epitaxial relationship is again best understood when considering first cell I[11] or cell II[9] (010) layers built up with isochiral chains and noting that *n*-pentane segments form a linear grating oriented parallel to [011]. Several packing modes are available for a new layer depositing on top of this exposed face (Figure 5 a–d), two of which have already been considered in connection with sPP crystal polymorphism. If the new layer is made of chains *antichiral* to the substrate ones, the gratings of the depositing and substrate faces in contact are parallel as in the crystal structure of cell II[6,9] (Figure 5a). A steric problem arises for deposition of chains *isochiral* to the substrate ones since the two grating orientations are nearly at right angles to each other. As shown in Figure 5b, this steric problem is normally relieved by $b/2$ shifts leading to the C-centered cell I in which the *n*-pentane segments are located in appropriate niches of the substrate layers.[9,11]

The newly observed epitaxial relationship derives from this packing scheme by noting that an alternative packing mode exists: the two gratings in contact can become nearly parallel if the top layer is rotated by 74° around the *a* axis of the unit cell. The (011) substrate and $(0\bar{1}1)$ bottom surface of the depositing layer, which both contain exposed *n*-pentane units, become parallel (Figure 5c). The chirality (assumed to be of only one hand) of the helices determines whether the rotation is clockwise or counterclockwise and accounts for the observation of two populations of sPP, tilted symmetrically relative to the major one.

The above analysis is made in terms of interacting contact faces and stresses the (homo)epitaxial aspects of the structural relationship. The latter can equally well, and more appropriately, be described as a *rotation twin*. Indeed, the depositing layer can be generated from the substrate one by a simple rotation–translation around a 2_1 screw axis parallel to [011] (in this halved cell) at the level $x/a = 1/4$ (cf. Figure 4). Several characteristics of this rotation twin axis are worthy of note: ideally, it should be parallel to the exposed helical path, which would ensure perfect parallelism of linear gratings of the layers in contact. In the present case, it is parallel to the nearest low-index axis, i.e. [011] or $[0\bar{1}1]$. In other words, the *sense of tilt* helps determine (in the present hypothesis of structures made of isochiral helices) the hand of interacting helices: right handed for tilts to the right and vice versa.

Note also that the rotation twin axis is oriented parallel to [011], which is the orientation of PE chains epitaxially crystallized on the sPP *bc* substrate plane (cf. Figure 3). This observation provides the link between the two present studies and explains in simple structural terms the 2-fold relation between sPP/PE and sPP/sPP chain axes tilt angles (37 and 74°, respectively).

The above reasoning is made for a structure based on isochiral helices, whereas the actual one consists predominantly of alternating helices of opposite hand, which blurr somewhat the molecular interactions described so far. In particular, the lattice matching (parallelism of (021) planes, in the normal cell with $b = 1.12$ nm) is maintained and results in parallelism of half of the *n*-pentane subunits in the contact planes. However, examination of the faces in contact suggests significantly less favorable interactions due to misalignments of the units that are not parallel to the rotation twin axis (Figure 5d). Details of the interactions would be difficult to work out and may imply local adjustments of chain conformation to minimize these steric conflicts. In comparison of the two models, epitaxial growth of sPP appears favored on substrates where, due to the vagaries of polymer chain attachment, a higher density of isochiral helices is present. Conversely, the observed incidence of this branching in sPP crystallized on *p*-ter- and *p*-quaterphenyl may reflect the influence of the organic substrate.

(b) Homoepitaxy in Bulk Crystallization. What impact might this homoepitaxy have on the bulk morphology of sPP, since it has been observed so far only for epitaxial crystallization of the sPP itself on polyphenyls? This impact should manifest itself by development of daughter lamellae with their plane at 74° to the parent

