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Crystalline Structure of Isotactic Poly(vinylcyclobutane) from Fiber Diffraction Spectra

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ABSTRACT: The crystalline structure of isotactic poly(vinylcyclobutane), claimed to be tetragonal, has been revised on the basis of fiber diffraction spectra. The chain symmetry is 4_1, as already assessed, but the conformation is different (the identity period is 6.91 Å and not 6.60 Å). The space group is the orthorhombic $P2_12_12_1$ with lattice constants $a = 17.14$ Å, $b = 8.99$ Å, and $c = 6.91$ Å. The excellent quality of the oriented samples allowed a full structure analysis and refinement. Integrated diffraction intensities, from a stretched fiber, measured with a Fuji image plate detector, have been utilized in a constrained refinement (the helix was assumed strictly of 4_1 symmetry and the C−C bond lengths were set to 1.54 Å) obtaining a final R index of 15%. The refined chain bond angles are 103 and 107°, and the chain torsion angles are 165 and 273°.

Introduction

Several isotactic vinylic polymers with a cycloalkyl side group were synthesized using Ziegler−Natta catalysts in the years 1960 and later by Overberger et al.,[1] and they were also studied by X-ray diffraction. Among these polymers was isotactic poly(vinylcyclobutane) (*i*-PVCB).[2] Years later a tetragonal unit cell with $a = 34.12$ Å and $c = 6.6$ Å was proposed[3] for this polymer on the basis of a few Bragg reflections given in ref 2. The proposed unit cell was almost the same as the one of isotactic poly(3-methyl-l-butene),[4] suggesting that the two polymers were isostructural. It is worth noting that even the structure of poly(3-methyl-1-butene) has been subsequently revised and a new unit cell assigned.[5]

Recently *i*-PVCB was again synthesized by us. The new material is highly crystalline and gives a powder diffraction pattern with sharp Bragg diffraction peaks after annealing; furthermore the new material can be oriented well by stretching.

The fiber diffraction pattern shows well-resolved Bragg peaks, including the few peaks already observed by Overberger.[2] The spectrum however contradicts the proposed tetragonal unit cell.[3] Moreover there is an evident polymorphism: unoriented samples, obtained by quenching from the melt and subsequent annealing, give a powder diffraction pattern which is different from that of simply annealed samples (the latter is consistent with the fiber). The structure analysis of the unoriented samples, based on powder diffraction spectra, will be reported elsewere.

This article concerns the new synthesis of *i*-PVCB and the study of fibrous samples only. The use of the imaging plate by Fuji for performing diffraction measurements gave data of excellent quality; this allowed performing an accurate structure refinement.

Experimental Section

Synthesis. Isotactic poly(vinylcyclobutane) was obtained by polymerization using a commercial heterogeneous catalyst: $TiCl_4$ supported on $MgCl_2$ treated with dibutylphthalate. A 0.03 g amount of the catalyst was dispersed (under nitrogen atmosphere) in a solution of 0.4 mL of $Al(i\text{-}C_4H_9)_3$ and 0.03 mL of $(t\text{-}C_4H_9)_2Si(OCH_3)_2$ in 5 mL of anhydrous toluene. After addition of 1 mL of vinylcyclobutane the suspension was stirred for 48 h at 50 °C. The reaction was interrupted by pouring the mixture into acidified methanol. The polymer was separated by filtration. Subsequently it was washed with acidic methanol and dried at 80 °C. The yield was 0.4 g of crystalline polymer.

Preparation of Samples. *i*-PVCB amorphous samples were obtained by quenching compression moulded samples (melting temperature 228 °C) in liquid nitrogen. Highly crystalline unoriented samples were obtained either by annealing the raw product or by annealing amorphous samples quenched from the melt. Highly crystalline oriented samples were obtained by stretching amorphous samples (draw ratio 400%) at 70 °C (glass transition temperature is ~60 °C) and annealing the fibers at 210 °C for 20 h.

