Studies on the Molecular Conformations of *racemic* Poly(*sec*-butyl) vinyl ether, of Poly-S-(*sec*-butyl) vinyl ether, and of Polyisopropyl vinyl ether in the Crystal State

by

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Dedicated to Prof. Dr. G. V. SCHULZ on the occasion of his 60th birthday

SUMMARY:
    The molecular conformations in the crystal state of isotactic *racemic* poly(*sec*-butyl) vinyl ether, poly-S-(*sec*-butyl) vinyl ether, and poly-*i*-propyl vinyl ether have been investigated by comparison of the X-ray diffraction intensities in the fiber spectra with the calculated intensity due to an isolated macromolecule. The chain conformation is the same in all cases; it is characterized by a helix with 17 monomeric units in 5 pitches, with a chain repeat of 35.5 Å. While the molecular conformation of poly-*i*-propyl vinyl ether has been fairly well defined, the corresponding conformations of the poly-(*sec*-butyl)-vinyl ethers have been found to be essentially analogous, apart from the exact location of the extra methyl group that the latter polymers possess with respect to poly-*i*-propyl vinyl ether. Four different sites are available for this methyl group, no significant difference being found among them from the calculated intensity distributions.
    Two different structural models are then proposed in order to explain the virtual identity in the diffraction spectra between *racemic* poly(*sec*-butyl) vinyl ether and poly-S-(*sec*-butyl)vinyl ether.

ZUSAMMENFASSUNG:
    Die molekularen Konformationen im Kristallzustand von isotaktischem *racemischen* Poly(*sec*-butyl)-vinyläther, Poly-S-(*sec*-butyl)-vinyläther und Polyisopropylvinyläther wurden durch Vergleich der Röntgenbeugung in Faserdiagrammen mit der für ein einzelnes Makromolekül berechneten Intensität untersucht. Die Konformation der Kette ist in allen Fällen dieselbe. Sie ist durch eine Helix mit 17 Monomereinheiten auf 5 Windungen und eine Identitätsperiode von 35,5 Å gekennzeichnet. Während die molekulare Konformation von Polyisopropylvinyläther recht sicher festgestellt werden konnte, wurden die entsprechenden Konformationen der Polybutylvinyläther als im wesentlichen analog befunden, abgesehen von der exakten Lokalisierung jener Methylgruppe, die die letzteren Polymeren zusätzlich besitzen. Es sind vier verschiedene Positionen für diese Methylgruppe möglich, da zwischen diesen keine deutlichen Unterschiede in den berechneten Intensitätsverteilungen auftreten.
    Es werden zwei verschiedene Strukturmodelle vorgeschlagen, um die im wesentlichen vorhandene Identität in den Beugungsbildern von *racemischem* Poly(*sec*-butyl)vinyläther und Poly-S-(*sec*-butyl-vinyläther zu erklären.

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Introduction

Crystalline isotactic polymers of *racemic* (*sec*-butyl)-vinyl ether and of *S*-(*sec*-butyl) vinyl ether have been synthesized with the aid of stereo-specific catalysts *)[1,2].

We thought it interesting to study the molecular structure in the crystal state of these polymers for two reasons: first in order to point out the structural analogies that can be foreseen between them and the crystalline isotactic poly-α-olefins and poly-alkyl vinyl ethers already studied; second, in order to connect the steric configuration of the asymmetric carbon atom present in the monomeric unit with the conformation assumed by the macromolecule.

The monomeric units (−CH$_2$−CH−) of crystalline isotactic vinyl poly-

$$R$$

mers are arranged along helices, the symmetry and periodicity of which along the chain depend on the steric requirements of the side group R.

In particular, the macromolecules of isotactic poly-4-methyl pentene-1 and of poly-4-methyl hexene-1 in the crystal state have a helix conformation containing 3.5 (7/2) monomeric units per pitch[3]. The chain conformation of crystalline isotactic poly-*i*-propyl vinyl ether is only slightly different, the monomeric units being arranged along helices containing 3.4 (17/5) monomeric units per pitch[4]. It seems, therefore, reasonable to expect that also the molecules of isotactic *racemic* poly(*sec*-butyl) vinyl ether and of poly-*S*-(*sec*-butyl) vinyl ether in the crystal state have a helix conformation not very different from that of the polymers mentioned above.

