Conformational and Packing Energy Calculations for Isotactic Poly(vinylcyclohexane): Crystal Structure of Form I

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ABSTRACT: The polymorphic behavior of poly(vinylcyclohexane) is discussed on the basis of conformational energy calculations on an isolated chain. The presence of two different modifications is in accordance with the energy minima present in the conformational energy maps. The packing of the chains in form I is analyzed on the basis of packing energy and structure factor calculations.

Introduction

Two polymorphic crystal forms have been described for isotactic poly(vinylcyclohexane) (PVCH).

Form I is the ordinary crystalline form which occurs in as-prepared and melt-crystallized samples and in extruded fibers. The crystal structure of form I of PVCH has been reported by Natta, Corradini, and Bassi.[1] Chains in 4/1 helical conformation are packed in a tetragonal unit cell with axes $a = 21.9$ Å and $c = 6.5$ Å; the space group suggested was $I4_1/a$.[1]

A second modification of PVCH, form II, has been described by Noether;[2] it occurs in fiber samples drawn at temperatures below 240 °C and it is transformed to form I by annealing above 260 °C. Form II is characterized by chains in a 24/7 helical conformation packed in a tetragonal unit cell with axes $a = 20.48$ Å and $c = 44.58$ Å.[2]

In this paper the polymorphic behavior of PVCH is discussed on the basis of conformational energy calculations on an isolated chain. Moreover the packing of the chains in form I is analyzed on the basis of packing energy and structure factor calculations.

Experimental Part

Isotactic PVCH was prepared with the $MgCl_2$/dioctyl phthalate/$TiCl_4$−phenyltriethoxysilane/Al$(C_2H_5)_3$ catalytic system, with a yield of 14 g (polymer)/[g (catalyst) × h] at 60 °C.

The polymer was extracted in boiling *n*-heptane to remove atactic and low molecular mass stereoregular fractions. The most stereoregular fraction of the polymer displays an inherent viscosity, measured in tetralin at 135 °C, of 0.77 dL/g and a melting temperature of 370 °C. This sample is essentially in form I, with traces of form II; annealing at 260 °C eliminates any traces of form II.

X-ray powder diffraction spectra were obtained with nickel-filtered Cu Kα radiation with an automatic Philips diffractometer.

The single molecule conformational energy maps were calculated using the methods already described for other isotactic polymers.[3,4] The intramolecular energy has been calculated as the sum of three terms

$$E = E_t + E_b + E_{nb}$$

where E_t is the sum of energy contributions associated with torsion angles (θ) around single bonds, which are assumed to have the functional form

$$E_t' = (K_t/2)(1 + \cos 3\theta)$$

E_b is the sum of energy contributions due to bond angle (τ) deformations, which are assumed to have the form

$$E_b' = (K_b/2)(\tau - \tau_0)^2$$

and E_{nb} is the sum of energy contributions due to the nonbonded interactions between atoms separated by more than two bonds, which are assumed to have the form

$$E_{nb}' = Ar^{-12} - Br^{-6}$$

The calculations of the conformational energy were performed on a portion of the isolated chain of PVCH shown in Figure 1. The nonbonded energy has been calculated by taking into account the interactions between the atoms of the first monomeric unit and the interactions between these atoms and the remaining atoms within spheres having radii twice the van der Waals distances for each pair of atoms. The potential energy constants are those reported by Flory.[5]

The packing energy is evaluated as half of the sum of the interaction energies between the atoms of one monomeric unit and all surrounding atoms of the neighboring macromolecules. The calculations were performed with the same parameters used for the conformational energy calculations. The interactions were calculated within spheres of radii equal to twice the sum of the van der Waals radii for each pair of atoms. The conformation of the chain, and hence the *c* axis, was kept constant. Indeed, the conformational preference is not likely to be influenced by the energy differences associated with packing efficiency if the energy differences between different conformations of the isolated chain are high.[6]

Measured structure factors (F_o) were equated to the square root of the experimental intensities corrected by $Lp = (1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta)$, $F_o = (I/Lp)^{1/2}$. The experimental intensities (I) were evaluated by measuring the areas of the peaks in the X-ray powder diffraction pattern, after substraction of the amorphous halo.

