JOURNAL OF MATERIALS SCIENCE 29 (1994) 6159–6166

Phase II to phase I crystal transformation in polybutene-1 single crystals: a reinvestigation

S. KOPP, J. C. WITTMANN, B. LOTZ
Institut Charles Sadron (CRM-EAHP), CNRS-ULP Strasbourg 6, rue Boussingault
67083 Strasbourg, France

The spontaneous phase II to phase I crystal–crystal transformation of polybutene-1 was investigated by electron diffraction and bright- and dark-field imaging of solution and thin-film grown single crystals. Whole single crystals were observed to transform with a single phase II to phase I orientational relationship and, in the case of multiple orientations, the transformed areas were not dependent on growth sectors. These results do not support the views of Holland and Miller of a "twinned" phase II to I transformation determined by growth sectors but are consistent with a transformation scheme introduced by Fujiwara. Nucleation and growth of the transformation are further discussed.

1. Introduction

The spontaneous crystal–crystal transformation from phase II to phase I in polybutene-1 (pBu1) was established in the very early works of Natta *et al.* [1,2]. This transformation has been investigated in some detail because it is a familiar solid-state crystal transformation in polymers, and, from a practical standpoint, limits considerably the applications of pBu1 [3]. Indeed, the transformation, which can take days or weeks, corresponds to a densification and introduces a shrinkage of, for example, moulded objects. The transformation depends on various physical treatments or chemical modifications. It is accelerated by quenching to a temperature less than the glass transition temperature, by high pressure, deformation, or by additives (plasticizers or nucleating agents). It is also accelerated by introduction of ethylene, propylene, etc., comonomers in the structure but is hindered when the comonomer is 4-methylpentene 1.

The structural aspects of the transformation are mostly known through a landmark work of Holland and Miller [4]. These authors obtained the three crystal phases of pBu1 in the form of solution-grown single crystals. Phase II, which is formed spontaneously in bulk crystallization, has a tetragonal unit cell and 11_3 helix conformation. This form transforms into phase I, which has a hexagonal or trigonal cell and a 3_1 helix (the related phase I′ has the same crystal structure as phase I but is formed directly, rather than being the result of transformation of phase II). Phase III has an orthorhombic unit cell and a 4_1 helix. Holland and Miller recorded diffraction patterns of phase II single crystals in the process of transformation into phase I. They showed that two orientations only of phase I are created, thus giving an overall "twinned" outlook to the phase I pattern, as illustrated in Fig. 1a. Furthermore, they state (but do not provide experimental support) that "the components of the phase I 'twin' arise from specific growth sectors of the parent phase II single crystal", as illustrated here in Fig. 1b which is adapted from their paper.

Fujiwara [5] investigated shear-induced transformation of phase II spherulites crystallized in a temperature gradient, in which (1 1 0) and ($\bar{1}$ 1 0) planes are parallel and normal to the gradient, respectively. Shearing along either one of these two families of planes resulted in a single phase I orientation (i.e. no "twinning"), with its $(1\,1\,.\,0)_\mathrm{I}$ plane parallel to the plane of shearing. Fujiwara suggested a transformation scheme illustrated in Fig. 2 in which $(1\,1\,0)_\mathrm{II}$ becomes $(1\,1\,.\,0)_\mathrm{I}$. These two planes are indeed made of isochiral helices, successive planes being antichiral, and the interhelix distance is similar: 1.06 and 1.02 nm, respectively. Transformation is thus possible with minimum helix displacement and no energetically unrealistic change of helix chirality.

Further work on the II–I phase transformation was performed by Gohil *et al.* [6] who investigated thin films with fibre-like orientation, and by Chau and Geil [7]. Both groups indicated that the transformation is nucleation controlled and results, for oriented thin films, in very small (10–20 nm) crystallographically coherent domains.

The present investigation was aimed at solving a contradiction between Fig. 1b and Fig. 2. Indeed, it is apparent that $(1\,1\,0)_\mathrm{II}$ and $(\bar{1}\,1\,0)_\mathrm{II}$ planes are parallel to the diagonals of the square phase II single crystals and therefore are symmetrically related to the (1 0 0) growth sectors and fold planes. As a consequence, if one accepts the transformation scheme suggested by Fujiwara [5], growth and/or fold planes cannot favour transformation in any particular set of $(1\,1\,0)_\mathrm{II}$ or $(\bar{1}\,1\,0)_\mathrm{II}$ planes, i.e. transformation should not be growth-sector dependent: Figs 1b and 2 are mutually incompatible.

