Analysis of chain folding in crystalline isotactic polypropylene. The implications of tacticity and crystallographic symmetry

V. Petraccone and B. Pirozzi
Dipartimento di Chimica, Università de Napoli, Via Mezzocannone 4, 80134 Napoli, Italy

and S. V. Meille
Dipartimento di Chimica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
(Received 20 August 1985; revised 5 March 1986)

Tacticity and crystallographic considerations are used to predict fold models for a perfect crystal of isotactic polypropylene (α-form). If we assume adjacent re-entry chain folding we conclude that the folding plane must be parallel to the (010) plane. This is in agreement with morphological experimental evidence. We also show that this result is likely to apply even to non-perfect crystals.

(Keywords: chain folding; isotactic polypropylene; adjacent re-entry)

INTRODUCTION

Morphological investigations of solution-$^{1-5}$ and melt-crystallized$^{6-11}$ α-form isotactic polypropylene (α-IPP) consistently show the basic structural unit to be a lath-like chain-folded crystal. The short direction of the laths is parallel to the reciprocal b^* axis, while the longitudinal direction coincides with that of the reciprocal a^* axis of the monoclinic structure; the fold surfaces are consequently best described as $(\bar{1}06)$ crystallographic planes[11]. The authors of several electron microscopy studies indicate the (010) plane as the most probable fold plane in α-IPP solution-grown crystals. The most relevant evidence is the crystal fracture morphology[1,4,5], but also the relative smoothness of the crystal faces supports this conclusion, while the absence of spiral growths in α-IPP suggests fold plane uniqueness.

The recent results on polypropylene crystals obtained by Wittmann and Lotz[12], showing fold orientation by decoration of the fold surface with crystallized polymer vapours, could be interpreted to be at variance with the above conclusions. These authors observe sectoring of the fold surface of α-IPP crystals and also imply fold orientations differing from (010). As we shall show later, in principle, the actual fold orientations may or may not coincide with the fold plane direction. If there is no such coincidence, fold orientation studies cannot be unequivocally correlated with the fold plane direction. We will return to this question after the presentation of our model.

Melt- and solution-grown lamellae of α-IPP are generally organized in dentritic structures$^{3,7-11}$ resulting from a three-dimensional 'cross-hatched' network. This habit has been found to originate in an unconventional twinning mode by which twins share the b axis and form an acute angle of 80° 40′. A number of different explanations, most of them involving some form of epitaxy, have been proposed for this twinning mode. Recently Clark and Spruiell[10] suggested that the epitaxial matching is between a supposed chain folding separation of 13.1 Å on the fold surface and twice the c axis.

Although the body of evidence indicating some chain folding regularity in α-IPP is large and appears to have possibly important morphological implications[9,10], to our knowledge only the inadequate model by Sauer *et al.*[1] has been proposed up to now.

We think that a better understanding of chain folding in α-IPP is desirable and in this paper we show that fold planes must indeed be parallel to the (010) plane, although the folding pattern is quite different from that previously proposed. Our conclusions are based on tacticity and crystallographic considerations under the hypothesis of adjacent re-entry. Similar arguments were used by Sadler *et al.*[13] to discuss chain folding in the case of isotactic polystyrene.

TACTICITY CONSIDERATIONS

In vinyl polymers (as in the case of IPP) the two main chain bonds adjacent to the substituted carbon atoms can be distinguished from a configurational point of view as (+) or (−) bonds[14], as shown in *Figure 1*. Consequently, for a conformationally regular chain, in which a chain axis can be recognized, two chain directions may be distinguished with respect to a reference axis (Z) parallel to the chain axis (see *Figures 2a* and *2b*).

