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An Unusual Chain Conformation: s(6*4/3) Helices in Form II of Isotactic Poly(vinylcyclopentane)

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ABSTRACT: The crystalline form II of isotactic poly(vinylcyclopentane) was studied on the basis of fiber X-ray diffraction and of potential energy calculations of both isolated and packed chains. The hypothesis of a s(6*4/3) conformation of the chain has been investigated in detail. According to our interpretation, s(6*4/3) helices, which represent an anomalous case among isotactic poly(α-olefins), result from the superposition of a basically s(2*4/1) conformation of the backbone chain and of side groups following one another with a regular sequence of three conformations, mainly different for their orientation. Slight deformations of the main chain torsion angles from s(2*4/1) symmetry are found to be relevant to improve the data fitting. The resulting structure is indicative of a quite singular polymorphism, mainly ascribable to the different conformations accessible to the side groups.

Introduction

Isotactic poly(vinylcyclopentane) (*i*-PVCP) was studied in the 1960s, when numerous stereoregular polyolefins were structurally characterized, mainly using X-ray diffraction.[1,2] Noether isolated three different crystalline forms and indexed the X-ray diffraction patterns of oriented samples.[2] Both forms I and II were found to have a body-centered tetragonal unit cell with $a = b = 20.14$ Å but different c edge and space group. It was reported that form I had $c = 6.5$ Å and space group $I4_1/a$, while form II had $c = 19.5$ Å and either $I4$ or $I4$ space group. Form III was found to have a tetragonal lattice with $a = b = 37.1$ Å, $c = 19.8$ Å, and space group $P4/mmm$ or $P4/nmm$. On these bases, helix symmetries were proposed, and they were named 4_1 (form I), 12_3 (form II), and 10_3 (form III).

Most isotactic poly(α-olefins) follow the rule that chain constitutional repeating units (CRU)[3] are geometrically equivalent.[4] In that case the IUPAC notation s(A*M/N) for helical symmetry[5] (where the helix class A identifies the number of skeletal chain atoms contained in the helix residue and the integer M identifies the number of helix residues contained in N turns) is redundant because A is always equal to 2, and the shortened notations 10_3 and 4_1 conveniently stand for s(2*10/3) and s(2*4/1). On the other hand, the notation 12_3 (intended to indicate that there are 12 CRU, $CH_2CH(C_5H_{11})$, in 3 turns) is not in clear correspondence with the IUPAC notation; in effect, if the equivalence principle were satisfied with $A = 2$ a 12_3 helix would be nothing but a 4_1 helix. Considering that both possible space groups for form II present a crystallographic 2_1 screw axis, which leads to an asymmetric unit of six CRU, Noether's 12_3 notation should correspond crystallographically to a s(12*2/3) symbol.

Noether did not verify its hypothesis of such an unusual helix by structure factor calculations: chain conformation, side group conformations, and orientation of the helix within the unit cell remained undefined. Therefore, the following questions arise: what exactly is the nature of the geometrical difference among units, and why does this difference appear?

As the reexamination of this intriguing problem seemed to us worthwhile, we have undertaken a novel study of *i*-PVCP based on the analysis of fiber diffraction spectra and on potential energy calculations of both isolated and packed chains, beginning with form II. Diffraction patterns were recorded using the image plate technique,[6] which allowed quantitative evaluation of diffracted intensity and structure factors. A model for this complex structure has been set up, assuming geometrical equivalence with $A = 6$, therefore reducing the number of independent carbon atoms from 42 to 21 and changing the line symmetry symbol from s(12*2/3) to s(6*4/3). Notwithstanding the poor crystallinity and the scarcity of data, the main features of the model turn out to be rather well-defined.

Experimental Section

i-PVCP has been polymerized following the same procedure discussed in ref 7. Fiber samples were obtained using a film cast from a chloroform solution. Films 0.1−0.2 mm thick were stretched with an Instron automated material testing system, at a temperature of 120 °C with a strain rate of 10 mm/min. The X-ray fiber diffraction pattern was quite similar to that published by Noether for form II, but some reflections of form III were also observed. The latter disappeared after annealing for 3 h at 170 °C.