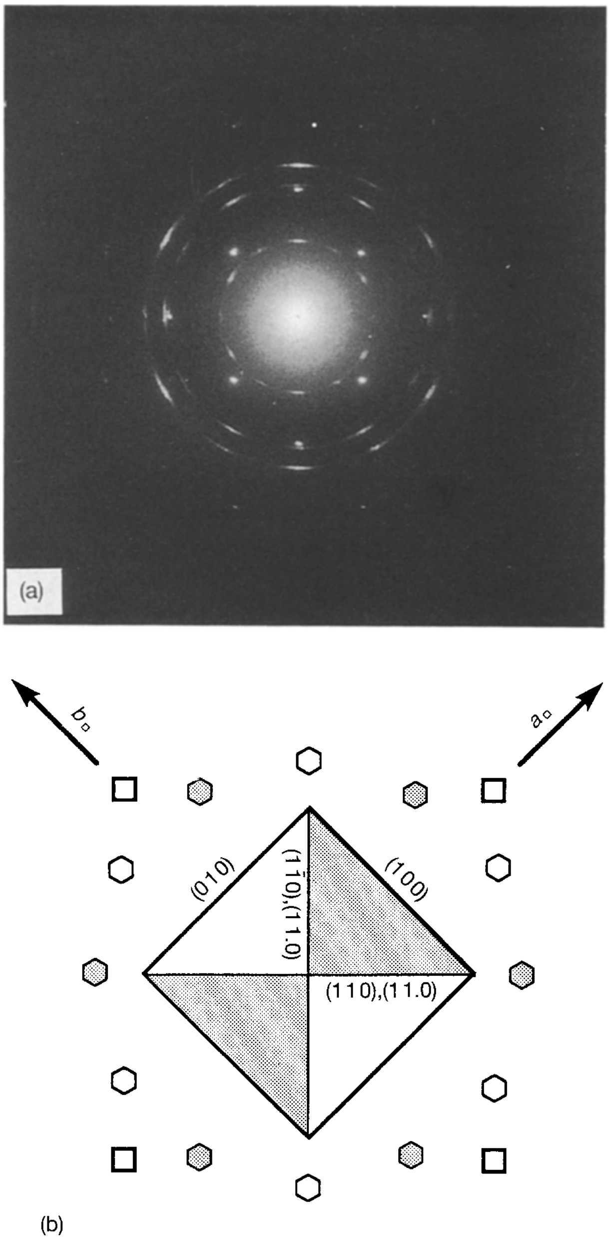

Figure 1 (a) Electron diffraction pattern of a lamellar single crystal of pBu1 initially in form II after partial transformation into form I. Note in the inner circle, the sharpness of the 1 0 0 and 0 1 0 spots of form II, as opposed to the arcing of reflections of form I. The presence of twelve spots of form I indicates the existence of two orientations at right angles of this form. (b) Origin of the two crystal lattice orientations of form I according to Holland and Miller [4]. The crystal is shown at the centre; its light and shaded growth sectors yield the light and shaded form I diffraction spots (hexagonal outline), respectively. Note also the relative form II (square 1 0 0 and 0 1 0 spots) and form I lattices orientation which implies parallelism of $(1\,1\,0)_{\mathrm{II}}$ and $(1\,1\,.\,0)_{\mathrm{I}}$ planes. This scheme is questioned in the present article.

Our experimental approach is similar to that of Holland and Miller [4] it rests on investigation of single crystals of phase II during or after transformation. It provides a straightforward answer to a problem that is recurrent in polymer science. As an illustration, a similar crystal–crystal transformation (but reciprocal to that of pBu because it goes from hexagonal to tetragonal) has been reported in single crystals of poly(α benzyl-*L*-aspartate) by Munoz-Guerra *et al.* [8] who also assumed, if only implicitely, a growth-sector dependent transformation.

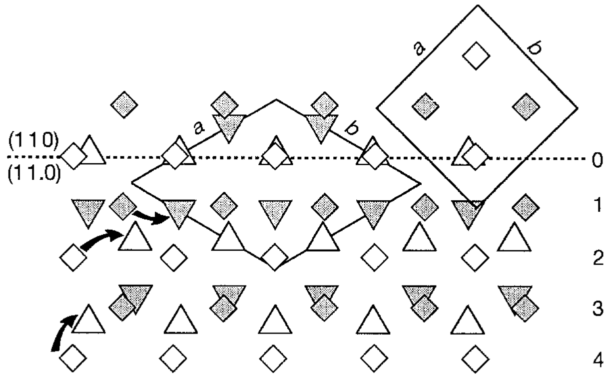

Figure 2 Transformation scheme from form II into form I according to Fujiwara [5]. A tetragonal cell of form II and a hexagonal (trigonal) cell of form I are indicated. 4_1 and 3_1 helices of forms II and I are represented as squares and triangles, respectively. The different helical hands are shown as light and shaded. The transformation is initiated in layer 0 and propagates both sideways and downwards. Note preservation of the helical hand in the transformation, a small contraction in the $(1\,1\,0)_{\mathrm{II}}$–$(1\,1\,.\,0)_{\mathrm{I}}$ horizontal planes, lateral shifts of chains in layers 1 and 2 and significant lattice shrinkage in the vertical direction, as manifested by helix movements in layer 4.

2. Experimental procedure

Two pBu1 samples of commercial origin (Aldrich) were used. Their molecular weights are 1.8×10^5 and 7.2×10^5. A low molecular-weight material obtained by fractionation of an experimental sample was also used. Results were almost independent of sample characteristics, which will not be specified further.

Single crystals of form II are known to transform fairly rapidly into form I when maintained in solution. For this reason, single crystals were not formed by isothermal crystallization, but rather by slow evaporation of a hot octanol solution spread on a glass cover slide. Faster crystallization was achieved and the crystals (of several micrometres lateral size) had well-developed growth faces. Transformation of the then dry crystals was slow (it took several days), whereas observation in the electron microscope could be performed within hours.