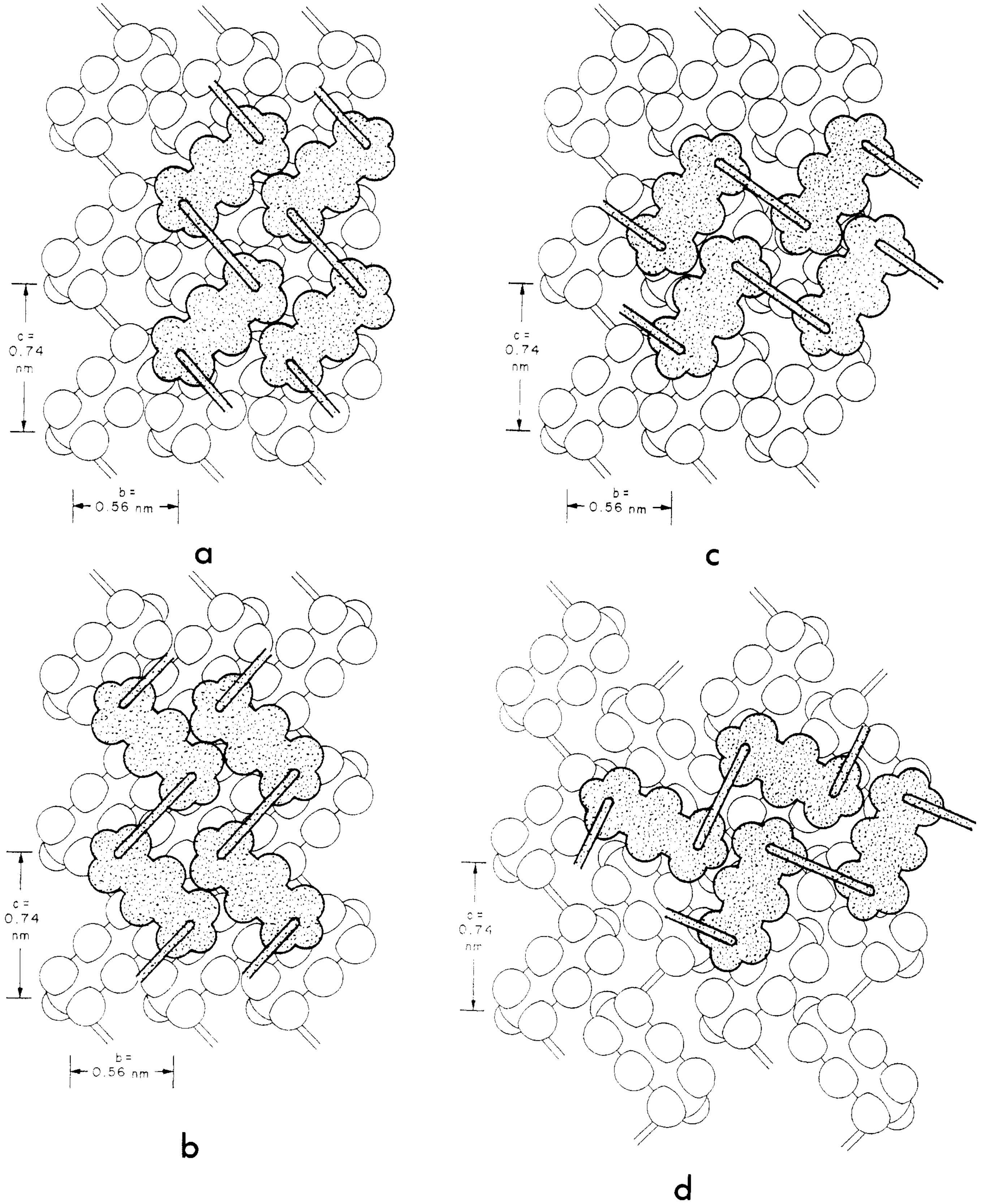

Figure 5. Various packing modes of *bc* layers of helices in sPP. (a) Packing mode as in cell II. The substrate layer (light lines) is made of right-handed helices as shown in Figure 2. The top layer (heavy lines) consists of left-handed helices, whose bottom (contact) surfaces are drawn in this figure. Note the parallelism of interacting stretches of CH_3, CH_2, and CH_3 units and interdigitation linked with a $c/2$ shift of the chains. (b) Packing of layers of isochiral chains as in cell I. Note the nearly right angle orientation of interacting stretches of CH_3, CH_2, and CH_3 units and $b/2$ shifts which ensure favorable interdigitation in niches of the opposite layers. (c) Alternative, homoepitaxial packing mode of layers of isochiral helices giving rise to the extra sPP chain orientations observed in Figure 4. Note in this model the near, but not perfect, parallelism of interacting stretches of CH_3, CH_2, and CH_3 units. For such right-handed helices, the new layer is tilted clockwise relative to the substrate; were the helices left-handed, the tilt would be counterclockwise. (d) Homoepitaxial packing mode as in (c), but assuming *bc* layers made of alternating right- and left-handed helices as in cell III. Note the more complicated pattern of interactions between the two layers in contact, which makes this scheme less probable than that displayed in (c).

