Energy Calculations for Isotactic Polypropylene: A Comparison between Models of the α and γ Crystalline Structures

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ABSTRACT: Packing energy calculations have been performed on both α and γ forms of crystalline isotactic polypropylene with the following objectives: (a) to compare the stability of the two crystal lattices; (b) to compare the effects of the up–down statistical disorder in the two polymorphs; (c) to investigate the stability of a possible alternative model for the γ phase; (d) to define a compromise structural model for γ-iPP satisfying both the crystallographic and energetic requirements. The results indicate very nearly identical values of the packing energies of the two lattices, the γ form and the α form displaying a preference for the up–down inversions to occur at closely related sites. While the alternative model for the γ structure shows a substantially higher packing energy, the minimum-energy structure deviates only marginally from the one refined from X-ray powder diffraction data. The compromise model shows a disagreement factor nearly as low as the value obtained considering only X-ray data and an energy only 0.4 kcal/mol of trimer higher than the minimum value.

1. Introduction

The recent determination of the crystal structure of the γ crystalline form of isotactic polypropylene (γ-iPP) revealed a totally new crystal architecture where non-parallel chain axes coexist within the same crystal lattice.[1,2]

The structure is well established: it is supported by quantitative analysis of X-ray powder diffraction profiles,[1] by morphological evidence,[3] and by electron diffraction data recently reported by Lotz et al.[4] The proposed γ-iPP crystal packing is free from severe intermolecular contacts and therefore qualitatively acceptable also from an energetic point of view. The present paper is mainly aimed at giving this statement a quantitative basis, founded on the widely accepted principles of molecular mechanics applied to crystal structure analysis.[5]

Further interest of packing calculations is also connected with the up–down statistics of iPP chains of approximate 3_1 helical symmetry, a feature which γ-iPP shares with the crystal structure of the α form of isotactic polypropylene (α-iPP; $C2/c$ crystal symmetry).[6] An additional feature common to α-iPP and to γ-iPP is that the two crystals may be described in terms of a common substructure consisting of two adjacent layers of parallel iPP chains related to each other by a center of inversion or by a glide plane. The result is the bilayer structure reported in Figure 1, where the 3-fold symmetry of the polymer chains is schematically represented by trigonal prisms.

The difference between α-iPP and γ-iPP is mainly due to the different juxtapositions of adjacent bilayers: in α-iPP chain axes parallelism is maintained, while a tilt of ±80° between neighboring bilayers is present in γ-iPP. The strong similarity of the two structures requires, in our opinion, a comparative study in order to assess the relative stability of the two polymorphs.

Although α-iPP has been already extensively studied by Corradini et al. under various crystal symmetries,[7] we decided to carry out an independent analysis on both polymorphs in order to obtain results which, being computed on the common basis of the same force-field parameters and the same optimization technique, can be quantitatively compared. It is worthwhile, however, anticipating that, as far as α-iPP is concerned, our results are in substantial agreement with those previously obtained by Corradini et al.

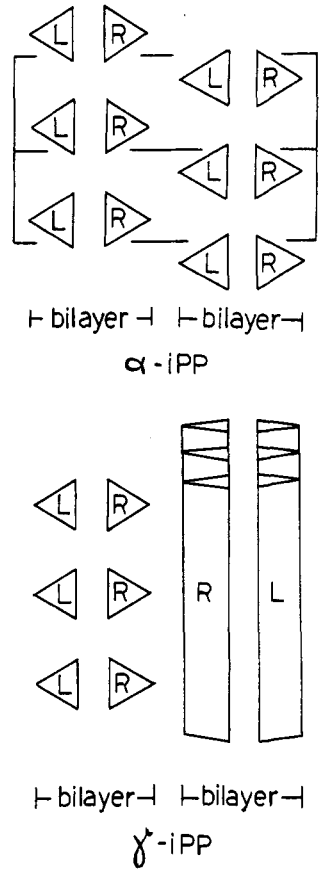

Figure 1. Schematic representation of the bilayer substructure, which is common to both α-iPP and γ-iPP, and of the different juxtapositions of adjacent bilayers. 3-fold polymer helices are represented by trigonal prisms.