Fibre Spectra of Racemic Poly(sec-butyl) Vinyl Ether and of Poly-S-(sec-butyl) Vinyl Ether

The polymer fibers suitable for X-ray examination were obtained by extruding from the melt thin polymer cylinders which were stretched along their axes and then annealed under tension in boiling water for about 30 hrs.

The X-ray diffraction spectra of the fibers thus obtained show a diffuse halo due to the amorphous phase, and sharp diffraction spots distributed along different layer lines, due to a crystalline phase. These diffraction

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spots are absolutely identical in position and intensity either in the polymers obtained from the optically active (sec-butyl) vinyl ether or in those obtained from the racemic monomeric mixture.

Table 1. Reflections present in the fiber spectra of crystalline isotactic *racemic* poly(sec-butyl) vinyl ether and poly-S-(sec-butyl) vinyl ether. The R and ζ reciprocal coordinates are expressed in $1/d$ scale (Å^{-1})

R \ ζ	0.0000	0.0564	0.0843	0.1407	0.1972	0.2815	0.3379
	vs 0.1103	vw 0.1226	w 0.1725	s 0.1206	m 0.0759	vw 0.1538	m 0.1219
	mw 0.1551	ms 0.1978		w 0.1609	ms 0.1122	vw 0.2387	
	w 0.2199	mw 0.2264		w 0.1991	w 0.1745		
	m 0.2452			w 0.2374			
				w 0.2731			

Table 2. Determination of the identity period along the chain axis for crystalline isotactic *racemic* poly(sec-butyl) vinyl ether and poly-S-(sec-butyl) vinyl ether, from the ζ experimental values

ζ (Å^{-1})	c/l (Å.)	l	c (Å.)
0.0564	17.73	2	35.46
0.0843	11.86	3	35.58
0.1407	7.107	5	35.54
0.1972	5.071	7	35.50
0.2815	3.552	10	35.52
0.3379	2.959	12	35.51

Conformational Analysis of Crystalline Isotactic Poly(sec-butyl) Vinyl Ethers and of Poly-i-Propyl Vinyl Ether

Table 1 reports the R(or ξ) and ζ coordinates (in the scale $1/d$, Å^{-1}) and the relative intensities of the various reflections of the fiber spectrum of poly(sec-butyl) vinyl ethers. In the "tilted" fiber spectra, with the fiber axis perpendicular to the rotation axis, a very sharp and intense equatorial reflection is observed; its BRAGG distance d corresponds to 2.09 ± 0.01Å.

The experimental data obtained so far are in good agreement with a chain repeat of 35.5 ± 0.20 Å and 17 monomeric units in the identity period (Table 2).

The number of helix pitches per chain repeat was determined by a qualitative comparison between the observed distribution of the diffracted intensity in the various layers of the fiber spectrum and the radial intensity distribution calculated for an isolated macromolecule with the following relationship, derived by Corradini and Pasquon[5] (*cf.* Crick, Cochran, and Vand[6]):

$$F^2(R,l) = \sum_n \left[\sum_j f_j \, J_n \, (2\pi \, Rz_j) \cos \left(\frac{2\pi l z_j}{c} - n\varphi_j \right) \right]^2 +$$
$$+ \sum_n \left[\sum_j f_j \, J_n(2\pi Rz_j) \sin \left(\frac{2\pi l z_j}{c} - n\varphi_j \right) \right]^2 \tag{1}$$

R is the radial cylindrical coordinate in reciprocal space (Å^{-1});

l is the index of the layer under consideration;

f_j is the atomic scattering factor of the j-th atom corresponding to the (R, l) reciprocal coordinates;

c is the identity period along the chain (Å.);

r_j, φ_j, and z_j are the cylindrical coordinates of the j-th atom of the monomeric unit (r_j, z_j in Å., φ_j in rad);

J_n is the Bessel function of n-th order (n being an integer);

$F^2(R,l)$ is the integral intensity due to a single macromolcule, in correspondence with the (R,l) coordinates.