Electron microscope investigations were performed using a Philips CM12 electron microscope. Illumination was maintained at a minimum level in view of the pBu1 electron-beam sensitivity and of the need to record in succession one electron diffraction pattern, several dark-field and bright-field pictures for a complete structural characterization. Under these illumination conditions, the search for adequate single crystals was helped by heavy Pt–C shadowing of the preparation at a shallow angle.

The structural investigation in dark-field imaging rests on the separation of form I and II *h k* 0 reflections in the diffraction pattern (cf. Fig. 1), which makes it possible to select independently reflections of the different phases, and therefore to "light" or "extinguish" the crystal forms which coexist within any single

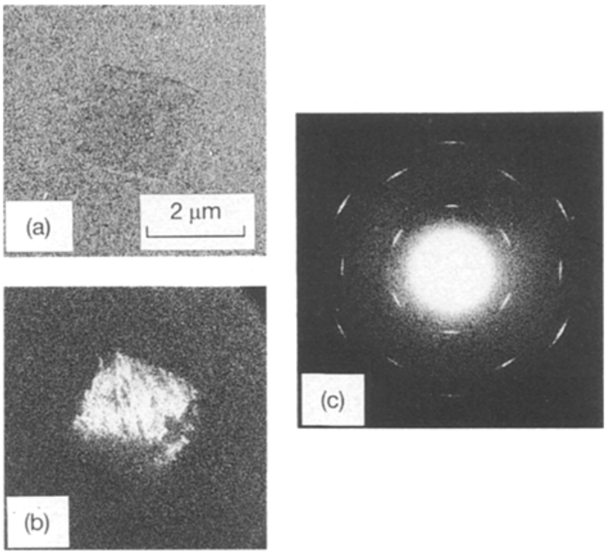

Figure 3 (a) Bright- and (b) dark-field pictures and (c) electron diffraction pattern of a crystal initially in form II displaying a single orientation of the form I lattice after transformation.

crystal. Most micrographs are recorded at a 3000 direct magnification on an X-ray film (Kodak DEF 5).

3. Results

Mostly monolamellar and some multilamellar crystals which experienced partial or complete transformation into form I have been investigated. However, our observations depart significantly from the results reported by Holland and Miller [4], and suggest that the crystal–crystal transformation is not growth-sector dependent. This conclusion is supported by observation of (i) crystals wholly transformed which display only a single form I orientation, and (ii) direct observation of the limits of form I domains which do not conform to initial form II growth-sector limits.

3.1. Single orientation of transformed phase I

The vast majority of the single crystals exhibit only one orientation of form I after transformation. Fig. 3a shows a small form II single crystal, as indicated by its square outline. Fig. 3c shows its diffraction pattern: the hexagonal symmetry and spacings indicate pure form I, i.e. complete transformation. Strikingly, this pattern reveals only one orientation of form I, and not the two orientations at right angles to each other described by Holland and Miller [4] (cf. Fig. 1). Dark-field imaging of the crystal confirmed that the major part of the crystal can be "lit" by selecting one diffraction spot: the form I domain extends over all four growth sectors, whereas only a small portion of the crystal is not in the diffracting position, probably for geometric reasons (Fig. 3b).

Fig. 4 shows a more complete set of electron diffraction, and bright- and dark-field pictures of two superposed crystals in near crystallographic register. The crystals are again nearly square, indicating their initial form II structure, whereas the diffraction pattern is of hexagonal symmetry with predominantly one orientation (a small component with the second orientation at right angles is visible on the original negatives but is lost on reproduction). Fig. 4c–f show dark-field pictures obtained by selecting in succession spots indexed as $\bar{4}2.0$, 22.0, $2\bar{4}.0$ and 03.0. The whole set confirms that transformed domains in phase I extend over all four growth sectors, irrespective of growth-sector limits of the parent form II crystal.

The dark-field pictures further reveal the fine structure of the domains which do not diffract uniformly but appear striated (cf. also Fig. 3b). Similar striations are observed in most dark-field pictures of polymer single crystals. They are usually associated with the geometry of the collapsed three-dimensional crystals: hollow pyramids of polyethylene, bowl-like crystals of poly-4-methyl-pentene-1 and polyoxymethylene, etc. The features are, in most cases, linked with the sectorization of the single crystals, and differ when the imaging planes are parallel, or at an angle to the growth planes. Although such features exist in Fig. 4c–f, the most conspicious striations are all oriented from lower left to upper right in the four dark-field pictures, irrespective of the specific diffraction spot selected and of the growth sectors. These striations correspond to transformed domains. They are parallel to one $\langle 110 \rangle$ diagonal of the parent form II single crystal. A closer examination indicates that these striations have breadth and length in the 10–50 nm and in the micrometre range, respectively.

3.2. Limits of form I domains

In several cases, it was possible to observe the two orthogonal orientations of form I after transformation. Representative examples are shown in Figs 5 and 6. Fig. 5 shows a crystalline entity which may result from impingement during growth of two non-coplanar crystals of form II, thus the development of a screw dislocation at the point of encounter. The whole entity has already transformed into form I, as confirmed by the diffraction pattern (Fig. 5b). Successive dark-field imaging using two nearby 22.0 reflections makes it possible to reveal the areas with different orientations of form I (Fig. 5c and d). In spite of the multilamellar nature near the centre of the crystalline entity, the complementarity of the diffracting areas in the two pictures is readily apparent. Note, in particular, the small triangular domain near the upper left corner (arrowed in Fig. 5d where it is diffracting) and the very clear vertical and horizontal limits of the larger diffracting domain, i.e. nearly parallel to $\{100\}$ of form II.

