

The Structure of Crystalline 1,2-Polybutadiene and of Other "Syndiotactic Polymers"

G. NATTA and P. CORRADINI, *Istituto di Chimica Industriale del Politecnico di Milano, Italy*

I. INTRODUCTION

Systematic x-ray and electron diffraction studies of polymers of 1,3-butadiene prepared by different anionic catalysts have permitted us to identify two types of highly crystalline materials. One of us (G.N.) has already reported at the Symposium on Macromolecules in Zurich¹ that their synthesis was carried out at the Institute of Industrial Chemistry of the Polytechnic Institute of Milan with the aid of different highly selective catalysts. The description of the preparation of these catalysts, which have allowed us for the first time to prepare these new polymers, will be separately published by one of us (G.N.) together with L. Porri.

Infrared analysis carried out by E. Mantica and D. Morero in our Institute has established that one type of these crystalline polymers obtained with heterogeneous catalysts represents a continuous 1,4-*trans* arrangement of the monomers. X-ray diffraction has shown that this material is dimorphous, having one crystalline modification that is stable at room temperature and another stable above 60°C. The x-ray melting point of a polymer having a molecular weight of the order of 100,000 is around 130°C.

The low temperature modification has an identity period of 4.9 Å. along the chain axis and a hexagonal packing with a period of $a = 4.54$ Å. perpendicular thereto, but the symmetry of the crystals, as a whole, is lower. The high temperature modification seems to have the chains in helicoid form.

The other crystalline polymer consists essentially of monomers in the 1,2 addition; infrared studies have shown that more than 90% of its double bonds are of the vinyl type and the residual 10% represents a mixture of *cis* and *trans*. The higher the proportion of 1,2 addition, the more crystalline is the material. Figure 1 shows the infrared registration curves of two different typical samples of the product.

In this article, we limit ourselves to describing the structure of the latter polymer, which, in our opinion, is the more interesting material and which we shall simply call 1,2-polybutadiene. We shall report on the structure of the two modifications of the 1,4-*trans*-polybutadiene in another paper together with the study of the structure of other crystalline polydienes.