The n and l integral values are subjected to the following condition:

$$\frac{l}{c} = \frac{n}{P} + \frac{m}{p} \tag{2}$$

where m is an arbitrary integral number, P is the pitch of the spiral, and p the periodicity per monomeric unit along the chain axis.

It is to be noted that Eq. (1) of the scattered intensity does not account for intermolecular diffraction effects. In addition to the ideal case of an isolated macromolecule, it would also hold exactly when the helices are randomly turned with respect to each other. Nevertheless, it always gives a qualitative picture of the intensity distribution in the X-ray pattern, and the better the statistical agreement, the greater is the number of observed reflections per layer[5,6].

It is well known that the smaller the lowest index n given by Eq. (2) on the layer under examination, the greater are on the average the values given by Eq. (1), and the more the intensity will be concentrated at low R values.

Table. 3. Lowest n index of the BESSEL functions, on the basis of a 17/5 helix, for each value of l (see expr. (2))

l	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
n	0	+7	−3	+4	−6	+1	+8	−2	+5	−5	+2	−8	−1	+6	−4	+3	−7	0

Table. 4. Parameters defining the main chain helical conformation of crystalline isotactic *racemic* poly(*sec*-butyl) vinyl ether and of poly-S-(*sec*-butyl) vinyl ether, assuming the same deviation from the staggered conformation for both the internal rotation angles $(300°−\sigma_1 = 180°−\sigma_2)$

Identity period	35.5 Å.
Number of pitches	5
Monomeric units contained in the identity period	17
C–C̆–C valency angles along the main chain.	114° 30′
C–C bond length	1.54 Å.
Radii of the helices along which the main chain carbon atoms are disposed	0.961 Å.
Internal rotation angles: (right-handed helix)	$\begin{cases} \sigma_1 = 290° \\ \sigma_2 = 170° \end{cases}$

On this basis, we have found that the distribution of the diffracted intensity in correspondence with the various values of l (*cf.* Fig. 1) agrees at least qualitatively with a helix with 5 pitches per chain repeat. The lowest value of the index n allowed on each layer of the fiber spectrum for a 17/5 helix (*cf.* Eq. (2)) is reported in Table 3. We have, therefore, concluded that the conformation of the main chain is defined by the data reported in Table 4, assuming that the methylene and tertiary carbon atoms of the main chain are disposed on helices with the same radius.
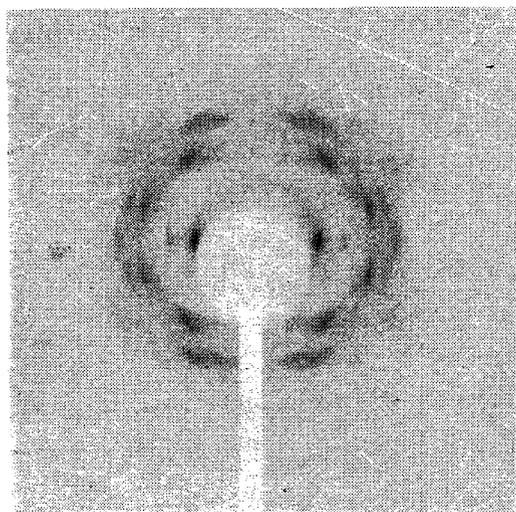

Fig. 1. Fiber spectrum of *racemic* poly(*sec*-butyl) vinyl ether

We arrived at identical conclusions in the definition of the chain structure of isotactic poly-i-propyl vinyl ether[4].

The R and ζ coordinates of the reflections present in the fiber spectrum of crystalline isotactic poly-i-propyl vinyl ether are reported in Table 5.