Conformational analysis considerations indicate that (+) bonds tend to assume rotation angles near to G^+ or T, while (−) bonds tend to assume rotation angles near to G^- or T. For an isotactic polymer, the attribution to (+) and (−) bonds of torsion angles respectively near to G^+ and T results in a left-handed (L) helix, while the assignment of torsion angles respectively near to T and G^- results in a right-handed (R) helix. In the case of IPP it is known that these attributions imply a L or a R 3/1 helix

0032-3861/86/111665$03.00

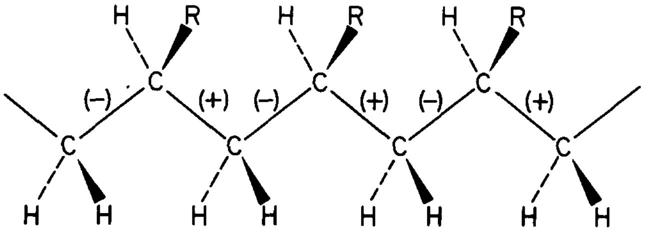


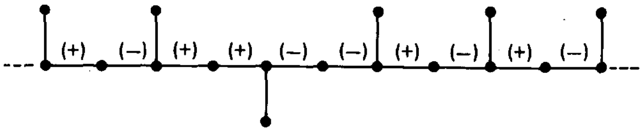
Figure 1 Definition of the configurationally enantiomeric (+) and (−) bonds in an isotactic vinyl polymer chain

respectively for the minimum energy conformations, which are present in the crystalline state[14]. For these conformations, if ΔZ is the difference in the coordinates (with respect to the reference axis) between the first atom of the lateral group and the carbon atom of the chain to which the lateral group is attached, we will have that, for a sequence as in *Figure 2a'*, ΔZ will be negative (lateral groups 'down') in the case of left-handed helix (L_d), while ΔZ will be positive (lateral group 'up') for a right-handed helix (R_u). The result will be opposite for the L and R helix respectively if we have a reversed bond sequence as in *Figure 2b'* (L_u,R_d). As a consequence there are 16 possible ways of coupling by a fold the four kind of helices (L_u,L_d,R_u,R_d) obtainable for an isotactic vinyl polymer if we introduce a reference axis parallel to the chain axis. If we now consider a perfectly (100%) isotactic vinyl polymer chain, in a fold we have necessarily an inversion in the direction of (+),(−) bond sequence relative to the reference axis (*Figure 3*). This constraint reduces the allowed folds to those indicated with 'yes' in the following scheme:

R_d	no	yes	yes	no
R_u	yes	no	no	yes
L_d	yes	no	no	yes
L_u	no	yes	yes	no
	R_d	R_u	L_d	L_u

Combinations that are symmetric with respect to the indicated diagonal are equivalent because they differ only in orientation relative to a reference frame. Of the four distinct existing possibilities, the encircled folds are isoenergetic because they are enantiomeric. The remaining two are non-equivalent because of the different orientation of the lateral groups with respect to the fold. The resulting three folding possibilities are presented in *Figure 4*.

It is important to observe that the described selection rules remain valid even if in the fold there are tacticity defects of the kind



by far the most usual in highly stereoregular IPP[15]; in fact such pairs of syndiotactic diads preserve the directionality of the isotactic chain.

CRYSTALLOGRAPHIC CONSIDERATIONS

The structure of IPP (α-form) is built up of layers of R and L helices packed in a monoclinic unit cell[16].

For thermodynamically stable crystals, the crystallographic symmetry is $P2_1/c$ (refs. 17–20). The packing of the helices, in this space group, viewed along the *c* axis, is shown in *Figure 5*. It is apparent from the figure that if we

