that a remarkable similarity governs the entire group of seaweed and animal polysaccharides. It was pointed out that κ-carrageenan and ι-carrageenan are capable of forming double helices in the aqueous state, a stereochemical property which perhaps is shared by the other structural polysaccharides. However, it may be significant that some of the possible carrageenan conformations were found to be sterically excluded for the same sulfated polysaccharides which we found were incapable of stabilizing casein micelles. Therefore, there is a distinct possibility that the casein stabilizing function of carrageenan may be dependent upon conformational properties.

The importance of the polymer size in respect to the stabilizing ability has been well established in the degradation studies. We do not know the reason for this dependency upon polymer size for a given sample, but note that a similar observation has been made for a correlation between the molecular weight of heparin and its anticoagulant activity. Braswell[19] has pointed out that the correlation can be confirmed only for fractions derived for the same sample but not for samples of different origin. Before the interaction mechanism between α_s-casein and carrageenan can be fully delineated it is clearly necessary to obtain a great deal more information about the purity and the molecular weights of the effective polysaccharides, and to determine to which extent the conformation of the polysaccharides is affected by the degradation treatments.

Finally, the hypothesis that the interaction depends in some way upon the stereochemical properties of carrageenan does not in our opinion preclude that other polysaccharides possessing different structure would also be capable of a similar interaction. Whether or not a polysaccharide exhibits the stabilizing ability may depend only upon the specific characteristics of the backbone structure and the relative location of the functional groups.

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Chain Conformation of Syndiotactic Poly(α-methylvinyl methyl ether) in the Crystalline State

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ABSTRACT: The chain structure of poly(α-methylvinyl methyl ether) in the crystalline state was investigated by using X-ray diffraction and conformational energy calculations. Bond angle deformations coupled to preferred internal rotation angles are included in our approach. In agreement with previous nmr results, this polymer is syndiotactic and in the crystalline state forms a 5_2 helix.

Combined application of X-ray diffraction and conformational analysis has been recognized as a powerful route to determining the chain structure of crystalline polymers.[4-7]

Parallel application of these two methods of investigation appears to be particularly useful for those polymers which are subjected to strong intramolecular interactions between nonbonded atoms or groups such as the polymers obtained from α-substituted vinyl monomers. The internal rotation angles defining the chain conformation tend in fact to depart appreciably from the "staggered" values. In addition, bond angle deformations must be considered, as has been suggested in the case of polyisobutene.[8] Only through a detailed analysis of the intramolecular conformational energy is it possible to select a few most probable chain models, which must then be checked against the X-ray data. These, in turn, contain information which can be regarded as distinct at four different levels. First, the measure of the repeat distance along the chain axis can usually be obtained without difficulty from an oriented

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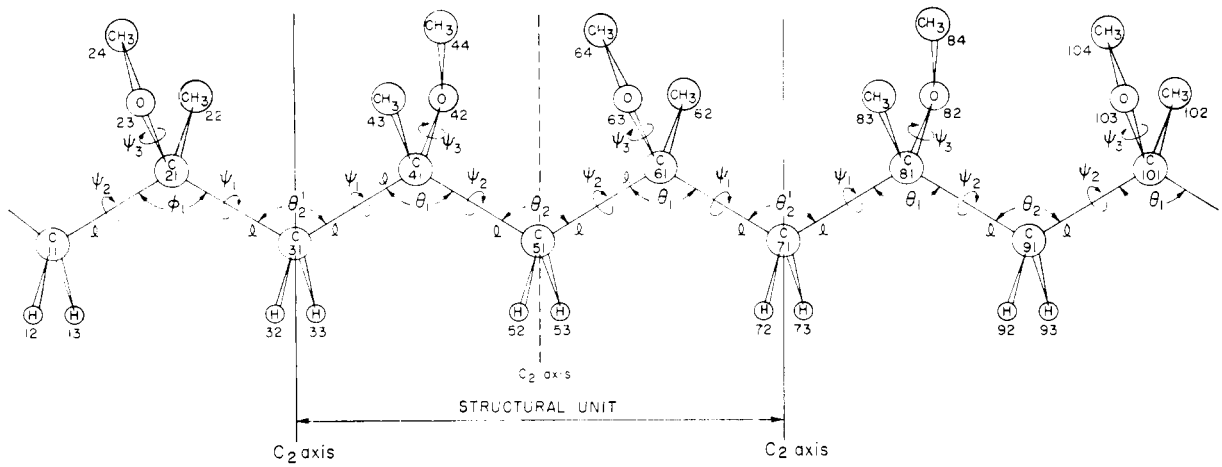