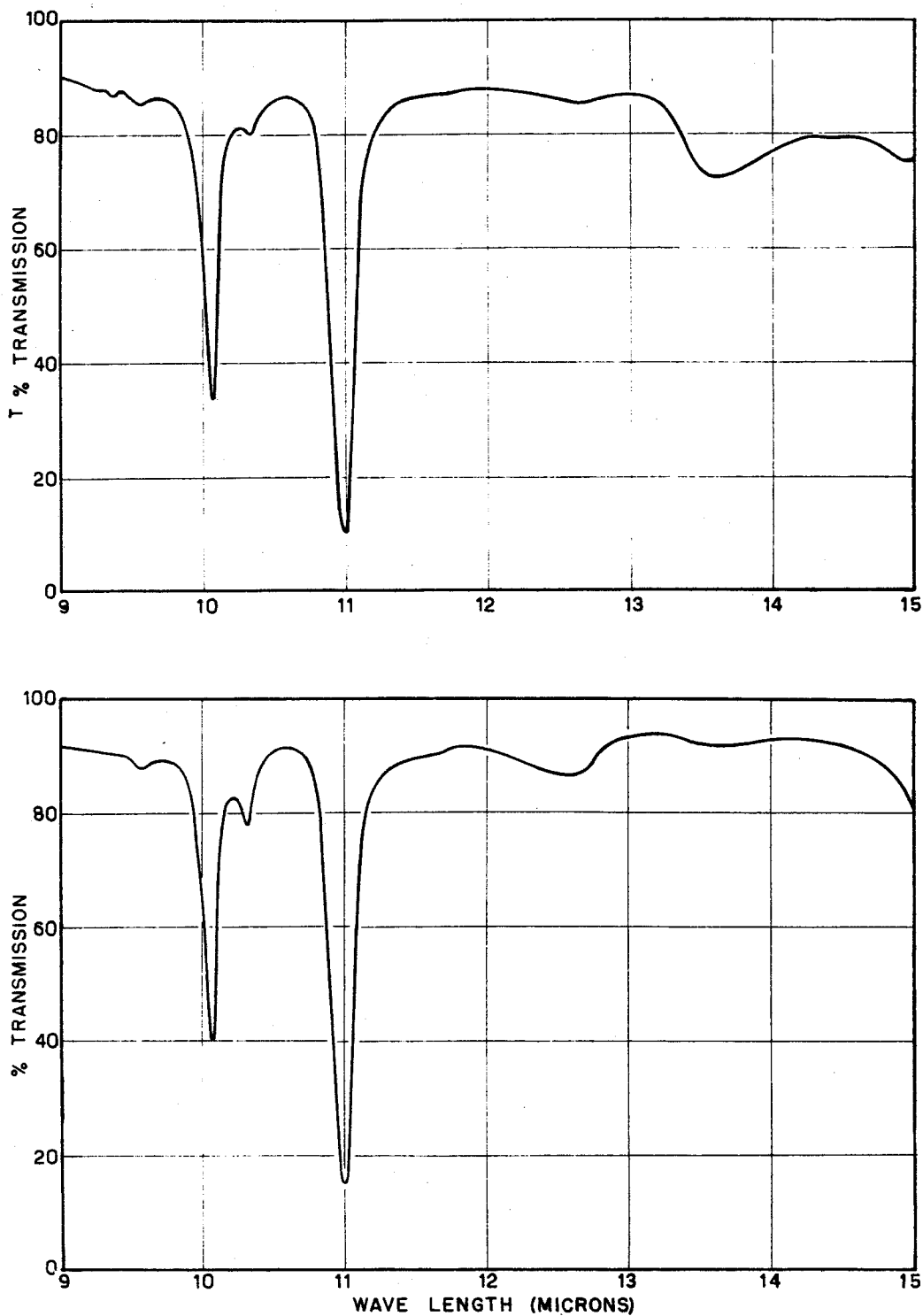


Fig. 1. Infrared absorption spectra of 1,2-polybutadiene.

The 1,2-polybutadiene to be described represents the first high melting (about $150^{\circ}\text{C}.$), highly crystalline polymer of butadiene that is linear and nonrubbery. Its melting point is higher than that of isotactic polybutylene ($125\text{--}130^{\circ}\text{C}.$) and very close to that of isotactic polypropylene ($160\text{--}170^{\circ}\text{C}.$),² which is in accord with the greater stiffness of the —CH=CH_2 group as compared with $\text{—CH}_2\text{—CH}_3$. Of equal interest is the fact that the 1,2-polybutadiene is the first case of a vinyl-type polymer, $(\text{CH}_2\text{—CHR})$, that

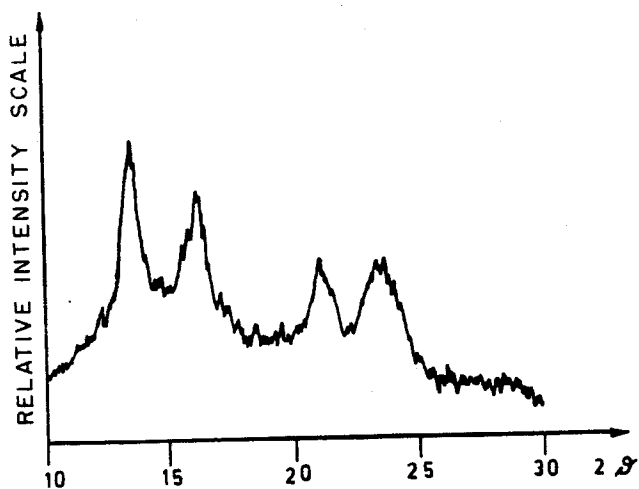


Fig. 2. Geiger counter registration curve of the reflections of 1,2-polybutadiene with $\text{CuK}\alpha$ radiation.

is highly crystalline but not isotactic. Indications of imperfect crystallinity have already been reported for a few known polyvinyl derivatives of nonisotactic character such as stretched fibers of polyvinyl chloride prepared with the aid of free radicals as initiators.³ The few and not sharp x-ray diffraction spots given by these materials were correlated with the presence of a planar zigzag chain with the substituents alternating in D- and L-configuration in respect to the plane of the zigzag. The absence of sharp and well-developed fiber diagrams did not permit a very profound study of the structural details of these materials.