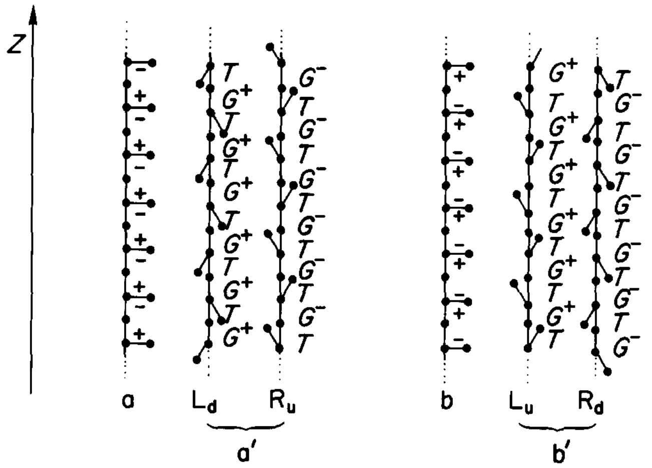


Figure 2 The two chain directions (a,b) of an isotactic vinyl polymer (with respect to a reference axis (*Z*)), determined by the two possible sequences of configurationally different (+) and (−) bonds. The corresponding minimum energy helical conformations for IPP, and the orientation relative to a reference axis of the bonds connecting the methyls to the main chain, are indicated for a and b respectively at a' and b'

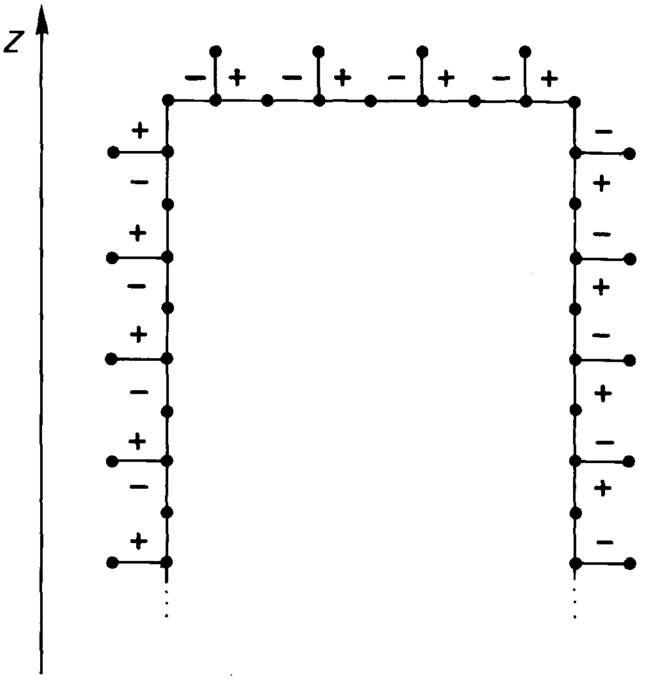


Figure 3 Folded isotactic vinyl polymer chain: note that in stems connected by a fold the (+),(−) bond sequence is inverted

assume adjacent re-entry, the encircled folds in the combination scheme also are ruled out because there are no such contiguous chains; therefore the only fold possibilities are between helices related by the same glide plane parallel to the (010) plane either directly or combined with a translation along the *a* axis. As a consequence folds must follow one another according to one of the eight possible paths described in *Figure 5*. As shown in the figure the indicated paths can be divided in two groups each comprising four equivalent paths. In conclusion only two energetically non-equivalent paths result. A common feature of all fold paths presented in *Figure 5* is that they proceed in a zig-zag fashion (similar to the one recently proposed for polystyrene[13]) connecting stems belonging to two distinct crystallographic layers, both parallel to the (010) plane and separated by 5.2 Å. These 'double layer' systems constitute the fold planes in our model; they extend themselves parallel to the (010) plane, although the orientations of the individual folds are respectively parallel to the (100), (140) and $(1\bar{4}0)$ crystallographic planes.