Diffraction Measurements. Oriented samples were examined using both photographic methods and recording techniques based on the Fuji imaging-plate system (BAS 2500). In the former case the fiber spectra were recorded by means of a cylindrical camera of 57.30 mm radius under vacuum, using graphite-monochromated Cu Kα and Cr Kα radiation. These films were used only for indexing the Bragg reflections and not to extract intensities. For intensity data collection the fiber spectrum (see Figure 1) was recorded by using graphite-monochromated Mo Kα radiation, and a flat Fuji image plate detector was placed orthogonal to the incident beam with a plate-to-specimen distance of 100 mm. The exposition time was 6 h at the power 50 kV × 25 mA. The exposed imaging plate was processed by the Fuji-BAS 2500 image plate reader and TINA software.[6]

The pixel size was choosen as 50 μm × 50 μm.

Integrated intensity data were obtained from the digitized fiber spectrum by using a homemade computer program.[7] This program isolates elliptical regions of the spectrum (with the

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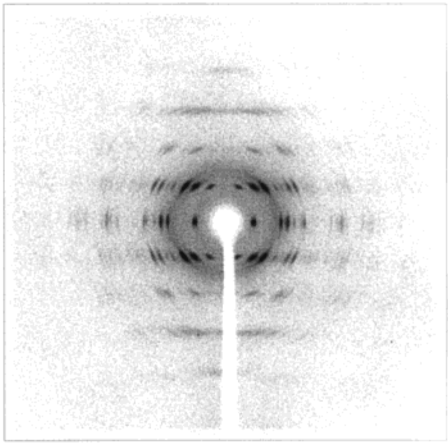


Figure 1. Digital image of the fiber diffraction spectrum of poly(vinylcyclobutane) recorded by a Fuji imaging plate, Mo Kα radiation, flat film camera, and film to sample distance 10 cm.

ellipsis parameters tunable case by case) and performs integration by summing the intensity over all pixels contained in the isolated regions, after subtracting the background value. Lorentz–polarization correction factors were applied on the integrated values. In case of partial overlap the intensities were obtained first integrating over the whole region and then dividing the result in parts proportional to the values obtained by integration in restricted areas.

As can be inferred from Table 1, we were able to extract integrated intensities of many more reflections from the imaging plate than could be measured on the photographic films. In particular this includes the measured $l = 2$ reflections which are all weak. The reasons for the increased sensitivity originate in several advantages of imaging plates over photographic films.[8] The quantum efficiency of IP is one, irrespective of the radiation used, the dynamic range is much larger than for films, and most importantly, this dynamic range is extended toward lower intensities, thus allowing the measurement of weak reflections.

Results and Discussion

Unit Cell, Space Group, and Chain Model. From the position of intensity maxima on the photographic films obtained with Cr Kα radiation, a right-angle unit cell was derived with the aid of an interactive computer program.[7] Cr Kα radiation was preferred to improve resolution; 14 equatorial and 20 upper layer reflections were measured. The resulting lattice constants were $a = 17.14$ Å, $b = 8.99$ Å, and $c = 6.91$ Å. The indexed reflections are the one listed in Table 1. The systematic absence of odd $h00$ and $0k0$ was observed. The absence of 001 was detected from the tilted fiber spectrum.

The observed c edge (chain repeat) close to values observed in other vinyl polymers with 4_1 helices[3–5,9,10] supports the previously proposed helix conformation. Indeed by assuming 1.54 Å chain bond lengths and 110° chain bond angles the observed identity period and the 90° angular repeat are well reproduced if chain torsion angles are set to ~156 and ~277° (both these angles are plausible). Moreover the calculated density agrees with the measured one (1.01 g cm^{-3}, flotation) if 8 repeating units per cell are present ($D_c = 1.03$ g cm^{-3}).