Oriented samples were examined using both photographic methods and image plate recording techniques.[6] In both cases fiber patterns were recorded under vacuum by means of a cylindrical camera of 57.30 mm radius, using Cr Kα radiation and a graphite monochromator. The exposed image plate of the final sample was processed by the Fuji-BAS 1800 image plate reader, choosing 100 μm × 100 μm pixel size (Figure 1). Integrated intensities were obtained from the digitized fiber pattern by using a computer program that draws peak by peak a family of equispaced level lines from the top to the background level (automatically singled out) and evaluates the integrated intensities as the summation of the areas enclosed in the level lines.[8] By applying the standard corrections for the Lorentz[9] and polarization factor,[10] a list of observed structure factors was obtained (Table 1).

Molecular and crystal structure modeling, calculations of structure factors, and verification of crystal packing were performed using the TRY program written by one of us[11] (TRY

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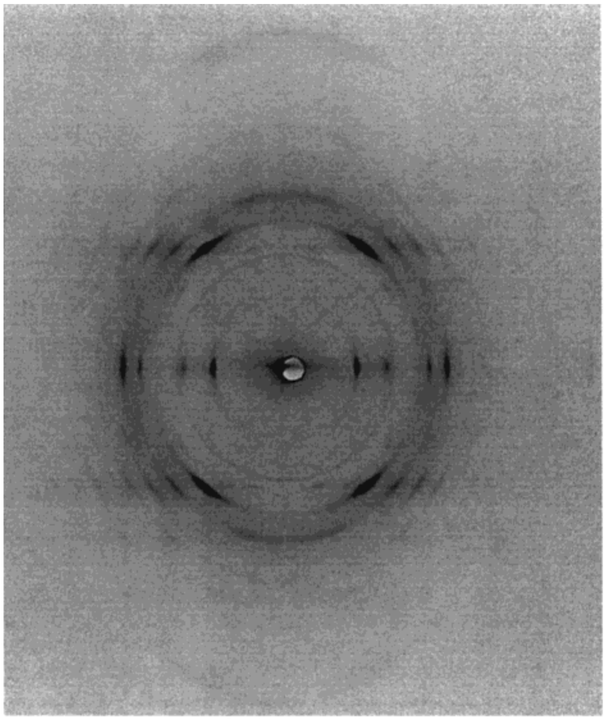

Figure 1. Fiber diffraction pattern of the Cr Kα radiation (with a graphite monochromator) from a sample of form II of *i*-PVCP, recorded by a Fuji image plate mounted on a cylindrical camera (57.3 mm radius) operated under vacuum.

is an interactive computer program which, making use of internal coordinates and overall roto-translation coordinates, assists in model building, model optimization, calculation of structure factors, check-up of packing, least-squares refinement, etc.). Potential energy calculations were performed building molecular models with TRY and computing the energy according to the MM3 force field[12] as coded in the TINKER package.[13]

A finite chain has been considered either isolated or surrounded by its eight nearest neighbors to simulate the crystal environment. In the two cases the chain was composed by 18 and 30 CRU, respectively. We computed the energy values of the six central units, which are poorly influenced by end effects. The energy values reported refer to a mole of CRU: $-CH_2CH(C_5H_{11})-$.

Preliminary Considerations

The fiber diffraction spectrum obtained by us is fully consistent with the unit cell proposed by Noether for form II: tetragonal body-centered lattice with $a = b =$ 20.14 Å and $c =$ 19.60 Å. The observed[2] density (0.954 g cm^{-3}) is well reproduced by this cell considering 4 × 12 CRU (0.964 g cm^{-3}). The indexed reflections (only $h + k + l = 2n$ are present) are reported in Table 1. Possible space groups are $I4$ (homochiral helices) or $I\bar{4}$ (heterochiral helices).

The identity period obtained from the X-ray fiber diffraction pattern (19.60 Å) is well compatible with a sequence of 12 $CH_2CH(C_5H_9)$ units; the value 19.60/12 = 1.63 Å is close to the helix pitch observed for other 4_1 helices of *i*-poly(vinylcycloalkanes) such as forms I of poly(vinylcyclobutane), 1.73 Å,[7] and poly(vinylcyclohexane), 1.62 Å.[22] One observes, however, a marked strength of the $hk0$ and $hk3$ layers as if the helix would be roughly 4_1. These findings suggested the idea that the chain conformation could be close to 4_1 for the backbone atoms and that the more complex s(6*4/3) helix could result from a variable orientation of cyclopentyl side groups and/or a variable conformation of the rings themselves.