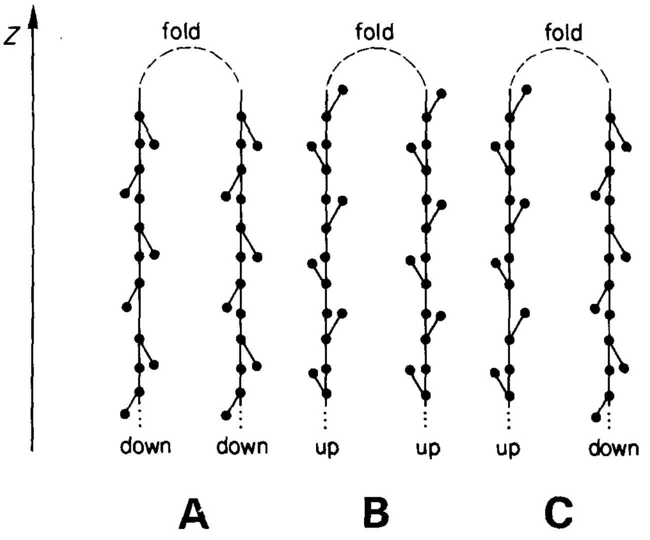


Figure 4 The three basic fold models. (A) Between pairs of down stems: the side groups of both stems are pointing away from the fold. (B) Between pairs of up stems: the side groups are pointing towards the fold. (C) Between an up stem and a down stem: the side groups point towards the fold in one stem and away from the fold in the other. The selection rules (see text) imply that folds (a) and (b) are feasible only between stems of opposite chirality, while fold (c) is possible only between stems with the same chirality. In the ordered $P2_1/c$ α-IPP, contiguous chains are only of opposite chirality and model (c) is therefore not feasible if adjacent re-entry is postulated

Thus far we have discussed folding in the thermodynamically most stable, crystallographically most ordered α-IPP modification. It is to this limiting $P2_1/c$ form that our working hypothesis of adjacent re-entry folding is most likely to apply. However α-IPP is known to show various degrees of disorder in the up and down positioning of the chains, as a consequence of different thermal histories (crystallization conditions, annealing procedures, etc.) while the unit cell and the ordered arrangement of the 3-fold R and L helices are unaltered[16–23]. In melt-crystallized α-IPP, order has been demonstrated to improve either on increasing the isothermal crystallization temperature[23] or on annealing in temperature ranges where melting–recrystallization phenomena[21,22] occur. A similar behaviour is also expected for solution-grown crystals of α-IPP, although we are not aware of any experimental work on this issue.