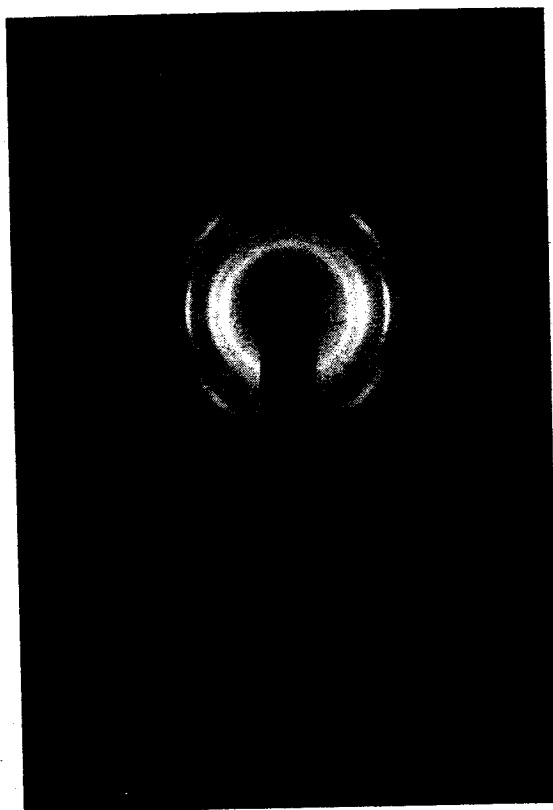


Fig. 3. X-Ray fiber diagram of 1,2-polybutadiene.

II. X-RAY INVESTIGATION

1,2-Polybutadiene, a white, easily moldable powder, was investigated with CuK_α radiation and a Geiger counter; it gives diffraction maxima distinctly different from those of isotactic poly- α -butylene²; they correspond to spacings of 6.60, 5.49, 4.20, and 3.80 Å.

The diffraction line of 3.80 Å. does not appear in samples that are molded at low temperatures in such a manner that a planar orientation is developed; this spacing, therefore, belongs to a set of planes, the last index of which is different from zero.² In fact, a rodlet of the polymer extended at high temperatures and cold-drawn produces a fiber diagram in which the first three reflections appear on the equator (Fig. 3), whereas the 3.80 Å. spot falls on the first layer line. The identity period along the fiber axis is 5.1 ± 0.1 Å.

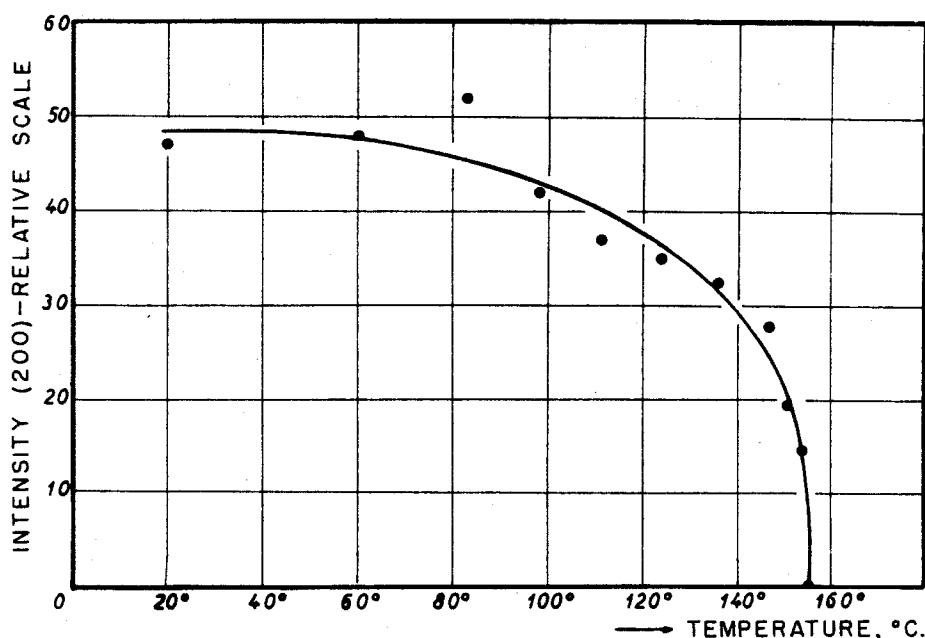


Fig. 4. Melting point curve of 1,2-polybutadiene taken with x-rays.