Table 1. Bragg Indices, *d* Spacings (Å), and Squared Structure Factors for Form II of *i*-PVCP (Fiber Spectrum)[a]

hkl	d_{obs}	d_{calcd}	F_{obs}^2	F_{calcd}^2
110		14.24		0
200	10.12	10.07	1601	1648
220	7.14	7.12	445	462
130 + 310		6.37		0
400	5.05	5.04	816	631
420 + 240	4.52	4.50	2905	2913
330		4.75		0
150 + 510		3.95		0
440		3.56		5
820 + 280		2.44		163
101		14.05		96
121 + 211		8.18		59
301		6.35		21
321 + 231		5.37		27
141 + 411	4.73	4.74	14	4
112		8.07		90
202		7.02		3
222	5.78	5.76	29	4
312 + 132	5.31	5.34		220
402	4.46	4.48	13	31
152 + 512		3.66		83
332	4.31	4.27		27
422 + 242	4.10	4.09		30
103	6.18	6.21	24	2
213 + 123	5.28	5.29	4531	4552
303	4.68	4.68	557	247
233 + 323	4.25	4.24	482	437
143 + 413	3.94	3.91	72	96
433 + 343 + 503	3.44	3.43	*	600
523 + 253	3.26	3.24		15
613 + 163		2.95		35
114	4.62	4.63	74	86
314 + 134	3.87	3.88	*	366

[a] For overlapped reflections, cumulated F^2 values are given. The isotropic thermal parameter B_{iso} (adjusted by trial) is 20 Å^2. F^2 values are in (electron/unit cell)^2 (48 CRU). F_{obs}^2 are given only for the reflections whose integration was possible; two weak reflections, discernible but nonintegrable, are marked with an asterisk.

As the helix repeat consists of 3 turns with 4 units per turn, the simplest way for obtaining a s(6*4/3) helix is that of a sequence of 3 conformations regularly repeating ...*ABCABC*.... If each turn is enhanced by an horizontal brace, one has (note that the fourth turn is identical to the first one)

$$\ldots\overbrace{ABCA}\overbrace{BCAB}\overbrace{CABC}\overbrace{ABCA}\ldots$$

The 3 conformations should not be necessarily different. For instance, also the sequence ...*ABAABA*... gives rise to a s(6*4/3) helix:

$$\ldots\overbrace{ABAA}\overbrace{BAAB}\overbrace{AABA}\overbrace{ABAA}\ldots$$

Considering rototranslational invariance, the n^3 three-unit combinations obtainable from n different conformations of the side groups reduce to n 4_1 helices and $(n^3 - n)/3$ s(6*4/3) helices.

Side Group Conformations

As far as the conformations of the cyclopentyl rings is concerned, one can refer to the simpler case of cyclopentane. As is well-known, this molecule is not planar. Long ago, Kilpatrick, Pitzer, and Spitzer[14]

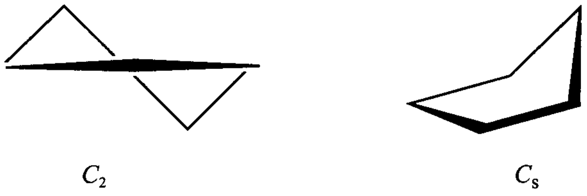

Figure 2. Two distinguishable conformation of a cyclopentyl ring. The left one has C_2 symmetry, while the right one has C_s symmetry.

showed by thermodynamic and spectroscopic arguments that the two degenerate out-of-plane vibrational normal modes of a planar cyclopentane have a very low frequency, thus leading to continuous out-of-plane displacements z_j's of the atoms of the ring ($j = 1, 2, ..., 5$), which can be calculated according to the equation

$$z_j = \sqrt{\frac{2}{5}}q \cos 2\left(\frac{2\pi}{5} j + \phi\right)$$

where q is the oscillation amplitude and ϕ is a phase angle running in the range $0-2\pi$. The potential energy of the cyclopentane is so flat that, during such low-amplitude motion, 20 energy minima of either C_2 or C_s symmetry are found (Figure 2).