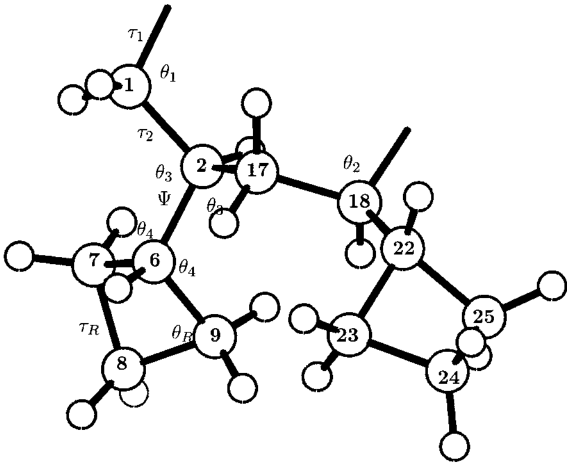
Thus the most likely hypothesis is that the crystal belongs to orthorhombic system and has a primitive space group with 4 general positions (a pair of consecutive units cannot be related by symmetry since 4_1 is not a symmetry element in orthorhombic system). To conciliate this with the 4_1 chain model, the 4 general positions must include a 2_1 symmetry.

Table 1. Bragg Reflections for Isotactic Poly(vinylcyclobutane) Observed on the Photographic Film (Cr Kα Radiation) and/or on the Fuji Imaging Plate (the Former Used Only for Indexing)[a]

h	k	l	F_{obs}^2	F_{calc}^2	d_{obs}	d_{calc}
2	0	0	232	141	8.63	8.57
1	1	0	206	247	7.98	7.96
1	2	0	477	453	4.34	4.35
0	2	0		11		4.49
4	0	0		7		4.28
4	1	0	516	410	3.88	3.87
2	2	0		103	3.99	3.98
3	2	0	131	75	3.53	3.53
5	1	0	40	70	3.20	3.20
4	2	0	69	88	3.11	3.10
6	0	0		2	2.86	2.86
2	3	0		6	2.82	2.83
6	1	0		1	2.73	2.72
5	2	0		33	2.73	2.72
7	1	0	31	20	2.37	2.36
6	2	0		0		2.41
0	4	0	65	35	2.24	2.25
5	3	0		6		2.26
1	4	0		1		2.23
2	4	0	168	52	2.17	2.17
8	0	0		40		2.14
7	2	0		1		2.15
3	4	0	21	5		2.09
8	1	0		1		2.08
6	3	0		1		2.07
9	1	0	97	73		1.86
5	4	0		18		1.88
7	3	0		6		1.90
1	5	0	140	89		1.79
6	4	0		11		1.77
2	5	0		5		1.76
9	2	0		0		1.75
10	0	0	19	38		1.71
10	1	0		7		1.68
3	5	0		4		1.71
6	5	0	33	8		1.52
11	1	0		7		1.53
1	0	1	62	62	6.40	6.41
2	0	1	355	201	5.37	5.38
1	1	1		146	5.21	5.22
0	1	1		23		5.48
2	1	1	692	702	4.59	4.62
3	1	1	51	74	3.94	3.95
1	2	1	11	42	3.65	3.68
0	2	1		3		3.77
4	0	1		1		3.64
4	1	1	183	155	3.37	3.37
2	2	1		35	3.43	3.45
3	2	1	326	311	3.14	3.14
5	1	1		3	2.91	2.91
4	2	1		4	2.83	2.83
0	3	1		16	2.75	2.75
1	3	1		4	2.72	2.71
2	3	1		8	2.63	2.62
6	1	1		5	2.54	2.53
5	2	1		36		2.54
3	3	1		11	2.47	2.48
7	0	1		26	2.31	2.31
4	3	1		29	2.31	2.31
7	1	1		29	2.24	2.24
5	3	1	21	22	2.15	2.14
1	4	1		10		2.12
0	4	1		7		2.14
2	4	1	33	28		2.07
7	2	1		35		2.05
8	0	1		12		2.05
0	1	2	40	13		3.22
1	1	2		23	3.17	3.17
2	0	2		5		3.20
2	1	2	8	15		3.02
3	0	2		0		2.96
0	2	2	83	15		2.75
4	0	2		16		2.69
1	2	2		20		2.70
4	1	2	16	30		2.58
2	2	2		8		2.61
6	2	2	27	22		1.98
4	3	2		7		2.00
7	0	2		0		2.00
5	3	2	59	39		1.89
1	4	2		15		1.87
0	4	2		5		1.88
6	3	2	32	23		1.77
8	1	2		8		1.78
3	4	2		1		1.79
0	1	3	13	25		2.23
1	1	3		0		2.21
2	0	3		1		2.22
2	1	3	64	60		2.16
3	0	3		14		2.14
3	1	3	7	26		2.08
2	2	3	16	23		1.99
4	1	3		9		1.98
4	2	3	35	15		1.85
5	1	3		5		1.87
2	3	3	11	3		1.79
5	2	3		9		1.76
6	1	3		4		1.76