Calculated structure factors (F_c) were computed as $F_c = (\sum|F_i|^2 M_i)^{1/2}$ where M_i is the multiplicity factor and the summation is taken over all reflections included in the 2θ range of the corresponding reflection peak observed in the powder spectrum. Only values greater than the observable limit are reported. The thermal factor $B = 8$ Å^2 and atomic scattering factors from ref 7 were also assumed here.

An agreement factor was calculated as $R' = \sum|F_o - F_c|/\sum F_o$.

Results and Discussion

Conformational Energy Calculations. Conformational energy calculations were performed on a portion of an isolated chain shown in Figure 1, by application of the equivalence principle[6] to successive

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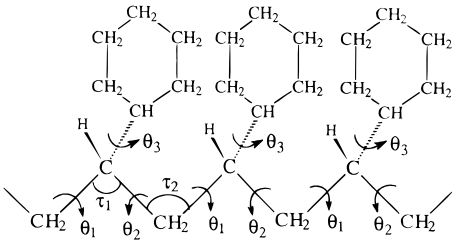

Figure 1. Portion of the chains of PVCH used in the conformational energy calculations. The definition of the torsion angles θ_1, θ_2, and θ_3 and the bond angles τ_1 and τ_2 is also shown.

Table 1. Bond Lengths and Bond Angles Used in the Conformational Energy Calculations of PVCH

	Bond Lengths (Å)		
C−C	1.53	C−H	1.10
	Bond Angles[a] (deg)		
C″−C′−C″	111.0	C′−C″−H	108.9
C′−C″−C′	113.0	H−C″−H	108.0
C″−C′−H	107.9		

[a] C′ indicates a methine carbon atom; C″ indicates a methylene carbon atom of the backbone.

constitutional units by assuming a line repetition group **s**(M/N) for the polymer chain. As a consequence the sequence of the torsion angles in the main chain is of the form ...$\theta_1\theta_2\theta_1\theta_2$... (Figure 1) and the calculations are for a short helical segment.

The geometrical parameters assumed in the present calculations are reported in Table 1.

A conformational energy map for PVCH, as a function of θ_1 and θ_2 is shown in Figure 2a. In this map for each pair of θ_1 and θ_2, the positions of the side groups (defined by the torsion angles θ_3) were varied in steps of 5°, to place them in the minimum energy position corresponding to that pair of θ_1 and θ_2. A detail of this map (with θ_3 varied in step of 2.5°) is reported in Figure 2b. The conformations of the cyclohexane rings have been fixed by assuming torsion angles of ±60°.[8] Two minima are present in the region $\theta_1 \approx G^+$, $\theta_2 \approx T$.

In the map of Figure 2b are also reported the loci of points corresponding to the **s**(4/1), **s**(24/7), and **s**(3/1) helical symmetries, with values of the unit twist $t = 2\pi N/M$ of 90, 105, and 120°, respectively, and the pairs of torsion angles corresponding to the experimental conformations observed in form I (point A, observed unit height $h = c/4 = 1.62$ Å) and in form II of PVCH (point B, observed unit height $h = c/24 = 1.86$ Å).

It is apparent that the conformations with symmetries 4/1 and 24/7 are very close to the absolute minimum of the map. They correspond to isodistortions for θ_1 and θ_2 from the precise *gauche* and *trans* values, due to the bulkiness of the lateral groups, already observed in various isotactic polymers.[9] A greater distortion of the torsion angles of the main chain is present in the helix 4/1, as revealed by the lower values of the unit height (1.86 Å for the 24/7 helix, 1.62 Å for the 4/1 helix).

It is worth noting that the relative minimum present in the map of Figure 2b is close to the dashed line corresponding to conformations with **s**(3/1) symmetry, however, no polymorphic form with **s**(3/1) helical chains has been observed until now for PVCH.

The general pattern of the maps of Figure 2 does not change significantly by slight variations of the bond angles of the main chain (e.g. for 112 and 114° for the bond angles at the methine and methylene carbon atoms, respectively).