2. Method of Computation

The aim of our computational approach is to keep the number of geometrical constraints and arbitrary assump-

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tions at a minimum, so that the optimization parameters coincide with the Cartesian coordinates of all the atoms of the asymmetric unit. This requires the adoption of a suitable force-field comprising, in addition to the nonbonded interaction parameters, also the terms referring to bond-length, bond-angle, and torsion-angle energies, as well as possible Coulombic or lone pair interactions. In the present work we have adopted the MM2 force-field parameters of Allinger and Yuh,[8] a choice that has already given satisfactory results in a number of previous studies.[9-11] The same nonbonded energy parameters were used to calculate both inter- and intramolecular interactions, this approximation being acceptable provided the unit cell dimensions are kept fixed at the experimental values.

The lattice parameters used for α-iPP were $a = 6.634$, $b = 20.976$, $c = 6.519$ Å and $\beta = 98.5°$;[12] for γ-iPP the following values, reported in ref 1, were adopted: $a = 8.54$, $b = 9.93$, $c = 42.41$ Å. A microcrystal is built up around the reference asymmetric unit according to the space group symmetry, with suitable dimensions which allow to us account for all relevant packing interactions and the convergence of long-range interactions as well. This is usually accomplished by taking into account all surrounding units with at least one atom located at a distance of 8 Å or less from the reference unit.[13]

The presence of statistical disorder with the consequent assumption of fractionary occupation factors for the atoms involves particular attention in the calculation of packing energy. Our energy minimization program allows for the coexistence of two or more alternative structures at any given site. In practice, the whole system under investigation may be divided into sections, each section being constituted by one or more structural alternatives, each one characterized by a given occupation factor. Of course the occupants of a given section ignore each other in agreement with the statistical nature of their copresence, while the interactions among different sections are summed up according to the occupancies. In the present case sections correspond to helices: thus, for the space groups *Fddd* of γ-iPP and *C2/c* of α-iPP, where up–down statistics of isochiral chains is considered, two equiprobable helices, related by a 2-fold axis normal to the helix axis, constitute a section and their interaction energies are weighted accordingly.

The first step in the present optimization procedure is typically performed by minimizing the energy of the isolated chain under the only constraint of reproducing the experimental repeat period. Subsequently the packing energy in the mentioned bilayer of chains (Figure 1) was minimized. From this common starting point the different structures were then generated, according to the respective symmetry operations, and subsequently optimized by minimizing the energy of the reference unit in the microcrystal with respect to all atomic coordinates. Thus, models were built independently from the available crystallographic coordinates, and only the experimental lattice parameters and symmetry were considered as established data in the optimization process.

In order to assess the reproducibility of our results, the computations for each model were then repeated several times by variously changing the starting point. While in the next sections we report on the analysis of the very lowest energy minimum for each model, here we anticipate two conclusions: (i) there is very little margin of uncertainty (on the order of 0.01 kcal/mol) with regard to the calculated relative stabilities of the different structures; (ii) in a few instances different runs led to models having

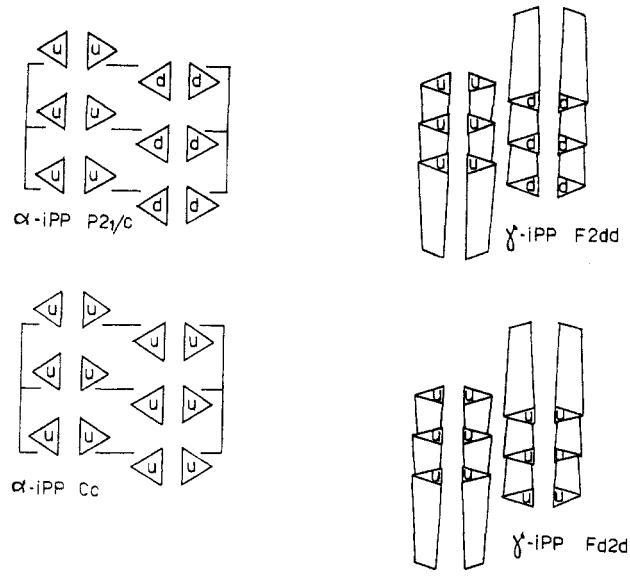

Figure 2. Relative orientations of polymer helices, in the different crystal symmetries, shown as viewed from the fold surface of a lamellar crystal.