Table. 5. Reciprocal R and ζ coordinates (Å^{-1}) of the reflexions present in the fiber spectrum of crystalline isotactic poly-i-propyl vinyl ether

ζ R	0.0000	0.0564	0.1407	0.1872	0.3379
	vs 0.1167 mw 0.1647 mw 0.2594	m 0.2076 w 0.2400	ms 0.1297 vw 0.2400	mw 0.0843 m 0.1232 vw 0.1816	ms 0.1167

As shown by a comparison with the data reported in Table 1, the distribution of the diffracted intensities on the various layers is very similar for the two polymers; therefore, it is to be expected that the macromolecules of isotactic poly(sec-butyl) vinyl ethers and poly-i-propyl vinyl ether have substantially similar conformations. The slight differences revealed by their X-ray diffraction spectra may be attributed only to the effect of the additional carbon atom that poly(sec-butyl) vinyl ethers possess with respect to poly-i-propyl vinyl ether. The analogy between the conformations of the macromolecules influences also their crystal packing; this is clearly shown by a comparison between the dimensions of the unit cells in the two cases, as will be seen in the following.

Let us first make a parallel examination of the diffraction spectra of poly-i-propyl vinyl ether and of poly(sec-butyl) vinyl ethers and of those of the corresponding isotactic poly-α-olefins, in which the oxygen atom is substituted by a ($-CH_2-$) group. The diffraction spectra of isotactic poly-4-methyl pentene-1 and of poly-4-methyl hexene-1 have been interpreted on the basis of a tetragonal unit cell[3,7]; analogously, all the reflections of the fiber spectra of the polyvinyl ethers under examination can be interpreted on the basis of tetragonal unit cells, having the following constants (Table 6).

The repetition period c being the same both for the two poly-α-olefins and for the two poly vinyl ethers, an enlargement of the unit cell takes place normally to the chain axes, which is of the same order of magnitude when passing either from poly-i-propyl vinyl ether to poly(sec-butyl) vinyl ethers or from poly-4-methyl pentene-1 to poly-4-methyl hexene-1.

Table 6. Constants of tetragonal unit cells

Polymer of	c (Å.) axis of macromolecule	a = b (Å.)
4-methyl pentene-1	13.80	18.60
4-methyl hexene-1	14.00	19.64
i-propyl vinyl ether	35.50	17.20
(sec-butyl vinyl) ether	35.50	18.25

Proposed Model of the Macromolecule of Isotactic Poly-i-propyl Vinyl Ether

At this point, we have tried to find a model of the poly-i-propyl vinyl ether macromolecule that, besides permitting a good space arrangement of the isopropyl side groups among themselves and with regard to the carbon atoms of the main chain, should qualitatively justify the distribution of the intensities in the diffraction spectrum. First we have assumed the same values of the valency angles and of the bond distances of the side group atoms as found on the average in low-molecular weight compounds ($C-\overset{\vee}{O}-C = 110°$, $C-\overset{\vee}{C}-C = 112°$, $C-O = 1.43$ Å, $C-C = 1.54$ Å).

In order to arrange the side groups, the internal rotation angles σ_3 and σ_4 occurring on the two C—O bonds are still to be defined
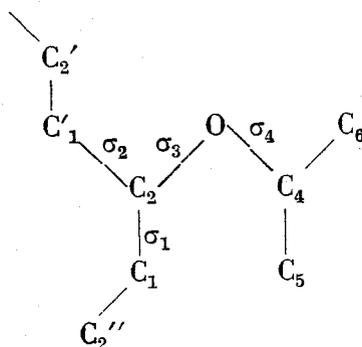
Assuming, for instance, that the sense of spiralization of the main chain is right-handed, i.e., that:

$$\sigma_1 = \overline{(C_{2''}C_1C_2)} \quad \overline{(C_1C_2C_{1'})} = 290°$$ and

$$\sigma_2 = \overline{(C_1C_2C_{1'})} \quad \overline{(C_2C_{1'}C_{2'})} = 170°$$

then if we put:

$$\sigma_3 = \overline{(C_1C_2O)} \quad \overline{(C_2OC_4)} = 280°$$ and

$$\sigma_4 = \overline{(C_2OC_4)} \quad \overline{(OC_4C_5)} = 280°$$

the shortest intramolecular distances, for atoms spaced by four or more bonds, become all of the order of 4 Å.
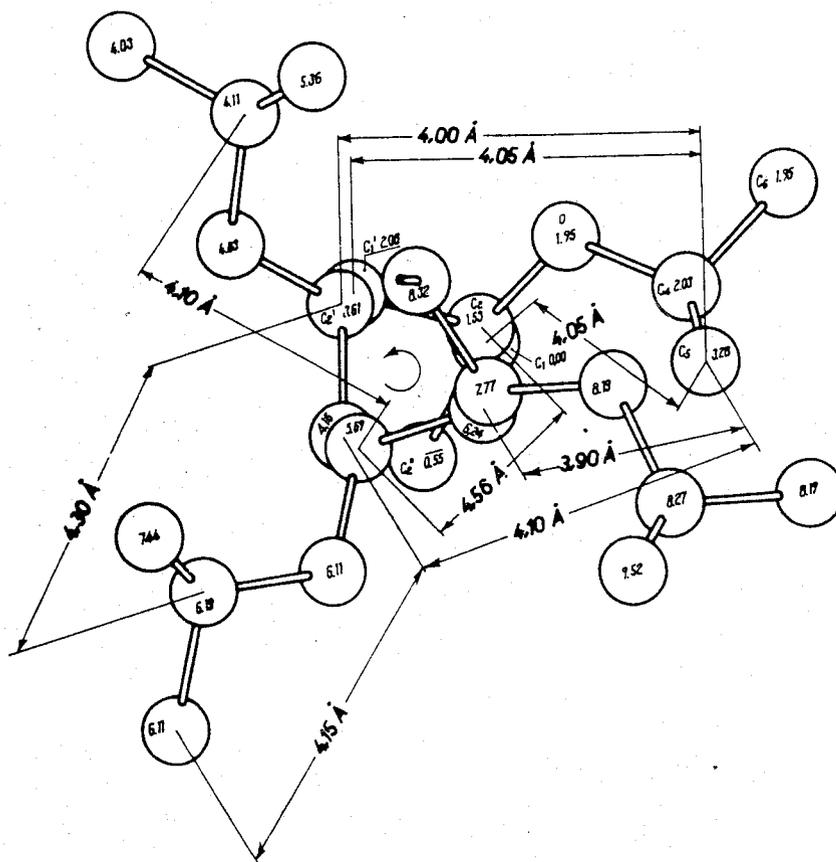

Fig. 2. Projection on a plane perpendicular to the chain axis of the proposed model of iso-tactic crystalline poly-*i*-propyl vinyl ether, omitting the hydrogen atoms. The most significant intramolecular contact distances are indicated

Any significant variation of σ_3 and σ_4 from the above reported values leads to a shortening of some contact distances. In particular, as it appears from Fig. 2, the C_5 atom is practically equidistant from all the nearest carbon atoms spaced by 4 or more bonds. If the groups consti-tuted by four carbon atoms linked by three successive bonds are con-sidered, it can be seen that none of them is considerably far from the energetically favoured *trans* or *gauche* conformations; moreover, all the intramolecular H—H distances are fully acceptable (see Fig. 5).

Finally, it seems worth mentioning that analogous values of the internal rotation angles around the C—O bonds have been found in other crystal-line polymers; in hexagonal polyformaldehyde 284°, [8], in isotactic poly-aldehydes 278°, [9] and in isotactic poly methyl vinyl ether 280° [10]. For all these reasons we have accepted the previously indicated conforma-tional model as the starting point for a more detailed analysis.

We have then checked the model by a comparison of the X-ray intensity due to a single macromolecule, calculated according to Eq. (1), with the diffracted intensity, in all the layers of the fiber spectrum. If the assumed molecular conformation is correct, the calculated intensity should qualitatively agree with the general pattern of the diffracted intensity, apart from intermolecular interference effects which are not allowed for by Eq. (1).