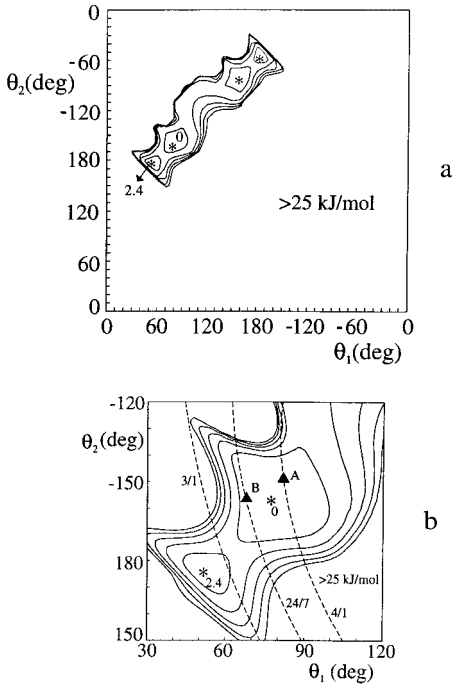

Figure 2. (a) Map of the conformational energy as a function of θ_1 and θ_2 in the **s**(M/N) line repetition group for $\tau_1 = 111°$ and $\tau_2 = 113°$. θ_1 and θ_2 are scanned every 10°, θ_3 is scanned every 5°, and minimum energy values are reported. The curves are reported at intervals of 5 kJ/mol of monomeric units with respect to the absolute minimum of the map assumed as zero. The values of the energies corresponding to the minima (indicated with asterisks) are also reported. (b) Detail of the energy map (a) with θ_1, θ_2, and θ_3 scanned every 2.5°. The curves are reported at intervals of 5 kJ/mol of monomeric units with respect to the absolute minimum of the map assumed as zero. The dashed curves correspond to the loci of points for which the helical symmetries are **s**(4/1), **s**(24/7), and **s**(3/1). The triangles indicate the experimental conformation 4_1 (A) and 24_7 (B), observed in forms I and II of PVCH, respectively.

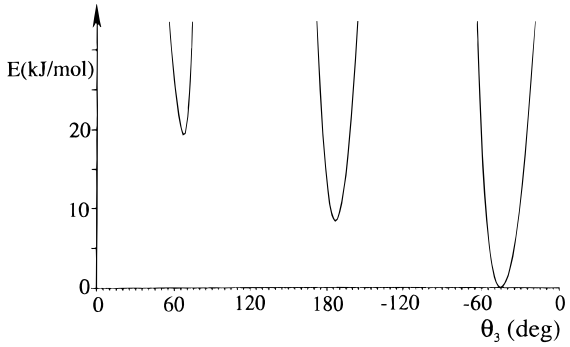

Figure 3. Conformational energy of PVCH as a function of θ_3 for the fixed values of $\theta_1 = 82°$ and $\theta_2 = -147°$ (4/1 helix). The absolute minimum of the curve has been assumed as zero.

According to this geometrical and energy analysis, a model of the chain of the form I of PVCH is built with the values of the dihedral angles along the main chain $\theta_1 = 82°$ and $\theta_2 = -147°$ (point A of Figure 2b).

The conformational energy curve of PVCH as a function of θ_3 for this fixed value of θ_1 and θ_2 is shown in Figure 3. It is apparent that the conformation of the lateral group with $\theta_3 = -45°$ corresponds to a deep energy minimum.

The projection along the chain axis and a side view of the model for the chain conformation of form I (4/1 helix) of PVCH are given in Figure 4.

Packing Energy Calculations and Crystal Structure of Form I. The X-ray powder diffraction spectrum

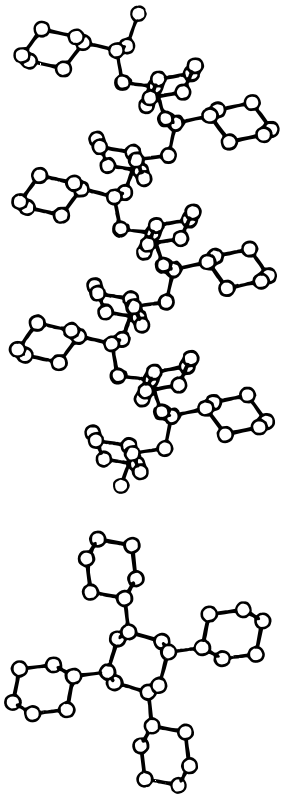

Figure 4. Side view and a projection along the chain axis of the model of the chain conformation of form I (4/1 helix) of PVCH.