Figure 1. Representation of the PMVME macromolecule. The main chain has been given an arbitrary zigzag planar conformation.

fiber spectrum. Together with the postulate of equivalence among the monomer units,[9,10] it is possible to exclude the vast majority of conformations. From the qualitative examination of the X-ray intensity distribution on the various layers of the fiber diagram, it is often possible to ascertain if a polymer chain has a helical structure containing N residues in M turns of the helix.[11] The X-ray diffraction intensity may be quantitatively compared with that calculated for a single, isolated chain, *i.e.*, the packing effects on the intensity distribution are neglected, to a first approximation.[11,12] Finally, the full comparison between observed and calculated X-ray amplitudes can be performed to account for the three-dimensional order.

In the present paper we will discuss the results of our combined X-ray–potential energy conformational analysis of syndiotatic poly(α-methylvinyl methyl ether) (PMVME, Figure 1), where the X-ray investigation has been carried out through the first three steps mentioned above. Only the detailed analysis of the structure factors has been omitted. One of us has also carried out a similar analysis for polyisobutene.[13]

Experimental Section

A. Monomer Synthesis. α-Methylvinyl methyl ether was prepared from methylacetylene and methanol using the method devised by Shostakovskii and coworkers.[14]

B. Polymerization. The polymer was synthesized using the method recently described by Goodman and Fan,[15] based on cationic catalysis.

C. X-Ray Fiber Spectrum. Oriented fibers of PMVME were obtained by annealing strips of polymer under stress at about 70°, followed by unidirectional stretching at about the same temperature. These oriented fibers were further annealed under the same conditions in order to produce maximum sharpness and intensity in the fiber pattern. Exposures ranging from 4 to 12 hr were made using nickel-filtered copper radiation and a Weissenberg camera (R 28.65 mm.). An X-ray tube operating at 45,000 V and 15 mA and fitted with a copper target was used. The radiation was filtered with a Ni foil, so that only the Cu Kα component was utilized (λ = 1.5418 Å).

Convention for the Definition of the Internal and of the Helical Coordinates of the Macromolecule

The variable parameters defining the integral geometry of the polymer chain are reported in Figure 1. The convention for the ith bond is that $\psi_i = 0°$ for the *cis* conformation of the three bonds $(i - 1, i, i + 1)$.[16] ψ_1 and ψ_2 are defined with respect to the main chain; ψ_3 is defined with respect to the C(4i + 1, 1)–C(4i, 1)–O–CH_3 sequence.

The helical symmetry is indicated as $s(N/M)2$ or $s(N/M)1$, depending on the presence or absence of a twofold axis orthogonal to the chain;[17] N is the (integer) number of residues, or structural units, per chain repeat, and M is the corresponding (integer) number of turns of the helix. Both kinds of helix symmetries are often referred to as N_M. The full repeat distance along the chain axis is indicated by c. The Bragg index along the same direction in reciprocal space is l. The chain repeat per structural unit—which in an $s(N/M)2$ symmetry generally corresponds to two monomer units—is indicated as d_s and is equal to c/N; and d_m is the chain repeat per monomer unit (see Figure 4).

The cylindrical coordinates of the ith atom of the helix, defined with reference to its axis, are indicated as (r_i, z_i, φ_i) with the positive direction of the φ coordinates increasing simultaneously with z along the helix.[11] In an $s(N/M)2$ symmetry, the difference in φ angles between two corresponding atoms of neighboring structural units is indicated as $\eta = 2\Theta$, where Θ can be defined as the angle between two successive twofold axes perpendicular to the chain (see Figure 4).

X-Ray Diffraction Analysis. The X-ray fiber spectrum is shown diagrammatically in Figure 2. The existence of three equatorial reflections whose d spacings

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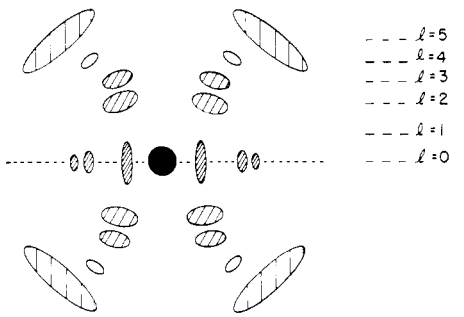

Figure 2. Diagrammatic representation of the X-ray fiber spectrum of PMVME (Cu Kα, radius of the cylindrical camera 28.65 mm).

are in the ratios $1:1/\sqrt{3}:1/2$ strongly suggests a hexagonal or pseudohexagonal packing among the chains with a distance between chain axes of 9.02 ± 0.15 Å.