[a] If column d_{obs} is empty, the reflection was not observed in the Cr spectrum. Note that reflections overlapped on Fuji plate (grouped between rules) may be resolved onto the Cr spectrum. In such cases distinct values are given for d_{obs}; else d_{obs} is repeated. F_{obs}^2 and F_{calc}^2 are in arbitrary units. F_{calc}^2 are those of structure B.

With rejection of the space groups having 2-fold axes or mirror planes as packing symmetry elements (these are notoriously very bad packing symmetries for helicized chains) only 3 possibilities arise: $P2_12_12_1$ (No. 19), $Pca2_1$ (No. 29), and $Pna2_1$ (No. 33). In the first case



Torsion angles: τ_1 = C1–C2–C17–C18
τ_2 = C2–C17–C18–C22
Ψ = C1–C2–C6–C7
τ_R = C6–C7–C8–C9

Bond angles: θ_1 = C2–C17–C18
θ_2 = C1–C2–C17
θ_3 = C1–C2–C6 = C17–C2–C6
θ_4 = C2–C6–C7 = C2–C6–C9

Figure 2. Internal coordinates (i.c.) for isotactic poly(vinylcyclobutane). The molecular model (two chemical units) is shown. The independent bond angles (4 values) and independent torsion angles (four values) are defined in the drawing. Furthermore the i.c. include the overall rotation Φ (angular cylindrical coordinate Φ of C6 atom) and the overall translation z_0 (z-coordinate of C6 atom). The labels of the C atoms are also indicated (see Table 3).

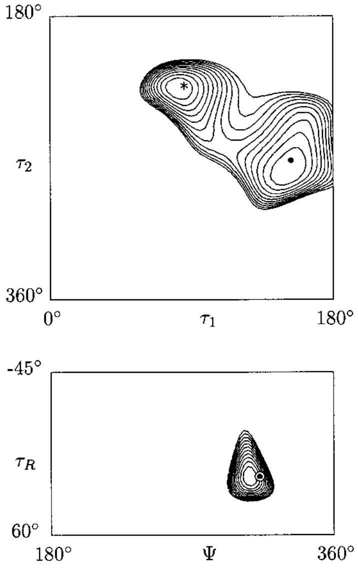


Figure 3. Potential energy maps vs chain torsion angles τ_1, τ_2 (top) and vs internal torsion angles Ψ, τ_R (bottom) for the isolated chain. Contour lines are traced every 0.05 kcal/mol (1 C_6H_{10} unit). The energy has been computed using the functions suggested by Halgren,[16] considering the van der Waals contributions, the torsional contributions, and the bending contribution only for the cyclobutyl bond angles. A bullet (●) superimposed indicates the actual structure. An asterisk (∗) indicates another combination of torsion angles of lower energy (0.50 kcal/mol lower) corresponding to a ∼7/2 helix. In both cases the internal coordinates kept fixed are those of Table 2. The nonplotted regions are devoid of minima.

helices are all of the same chirality; in the other two cases crystallites should contain both left- and right-handed helices, an outcome more frequent in polymeric structures. Anyway, systematic extinctions foreseen in the last two cases are contradicted by the well-resolved Cr Kα spectrum, while they confirm $P2_12_12_1$.