The powder diagram was obtained in a camera capable of operating at different temperatures and described elsewhere.² It was found from the disappearance of the diffraction lines that the material fuses completely at 154°C. The temperature spread, which is shown in Figure 4, corresponds to the normal behavior of high polymers and can only partly be attributed to the pressure of monomer units in different configurations which form amorphous areas.

III. ELECTRON DIFFRACTION STUDIES

We have already observed with other polymers that in many cases it is advantageous to study the diffraction of electrons by thin layers of polymers because in such thin films the polymer molecules tend to assume a

preferred orientation spontaneously. Also with crystalline 1,2-polybutadiene electron diffraction studies have proved to be very useful. Very thin layers (about 100 Å. thick) of the polymer were made by evaporation of a benzene solution on water and showed all the polymer molecules to be oriented with their axes perpendicular to the plane of the layer. These films were examined on a copper screen with a Finch electron diffraction camera in cooperation with I. W. Bassi.

IV. INTERPRETATION OF THE DIAGRAMS

The transmission diagrams obtained with electrons can be considered as a direct representation of a section of the reciprocal lattice by a plane passing through its origin. In our special case, where the crystallites are very small and parallel to a crystallographic direction c (coinciding with c), the set of their reciprocal lattices is given by concentric circles formed by the intersection with planes perpendicular to c (spaced by $1/c$) and cylinders coaxial to c with a radius $1/d(hk0)$. If one irradiates a thin film perpendicular to its surface with electrons, the reflection plane cuts the reciprocal lattice in a set of circles with radii $1/d(hk0)$, because a and b are perpendicular to c . The diagram contains only reflections indexed by $(hk0)$, which form a set of circles with the radii r

$$r = \lambda R d(hk0)$$

where λ = wave length and R = distance between sample and photographic plate. Figure 5 shows such a diagram.

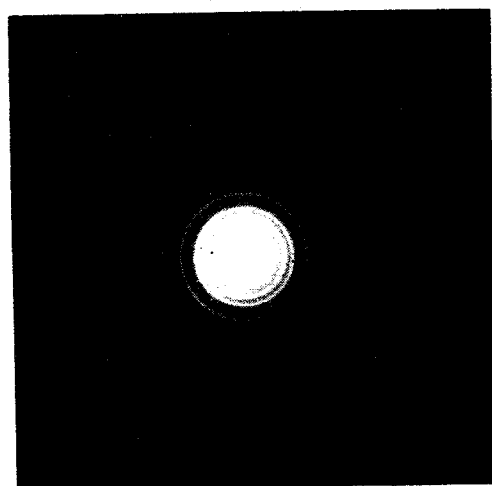


Fig. 5. Electron diffraction diagram of a thin film of 1,2-polybutadiene beam perpendicular to plane of film.



Fig. 6. Same diagram with oblique irradiation.

If the film is rotated by an angle δ in respect to the previous position so that its plane is now inclined to the beam at $(90^\circ - \delta)$, the reflection plane now cuts the reciprocal lattice in points falling on parallel straight lines

which are the intersections of the reflection plane with reciprocal lattice planes distanced from each other by $1/c$. The distance between these straight lines is $\lambda R/c \sin \delta$. Each reflection also falls on a circle of the radius $\lambda R/d(hkl)$. Figure 6 shows a pattern of this type and Table I the figures obtained from it.