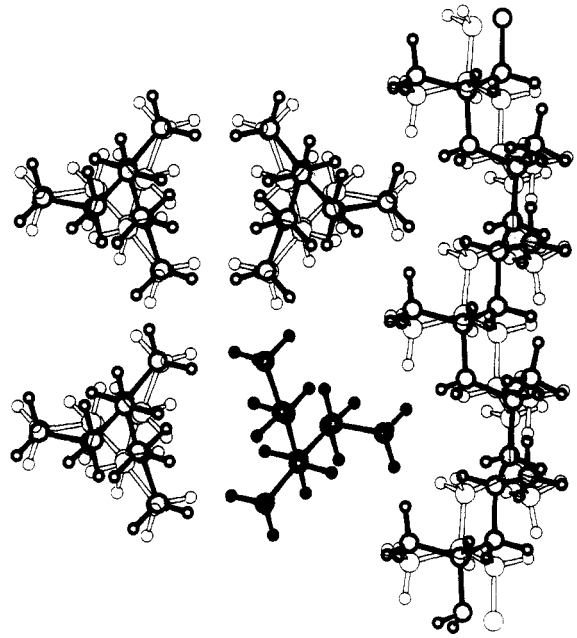

Figure 3. Computed structure corresponding to the minimum total energy for γ-iPP.

nearly the same energy but showing appreciable discrepancies in atom positions (root-mean-square (rms) deviations on the order of 0.05 Å on the atomic coordinates).

3. Results

The total energy of the reference unit in the microcrystal can be separated into different contributions in a way that, although arbitrary, may give some insight into the main features characterizing the crystal lattice. This approach is particularly relevant in the present case because the two crystal structures to be compared, while differing substantially, share three major features: (i) the 3_1 helical chain conformation; (ii) the bilayer substructure; (iii) the presence of up–down statistics.

The symmetries taken into consideration are *Fddd*, *F2dd*, and *Fd2d* for γ-iPP and *C2/c*, $P2_1/c$, and *Cc* for α-iPP. There is a one to one correspondence between the three γ-iPP and the α-iPP space groups: *Fddd* and *C2/c* are both characterized by crystallographic up–down statistics; *F2dd* and $P2_1/c$ as well as *Fd2d* and *Cc* present a

Table I
Total and Partial Energies (kcal/mol of Trimer) of the γ-iPP and α-iPP Structures with Different Crystal Symmetries

			γ-iPP				α-iPP		
			Fddd	*Fd2d*	*F2dd*		*C2/c*	*Cc*	$P2_1/c$
intramolecular	contribution	A	10.76	10.75	10.77		10.79	10.83	10.83
monolayer	no up–down inversion	B′	−3.96	−3.98	−3.93		−3.80	−3.82	−3.81
	up–down inversion	B″	−3.60				−3.47		
	average	B	−3.78				−3.63		
bilayer	glide plane	C′	−5.08	−5.13	−5.31		−5.13	−5.27	−5.29
	center	C″	−4.74				−4.77		
	average	C	−4.91				−4.95		
interaction between bilayers	180° rotation around *b*	D′	−4.75	−4.73		glide plane	−4.78	−4.69	
	180° rotation around *a*	D″	−4.69		−4.61	center	−4.72		−4.77
	average	D	−4.72			average	−4.75		
total energy			−2.65	−3.09	−3.08		−2.54	−2.95	−3.04

similar orientational relationship between neighboring chains of adjacent bilayers: the orientation is the same (down–down or up–up) in *Cc* and *Fd2d* and opposite in $P2_1/c$ and *F2dd*. A schematic representation of the described features is reported in Figure 2, while the minimum-energy structure is displayed in Figure 3.