Table 2. Internal Coordinates for *i*-PVCB Obtained by Least-Squares Refinement with Standard Deviations in Parentheses[a]

i.c.	A	B	C
θ_1 (deg)	110	103(2)	
θ_2 (deg)	110	107(5)	
θ_3 (deg)	110	107(4)	113.9(18) 107.0(26)
θ_4 (deg)	110	128(3)	135(1) 130(3)
τ_1 (deg)	156	165(3)	
τ_2 (deg)	277	273(1)	
Ψ (deg)	−60	−47(8)	−20(10) −35.8(10)
Φ (deg)	−17	−21(1)	−27(1)
z_0 (Å)	1.30	1.27(6)	1.08(6)
τ_R (deg)	27	21(7)	14(4)
θ_R (deg)	86	88	89
B_{iso} (Å^2)	6.0	6.00	6.10
R_1	0.22	0.152	0.146
R_2	0.28	0.178	0.176

[a] In column A the coarse values obtained by visual adjustment are given. Column B refers to the refinement done within the strictly 4_1 model (10 parameters). Column C refers to the refinement done waiving the 4_1 condition for side groups only and retaining the same cyclobutane internal conformation. In both cases the least-squares refinement has been done by imposing two constraints: fixed value 6.91 Å to the identity period and the value 90° for the angular repeat.

Structure Analysis. This structural problem was not faced considering atomic coordinates (there are 12 independent carbon atoms leading to 36 independent positional parameters; this large number of parameters cannot be refined against the 37 observed intensities) but in terms of internal coordinates (i.c.). In fact a coarse structure analysis can be done by assuming strict 4_1 chain symmetry, fixed bond lengths and angles, chain torsion angles 156 and 277° (which reproduces the observed repeat; see above), and the 27° torsion angle for the C_4 ring (experimental value coming from NMR spectra[11]). Figure 2 shows the resulting molecular model. At this level three independent i.c. need to be determined: the chain overall rotation angle Φ; the chain shift z_0 along chain axis; the torsion Ψ around the bond between the chain and the cyclobutyl group. Adjustment by trial of Φ, z_0, and Ψ was done using TRY,[12] a general program for modeling polymeric structures by systematic use of internal coordinates and using as figures of merit the R_1 and R_2 disagreement indices of observed−calculated structure factors and the lattice energy. TRY allows performing systematic exploration of variable space, monitoring both packing energy and R indices. As described in Table 2, column A, one obtains a realistic coarse model with $\Phi = -1600°, \Psi = -60°$, and $z_0 = 1.30$ Å, with an R_1 index of 0.22 and quite reasonable packing distances.

Structure Refinement from Fiber Data. Structure refinement was done by considering again internal coordinates but a more flexible model in which also chain torsion angles and bond angles are varied. There are 10 independent i.c.: the above mentioned Φ, Ψ, and z_0 plus the torsion angles τ_i and the bond angles θ_i as defined in Figure 2. Bond-length refinement was not

Table 3. Fractional Coordinates of the Asymmetric Unit of *i*-PVCB for Model A (4_1 Molecular Symmetry)[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
C1	0.0534	−0.1000	0.4595
C2	0.0595	−0.0673	0.2413
H3	0.0829	−0.2023	0.4964
H4	0.0777	−0.0105	0.5443
H5	0.0076	−0.1147	0.1776
C6	0.1438	−0.1074	0.1846
C7	0.1914	−0.2460	0.2407
C8	0.2463	−0.2107	0.0702
C9	0.1797	−0.1184	−0.0191
H10	0.1322	−0.0090	0.2696
H11l	0.1593	−0.3482	0.2199
H12	0.2198	−0.2345	0.3795
H13	0.2604	−0.3080	−0.0146
H14	0.2955	−0.1432	0.1127
H15	0.1994	−0.0122	−0.0732
H16	0.1442	−0.1824	−0.1176
C17	0.0525	0.1018	0.2095
C18	0.0353	0.1134	−0.0087
H19	0.1061	0.1580	0.2464
H20	0.0055	0.1482	0.2943
H21	0.0602	0.0145	−0.0724
C22	0.0563	0.2741	−0.0654
C23	0.1290	0.3650	−0.0093
C24	0.1105	0.4696	−0.1798
C25	0.0621	0.3427	−0.2691
H26	0.0047	0.2521	0.0196
H27	0.1826	0.3038	−0.0301
H28	0.1230	0.4191	0.1295
H29	0.1616	0.4965	−0.2646
H30	0.0751	0.5634	−0.1373
H31	0.0064	0.3802	−0.3232
H32	0.0957	0.2748	−0.3676