Fig. 6 illustrates further the irregular outline of transformed domains, revealed here with a single dark-field picture. Note that the domain limits coincide with the initial growth sector boundary only along a small fraction of the overall contour (arrowed in Fig. 6b).

A variety of similar observations indicates that, whenever two orientations of form I coexist in any single crystal, the limits of the two types of domain do not display any simple or clear-cut pattern, but rather have an irregular outline.

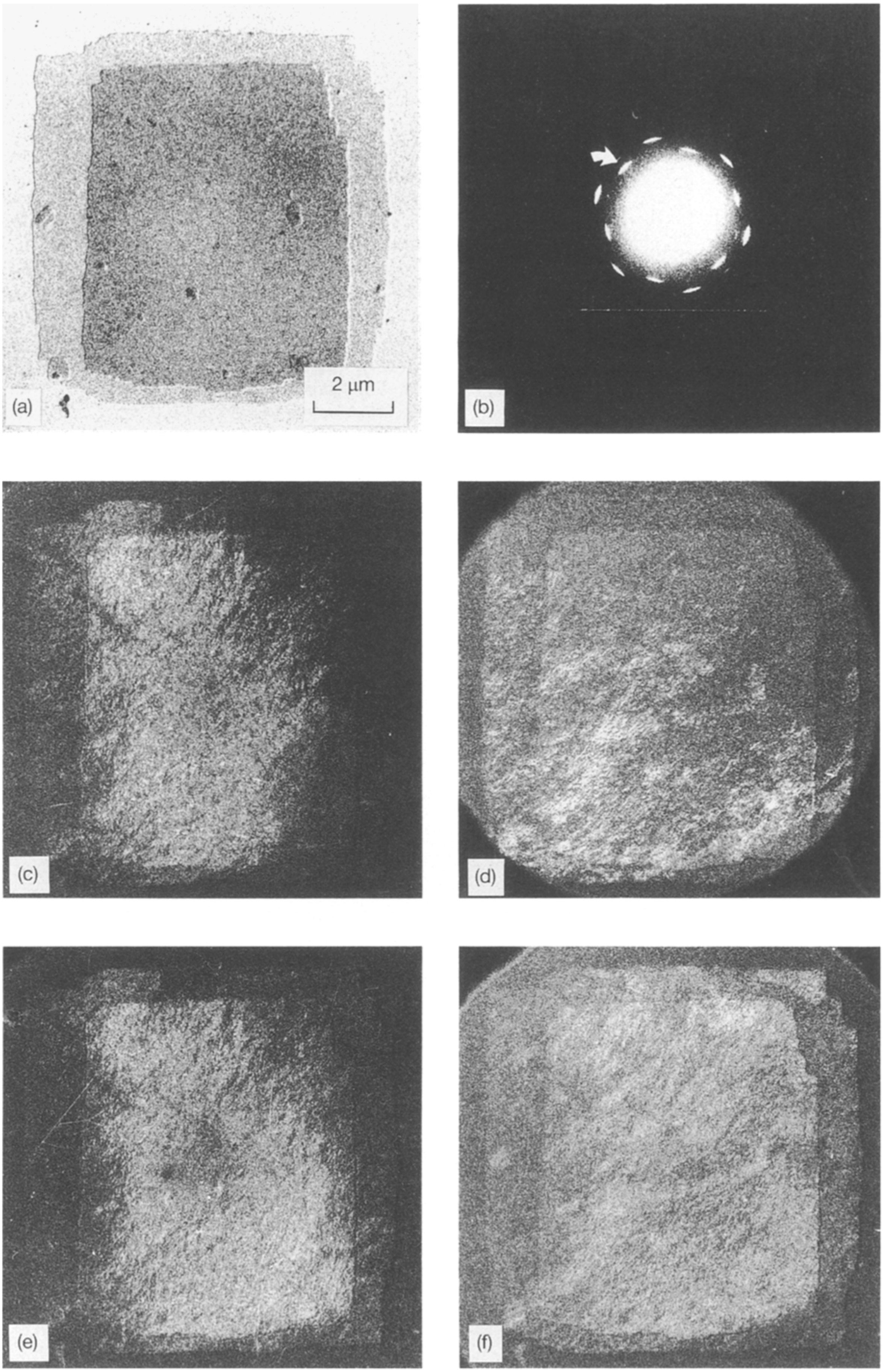

Figure 4 (a) Bright-field image, (b) electron diffraction pattern and (c–f) several dark-field pictures taken with reflections (c) $\bar{4}2.0$, (d) 22.0, (e) $2\bar{4}.0$ and (f) 03.0 of two superposed crystals of form II after transformation into form I. Note the striae (diffracting domains) parallel to lower left to upper right diagonal of the square form II crystal. The relative orientation of diffraction pattern and crystal confirms that $(1\,1.0)_I$ planes (22.0 reflection arrowed) are parallel to *this* diagonal of the crystal, which thus corresponds to the dashed line in the transformation scheme illustrated in Fig. 2 (and cf. Fig. 8).