The cylindrical coordinates of the atoms of the monomeric unit of poly-i-propyl vinyl ether which are derived from the model described above are:

	r (Å.)	c (Å.)	φ (rad)
C_1	0.96	0.00	0.0000
C_2	0.96	1.53	0.1658
O	2.31	1.95	0.3578
C_4	3.23	2.03	−0.0349
C_5	3.30	3.28	−0.2880
C_6	4.63	1.95	0.1309

The F^2 values calculated for each layer are reported in Fig. 3. The calculation has been performed by taking into consideration, for every l-th layer, only the BESSEL functions whose index n is < 5 (cf. Table 3).

The intensities of the observed reflections agree satisfactorily with the pattern of the calculated intensity. The agreement between observed and calculated values for the layers with $l = 7$ and $l = 10$ seems very significant; in fact, they have very different intensity distributions (the 7th layer has rather strong intensities, while the 10th layer is completely absent), though depending on a BESSEL function with the same low index ($n = 2$).

Calculations performed even on models slightly different from that described, never led to an intensity distribution consistent with the experimental data on the two layers under examination.

In Fig. 4 we show the proposed model of the macromolecule of crystalline isotactic poly-i-propyl vinyl ether.
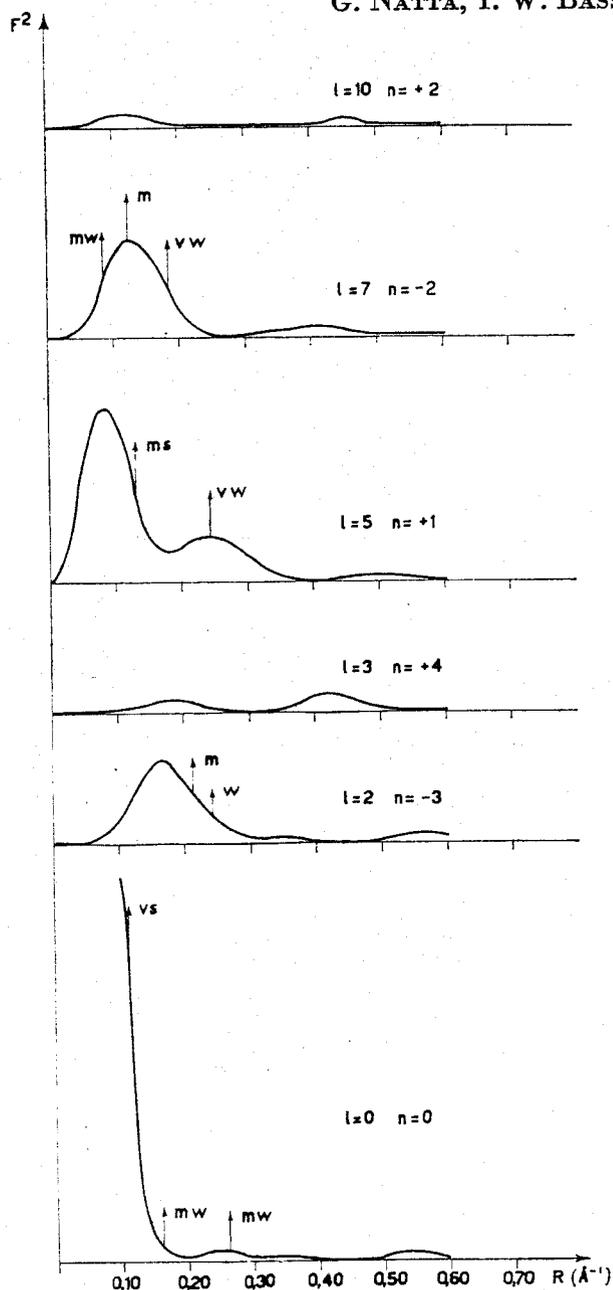
Fig. 3. Comparison between the calculated $F^2(R, l)$ function and the diffracted intensities (arrows) for crystalline isotactic poly-i-propyl vinyl ether