Both crystallographic analysis and packing energy

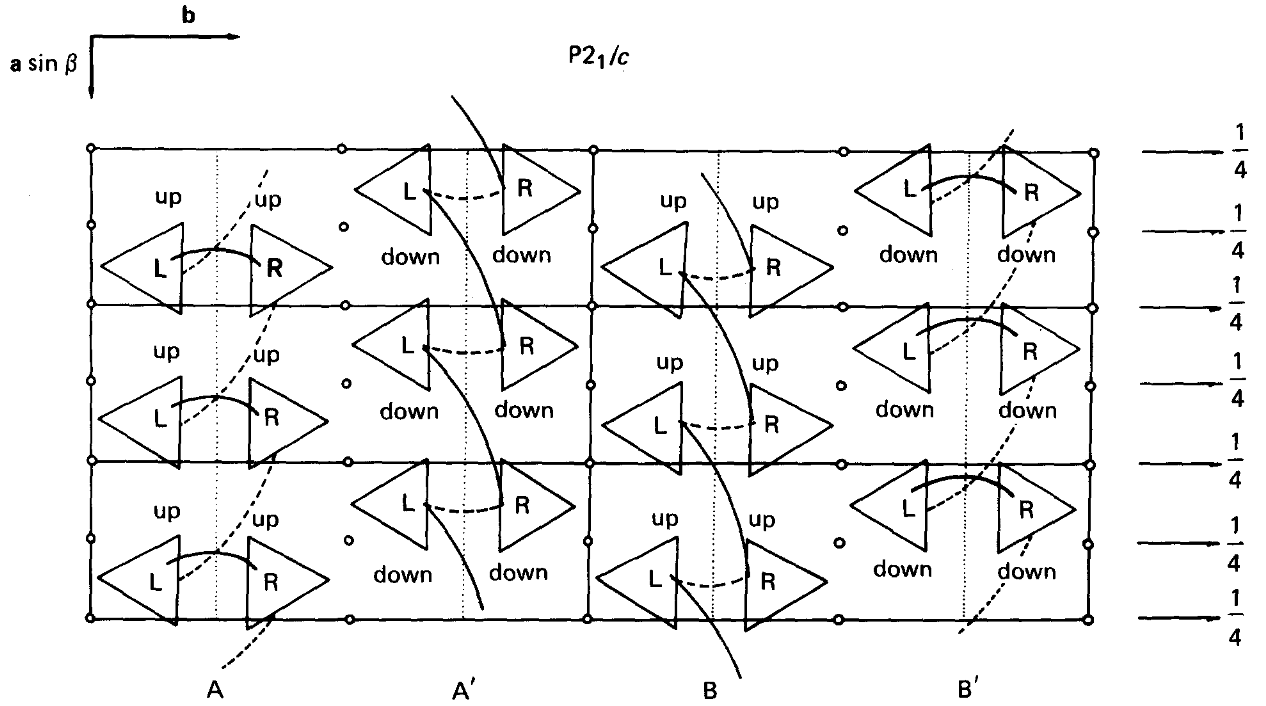


Figure 5 Possible fold paths in α-IPP assuming a perfect $P2_1/c$ crystal and adjacent re-entry. The mode of packing of right-handed (R) and left-handed (L) helices is given as a projection along the *c* axis. Full lines indicate folds on the fold surface towards the observer while dotted lines represent folds pointing away from the observer. Paths (A) and (B) are non-equivalent because in path (A) the shorter (100) folds are between stems with side groups pointing towards the fold (see *Figure 4b*) while the longer (140) folds occur between stems having the methyls pointing away from the fold (see *Figure 4a*). In (B) on the contrary the shorter folds are between down stems (see *Figure 4a*) and the longer $(1\bar{4}0)$ folds are between up stems (see *Figure 4b*). (A′) and (B′) are possible paths which are completely equivalent respectively to (A) and (B) from which they differ only in their orientation with respect to the reference coordinate system. Four other energetically equivalent paths, respectively related to the ones pictured in the figure by the indicated glide planes parallel to (010) plane (dotted lines), are also possible

calculations[17,19,20] performed to achieve a better understanding of the disordered structure are highly relevant to our discussion. The common conclusion of these works is that up–down disorder within layers of chains parallel to the (010) planes is extremely unfavourable and unlikely: in fact, good packing requires that chains related by an *a* axis translation have the same chirality and the same directionality. Statistical disorder is therefore attained preferentially orthogonally to the (010) planes, joining sets of layers with ordered $P2_1/c$ symmetry after a rotation of 180° around the *b* axis.

Our analysis of folding in α-IPP indicates that folds connect double layers of stems as shown in *Figure 5* rather than chain stems belonging to the same crystallographic plane as found in most polymer crystals. It is worth mentioning that disorder has been proposed[19,20] to be most likely exactly at the interface of such a double layer of stems.

The above description of up–down statistical disorder in α-IPP weakens the simple chain folding model proposed by Sauer *et al.*[1] These authors suggest folding between chains related by an *a*-axis translation. We have seen however that chains belonging to the same plane parallel to the (010) plane appear to have the same directionality not only in the ordered but also in the disordered structure. Therefore folds of this kind cannot be statistically relevant in highly isotactic α-IPP.

CONCLUSIONS

The fold pattern resulting from our analysis under the hypothesis of adjacent re-entry differs from the previously proposed ones in the following aspects:

(a) folds occur always between stems of opposite chirality;

(b) a regular adjacent re-entry fold pattern requires two distinct folds, one with a (100) orientation, the other with a (140) or $(1\bar{4}0)$ orientation;

(c) the resulting unique fold plane is parallel to the (010) crystallographic plane but arises from a combination in a zig-zag pattern of folds with (100) and (140) or $(1\bar{4}0)$ orientation;

(d) our model implies that the fold surfaces can either be disordered, if there is no correlation between the folds of different double layer systems (see *Figure 5*), or, if such correlation exists, sectors with different fold orientation may arise.