According to the "pseudorotation" model, the molecule fluctuates very rapidly between these minima, which correspond to $\phi = 0°, 18°, 36°, ..., 342°$. NMR and Raman measurements have led support to such a model.[16,17] In effect, C_s and C_2 conformers of cyclopentane are practically degenerate, and their interconversion through the pseudorotation pathway is almost barrierless ($E < 0.01$ kcal mol^{-1}).[17,18] A slight improvement of this first pseudorotation model was introduced by Adams, Geise, and Bartell, who imposed fixed lengths of the C−C bonds during pseudorotation;[16,19] hereafter, we will refer to such improved model. The adoption of a pseudorotation model, together with the fact that experimental estimates of q span a narrow range (0.43−0.47 Å), gives the practical advantage of defining the conformation of the ring in terms of the single variable ϕ. The extreme flexibility of the cyclopentyl ring should discourage to consider the above different conformations as possible candidates to solve our problem; however, it should also be considered that the pseudorotation can be hindered by interactions with other groups of the same chain or of nearby chains in the solid state.

A second but reasonably more important source of unlikeness for the side groups is the group-to-chain orientation, which can be defined by the torsion angle $\chi = \mathrm{H_{ring}-C_{ring}-C_{chain}-H_{chain}}$ (Figure 3). Since helicized chains turn into their mirror images (of opposite handedness) if the signs of all torsion angles are changed, T, G^+, G^- values for χ angles turn into T, G^-, G^+, upon changing helix chirality. To discuss the side group orientation independently from the chirality of the chain, it is practical to distinguish the three conformers χ_T, χ_G, and $\chi_{\bar{G}}$, defined in analogy to Flory's nomenclature.[20]

Indicating as C_α and C_β, the carbon atoms which are in α and β position with respect to the main chain methine carbon, one observes that in both the χ_T and $\chi_{\bar{G}}$ conformers a carbon atom of the chain and one of the C_β's of the side group undergo a strongly unfavorable 1,3-syndiaxial interaction, while such an interaction is absent in conformer χ_G. On the other hand, in both χ_G and $\chi_{\bar{G}}$ states one of the two C_β's of the side group undergoes two unfavorable *gauche* interactions. Considering the standard energetic ordering of conformational effects,[20] one expects that the energy scale of the rotamers shown in Figure 3 should be $E(\chi_G) < E(\chi_T) < E(\chi_{\bar{G}})$. Indeed, in isotactic poly-α-olefins bearing an acyclic side group with a tertiary C_α only the χ_G conformation has been observed in the solid state.[21] However, with a cyclic side group the situation is more delicate. On one hand, the χ_G conformer has been observed for *i*-poly(vinylcyclohexane), for which the energy of χ_G has been estimated to be ∼2 kcal mol^{-1} lower than that of χ_T.[22] On the other hand, the χ_T conformation was recently observed in our laboratory for form II of *i*-poly(vinylcyclobutane).[7] We checked by molecular mechanics calculations that the χ_T conformer is the most stable one (by more than 2 kcal mol^{-1}). Indeed, the puckering of the four-membered ring reduces the severity of the 1,3-syndiaxial interaction. Considering these different cases, it can be thought that for *i*-PVCP both χ_T and χ_G conformations could be energetically accessible.

Conformational Analysis in the Isolated Chain and Model Optimization

The above hypothesis has been investigated by means of potential energy calculations (see details in Experimental Section). Initially, we built a 4_1 right-handed chain model (all units geometrically equivalent) imposing standard values for C−C bond lengths, C−H bond lengths, and C−C−C angles (1.54 Å, 1.09 Å, and 109°, respectively). Main chain torsion angles θ_1 and θ_2 (Figure 4) were initially set to 83.98° and 207.11°, values which reproduce the angular repeat (90°) and the helix pitch of $c/12$. (These values are not unique,[21,22] but reasonable deviations from their values are not critical in determining the essential features of the energy map presented below.)