Diffuse layer lines appear at meridional coordinates ζ in reciprocal space: $\zeta_{\mathrm{I}} = 0.123$ Å^{-1}, $\zeta_{\mathrm{II}} = 0.179$ Å^{-1}, $\zeta_{\mathrm{III}} = 0.294$ Å^{-1}.

Assuming a chain repeat $c = 16.6 \pm 0.5$ Å, the three meridional coordinates noted above are in good agreement with l indices equal to 2, 3, and 5, respectively ($\zeta_{l=1} = 0.060$ Å^{-1}).

Cochran, Crick, and Vand first prepared an elegant expression for the structure factor of an isolated chain having a helical conformation.[11] The corresponding expression for the intensity on the lth layer integrated along the Ψ cylindrical coordinate, as given by Corradini and Pasquon,[12] reads

$$I(R, l) = \sum_n \left[\sum_i f_i J_n(2\pi R r_i) \cos\left(2\pi \frac{l z_i}{c} - n\varphi_i\right)\right]^2 + \sum_n \left[\sum_i f_i J_n(2\pi R r_i) \sin\left(2\pi \frac{l z_i}{c} - n\varphi_i\right)\right]^2 \quad (1)$$

where J_n corresponds to the Bessel function of integer order n. Possible values of the latter parameters are those which satisfy the relationship

$$l = Mn + Nm \quad (2)$$

where m is any integer, positive or negative, including zero. Since the average values of the Bessel functions decrease steadily with increasing n for the limited values of the variable under consideration, the N and M integers are chosen so that the lowest n values derived from expression 2 correspond to the l layers with highest (average) diffraction intensity.

By assuming a helical structure of the chain with five structural units (residues) in either two or three pitches, (*i.e.*, $N = 5$ and $M = 2$ or 3 in expression 2), the distribution of intensities on the X-ray diffraction pattern agrees with the presence of low-order Bessel functions in the three layers indicated above. Table I shows that the nonobserved layers are characterized by higher order Bessel functions. This allows us to conclude that in either case this polymer acquires a helical conformation with five structural units per repeat, and a period per structural unit $d_s = 3.32 \pm 0.1$ Å ($= c/5$). Such a distance is obviously incompatible with the presence of only one monomer unit (the maximum repeat, in the fully extended conformation, is approximately 2.5 Å), nor does it seem likely to include three or more units. We have therefore concluded that each structural unit

TABLE I

THE LOWEST VALUES OF THE INDICES OF THE BESSEL FUNCTIONS CONTRIBUTING TO THE X-RAY INTENSITY ON THE VARIOUS LAYERS, FOR DIFFERENT 5_M ($M = 1 \sim 4$) HELICES[a]

l, index of the layer	j (lowest index of the Bessel function)				Av intensity of layer[b]
	5_1	5_2	5_3	5_4	
0	0	0	0	0	s
1	1	−2	2	−1	
2	2	1	−1	−2	m
3	−2	−1	1	2	w
4	−1	2	−2	1	vvw
5	0	0	0	0	vw
6	1	−2	2	−1	

[a] See expression 2. [b] s = strong; m = medium; w = weak; vw = very weak; vvw = extremely weak.

comprises two monomer units. This is possible, according to the equivalence principle,[9,10] only if the two monomer units in each structural unit are connected by a twofold axis orthogonal to the chain axis. Consequently, the polymer must be syndiotactic[15,17] in agreement with previous nmr results.[15,18–20] The density of the polymer calculated from X-ray data is 1.06 g/cm^3, in good agreement with the experimental value 0.950 g/cm^3.

In the case of a syndiotactic vinyl polymer having an $[s(N/M)2]$ chain symmetry, the internal rotation angles ψ_1 and ψ_2 follow in the sequence (----$\psi_1\psi_1\psi_2\psi_2\psi_1\psi_1$-$\psi_2\psi_2$----) (Figure 1). They are related to the identity period per monomer unit d_m and the angle of rotation between two consecutive twofold axes through the following equations[21]

$$d_m = \frac{l}{2 \sin \Theta}[(1 - \cos\theta_1)(1 - \cos\theta_2) \sin(\psi_1 + \psi_2) - \sin\theta_1 \sin\theta_2(\sin\psi_1 + \sin\psi_2)]$$
$$\cos\Theta = \cos^2\frac{\theta_1}{2}\cos\theta_2 - {}^1/_2 \sin\theta_1 \sin\theta_2(\cos\psi_1 + \cos\psi_2) - \sin^2\frac{\theta_1}{2}(\cos\theta_2 \cos\psi_1 \cos\psi_2 + \sin\psi_1 \sin\psi_2) \quad (3)$$