Molecular Conformation of Isotactic Poly(sec-butyl) Vinyl Ethers

On the basis of the similarity in intensity distribution between the diffraction spectra of poly-i-propyl vinyl ether and of poly(sec-butyl) vinyl ethers we have examined the interatomic contacts occurring within the macromolecule of poly-i-propyl vinyl ether, in the previously assigned conformation, by introducing a methyl group, linked either to C_5 or to C_6 (Fig. 5) in the various possible sites. As results from Fig. 6, two of the six different sites which can be occupied by the C_7 atom of the methyl group must be discarded (C_7B and C_7C) since they give rise to unusual contact distances. Therefore, on the basis of Eq. (1) we have calculated the intensity distribution on the various layers of the fiber spectrum for the remaining four positions.
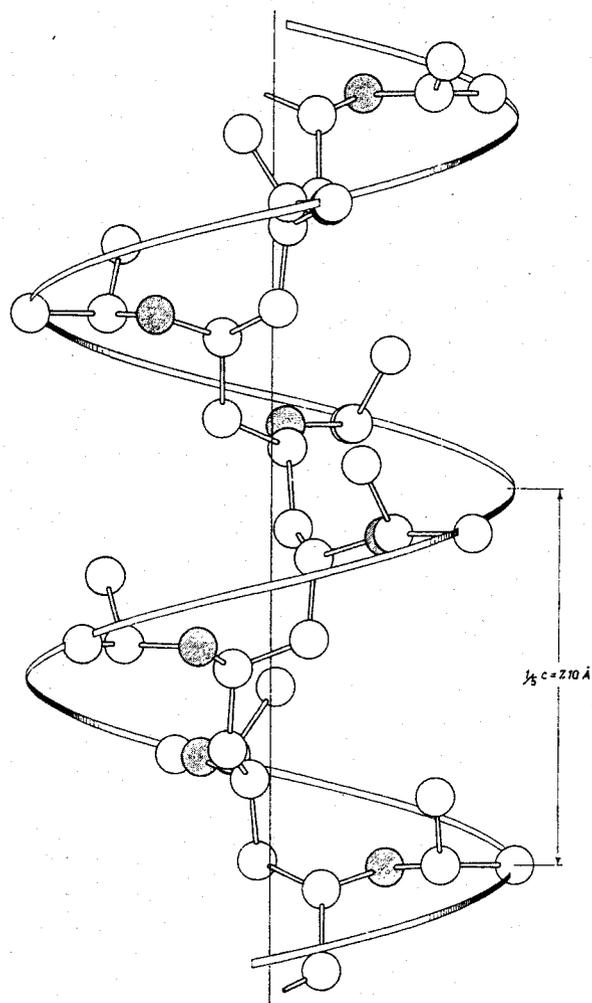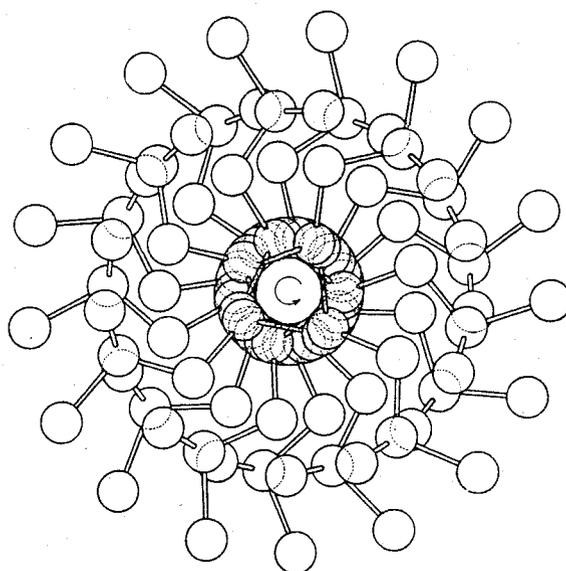
90

Fig. 4a   Fig. 4b

Fig. 4. Side (4a) and end (4b) views of the macromolecule of isotactic crystalline
poly-i-propyl vinyl ether

Unfortunately, the examination of the calculated intensity on all the
layers is scarcely significant, since the four positions lead to almost equi-
valent results, in substantial agreement with the experimentally observed
intensity distribution. Although careful examination of the calculated
intensity on the 3rd and on the 10th layer, which are not detectable in
the case of poly-i-propyl vinyl ether ($cf.$ Tables 1, 2 and 5), seems to in-
dicate that the site $C_{7''}$ is slightly favoured, we think that no decisive
choice may be derived from so small evidences.