The energy of such 4_1 helix was computed as a function of the torsion angle χ and the pseudorotation phase ϕ, varying χ by steps of 10° and ϕ by steps of 18° (that is spanning all C_2 and C_s conformers). The resulting energy map $E(\chi,\phi)$ is shown in Figure 5. One observes two low-energy regions which correspond to the discussed χ_T and χ_G conformations. The two regions are both rather broad with respect to the ϕ angle, but the χ_G region is broader. (The extensions of the two regions are in ∼1:3 ratio if the limit of 1 kcal mol^{-1} is considered.) This points to a more hindered pseudorotation in the χ_T case.

Recalculating the energy map with finer graining (2°), one obtains in the χ_G region two minima (both with $\chi = -67°$ and with $\phi = 54°$ and $-72°$), almost isoenergetic and ∼0.8 kcal mol^{-1} more stable than the χ_T minimum ($\chi = -166°$, $\phi = 0°$). We verified that the energetic features discussed are mainly dictated by ring-to-chain and not by ring-to-ring interactions. In effect, the inaccessible values to ϕ correspond to the ring pointing toward the main chain. The presence of the two similar-energy conformations, χ_T and χ_G, might be a reasonable explanation for the formation of a s(6*4/3) helix provided that the χ rotation is sufficiently hindered. Therefore, besides the two 4_1 helices, $(\chi_T)_4$ and $(\chi_G)_4$, we built two kinds of s(6*4/3) helices: $(\chi_T\chi_T\chi_G)_4$ and $(\chi_G\chi_G\chi_T)_4$. In all cases the pseudorotation angle ϕ was initially set to $\phi = 0$ for χ_T and tried between −90° and 90° for χ_G. We tested whether the pseudorotations of the rings of the same chain were correlated in the case of s(6*4/3)

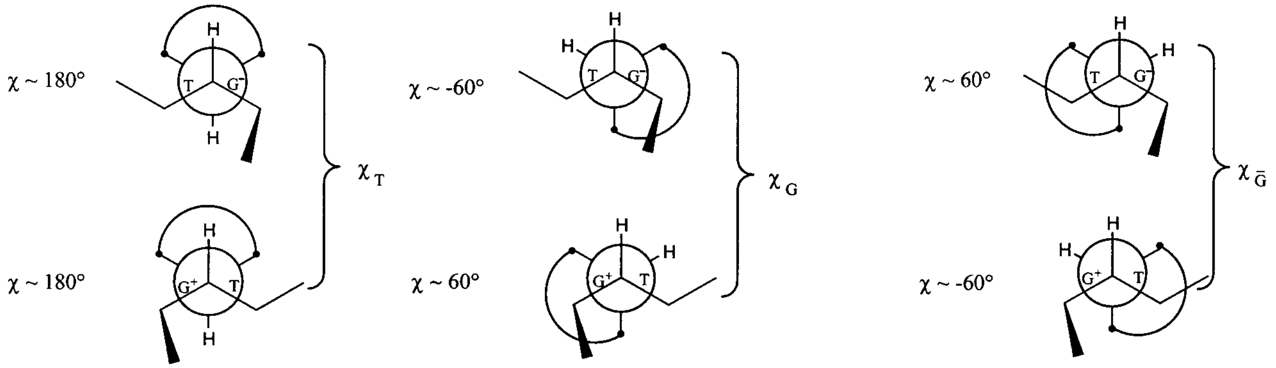

Figure 3. Newmann projections of the three rotamers expectable from a 3-fold rotational barrier for the ring-to-chain torsion angle χ in the case of a right-handed (top) and a left-handed (bottom) helix of an isotactic vinyl polymer with a cyclic side group.