In the present paper the notion of mutual orientation for parallel chains actually refers to the relative orientation of the vectors associated to the bonds from the tertiary carbon atom to the methyl, with respect to the common chain axis direction. Briefly, chains having the same orientation are isoclined; chains of opposite orientation are anticlined. For nonparallel helices the idea of mutual orientation has to be extended: it can become meaningful, e.g., with respect to the bisectrix of the interaxial angle. Of the two possible choices, i.e., the *a* or the *b* axis in the case of γ-iPP, we have chosen the second because the *b* axis is normal to the lamellar surface and because the angle between the chain axis directions and the *b* axis is smaller (40°) than the one with the *a* axis (50°).

The contribution of intramolecular energy (contribution A in Table I) to the total energy is practically identical in α-iPP and in γ-iPP in all the different space group symmetries. This reflects the essential invariance of the 3_1 helix conformation in iPP: in fact the energy differences between the optimized isolated helix conformation and the crystalline conformation in both α and γ-iPP are less than 0.2 kcal/mol of trimer.

The next objective is the determination of the contribution of one single layer of helices related to each other by a simple translation occurring along *a* in α-iPP and along *a* + *b* in γ-iPP (contribution B in Table I). In the case of the *C2/c* and *Fddd* symmetries, where the up–down statistics is crystallographic, we have analyzed two different situations: in the first one the reference unit is an Lu (lefthanded–up) helix and so are all other helices in the layer, while in the second one the Lu reference helix is flanked by Ld (lefthanded–down) helices. These two cases correspond to contributions B′ and B″ in Table I, while the B contribution is the average. It is apparent that an inversion of the orientation between helices related by a simple translation involves a small but significant increase in the interaction energy, and this holds both in α-iPP and γ-iPP. Moreover, this intralayer packing contribution appears to be slightly more favorable in γ-iPP than in α-iPP probably due to the different spacings between neighboring chains (6.64 Å in α-iPP and 6.55 Å in γ-iPP).

In the third step we evaluate the energy involved in the formation of bilayers like the ones reported in Figure 1. Note that although similar, bilayers in the α and in the γ form present small but significant differences which are likely to be related to the different interbilayer packing of the two structures. In both modifications two different elements of symmetry may relate to each other the helices of adjacent layers within a bilayer: an inversion center or a glide plane. In space groups *Fddd* and *C2/c* both elements are active. In order to analyze the packing in these space groups the two elements of symmetry have been activated separately (contributions C′ and C″), while C represents the statistically weighted contribution of a packing generated by both symmetry operators. Our results indicate a marked preference for the glide symmetry.

The final step, and the only one that unequivocally distinguishes α-iPP from γ-iPP, concerns the interaction between adjacent bilayers. As already stated, in α-iPP all chains are parallel, and adjacent bilayers contact each other through layers of helices of opposite chirality. On the contrary in γ-iPP the interaction between bilayers occurs through helices of the same chirality (see Figure 1), the tilt angle between the chain axes of adjacent bilayers being 80° if the contact occurs via L helices and −80° if R helices interact.