[a] The hydrogen atoms were calculated by assuming C−H bond lengths 1.08 Å, local C_{2v} symmetry for all CH_2 groups with H−C−H angles 108° (115° in the ring; see ref 10), and C−C−H angles for CH groups equal to the corresponding C−C−C angles (θ_3 and θ_4).

attempted, instead. The D_{2d} symmetry in the cyclobutane ring was maintained. The bond angle θ_R within the cyclobutane ring is a function of τ_R if one assumes that the cyclobutane ring maintains the D_{2d} symmetry. The mentioned i.c. are not however strictly independent quantities since the four values θ_1, θ_2, τ_1, and τ_2 must obey to two constraints: a fixed axial repeat per monomeric unit (one-fourth of the *c* cell edge) and a fixed angular helix repeat of 90°. Structure refinement for *i*-PVCB, against the intensity data, was performed, yet using TRY. This program applies the least-squares method[13] adjusting just the i.c. rather than atomic coordinates.

The minimized quantity was $\sum_k w_k(F_o^2 - F_c^2)^2$ with unitary w_k values, whereby for overlapping reflections the integral F_o^2 was used together with the sum of F_c^2 for the reflection contributing. For taking into account the mentioned constraints on axial and angular repeats the program makes use of the Lagrange multiplier method.[14]

Refinement was done first adjusting the i.c. controlling the chain backbone conformation, then the other, and at last all i.c. altogether. Refinement cycles were iterated till all shifts become negligible (4−5 cycles are sufficient). The results are listed in Tables 2 and 3. It is evident that all bond angles are close enough to the idealized 109.5° of the regular tetrahedron, except those concerning the highly strained cyclobutyl ring and also the θ_1 chain angle. Additional refinements were performed by partly waiving the 4_1 molecular symmetry. Allowing different orientations for the cyclobuthyl groups increases the number of parameters by only 3. Column C in Table 2 shows the resulting model, whose significance against the one in column B was tested by calculating the ratio $R_1(B)/R_2(C) = 1.04$. This value is below that one calculated by Hamilton at a significance level of 0.05 considering a less constrained model with 3 more parameters and 24 degrees of freedom.[15] Apparently the restricted model B is the maximum information that can be extracted from the data.

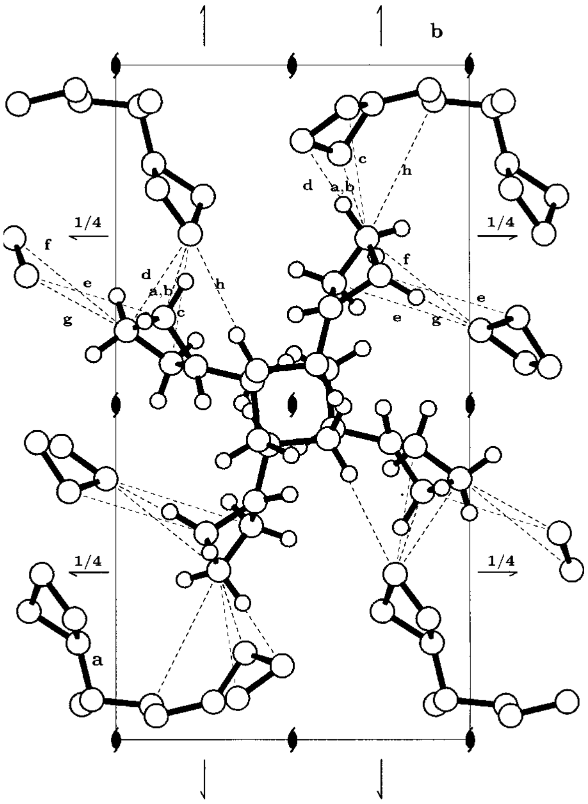


Figure 4. Crystal packing of *i*-PVCB. The structure is represented by omitting H atoms except for the central chain. The shortest C···C packing distances are $a = 3.73$ Å, $b = 3.78$ Å, $c = 3.91$ Å, $d = 3.98$ Å, $e = 4.04$ Å, and $f = 4.08$ Å. Note that the origin of the unit cell ($P2_12_12_1$ symmetry) is placed *differently* from the usual convention; this choice is imposed by the program TRY.[12]