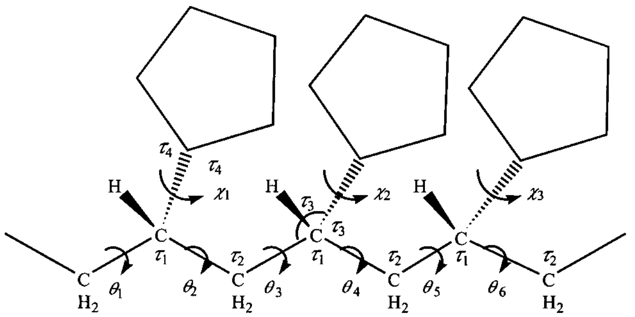

Figure 4. Definitions of the relevant torsion and valence angles, which were varied to set up models of 4_1 and s(6*4/3) helices of *i*-PVCP. The chain-to-ring torsions χ are defined with respect to the two hydrogen atoms bonded to the ring and to the chain methine. In the 4_1 helices and in the first models of s(6*4/3) helices the 4_1 symmetry was imposed for the backbone for the main chain ($\theta_1 = \theta_3 = \theta_5$, $\theta_2 = \theta_4 = \theta_6$).

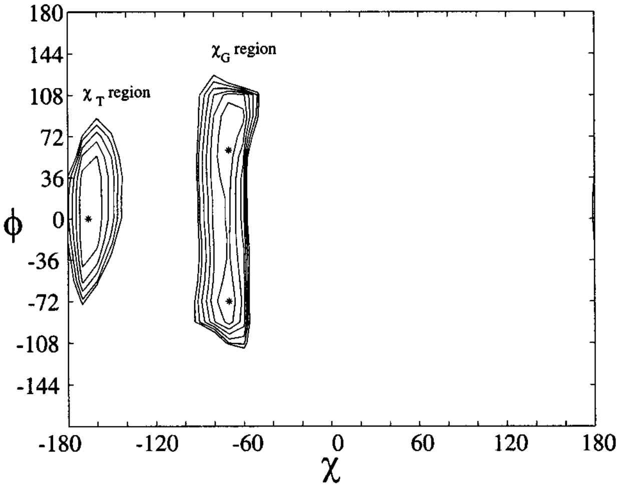

Figure 5. Potential energy map of a 4_1 helix as a function of the ring-to-chain torsion χ and the cyclopentyl pseudorotation phase ϕ. The curves are reported at intervals of 1 kcal mol^{-1} of CRU above the absolute minimum of the map. The minima in the low-energy regions (named χ_T and χ_G) are marked with asterisks.

helices, and we found that if the (*i*)-th ring is in the χ_T conformation, the ring ($i - 4$)-th cannot have a χ_G conformation with $\phi \sim -72°$, because the two rings point in opposite directions, producing severe contacts. In other cases we did not observe any severe contacts between (*i*)-th and ($i - 4$)-th rings.

The models with low enough initial energy have been optimized as a function of phases and amplitudes of the rings as well as torsion and valence angles of the ring-to-chain bond and of the backbone chain. The angular repeat of the 4_1 helix was imposed during minimization. The results are resumed in Table 2. As can be observed, the minimization lowered considerably the energy of the $(\chi_T)_4$ chain as compared to the $(\chi_G)_4$. This can be ascribed to the relaxation of the dihedral angles of the main chain. In fact, the increase of the θ_1 angle (cf. Figure 4 and Figure 3) by ~2° lowers the 1,3-syndiaxial interaction. As far as s(6*4/3) helices are concerned, the $(\chi_T\chi_T\chi_G)_4$ helix has an energy close to that of the $(\chi_T)_4$ helix and lower than all the others. Considering the small energy differences, even the $(\chi_G\chi_G\chi_T)_4$ helix should be considered likely.

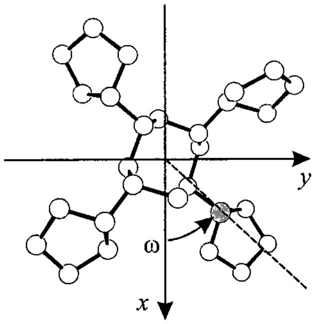

Figure 6. Definition of the overall rotation ω of the chain inside the unit cell. The height of the carbon atom indicated in black defines the variable z_0.