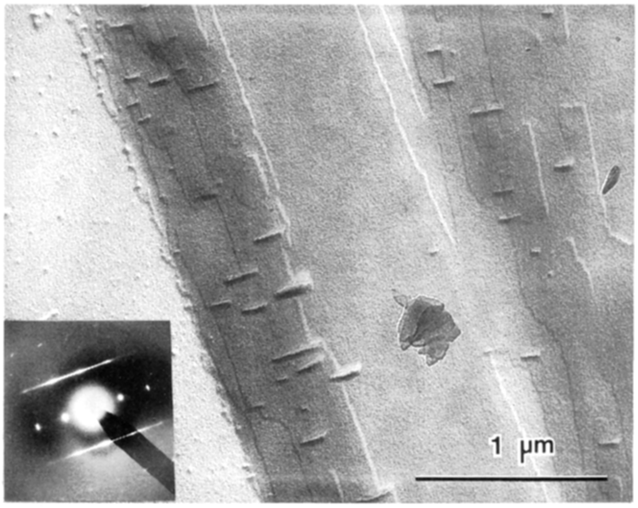

Figure 6. Transmission electron micrograph of lamellar edges of sPP single crystals grown in a thin film displaying edge-on lamellar growth. Original crystals were grown at 140 °C, partially melted in a steep temperature gradient, and recrystallized. Pt—C shadowing at $\tan^{-1} = 1/3$. Insert: electron diffraction pattern from the corresponding area.

ones, as in the well-documented and more conspicuous "quadrite" structure of α phase isotactic polypropylene.[3-5] Although no morphological impact of comparable magnitude exists in sPP, several suggestions of its occurrence can be found in the crystalline morphology of lamellar crystals grown in thin films. Small overgrowths may develop at the lateral edges of crystals submitted ot a steep heating gradient and recrystallized as shown in Figure 6. These overgrowths have all the characteristics associated with sPP/sPP epitaxial crystallization described above: location of the nucleation site on the (100) face, orientation of the lamellar plane at nearly right angles to the flat-on parent crystal (the orientation of the crystal on edge cannot be determined precisely, given the limited growth in the vertical direction), and presumably, preservation of the crystallographic *a* axis orientation. While absolute proof would rest on diffraction evidence, the above indications suggest that sPP homoepitaxy may occur to a limited extent in crystallization from the melt (especially for fast crystallization as, e.g., in injection molding), even though its limited extent precludes repetitiveness and significant impact on the overall crystal morphology.

3. Structural Requirements for Polymer Homoepitaxy. The present sPP/PE and sPP/sPP epitaxies bear very strong similarities with corresponding ones involving the α phase of isotactic polypropylene: α iPP/PE epitaxy[2] and α iPP/α iPP homoepitaxy.[5] In combination, these two studies help underline the main structural requirements for epitaxy and homoepitaxy of polymers.

The α iPP contact faces involved are lateral faces lined with methyl groups; epitaxies involve only fairly weak van der Waals forces.[15] More importantly, the *high symmetry* of the iPP contact faces is a key factor: they are built up of a lozenge-shaped array of methyl groups. Not unexpectedly, the rotation twin axis is parallel to the diagonal of the lozenge (either long or short diagonal). The short diagonal ([101] direction of the unit cell) is the bisector of the monoclinic β angle. It is also the direction along which PE chains align in the PE/iPP epitaxy. An original feature in α iPP stems from the fact that its structure is "polar": since contact faces are made of helices of one hand only, the tilt of PE chains, or the sense of rotation of the homoepitaxy, makes it possible to determine the hand of helices involved. Furthermore, homoepitaxy can generate only two relative lamellar orientations,[5] a feature also linked with the pecularities of the α phase crystal structure.[16]

The *bc* contact face of sPP is a fairly "flat" and featureless surface which can accommodate depositing chains at different sites. When analyzing packing energies for the various structures described as cells I, II, and III, Corradini et al. did not find any significant differences: the various packings are nearly isoenergetic.[17] With regard to possible homoepitaxy, the sPP contact face is, however, characterized by a low symmetry since *b* and *c* cell dimensions differ by over 25%. Whereas this is quite compatible with heteroepitaxy (for example with PE), it is a priori less favorable for homoepitaxy since a two-dimensional lattice match as in α iPP is precluded. As indicated earlier, the physically most plausible homoepitaxy rests on a *one-dimensional lattice match* and involves nucleation of patches of isochiral helices at defect sites, which build up an oblique, linear grating.