Like in the previous steps we must take into account the up–down mutual orientation of contacting chains. In the case of *Fddd* and *C2/c* symmetries both orientations are statistically present, in *F2dd* and $P2_1/c$ two adjacent bilayers contact each other through chains of opposite orientation, and in *Fd2d* and *Cc* this contact occurs through chains of the same orientation. Contributions D′, D″, and D summarize, in Table I, the energies pertaining to these different contacts. D′ refers to contacts between chains of the same orientation and the same chirality in γ-iPP and of opposite chirality in α-iPP, while D″ pertains to contacts between chains of opposite orientation and with the same chirality relations as in D′. In γ-iPP the interaction between bilayers contacting through chains with the same orientation (contribution D′) appears to be slightly more favorable than that involving chains with opposite orientation (contribution D″), the same difference being calculated in α-iPP. Comparison of contributions D′ and D″ with C′ and C″ in the case of α-iPP confirms the conclusions of Corradini et al.[7] concerning the most probable location of up–down disorder in α-iPP. According to the previous and the present study it is in fact somewhat more likely an inversion of the chain orientation to occur astride the contact plane between two bilayers than within the bilayer itself, the former event being almost energy insensitive, while the latter involves about 0.3 kcal/mol of trimer. It should be noted, however, that while the relative order of stability of the different α-iPP packings coincides with previous studies, the computed energy differences in our case are about 30% of the already small values found by Corradini et al. Similar conclusions can be reached with respect to γ-iPP: contributions C′ and C″ and D′ and D″ in space group *Fddd* are indeed closely comparable with the corresponding contributions in *C2/c*

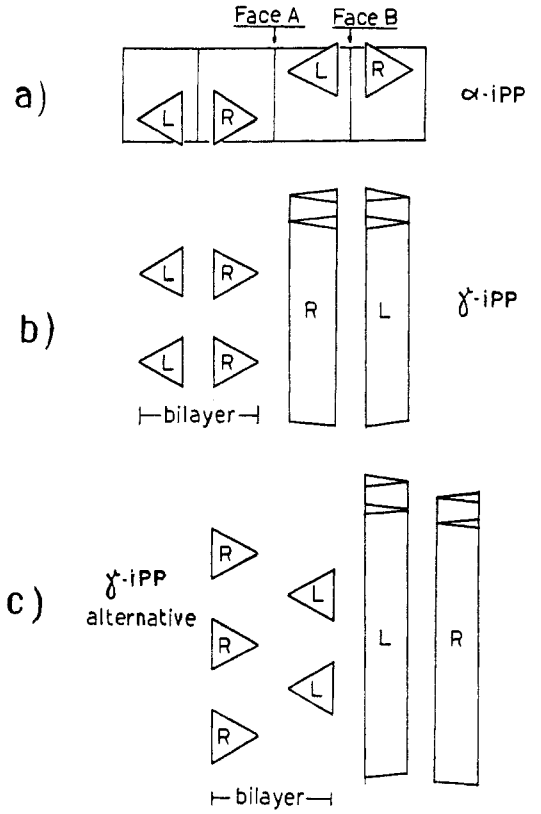

Figure 4. Two different models describing the possible crossing of neighboring polymer chains: (a) actual α-iPP structure where surfaces A and B indicate the possible exposed faces in α-iPP single crystals; (b) actual arrangement in γ-iPP; (c) schematic representation of the alternative γ-iPP structure.

for α-iPP, indicating that also in this case the change of orientation is more likely to occur at the interface between different bilayers rather than within a bilayer. An inversion occurring within a single layer (see contributions B′ and B″) involves, both in α-iPP and in γ-iPP, an energy difference of more than 0.3 kcal/mol of trimer.

To test the effect of the choice of the unit cell parameters on the packing energy, we have analyzed the γ packing (*Fddd* symmetry) adopting the low-temperature unit cell data[2] (a = 8.51, b = 9.95, c = 41.68 Å). Results indicate that all energy values are slightly shifted by a nearly constant amount, leaving energy differences and atom positions almost unchanged so that our analysis, as far as it concerns differential effects within a given cell, may be considered largely independent from the choice of the cell dimensions.

By summing up all the contributions A through D, we obtain the total (inter- + intramolecular) energy of the reference unit in the microcrystal, reported for the various space groups analyzed in the last row in Table I. These results indicate that the stability of the α-iPP and γ-iPP crystal lattices is nearly identical, and this conclusion applies also to space groups where no up–down statistics is present.

A distinct analysis was devoted to the evaluation of the potential energy pertaining to a possible (in principle) alternative structure for γ-iPP.