The angle η between two consecutive twofold axes connected by the helix symmetry (1 and 3 in Figure 4) is $360° \times 2/5 = 144°$ and $360° \times 3/5 = 216°$ for the 5_2 and 5_3 helix, respectively. The relationship between η and Θ is either $\eta = 2\Theta$ or $\eta = 360° - 2\Theta$, depending on the relative orientation of the twofold axes (1 and 2 in Figure 4) associated with the internal coordinate systems of two consecutive $-CH_2-$ units. In the present case, it turns out that the only reasonable chain models involve methylene units whose H atoms point alternatively toward and away from the chain axis. Therefore the second relationship between η and Θ above is

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the correct one. Consequently, the Θ values expected for a 5_2 and for a 5_3 helix are 108 and 72°, respectively.

In the following section we will discuss the results of our conformational energy calculations as a function of the internal rotation angles ψ_1, ψ_2, and ψ_3 and of the bond angles on the main chain. We compare the d_m and Θ values corresponding to the energy minima with the expected values of 1.66 ± 0.05 Å and 108° for the 5_2 helix, and 1.66 ± 0.05 Å and 72° for the 5_3 helix, respectively, showing that the first model is close to the most stable conformation corresponding to our results. Subsequently, we will refine the resulting model by analysis of the X-ray fiber spectrum.

Calculation of the Conformational Potential Energy. Contributions to the internal potential energy for different conformations of the polymer chains may arise from the following sources: (1) inherent potentials for the rotations around single bonds, (2) van der Waals interactions between nonbonded atoms and/or groups within or connected to the chain backbone, (3) chain strain energy connected with the bending of the C–C–C angles from their normal values, (4) electrostatic interactions of polar groups in the polymer chain.

As a first approximation, the interaction of type 4 is not taken into account in our calculations. Therefore, the energy equation may be represented by

$$U = U_{rot} + U_{nb} + U_{st} \quad (4)$$

where the three forms on the right-hand side correspond to contributions of type 1, 2, and 3, respectively. The equation for U_{rot} is

$$U_{rot} = \sum_i \frac{U_{0i}}{2}(1 - \cos 3\psi_i) \quad (5)$$

and the Lennard-Jones potential functions are used for the nonbonded-interaction energies

$$U_{nb} = \sum_{i<j}\left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}\right] \quad (6)$$

Here the parameter U_{0i} is the rotational energy barrier for the ith bond. U_0 is taken as 3.0 kcal/mol for a C–C bond, *i.e.*, close to the value reported for ethane,[22] and 1.07 kcal/mol for a C–O bond, as has been suggested for methanol.[23] The parameters B_{ij} are calculated in the Slater–Kirkwood approximation.[24,25] For simplification, the methyl groups have been treated as spherically symmetrical bodies, attributing to their polarizability the same value given for methane ($\alpha_{CH_4} = 2.6 \times 10^{-24}$)[26] and to their equivalent outer shell electron number the value 22,[27] only slightly smaller than that attributed to the methane molecule ($N_{CH_4} = 24$).[28] Values of A_{ij} are obtained by requiring U_{nb} to be a minimum at a distance r_{ij}^0 equal to the sum of the van der Waals radii of the interacting species ($r_{CH_3} = 2.0$ Å).

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TABLE II
PARAMETERS OF THE VAN DER WAALS INTERACTIONS[a]

$$U_{nb} = \sum_{i<j}\left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}\right]$$

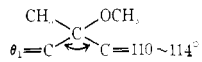
Interactions	A_{ij}	B_{ij}
H——H	4,709	49.29
CH_3——CH_3	5,636,100	2,752
C——C	293,990	380.6
O——O	89,397	245.26
C——H	39,698	133.48
C——CH_3	1,301,975	1,014.9
H——CH_3	185,540	345.6
O——H	19,835	102.4
O——C	162,140	302.03
O——CH_3	754,960	821.4

Bond lengths l

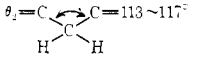
C–C 1.53 Å C–O 1.43 Å C–H 1.10 Å

Bond angles θ

C–C–O = C–O–C = 110°



C–C–H = H–C–H = 109°



[a] The values of r are in ångström units and energies are in kilocalories per mole of atomic pairs.

All the A_{ij} and B_{ij} parameters are reported in Table II. Nonbonded interactions between atoms separated by not less than three and not more than five bonds have been considered.