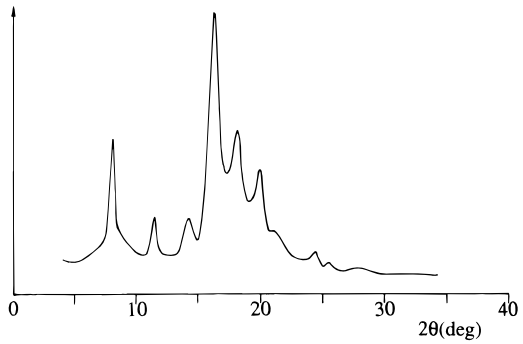

Figure 5. X-ray powder diffraction spectrum of form I of PVCH.

of form I of PVCH is shown in Figure 5. The reflections observed in the Geiger spectrum are listed in Table 2. All the reflections are accounted for by the tetragonal unit cell with axes $a = 21.9$ Å and $c = 6.5$ Å proposed by Natta, Corradini, and Bassi.[1] Although structure factor calculations were not reported in ref 1, the space group $I4_1/a$ was proposed from the absence of hkl reflections with $h + k + l = 2n + 1$ and $hk0$ with $h = 2n + 1$ and $k = 2n + 1$.

We have performed packing energy and structure factor calculations for various models of packing characterized by the body-centering of the lattice, the presence of enantiomorphous chains having 4_1 and 4_3 crystallographic symmetry, and a repeating unit corresponding to one monomeric unit. If the chains are anticlined, the resulting space group is $I4_1/a$; if the chains are isoclined, the space group is $I4_1cd$. In both cases there is the systematic absence of hkl reflections with $h + k + l = 2n + 1$. For the space group $I4_1/a$ the $hk0$ reflections with $h = 2n + 1$ and $k = 2n + 1$ are systematically absent, while for the space group $I4_1cd$ there are systematic absences of the $0kl$ reflections when $l = 2n + 1$ and $k = 2n + 1$, of the $h0l$ reflections when $l = 2n + 1$ and $h = 2n + 1$, and of the hhl reflections when $2h + l = 4n + 1$ and $l = 2n + 1$.

Table 2. Diffraction Angles 2θ, Bragg Distances d_{obs}, and Intensities I of the Reflections Observed in the X-ray Powder Diffraction Spectrum of Form I of PVCH (Figure 5)[a]

hkl	2θ (deg)	d_{obs} (Å)	d_{calc} (Å)	I[b]
200	8.1	11.0	10.95	s
220	11.4	7.76	7.743	m
101	14.2	6.24	6.231	m
211	16.3	5.44	5.416	vs
420	18.1	4.90	4.897	s
321	20.0	4.44	4.438	ms
411	21.5	4.13	4.113	w
431	24.6	3.62	3.632	w
521	25.6	3.48	3.448	w
611	28.3	3.15	3.149	w
800	32.7	2.74	2.737	w

[a] The indices hkl and the calculated Bragg distances d_{calc} are given for the tetragonal unit cell with axes $a = 21.9$ Å, $c = 6.5$ Å. [b] vs = very strong, s = strong, ms = medium strong, m = medium, w = weak.

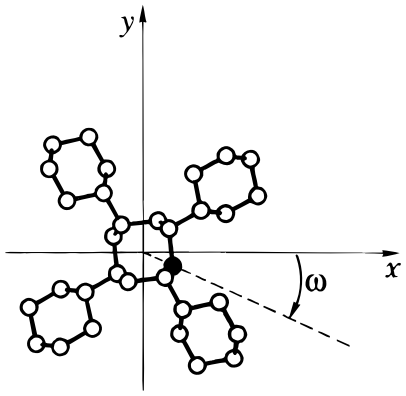

Figure 6. Definition of the variables used in the packing energy calculations. ω is the angle of rotation of the 4/1 helix of form I around the chain axis. ω is positive for an anticlockwise rotation. The height of the carbon atom indicated by the black ball defines the coordinate z (Å).