Any possibility that the methyl group is far apart from one of the four
positions above examined, seems very improbable. In fact these positions
are largely favoured in intramolecular energy both because they do not
contrast with the principle of the staggered bonds[11,12] and because they
give rise to acceptable intramolecular contact distances; on the other

hand, the intermolecular interactions are generally of a rather secondary importance in determining molecular conformations, so that they should not lead to substantial modifications of the above deduction.

a)   b)

Fig. 5. End view of the monomeric unit conformation of isotactic crystalline poly-*i*-propyl vinyl ether (a). End view of the possible conformations of the monomeric unit of crystalline isotactic *racemic* poly(*sec*-butyl) vinylether (b); the positions that may be assumed by the carbon atom C_7 of the methyl group are indicated

Fig. 6. End view of the macromolecule of crystalline isotactic *racemic* poly(*sec*-butyl) vinyl ether when the carbon atom C_7 occupies the C_7B or the C_7C sites (see Fig. 5). The shortest interatomic distances are indicated

Conclusions

The proposed molecular conformation of isotactic poly-i-propyl vinyl ether in the crystal state seems to be sufficiently proved both with respect to the intramolecular contacts, and with respect to the agreement between diffracted and calculated X-ray intensities (see Figs. 3 and 5a). Owing to the great analogy in intensity distribution between the diffraction spectra of the two polymers, the crystalline poly *racemic* (*sec*-butyl) vinyl ether must be attributed a very similar molecular conformation to that of poly-i-propyl vinyl ether, while the position actually assumed by the C_7 methyl group cannot be quite apart from one of the four sites shown in Fig. 5, discarding C_7B and C_7C. Any choice between them seems impossible with the data at hand. The same conclusions hold for crystalline poly-S-(*sec*-butyl) vinyl ether, whose X-ray spectra are indistinguishable from those of the polymer obtained from the racemic monomeric mixture.

The reasons why the two crystalline poly(*sec*-butyl) vinyl ethers show the same X-ray fiber diagram may be related to two distinct hypotheses.

The first consists in supposing that in the polymer formed by the racemic monomer mixture each macromolecule consists of fairly long isotactic sequences of (R) or (S) units and that only crystals containing isomorphous units are formed on crystallization. Apart from the optical sign, every crystal should be identical with those present in the polymer obtained from the optically active monomer.

Alternatively, it could be supposed that a statistical distribution of the C_7 methyl groups within the four sites previously discussed takes place, so that again the crystals corresponding to the two kinds of polymers are practically indistinguishable, from a statistical viewpoint. Examination of the X-ray pattern of Fig. 1 seems to be in agreement with the latter hypothesis, since paracrystalline distortions are revealed, which correspond to a value of the g parameter (the standard deviation of the GAUSSIAN distribution of the lattice statistics, divided by the average lattice vector) of about 5 % (to be compared with a value of 15 % resulting from poly acrylonitrile[13]). The corresponding fluctuations in the lattice dimensions should allow a good space filling of the disordered chains both in the case of the *racemic* and of the poly-S-(*sec*-butyl) vinyl ether.

We are also very much indebted to Prof. P. Pino who kindly supplied us with the samples of isotactic *racemic* poly(*sec*-butyl) vinyl ether and of poly-S-(*sec*-butyl) vinyl ether and for his helpful criticism. Our thanks are also due to Prof. P. Corradini who encouraged us in the course of this work. Finally, we wish to acknowledge the very useful suggestions by Prof. R. Hosemann about the paracrystalline disorder present in the poly(*sec*-butyl) vinyl ethers.

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