Finally, the strain energy for the bending of the chain bond angles (U_{st} in expression 4) has been evaluated according to the assumption of elastic deformations. For simplicity, all the angles indicated as θ_2 and θ_2' in Figure 1 have been assumed to be identical at the present stage, although they are not all related by the chain symmetry (half of them are in chain bonds characterized by the ψ_1 rotation, the other half are in bonds with ψ_2). Following Bixon and Lifson,[29] we have put

$$U_{st} = 80[(\theta_1 - \theta_1^0)^2 + (\theta_2 - \theta_2^0)^2]\left(\frac{2\pi}{360}\right)^2 \quad (7)$$

ignoring, as a first approximation, the difference between the two chain carbon atoms of each monomer unit. θ_1^0 and θ_2^0—the zero-strain bond angles—have been set equal to 110 and 112°, respectively. Changes in bond angles have been considered only for the main skeleton. However, we have always calculated conformational energy maps using fixed values of θ_1 and θ_2, which implies that the U_{st} term is a constant for each map.

We have expressed the conformational potential energy of the macromolecule as

$$U = U_M + U_{SC} \quad (8)$$

where the symbol M and SC stand for "main chain" and "side chain," respectively. U_M includes all energy contributions except those arising from the rotation around the C–OCH_3 bond (ψ_3 in Figure 1) and from the nonbonded interactions involving the methyl group linked to the oxygen atom. Both these energy contributions are included in U_{SC}. Aside from the bond

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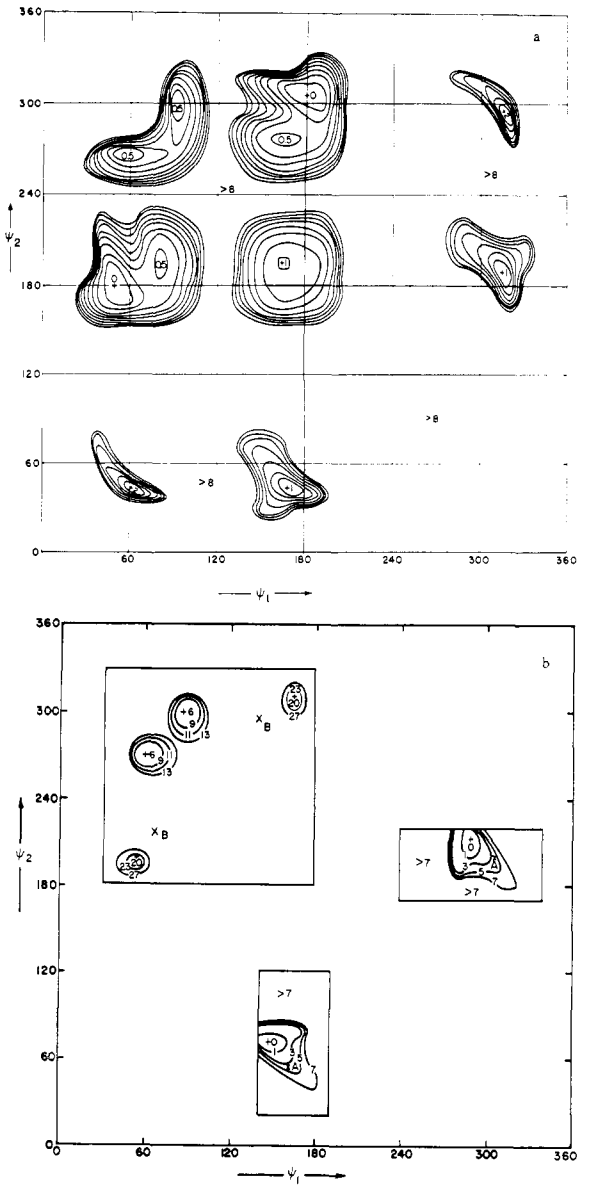

Figure 3. (a) The internal conformation energy of the main chain for syndiotactic poly(α-methylvinyl methyl ether), U_M; the valence angles in the main chain are $\theta_1 = 114°$, $\theta_2 = 117°$. (b) The overall internal conformational energy, $U_M + U_{SC}$, for syndiotactic poly(α-methylvinyl methyl ether) around the energy minima of U_M in the (ψ_1, ψ_2) space. The values of ψ_3 have been chosen in such a way as to minimize U_{SC}.

angles, therefore, U_M is a function of ψ_1 and ψ_2 only, while U_{SC} depends on ψ_1, ψ_2, and ψ_3. We have tabulated U as a function of ψ_1 and ψ_2, assuming implicitly that the value of ψ_3 is that which minimizes U_{SC} for each (ψ_1, ψ_2) combination. The assumption does not introduce any approximation as long as we are looking for the minima of the conformational energy function.