Table 2. Minimum-Energy Values (kcal/mol of CRU) for Optimized Isolated Chains of *i*-PVCP in Different Conformations, Referred to Their Lowest Value (32.8 kcal/mol)

helix	*E* (kcal/mol)
$(\chi_T)_4$	0.0
$(\chi_G)_4$	0.7
$(\chi_T\chi_T\chi_G)_4$	0.0
$(\chi_G\chi_G\chi_T)_4$	1.0

Optimization of Crystalline Structure

The next step in the work has been done considering the packing energies and, in the case of form II, comparing the experimental diffraction pattern with the ones calculated for the two chain models and both possible space groups *I*4 and $I\bar{4}$. In the final stage the fit has been done by using the least-squares method. In a first set of calculations, only two parameters were varied: the rotation angle ω of the chain around its axis and, for the $I\bar{4}$ space group, the height z_0 of the chain in the unit cell (Figure 6). The results obtained in this stage are shown in Table 3. It can be noted that the

Table 3. Calculated Potential Energies (Referred to the Lowest Value 28.7 kcal/mol) and Disagreement Indices for Diffraction Data Obtained for *i*-PVCP According to Different Packing Models and Chain Conformations[a]

helix	$I4_1/a$	$I4$	$I\bar{4}$, 4_1 backbone		$I\bar{4}$, 6*4/3 backbone		$I\bar{4}$, LS refinement	
$(\chi_T)_4$	$E = 0.0$							
$(\chi_G)_4$	$E = 1.7$							
$(\chi_T\chi_T\chi_G)_4$		$E = 7.0$	$E = 1.4$	$R_1 = 0.39$	$E = 5.5$	$R_1 = 0.27$		
$(\chi_G\chi_G\chi_T)_4$		$E = 6.8$	$E = 3.3$	$R_1 = 0.33$	$E = 3.2$	$R_1 = 0.14$	$R_1 = 0.085$	$R_2 = 0.065$

[a] Disagreement indices have been computed as $R_1 = \sum||F_{obs}| - |F_{calcd}||/\sum|F_{obs}|$ and $R_2 = \sum|F_{obs}{}^2 - F_{calcd}{}^2|/\sum(F_{obs}{}^2)$. In case of overlap $|F_{calcd}|$ is the square root of the sum of the overlapped $F_{calcd}{}^2$.

packing obtained with symmetry $I4$, i.e., with homochiral helices, is very poor. Therefore, we choose the $I\bar{4}$ symmetry.

Despite reasonably good packing energy (2.7 and 1.8 kcal mol^{-1} for the $(\chi_T\chi_T\chi_G)_4$ and the $(\chi_G\chi_G\chi_T)_4$ helices), the agreement between calculated and observed diffracted intensities is initially very bad. Therefore, we tried to improve the model, allowing torsion angles of the main chain to be different. This sounds reasonable if one considers that the χ_G and χ_T conformations imply different ring-to-chain distances. In effect (see Table 3), upon minimal changes of these angles, the R_1 values decreased considerably. The two models $(\chi_G\chi_G\chi_T)_4$ and $(\chi_T\chi_T\chi_G)_4$ behave differently, however: for the former one obtains $R_1 = 0.14$ and simultaneously a good packing energy; the best R_1 index of the latter, instead, is worse than that of the former and is even associated with a high energy. Therefore, the $(\chi_G\chi_G\chi_T)_4$ is certainly the only convincing conformation.

The final structure refinement has been attempted by the least-squares method, once again using internal coordinates and the TRY program, which minimizes the disagreement index $R_2 = \sum| F_{obs}{}^2 - F_{calcd}{}^2|/\sum(F_{obs}{}^2)$. In the case of overlap, the sum of the overlapped $F_{calc}{}^2$ was matched with the $F_{obs}{}^2$ value. The minimization was carried out performing repeatedly "block refinement" cycles over 4−5 variables, constraining the pitch and the angular repeat of the helix. As expected from energy calculations, the R_2 minimization is ill-conditioned as far as the phases ϕ and the amplitudes q are concerned. Therefore, we decided to fix the conformation of the rings setting all phases ϕ to zero (see Figure 2) and all amplitudes q to 0.43 Å.[19] In the last refinement steps also the C−C bond lengths were adjusted, using two distinct values for chain backbone and for side groups. The rather surprising result was that the first bond length (initially 1.54 Å) is only marginally changed (1.53(2) Å), while the second bond length reduces to 1.46(1) Å. This result is in line with the easy pseudorotation of the rings. Indeed, it is well-known that X-ray determination of bond lengths is affected by librational shortening,[23] and many examples of structures with cyclopentyl fragments with C−C bond well shorter than 1.46 Å can be easily found in single-crystal crystallographic databases.[24] Even the unusually small value of the valence angle τ_4 is not particularly significant due to conformational disorder. The final values of disagreement indices obtained are $R_1 = 0.085$ and $R_2 = 0.065$. The final values of the internal coordinates, with the associated standard errors, are given in Table 4, and the resulting crystal structure is shown in Figure 7.