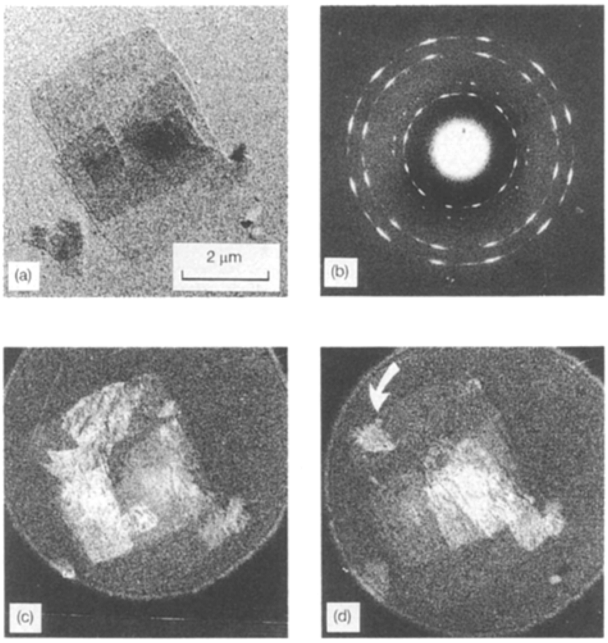

Figure 5 Electron diffraction pattern, bright-and dark-field pictures of a crystal of form II after transformation into form I with two orientations of the latter form. The dark fields were imaged through reflections characteristic of the two different orientations.

3.3. Multilamellar crystals

Multilamellar crystals are less informative regarding the transformation process. They display an overall diffraction pattern with two orientations. In the crystal shown in Fig. 7, various zones have been selected to determine the local organization. As is apparent in the insets, either one or two orientations of form I are generated during the crystal–crystal transformation.

4. Discussion

The early scheme of Holland and Miller [4] linked the transformation of phase II pBu1 single crystals into "twinned" orientation of phase I with existence of growth sectors of the parent crystals. Because differences in fold orientation are the most conspicuous feature of growth sectors, this scheme provided a potential means to investigate structural links between the crystalline core and fold surface structure of polymer lamellae via a mechanism (a crystal–crystal transformation) seldom considered in this context.

This scheme has already been questioned by the observations of Chau and Geil [7], who report that two form I orientations are created within a single growth sector. However, the crystals examined had irregular growth faces, which left open the possibility of microsectorization and serration of the macroscopic growth faces. The present results are clearly in contradiction with the scheme of Holland and Miller [4], especially when a single orientation of form I is generated in all four growth sectors upon transformation of the parent phase II single crystal. These results are now analysed (i) in crystallographic terms, in connection with the transformation mechanism suggested by Fujiwara [5], and (ii) in connection with the nucleation and growth mechanisms proposed so far.

4.1. Crystallographic aspects of the transformation

The transformation scheme introduced by Fujiwara [5] takes into account strong crystallographic features: interhelical distance and chirality of helices in parent $(1\,1\,0)_{\mathrm{II}}$ and daughter $(1\,1\,.\,0)_{\mathrm{I}}$ planes. Our experimental results appear to support this transformation scheme, mainly through the impact of the significant dimensional changes associated with the crystal-structure modification, a feature which had not been taken into account so far.

The phase II to I transformation scheme of Fig. 2 induces highly anisotropic dimensional changes. Along the chain axis, the rise per residue increases by