A possible model of packing with lower symmetry than $I4_1cd$, with two neighbor enantiomorphous chains assumed independent (not related by any element of symmetry) and isoclined, corresponding to the space group $I4_1$, was also considered. This space group has been found for form III of isotactic poly(4-methyl-1-pentene)[10] and gives only the systematic absence of hkl reflections with $h + k + l = 2n + 1$.

For the packing energy calculations the position of the chain axis inside the unit cell has been fixed at the fractional coordinates $x/a = y/b = 0.25$ (corresponding to the position of the crystallographic 4_1 axis of symmetry in the cited space groups) so that the lattice energy has been calculated by maintaining the axes of the unit cell constant, varying only two parameters: the orientation of the chain around its axis (represented by the angles ω defined in Figure 6) and the z coordinate that defines the relative height of the chain in the unit cell.

The packing model corresponding to the space group $I4_1cd$ should be ruled out due to the presence in the X-ray powder diffraction spectrum of $h0l$ reflections with h and l odd (e.g. 101 reflection, see Table 2), which are extinct in the space group $I4_1cd$. On the other hand this model gives always high values of the packing energy.

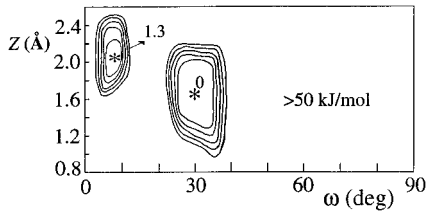

Figure 7. Map of the packing energy of form I of PVCH as a function of ω and z (defined in Figure 6), for the space group $I4_1/a$. The conformation of the 4/1 helical chains and the axes of the unit cell are maintained constant. The curves are reported at intervals of 10 kJ/mol of monomeric unit with respect to the absolute minimum of the map assumed as zero. The value of the energies corresponding to the minima (indicated with asterisks) are also reported.

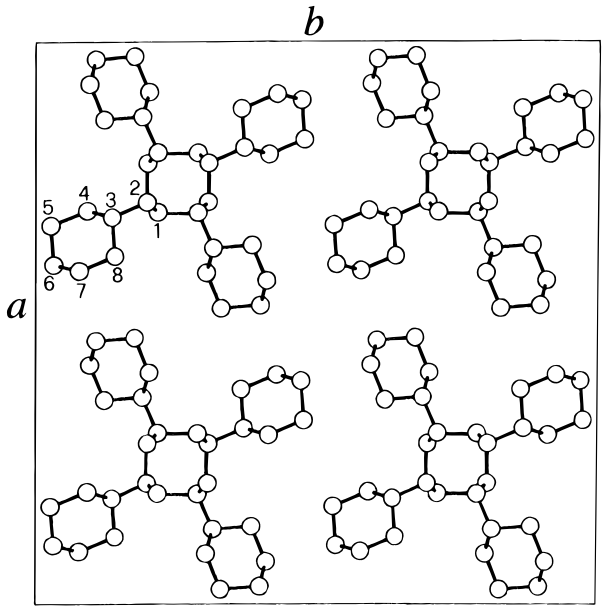

Figure 8. Model of packing for the form I of PVCH for the space group $I4_1/a$.

The map of the packing energy as a function of ω and z for the space group $I4_1/a$ is reported in Figure 7. The map repeats identically after a rotation of $\omega = \pm t = \pm 90°$ (where t is the unit twist) and a translation of $z = \pm h = \pm c/4$ (where h is the unit height). Therefore only the portion of the map with ω in the range $0-90°$ is reported. Two different energy minima are present in the map.

Calculations of structure factors for the space group $I4_1/a$ have been performed for models of packing corresponding to the energy minima of Figure 7.

A good agreement between observed and calculated structure factors is obtained for the model of packing corresponding to the absolute minimum of the map of Figure 7 ($\omega = 33°$ and $z = 1.66$ Å) and shown in Figure 8.