U_M has been calculated by rotating both ψ_1 and ψ_2 at intervals of 10°, and considering several different combinations of θ_1 and θ_2, *i.e.*, the two chain angles C–C–C of the monomer unit (Figure 1). The CH_3–C–C, the CH_2–C–O, and the C–O–CH_3 angles have been given fixed values of 112, 110, and 110°, respectively. The lowest values of the U_M have been obtained for θ_1 and θ_2 equal to 114 and 117°, respectively. Correspondingly, we have calculated the U_{SC} contribution, varying

TABLE III
CONFORMATIONAL ENERGY FOR $\psi_1 = 150°$, $\psi_2 = 70°$, $\psi_3 = 80°$ AND DIFFERENT COMBINATIONS OF THE CHAIN BOND ANGLES

Chain bond angles		Conformational energy		
θ_1	θ_2	U_M	U_{SC}	$U = U_M + U_{SC}$
112	115	8.27	7.71	15.98
112	117	5.91	7.16	13.07
114	115	6.91	7.71	14.62
114	117	5.01	7.17	12.18
116	115	6.18	7.71	13.89
116	117	4.72	7.17	11.89

ψ_3 at intervals of 10° and recording the minimum value for each combination of ψ_1 and ψ_2 (Figure 3a). U_{SC} was then added to U_M to obtain the total conformational energy U (Figure 3b). To save computer time, the evaluation of U_{SC} has been carried out only in the regions around the minima of the U_M map. Calculations were also performed in some other points, chosen at random to make sure that no additional low energy minimum could arise in the resulting U map. The lowest minimum corresponds to $\psi_1 = 150°$, $\psi_2 = 65°$, ψ_3 (not indicated on the map) = 80°. As a check of our assumption for the chain bond angles, we have calculated the total energy U for the same values of ψ_1, ψ_2, and ψ_3, with different (θ_1, θ_2) values. The results are reported in Table III. The combination with $\theta_1 = 114°$, $\theta_2 = 117°$, which has been adopted to calculate the energy maps of Figure 3a and 3b, is very close to the lowest conformational energy. The two crosses labeled A and B in Figure 3b correspond to a 5_2 and 5_3 helix, respectively, both conformations being characterized by a chain repeat per unit equal to the experimental value ($d_M = 1.66 \pm 0.05$ Å). It is important to stress that, for given values of θ_1, θ_2, d_m, and Θ, there is a unique solution of the system (3) for ψ_1 and ψ_2: a displacement of ±5° in these two angles leads to a change of about ±0.1 Å in d_m. It is apparent that the conformation represented by A ($\psi_1 = 160°$, $\psi_2 = 55°$, $\psi_3 = 80°$) is more satisfactory; it deviates by 10–15° in ψ_1 and ψ_2 from the *lowest* energy minimum. The conformational energy of A changes slowly with ψ_3; a change of ±15° in this angle does not increase the energy by more than 1.5 kcal/monomer unit. As a consequence, relatively wide variations from the calculated ψ_3 value can be expected because of packing forces in the crystal and approximations involved in our analysis.

Comparison of the Calculated Intensity Diffracted by the Isolated Helix with the Experimental X-Ray Diagram. Calculation by expression 1 of the X-ray intensity diffracted by the model represented as point A in Figure 3b does not lead to a satisfactory agreement with the observed intensity distribution—compared with the fiber spectrum reported in Figure 2—essentially because of the exceedingly low intensity calculated on the layer with $l = 3$. Consequently, we have looked for a modified, more satisfactory model according to the following criteria.

(a) The θ_2 and θ_2' bond angles (see Figure 4) may be assigned different values, provided the corresponding

TABLE IV
GEOMETRICAL PARAMETERS OF PMVME IN THE CRYSTALLINE STATE

Bond lengths, Å	Bond angles, deg	Internal rotation angles, deg
C(1)–C(2) 1.54	C(2′)–C(1)–C(2) 123.1 (θ_2')	C(3)–C(2′)⟲C(1)–C(2) 157.2 (ψ_1)
C(2)–C(3) 1.54	C(1)–C(2)–C(3) 112.2 (θ_1)	C(1)–C(2)⟲C(3)–C(2″) 59.2 (ψ_2)
C(3)–C(4) 1.54	C(2)–C(3)–C(2″) 108.2 (θ_2)	C(3)–C(2)⟲O(1)–C(5) 67.2 (ψ_3)
C(3)–O(1) 1.45	C(1)–C(2)–C(4) 118.2	
C(5)–O(1) 1.45	C(1)–C(2)–O(1) 112.0	
	C(3)–C(2)–O(1) 105.4	
	C(3)–C(2)–C(4) 106.8	
	C(4)–C(2)–O(1) 107.0	

Cylindrical Coordinates for the Monomer Unit

	r, Å	z, Å	φ, deg
C(1)	0.67	0.00	0.0
C(2)	1.64	1.07	30.0
C(3)	2.15	1.61	72.0
C(4)	2.00	2.32	3.1
C(5)	4.05	1.61	31.0
O(1)	3.05	0.56	30.0

strain energy does not increase by more than 1–2 kcal/monomer unit.