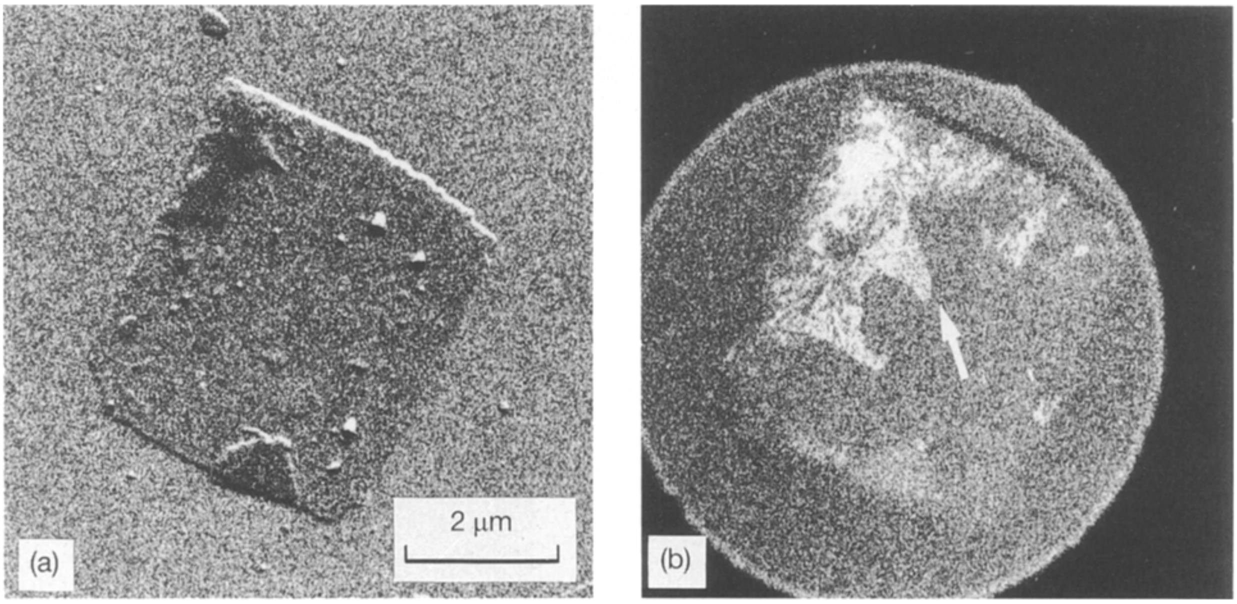

Figure 6 Bright-and dark-field pictures of a crystal of form II after transformation into form I with two orientations of the latter form. Note the irregular, curved outline of the limits of transformed sector, only partly parallel to growth-sector limits (arrowed).

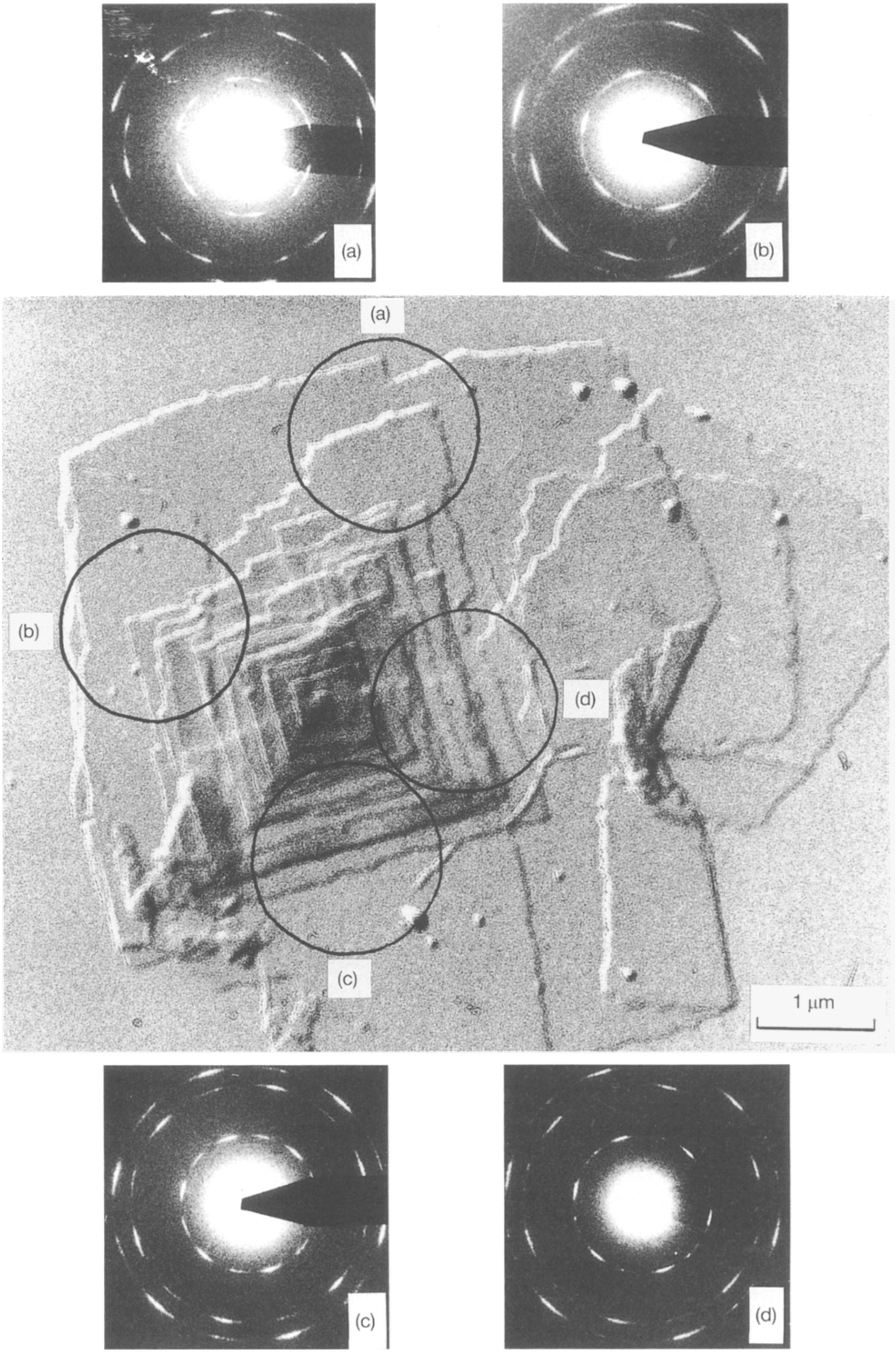

Figure 7 Montage of a multilamellar crystal and various diffraction patterns of selected zones (indicated). Relative orientation of diffraction patterns and bright field is not respected: the patterns indicate the presence of either one or two form I orientations. No detectable form II is present.