As discussed by Lotz and Wittmann,[14] branching in α-iPP involves, at the contact plane between lamellae, a crossing event between the chain axes which is very similar to the one later shown to occur in γ-iPP.[2] It was also suggested[14] that this crossing event can occur, in principle, in two different ways corresponding to the two different exposed crystal surfaces, i.e., plane A or plane B in Figure 4a. In the first case, if we represent schematically the 3_1 helices as trigonal prisms, the crossing chains contact each other through one edge (Figure 4b), while in the second case the contact occurs between chains facing each other through a side (Figure 4c).

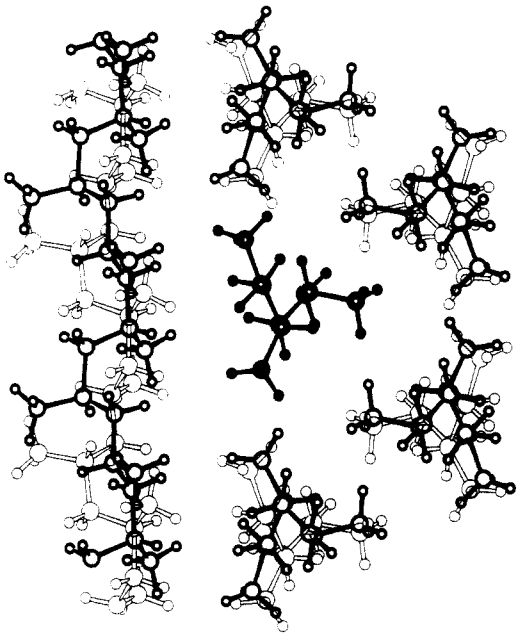

Figure 5. Possible alternative structure for γ-iPP, computed within the *Fddd* space group, the same adopted for the observed structure.

The first kind of interaction is the one actually observed in γ-iPP, while the second kind can give rise to an alternative γ structure with the same crystal symmetries (*Fddd*, *F2dd*, and *Fd2d*). The optimized alternative packing for the *Fddd* symmetry is shown in Figure 5.

The energy of the optimized alternative structure is 3.93 kcal/mol of trimer for *Fddd* and respectively 2.33 and 0.16 kcal/mol of trimers for *F2dd* and *Fd2d*. Comparing these values with those reported in Table I, it is apparent that equivalence of the two possible crossing events between polymer chains is not confirmed from the energy point of view, the alternative γ structure being much less stable than the observed one, particularly when up–down statistics is present. The present conclusion is indeed consistent with Rietveld refinement results,[1,2] while recent atomic force microscopy observations by Lotz et al., showing that contact faces of α-iPP[15] and γ-iPP,[16] epitaxially crystallized on benzoic acid, involve surfaces of type A rather than B (refer to Figure 4a), also appear supportive.

4. Comparison with the Crystallographic Model

The positional parameters of the structure (model II) calculated through the present energy minimization procedure for space group *Fddd* show a rms deviation of the carbon atom positions from the coordinates of the crystallographic model (model I), determined by Rietveld analysis,[1] of 0.17 Å, a rather low value that indicates a good agreement between the two different approaches. This is a nontrivial result if we consider that powder X-ray diffraction profiles from crystalline polymers usually display few peaks which, due to their broadness, give rise to relevant overlapping. This scarce structural information is partially compensated by the high accuracy in intensity data detection and by the adoption, in our optimization routine, of a set of generalized coordinates which minimizes the number of refinable parameters by taking into account all kinds of available structural information.

Table II
Fractional Coordinates of Carbon Atoms in Model III

	x	y	z
C(1)	−0.1391	−0.0921	0.0452
C(2)	−0.1098	−0.0289	0.0779
C(3)	−0.2625	0.0248	0.0925
C(4)	0.0121	0.0860	0.0763
C(5)	0.1769	0.0487	0.0641
C(6)	0.2501	−0.0646	0.0840
C(7)	0.2886	0.1711	0.0638
C(8)	0.2397	0.2927	0.0434
C(9)	0.2156	0.2524	0.0087

As a consequence model I is not to be considered as rigorously defined as a structural model derived, say, from single-crystal diffraction data. This leaves, in our opinion, some margin of indeterminacy which can be conveniently reduced by energy calculations, i.e., by taking into account the structural details of model II.