(b) The severe restrictions to the values of the CH_2–C–CH_3 and CH_2–C–O bond angles must be somewhat reduced. With reference to expression 7, a change of 6° from the zero-strain value of these bond angles entails a strain energy lower than 1 kcal/monomer unit, which has been assumed to be acceptable in considera-

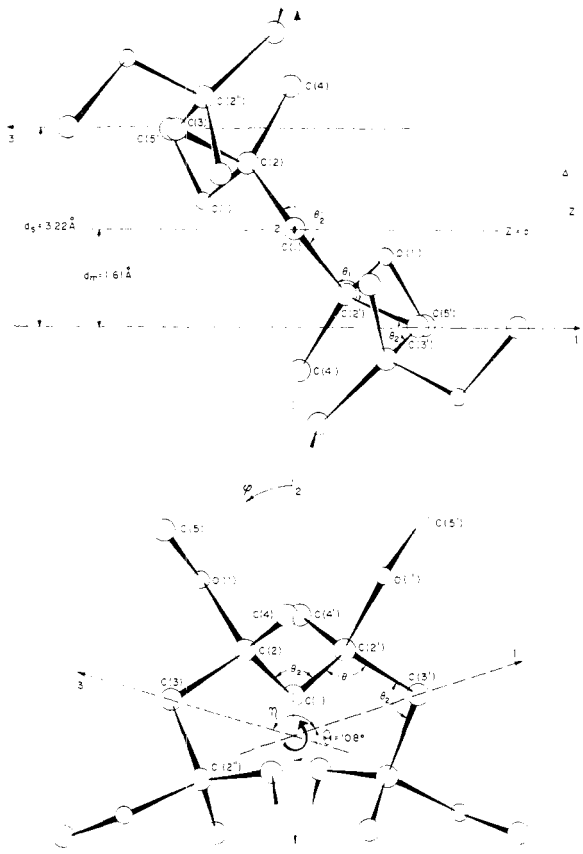

Figure 4. The resulting chain model of PMVME in the crystalline state.

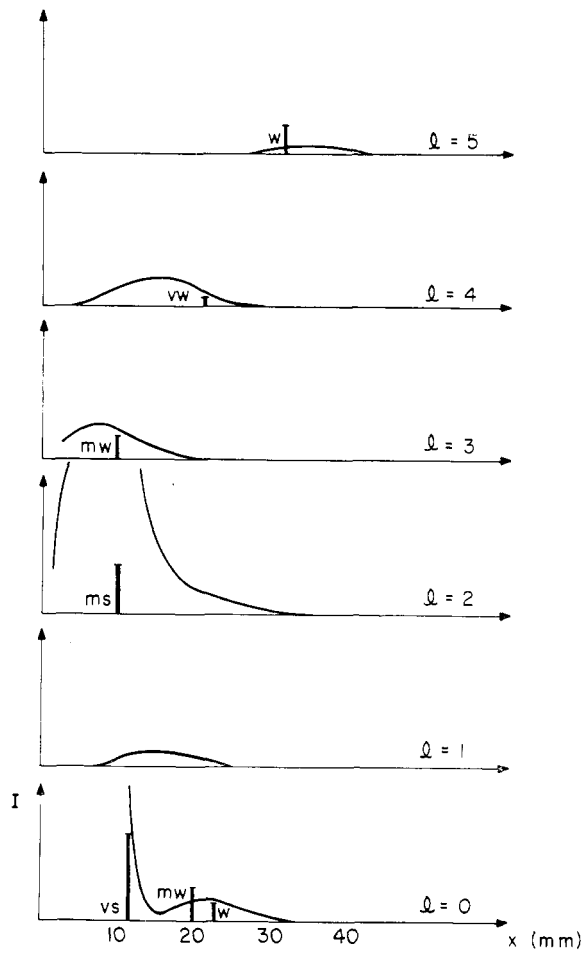

Figure 5. Comparison between observed and calculated X-ray intensities (the latter have been corrected for the Lorentz polarization). The x coordinate (in millimeters) corresponds to the distance from the meridional line in the spectrum reported in Figure 2. The intensities are given in arbitrary units.

tion of the strong nonbonded interaction energies involved in our system.