15.5% upon transition from 11_3 to 3_1 helix conformation (from 0.191 nm to 0.2167 nm rise per residue). This dimensional change is not visible in the $hk0$ projection investigated here, but is clearly revealed in epitaxially crystallized films [9]. The chain cross-section is reduced by a larger factor, − 17.7%, which accounts for the overall densification on transformation. This reduction is, however, highly anisotropic in the scheme of Fujiwara [5]: in the $(1\,1\,0)_{II}$–$(1\,1\,.\,0)_I$ planes which is maintained in the transformation (horizontal in Fig. 2), the interhelical distance is reduced by only 4% (from 1.06 nm to 1.02 nm). The main part of the contraction takes place in a direction normal to these planes: on average, the interplanar distance is reduced by nearly 20%, from 0.525 nm to 0.442 nm (cf. in Fig. 2, the vertical shift of plane labelled 4).

As illustrated in Fig. 8, we suggest that the striations parallel to $(1\,1\,0)_{II}$ planes (now $(1\,1\,.\,0)_I$ ones) result from, and reflect these highly anisotropic dimensional changes. Several features support this statement. First, the orientation of the phase I pattern relative to the square phase II crystal indicates that $(1\,1\,0)_{II}$ and $(1\,1\,.\,0)_I$ planes which are maintained in the transformation are parallel to the striations. Second, the contraction involves considerable molecular displacements–actually movements of whole crystallographic planes. The diffracting domains 10–50 nm wide at most give an indication of the actual displacements that are tolerable within the lattice. The non-diffracting striae within the transformed zones would thus mainly include gaps generated by the transformation, in addition to zones extinct because of inadequate diffraction conditions. It is clear, however, that in transformed crystals each small, individual domain of crystallographic coherence revealed by dark-field experiments is not generated by its own nucleation event. On the contrary, the single phase I unit-cell orientation and structure of transformed domains in Figs 4c–f and 5 suggests that the transformation spreads "laterally" through $(1\,1\,0)_{II}$ planes which are maintained. Through partial decohesion due to shrinkage, small, bent crystal domains are created, but these domains remain interconnected because the transformation "zig-zags" laterally throughout the whole crystal.

To sum up, several experimental findings support the mechanism proposed by Fujiwara [5] which rests on the fact that $(1\,1\,0)_I$ and $(\bar{1}\,1\,0)_I$ planes do not play symmetrical roles once the transformation is initiated: the very existence of a single orientation of phase I, the formation of small, elongated and wavy domains parallel to the diagonal along which transformation takes place, and the development of waviness itself which results from significant crystal shrinkage in one direction only. This shrinkage and resulting waviness account for the arcing of phase I reflections as opposed to the sharpness of parent phase II single-crystal spots (Fig. 1a). It also provides an explanation for the observed small domain size in transformed crystals and therefore helps reassess the respective roles of nucleation and growth in the transformation.

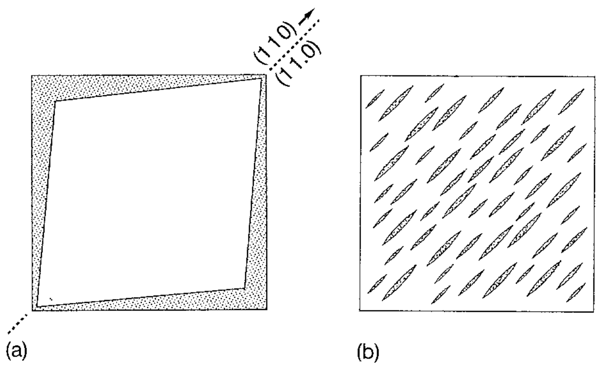

Figure 8 (a) Shrinkage (shaded area) of a square phase II crystal upon conversion to phase I when the indicated $(1\,1\,0)_I$–$(1\,1\,.\,0)_{II}$ plane is maintained in the transformation. (b) Development of cracks and elongated domains to accomodate this shrinkage when the overall crystal dimensions are constrained.

4.2. Nucleation and growth of the transformation

The detailed initial stages of the phase II to phase I transformation are not known at a molecular level, but nucleation density is increased, in bulk crystallized pBu1, by mechanical (high pressure, cold forging) or thermal (quenching below T_g) stresses. Nucleation is often considered to be the rate-determining step, but seemingly for opposite reasons: Goldbach [10, 11] and Gohil *et al.* [6] indicate that it is a slow process (and thus controls the overall transformation) whereas Chau and Geil [7] indicate profuse, instantaneous nucleation at early stages of the transformation, followed by a second process of random nucleation. Gohil *et al.* [6] also observed the formation of numerous, small transformed domains in thin films produced by melt stretching, and associate this profuse nucleation with the existence of taut interlamellar tie molecules.

The present single crystals, being produced by thin-film growth upon evaporation of a polymer solution, experience minimum mechanical disturbance, possibly not even stresses associated with sedimentation on a substrate. Under such conditions, the nucleation rate is small in monolamellar crystals, and is therefore the rate-determining step: some crystals are not transformed after one month [11], and single orientation of the transformed phase I indicates comparatively rapid propagation of the transformation within the whole crystalline lamella after the nucleation event. In the light of the present results, it appears that profuse nucleation was inferred by Chau and Geil [7] on the assumption that each small domain must be created by a different nucleus; this hypothesis is invalidated by our observations, but could not be tested in their experiments, because the two possible orientations coexisted in any single crystal and even growth sector.