The R_2 values (B model) for equatorial and upper layer reflections are respectively 0.152 (15 groups of reflections) and 0.150 (22 groups of reflections), and separated R_2 values for the *l* even and *l* odd reflections are respectively 0.211 and 0.138. Because of these values and the excellent packing, which allows an equilibrated distribution of C···C contacts, the hypothesis of left and right helices in a random substitution was not pursued.

Conformational Energy of the Isolated Chain. The chain structure obtained has been tested from the point of view of the conformational energy of the isolated chain. Figure 3 shows plots of the energy calculated against τ_1, τ_2 torsion angles and against Ψ, τ_R torsion angles, considering[16] the van der Waals contribution, the torsional contribution, and the bending contribution only for C−C−C angles of the cyclobutyl ring. It is

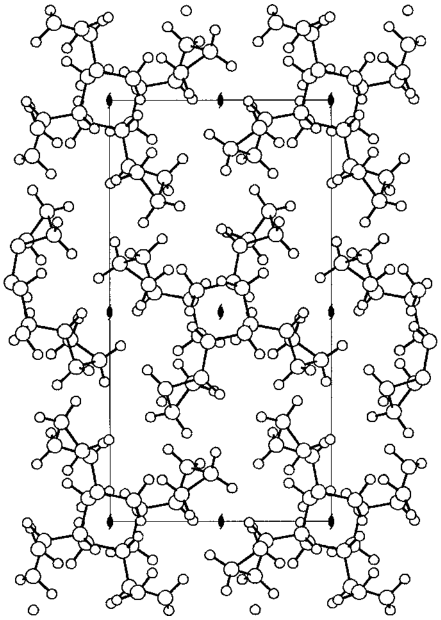


Figure 5. Helices pattern in fibrous *i*-PVCB.

evident that the chain crystallographic structure earns further credibility by the vicinity to a relative minimum of the potential energy function. Indeed there is another minimum, of energy only 0.50 kcal/mol lower, which could correspond to a 7/2 helix. This structure could be considered as a candidate model for the structure existing in unoriented samples obtained by crystallization from the melt.

Crystal Packing and Discussion. The final crystal structure of *i*-PVCB is shown in Figure 4 where also the shortest nonbonded C···C interactions (all are through the cyclobutyl groups) are indicated. The structure appears as a largely distorted hexagonal arrangement with axis-to-axis distances of 9.0 and 9.7 Å (see Figure 5).

The 4_1 helix has been observed also in several isotactic polyolefins.[3−5,9,10] Frequently 4_1 helices with bulky side groups pack in tetragonal space groups, while less symmetrical packings are observed in the case of smaller side groups. This is for instance the case of the form III of isotactic poly(3-methyl-1-butene), believed to be isostructural to *i*-PVCB[4] but with monoclinic symmetry instead.[5] An orthorhombic arrangement, with the same $P2_12_12_1$ space group, is present also in poly(1-butene) (form III).[10] Corradini et al. observed that 4_1 helices have a special bent for the tetragonal packing when the ratio of backbone radius to the helix radius is in the interval 0.3−0.8.[17] In our case this is really fulfilled, but the Corradini rule is not obeyed. Note however that Corradini considers only packings of enantiomeric helices, while in our case helices are all of the same chirality.

All things considered, the adoption of the recording techique based on the Fuji imaging plate seems to give reliable structural refinements, at least when structural parameters are small enough. Surely the increasing of spectral resolution (note from Table 1 that reflection overlap is frequent) could improve the results. This could be obtained by using longer wavelength and/or a more appropriate instrument, e.g. a cylindrical camera with larger radius.

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