Similar homoepitaxies may well be observed for other polymers with appropriate crystal structures, i.e. those characterized by highly symmetrical potential contact planes. The search for such polymers is considerably aided by crystal morphology, since these homoepitaxies result in significantly different orientations of mother and daughter lamellae—that is in *lamellar branching*. Dr. Muñoz Guerra brought to our attention the "netlike" lamellar morphology of solution-crystallized polyamide 3 which appears to result from nearly orthogonal lamellar branching.[18] The detailed crystal structure of polyamide 3 is not known, but the *c* and *a* parameters of its unit cell are almost equal. As a result, its hydrogen-bonded sheets must have highly symmetrical lateral faces, as well as relatively weak van der Waals interactions with their neighbors: both features are favorable ingredients for homoepitaxy.

Conclusions

As its α phase isotactic counterpart, syndiotactic polypropylene exhibits two epitaxial relationships: a heteroepitaxy with PE and a rather subtle and infrequent homoepitaxy. Both epitaxies have been analyzed by taking advantage of epitaxial crystallization of sPP itself on linear oligophenyls. Control of the contact planes through a sequence of epitaxial crystallizations helps establish the PE/sPP structural relationships: these are contact through $(100)_{\mathrm{sPP}}$ and $(110)_{\mathrm{PE}}$ planes and parallelism of the PE chain with the $[011]_{\mathrm{sPP}}$ direction (which is nearly parallel to the exterior path of the sPP helix).

The sPP homoepitaxy was manifested and analyzed when examining sPP epitaxially crystallized on linear oligophenyls. The homoepitaxy is only a rare and marginal feature in bulk crystallization, but explains occasional development of small, immature daughter lamellar overgrowths at nearly right angles to the parent lamellae. Its structural grounds are similar to the PE/sPP epitaxy: parallelism and matching of (011) and $(0\bar{1}1)$ planes of the twin components in the (100) contact plane. It is best described as a 2_1 rotation twin around an axis parallel to [011] (when $b = 0.56$ nm).

The analogous behaviors of sPP and α iPP in terms of epitaxy underlines the symmetry requirements imposed on the contact face, especially for homoepitaxy. Whereas the α iPP contact face fulfills these requirements with its two-dimensional, lozenge-shaped grating of methyl groups, the less favorable rectangular (100) plane of sPP offers only a one-dimensional grating materialized by parallel stretches of pseudo *n*-pentane units. This less favorable structure, which moreover is only a minor constituent of the contact face (occurring at defect regions), explains the limited presence of this homoepitaxy in actual bulk crystallization of syndiotactic polypropylene.

Acknowledgment. M.S. is grateful to EXXON Chemicals International, Inc., for financial support.

References and Notes

(1) Wittmann, J. C.; Lotz, B. *Prog. Polym. Sci.* **1990**, *15*, 909.

(2) Lotz, B.; Wittmann, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1559.

(3) Khoury, F. *J. Res. Natl. Bur. Stand.* **1966**, *70A*, 29.

(4) Padden, F. J., Jr.; Keith, H. D. *J. Appl. Phys.* **1966**, *37*, 4013.

(5) Lotz, B.; Wittmann, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1541.

(6) Lovinger, A. J.; Davis, D. D.; Lotz, B. *Macromolecules* **1991**, *24*, 552.

(7) Petermann, J.; Xu, Y.; Loos, J.; Yang, D. *Polym. Commun.* **1992**, *33*, 1096.

(8) Stocker, W.; Schumacher, M.; Graff, S.; Lang, J.; Wittmann, J. C.; Lovinger, A.; Lotz, B. *Macromolecules*, preceding paper in this issue.

(9) Lotz, B.; Lovinger, A.; Cais, R. E. *Macromolecules* **1988**, *21*, 2375.

(10) Satou, M.; Watanabe, Y.; Hayashi, H. *J. Polym. Sci. Polym. Phys. Ed.* **1972**, *10*, 835.

(11) Corradini, P.; Natta, G.; Ganis, P.; Temussi, P. A. *J. Polym. Sci., Part C: Polym. Lett.* **1967**, *16*, 2477.

(12) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1837.

(13) Turner, J. D.; Lingafelter, E. C. *Acta Crystallogr.* **1955**, *8*, 551.

(14) Ferro, D. R., Brückner, S.; Meille, S. V.; Ragazzi, M. *Macromolecules* **1992**, *25*, 5231.

(15) Meille, S. V.; Brückner, S.; Porzio, W. *Macromolecules* **1990**, *23*, 4114.

(16) Natta, G.; Coradini, P. *Nuovo Cimento, Suppl.* **1960**, *15*, 40.

(17) Corradini, P.; Pirozzi, B.; Napolitano, R. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1991**, *2*, 341.

(18) Munoz-Guerra, S.; Fernandez-Santin, J. M.; Rodriguez-Galan, A.; Subirana, J. A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 733.