All C...C packing contacts are among cyclopentyl rings. Some of them are rather short (e.g., 3.44 Å), but the above-discussed disorder in cyclopentyl groups makes of little significance this finding. Furthermore, it can be observed that varying by only 1° the angle ω (a variation of just 1.2 σ) the shortest packing C...C contact rises to 3.60 Å.

Table 4. Internal Coordinates of the Final Model of Form II of *i*-PVCP[a]

b_1	1.53(2) Å	θ_4	80.7(6)°
b_2	1.46(2) Å	θ_5	−145.8(19)°
τ_1	113.4(7)°	θ_6	84.1(11)°
τ_2	110.4(10)°	χ_1	70(6)°
τ_3	112.2(15)°	χ_2	72(8)°
τ_4	105.0(14)°	χ_3	171(9)°
θ_1	−152.5(11)°	w	67.3(6)°
θ_2	81.5(5)°	z_0	5.48(12) Å
θ_3	−148.7(7)°		

[a] The C−C bond lengths are b_1 for main chain bonds and b_2 for cyclopentyl rings, while the other coordinates given in the table are defined in Figures 4 and 6. C−H bond lengths are fixed to 1.08 Å and C−C−H bending angles to 109°. The phases ϕ and the amplitudes q of the rings are set to 0 and 0.43 Å, respectively.

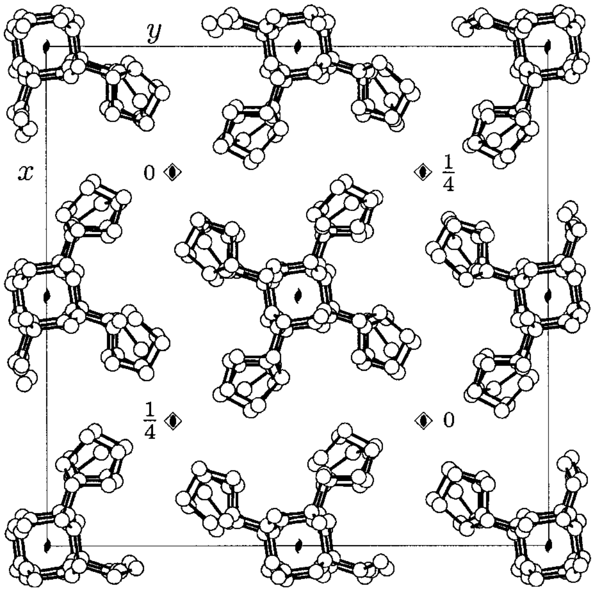

Figure 7. Crystal packing of *i*-PVCP. Note that the origin of the unit cell ($I\bar{4}$) is placed differently from the usual convention.

By inspection of the final observed/calculated structure factor fit (see Table 1), two specific disagreements are apparent: the (433) + (503) + (343) and (314) + (134) reflections which, although visible, were not sufficiently strong to be correctly integrated; their computed values are rather high. It must be noted that both these reflections were classified as "strong" by Noether.[2] In the future investigations planned for the other crystalline forms of *i*-PVCP, we hope to get more sharp diffraction spectra and to perform a more accurate determination of diffracted intensities also for form II.

Conclusions

The model proposed here for form II of poly(vinylcyclopentane) consists of a main chain slightly different from a 4_1 helix with side groups following one another with a regular sequence of 3 conformations, mainly different for their torsion angles χ (Figure 4). This structure is rather uncommon since macromolecular polymorphs differ usually for packing and/or for the main chain conformation. While it is well-known that different dispositions of the side groups can give rise to different liquid crystalline phases,[25] different crystalline phases ascribable to side groups are certainly rarer[26,27] and, to the best of our knowledge, have not been reported for vinyl polymers.

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