The situation is more blurred for multilamellar crystals or multilamellar thin films investigated by Gohil *et al.* [6]. In the latter films, in which the lamellae are observed edge-on as opposed to flat-on as in the present study, the small size and apparent absence of connection between diffracting domains may also result from the lateral shrinkage on transformation: the resulting waviness of transformed domains places most of them out of diffraction conditions when observed normal to the chain axis.

In our study, multilamellar crystals always appear transformed. This enhanced nucleation rate relative to monolamellar lamellae, and frequent formation of "twinned" orientation of phase I suggests nucleation mechanisms specific to multilamellar crystals. Indeed, we have never observed a single orientation of phase I, as could be expected if a single nucleation event propagates by spiralling throughout the screw dislocation. It is therefore tempting to invoke stresses created on sedimentation, but their nature and mode of action are open to conjecture. Such stresses, and therefore likely nucleation sites, could be concentrated near the centre of the screw, where crystal deformation is maximum. Alternative mechanisms might be envisaged. In particular, surface interactions between the fold surfaces of superposed lamellae may be operative. Such interactions are known to generate dislocation networks in polyethylene single crystals [12, 13]. i.e. to induce stresses within the crystal lattices. Investigation of these interactions and discrimination from stresses generated by screw dislocations would require investigation of superposed, individual lamellar crystals as performed in the elegant work of Sadler and Keller [12, 13]. The present preparation conditions and experimental difficulties of observation of pBu1 single crystals have not yet allowed a similar study.

5. Conclusions

Investigation by electron diffraction and dark- and bright-field electron microscopy of phase II polybutene-1 single crystals in the process of, or after, transformation into phase I indicates that:

1. The orientational relationship of the two phases is as determined by Holland and Miller [4] and as assumed in the transformation process put forth by Fujiwara [5]. In particular, it is characterized by parallelism of one set of $(1\,1\,0)_{\mathrm{II}}$ planes and its resulting $(1\,1\,.\,0)_{\mathrm{I}}$ planes.

2. The double, "twinned" orientation of form I after transformation observed by Holland and Miller [4] is found in many crystals, but the vast majority of transformed monolamellar crystals display a single phase I orientation. The link between growth sectors of parent phase II crystals and orientation of phase I indicated by Holland and Miller is not confirmed. In particular, the single phase I orientation is incompatible with such a link.

3. Dark-field imaging confirms that boundaries between differently oriented phase I domains in general do not follow growth sector boundaries. Further, dark-field pictures indicate that, upon transformation, phase I domains are composed of small wavy and elongated microdomains 10–50 nm wide and up to ~ 1 μm long, which are parallel to one diagonal only of the parent phase II crystal.

4. All these observations are consistent with the transformation mechanism introduced by Fujiwara [5]. The fine structure of transformed domains is a logical consequence of the highly anisotropic lattice dimensional changes implicit in the intralamellar propagation of the transformation (approximately -4% in $(1\,1\,0)_{\mathrm{II}}$ planes transformed into $(1\,1\,.\,0)_{\mathrm{I}}$ planes, and approximately -20% in a direction normal to these planes).

5. Formation of numerous microdomains is compatible with a single or with limited phase I nucleation events. Previous conclusions which linked the multiplicity of microdomains with profuse nucleation need to be reassessed.

6. The exact nature of the mechanisms (stresses) which initiate the transition, and their molecular translation in terms of crystal phase transition are not yet determined. Routes to analyse possible interlamellar interactions are suggested.

7. In more general terms, the present investigation stresses the crystallographic aspects of the phase II to phase I transformation (i.e. Fig. 2) as opposed to more subtle and potentially more enlightening fold surface–crystalline core interactions implicit in the incorrect growth-sector dependent mechanism illustrated in Fig. 1b.

References

1. G. NATTA and P. CORRADINI, *Nuovo Cimento, Suppl.* **15** (1960) 40.
2. G. NATTA, P. CORRADINI and I. W. BASSI, *ibid.* **15** (1960) 52.
3. L. LUCIANI, J. SEPPALA and B. LÖFGREN, *Prog. Polym. Sci.* **13** (1988) 37.
4. V. F. HOLLAND and R. L. MILLER, *J. Appl. Phys.* **35** (1964) 3241.
5. Y. FUJIWARA, *Polym. Bull.* **13** (1985) 253.
6. R. M. GOHIL, M. J. MILES and J. PETERMANN, *J. Macromol. Sci. Phys.* **B21** (1982) 189.
7. K. W. CHAU and P. H. GEIL, *J. Mater. Sci.* **21** (1986) 3002.
8. S. MUNOZ-GUERRA, J. M. FERNANDEZ-SANTIN, C. ALEGRE and J. A. SUBIRANA *Macromolecules* **22** (1989) 1540.
9. S. KOPP, J. C. WITTMANN and B. LOTZ, *Polymer,* **35** (1994) 908.
10. G. GOLDBACH, *Angew. Makromol. Chem.* **29/30** (1973) 213.
11. *Idem, ibid.* **39** (1974) 175.
12. D. M. SADLER, and A. KELLER, *Kolloid Z. Z. Polym.* **239** (1970) 641.
13. *Idem, ibid.* **242** (1970) 1081.

Received 12 October 1993
and accepted 21 March 1994