Following a procedure already adopted in a previous study,[9] we define a compromise model (model III) between models I and II. This is accomplished by linking carbon atoms to the positions of model I through fictitious springs of a properly adjustable elastic constant.

A number of energy minimizations is then performed by progressively reducing the strength of the springs so that the energy path in the transition from model I to model II can be monitored. It is usually found that the most relevant energy decrease occurs in the first steps of the path, corresponding mainly to small intramolecular rearrangements, while possible rototranslational changes occur near the end of the path and involve rather low energy decreases corresponding to relatively large positional changes. Our strategy for defining the compromise model is that of locating it, on the energy path, just at the end of the initial strongly decreasing step. In this way we get the greatest energy decrease at the expense of the smallest deviations from the crystallographically optimized model.

Model III, whose fractional coordinates are reported in Table II, has been obtained in this way, and a calculation performed in order to test its compatibility with crystallographic data gave a disagreement factor $R_2' = 0.117$ (where $R_2' = \sum|I_o - I_c|/\sum I_{net}$ and $I_{net} = I_o - I_{background}$, the summation being performed over all points of the experimental diffraction profile) between the observed and the calculated powder X-ray diffraction profiles. The modest increase of R_2' for model III relative to the value obtained for model I ($R_2' = 0.114$) involves an energy decrease of 2.94 kcal/mol of trimer which corresponds to the 88% of the energy difference between model I and model II, and the rms deviation of model III relative to model I is only 0.06 Å.

5. Concluding Remarks

According to the present energy minimization, the γ-iPP structure appears to be at least as stable as the α-iPP structure, and this is not a trivial conclusion considering the substantial differences between the two crystal lattices.

The small energy differences between the two polymorphs, 0.11 and 0.05 kcal/mol of trimer for space groups with and without statistical up–down disorder, respectively, are of borderline significance, but both values suggest that, in the case of infinite crystals, the γ phase should be slightly more stable than α-iPP. It is interesting to note that the computed energy difference between the two alternative ordered α-iPP space groups considered (*Cc* and $P2_1/c$) is of the same magnitide (0.09 kcal/mol of trimer. The higher stability of $P2_1/c$ packing for α-iPP is consistent with experimental observations:[17,18] indeed annealing the statistical disordered $C2/c$ α-iPP leads to an increased $P2_1/c$ rather than *Cc* content. Furthermore, energy differences of the same order of magnitude were computed, with the present approach, in other packing studies involving polymorphic behavior. In the case of α- and γ-polypivalolactone[10] and isotactic α- and β- 1,4-*cis*-poly(2-methyl-1,3-pentadiene),[11] the energy differences between the two polymorphs were respectively 0.28 and 0.26 kcal/mol, and in both cases the lower melting polymorph coincided with the one indicated as the less stable by packing energy calculations.

As far as disorder is involved, our analysis is in qualitative agreement with the conclusions of Corradini et al. concerning the most probable location of up–down inversions in α-iPP at the contact planes between bilayers. Similar considerations also apply to γ-iPP. For both crystal structures, however, the differences between ordered and statistical up–down packings are considerably smaller than the already modest values suggested by previous computations on the α form. The consequence is that disorder within bilayers, although less probable, should not in any way be ruled out.

The two possible, in principle, different ways of describing the crossing event occurring between the iPP chain axes show a remarkable difference in the potential energy involved so that we may conclude that also in α–α branching of iPP lamellae the most probable model for describing the crossing chains at the lamellar interface is the one determined from the γ-iPP structure analysis.

Finally a refined set of positional coordinates is proposed for γ-iPP that achieves a satisfactory compromise between the model refined from crystallographic data and the model optimized relative to conformational and packing energy.

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Registry No. γ-iPP (isotactic homopolymer), 25085-53-4.