A comparison between observed structure factors $F_o = (I/Lp)^{1/2}$, from the X-ray powder spectrum of form I (Figure 5), and those calculated $F_c = (\Sigma|F_i|^2M_i)^{1/2}$, for the space group $I4_1/a$ for the models of Figure 8, is reported in Table 3. A fairly good agreement is apparent. The value of the agreement factor R' for the observed and unobserved reflections, as grouped in Table 3, is 10%.

The fractional coordinates of the asymmetric units for the model of Figure 8 of form I are reported in Table 4.

As described above an alternative model of packing characterized by enantiomorphous and isoclined chains, corresponding to the space group $I4_1$, was also considered. Although the $hk0$ reflections with $h = 2n + 1$ and $k = 2n + 1$ are not systematically extinct in the space group $I4_1$, it is possible to build a packing model in which the corresponding intensities may be calculated as very low. This is due to the fact that the projections in the ab plane of the two low-energy models $I4_1/a$ and $I4_1$ are very similar. Therefore the available X-ray diffraction data do not allow one to exclude the space group $I4_1$.

Structure factor calculations for a model in which each chain is statistically substituted by the corresponding anticlined chain indicate that the presence of statistical disorder in the positioning of up and down isomorphous helices at each site of the lattice cannot be excluded.

Table 3. Comparison between Observed Structure Factors, F_o, Evaluated from the X-ray Powder Diffraction Spectrum of Form I of PVCH (Figure 5), and Those Calculated, $F_c = (\Sigma|F_i|^2M_i)^{1/2}$, for the Model of Form I of PVCH of Figure 8, for the Space Group $I4_1/a$

hkl	d_{obs} (Å)	d_{calc} (Å)	$F_o = (I/Lp)^{1/2}$	$F_c = (\Sigma\|F_i\|^2M_i)^{1/2}$	
200	11.0	10.95	192	192	
220	7.76	7.743	186	181	
101	6.24	6.231	218	202	
400		5.475		171	
	5.44		682		731
211		5.416		711	
420		4.897		401	
	4.90		421		417
301		4.854		115	
321	4.44	4.438	459	429	
411	4.13	4.113	207	270	
431		3.632		332	
	3.62		386		417
501		3.632		252	
620		3.463		48	
	3.48		111		79
521		3.448		63	
112		3.181		189	
611	3.15	3.149	266	135	321
202		3.116		221	
222		2.997	n.o. (84)[a]	89	
312		2.942	n.o. (85)[a]	157	
631		2.917	n.o. (86)[a]	90	
402		2.795	n.o. (90)[a]	77	
332		2.750		69	
800	2.74	2.737	190	113	189
721		2.730		134	

[a] Reflections not observed (n.o.) in the Geiger spectrum. The numbers in parentheses represent values of F_o corresponding to the threshold intensity, taken as equal to half of the minimum observed.

Table 4. Fractional Coordinates of the Asymmetric Units in the Model of Figure 8 of Form I of PVCH for the Space Group $I4_1/a$[a]

	x/a	y/b	z/c
C_1	0.303	0.215	0.255
C_2	0.285	0.196	0.475
C_3	0.312	0.133	0.528
C_4	0.300	0.089	0.347
C_5	0.326	0.026	0.399
C_6	0.396	0.031	0.438
C_7	0.407	0.075	0.619
C_8	0.381	0.138	0.566

[a] The asymmetric unit corresponds to the monomeric unit labeled in Figure 8.

Conclusions

The polymorphic behavior of PVCH has been interpreted on the basis of conformational energy calcula-

tions on an isolated chain. In particular it has been shown that the absolute conformational energy minimum is very close to the experimental conformations with symmetries 4/1 and 24/7, observed for form I and form II of PVCH, respectively.

The packing of the chains in form I has been analyzed on the basis of packing energy and structure factor calculations. Chains with fourfold helical symmetry are packed in the tetragonal unit cell with axes $a = 21.9$ Å and $c = 6.5$ Å proposed by Natta, Corradini, and Bassi.[1] The calculations confirm the preliminary model of packing proposed in ref 1. Every 4_1 helical chain is surrounded by four enantiomorphous 4_3 chains and vice versa; the unit cell is body centered. A good agreement between calculated and observed intensities is obtained for space group $I4_1/a$.

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