The outlined model appears to be in broad agreement with the morphological investigations suggesting that fold planes in α-IPP are parallel to the (010) crystallographic planes[1,5] while the limited available evidence on fold orientations in α-IPP obtained by crystal decoration techniques[12] does not conflict with our results. The hypothesis of the statistical relevance of adjacent re-entry appears to be thus justified at least in the case of solution-grown α-IPP crystals. We have also shown that this result is likely to apply also to non-perfect crystals.

With respect to energetic feasibility of the proposed models, it should be stressed that previous calculations[24,25] show that helix inversion energies in IPP are modest. Detailed conformational energy calculations of the surface energy of the folds, to be compared with available experimental data, are in progress.

ACKNOWLEDGEMENTS

We thank Professors G. Allegra and P. Corradini for useful discussions and encouragement. We thank the 'Ministero della Pubblica Istruzione' (Italy) for financial support.

REFERENCES

1 Sauer, J. A., Morrow, D. R. and Richardson, G. C. *J. Appl. Phys.* 1965, **36**, 3017
2 Morrow, D. R., Sauer, J. A. and Woodward, A. E. *J. Polym. Sci., Polym. Lett. Edn.* 1965, **3**, 463
3 Khoury, F. *J. Res. Natl. Bur. Stand.* 1966, **A70**, 29
4 Kojima, M. *J. Polym. Sci. (A-2)* 1967, **5**, 597
5 Martuscelli, E., Pracella, M. and Zambelli, A. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 619
6 Geil, P. H. 'Polymer Single Crystals', Interscience, New York, 1963, p. 214
7 Padden, F. J. and Keith, H. D. *J. Appl. Phys.* 1966, **37**, 4013
8 Padden, F. J. and Keith, H. D. *J. Appl. Phys.* 1972, **44**, 1217
9 Lovinger, A. J. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 97
10 Clark, E. S. and Spruiell, J. E. *Polym. Eng. Sci.* 1976, **16**, 176
11 Norton, D. R. and Keller, A. *Polymer* 1985, **26**, 704
12 Wittmann, J. C. and Lotz, B. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 205
13 Sadler, D. M., Spells, S. J. Keller, A. and Guenet, J. M. *Polymer* 1984, **25** (*Commun.*), 290
14 Corradini, P. in 'The Stereochemistry of Macromolecules' (Ed. A. D. Ketley), Dekker, New York, 1968, Vol. III, p. 1
15 Wolfsgruber, C., Zannoni, G., Rigamonti, E. and Zambelli, A. *Makromol. Chem.* 1975, **176**, 2765
16 Natta, G. and Corradini, P. *Nuovo Cim. Suppl.* 1960, **15**, 40
17 Mencik, Z. *J. Makromol. Sci., Phys.* 1972, **B6**, 101
18 Hikosaka, M. and Seto, T. *Polym. J.* 1973, **5**, 111
19 Corradini, P., Giunchi, G., Petraccone, V., Pirozzi, B. and Vidal, H. M. *Gazz. Chim. Ital.* 1980, **110**, 413
20 Corradini, P., Petraccone, V. and Pirozzi, B. *Eur. Polym. J.* 1983, **19**, 299
21 Guerra, G., Petraccone, V., Corradini, P., De Rosa, C., Napolitano, R., Pirozzi, B. and Giunchi, G. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1029
22 De Rosa, C., Guerra, G., Napolitano, R., Petraccone, V. and Pirozzi, B. *Eur. Polym. J.* 1984, **20**, 937
23 De Rosa, C., Guerra, G., Napolitano, R., Petraccone, V. and Pirozzi, B. *J. Thermal Anal.* 1985, **30**, 1331
24 Bruckner, S., Malpezzi Giunchi, L. and Allegra, G. *Macromolecules* 1980, **13**, 946
25 Corradini, P., Guerra, G. and Barone, V. *Eur. Polym. J.* 1984, **20**, 1177