(c) Assuming, as a first approximation, that the energy map reported in Figure 3b still holds some validity after the changes in bond angles, ψ_1 and ψ_2 should be modified so that the representative point A moves toward the minimum of the potential energy function.

(d) From what has been said at the end of the previous section, ψ_3 may have any value in the range 65–95°,

(e) The d_m value must remain in the range 1.66 ± 0.05 Å, and the Θ angle must remain equal to 108° (see expression 3 and Figure 4).

On the basis of trial and error methods, the best agreement with the experimental X-ray distribution has been obtained with the model reported in Figure 4, where $\theta_1 = 112°$, $\theta_2 = 108°$, $\theta_2' = 123°$; $\psi_1 = 157°$, $\psi_2 = 59°$, $\psi_3 = 67°$. The full list of the geometrical parameters corresponding to the model of Figure 4 is reported in Table IV. Figure 5 shows the calculated X-ray profiles, and the observed X-ray intensities are also indicated in conventional notation. An isotropic thermal factor equal to 4 Å^2 has been applied to all atoms, hydrogens omitted. The agreement is clearly satisfactory.

Conclusions

The present study represents a characteristic example of a polymer conformational analysis where two different techniques—X-ray and potential energy calculations—are employed in an alternate sequence, leading to a progressive refinement of the chain model.

It also emphasizes the importance of considering the bond angle flexibility in crowded molecules. As a matter of fact, no improvement from model A of Figure 3b—unacceptable from the X-ray point of view—seems possible if this kind of molecular deformability is not taken into account. On the other hand, analysis of Table III is in itself sufficiently indicative of the possibility of achieving significant energy stabilization through bond angle deformation.

Acknowledgment. We want to thank Dr. Hung-Tsung Chen for his helpful discussions in formulating our program. We also wish to thank the National Institutes of Health for their support through Grant GM 08974.

Second and Fourth Moments of Vinyl Polymer Chains

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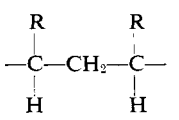
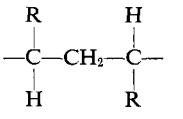
ABSTRACT: Configuration partition functions, z, and second and fourth moments, $\langle r^2\rangle_0$ and $\langle r^4\rangle_0$, of the end-to-end vector **r**, for vinyl polymer chains are calculated as functions of chain length (n), of the statistical weight parameter (ω) representing steric repulsions between groups separated by four bonds, and of the average stereochemical configurations of dyads comprising the chain. For small steric repulsions in the aforementioned conformations, *i.e.*, for $\omega > 0.10$, the characteristic ratio $C_n = \langle r^2\rangle_0/nl^2$ in the limit of long chains is comparatively small (<7) and nearly independent of the degree of stereoregularity throughout the range from isotactic to syndiotactic. For stronger repulsions, *i.e.*, for $\omega \approx 0$, C_n is much larger for isotactic than for syndiotactic chains; for atactic chains, it is lower than for either of the stereoregular forms. Characteristics of chains varying in stereoregularity *from isotactic to atactic* are fairly well reproduced by calculations for isotactic chains with ω varied artificially in the range from 0 to 0.1. Anomalous behavior of the ratio $\langle r^4\rangle_0/\langle r^2\rangle_0^2$ for syndiotactic chains is traced to the suppression of nonplanar conformations for tetrahedrally bonded chains in the limit $\omega = 0$.

Two aspects of the structure of vinyl polymers $-CH_2CHRCH_2CHR-$, etc., set them apart from other kinds of long chain molecules. First, steric interactions involving the substituent R, assumed to be of the size of CH_3 or larger, severely limit the conformations available to the chain. Second, alternate skeletal atoms being asymmetric, the characteristics of the chain may depend decisively on the stereochemical configurations of these centers of asymmetry. The stereochemical configuration of the chain is appropriately defined through specification of the symmetry of each of its successive dyads, which may be either *meso* (*m*)



or racemic (*r*)



The two species of the mirror-image pair (*dl* and *ld*) comprising the latter form need not be differentiated for our purposes. The stereochemical configuration of a sequence is then adequately specified by ...*mrrmr*..., for example.

Limitations on the spatial configuration of the chain molecule are markedly dependent on the *stereochemical* configurations of the asymmetric centers –CHR–. They are most severe in isotactic chains, which, if the ultimate in structural purity could be attained, would be exclusively *meso*. Interspersion of racemic dyads greatly increases the spatial configurations available, as measured by the configuration partition function, for example (*cf.* the following).