TABLE I

$$\lambda R = 5.435 \times 10^{-8} \text{ cm.}^2$$

$2r$ (mm.)	Equator		First layer line	
		Intensity	$2r$ (mm.)	Intensity
8.3	<i>s</i>		14.3	<i>s</i>
9.9	<i>s</i>		19.9	<i>w</i>
12.9	<i>s</i>		28.2	<i>w</i>
16.9	<i>ms</i>			
19.2	<i>mw</i>		23.2	<i>ms</i>
21.4	<i>m</i>		27.3	<i>mw</i>
25.8	<i>m</i>		28.6	<i>w</i>
29.5	<i>w</i>		30.7	<i>w</i>
30.7	<i>w</i>		32.9	<i>mw</i>

The equatorial reflections (Fig. 7) can all be explained on the basis of a plane rectangular lattice with $a = 10.98 \pm 0.10$ A. and $b = 6.60 \pm 0.05$ A. In order to index the higher layer lines we have used the construction indicated in Figure 7. On the line OP we plot, beginning at O , segments OP ($hk0$), which are proportional to all possible values of $1:d(hk0)$. One does the same on the parallel lines $O'P'$, $O''P''$, which are drawn at distances proportional to $1/c$. If the lattice is orthorhombic, the circles with radii proportional to $1:d(hkl)$ and with the center in O will intersect the line $O'P'$ with $l = 1$, $O''P''$ when $l = 2$ at points $P'(hkl)$ or $P''(hk2)$, respectively, which give us the indices of the reflections. Figure 7 shows that this construction can be successfully applied in our case.

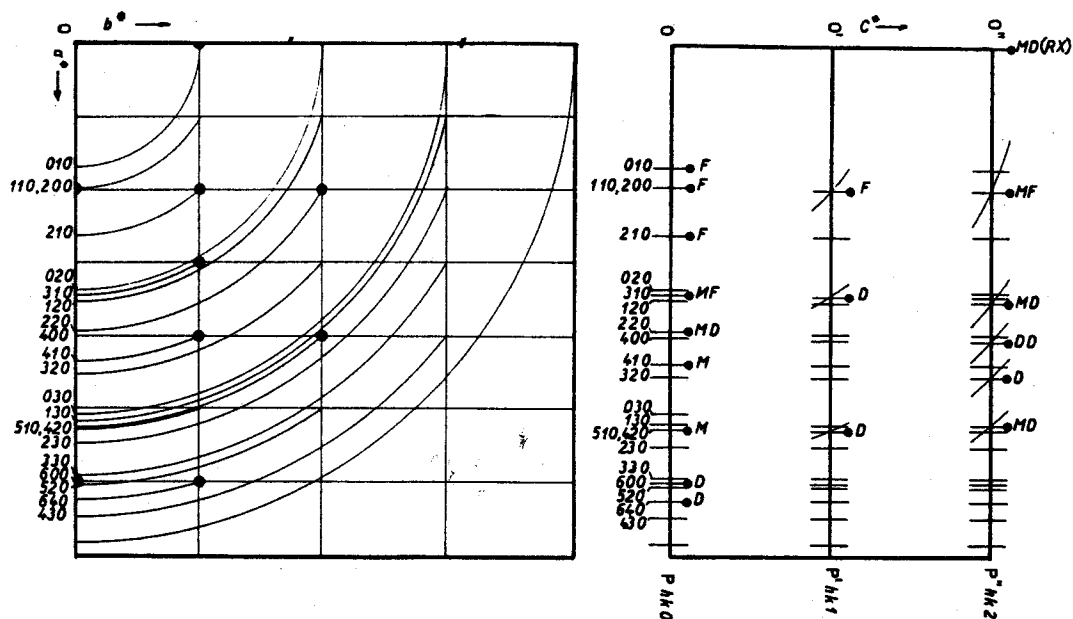


Fig. 7. Reconstruction of the reciprocal lattice of 1,2-polybutadiene.

The best evaluation leads to an elementary cell with $a = 10.98$ Å., $b = 6.60$ Å., and $c = 5.14$ Å. The theoretical density (assuming four monomers in the cell) is 0.963. This must always be higher than the experimental value (0.92) because of the presence of less dense amorphous areas.

The absence of reflections $0kl$, for $l = 2n + 1$ and $h0l$ for $h = 2n + 1$, which may not be completely conclusive because of possible very small intensities, and considerations of packing possibilities of the molecules indicate $P6cm$ as the most probable space group.

V. DETERMINATION OF THE STRUCTURE

For simplicity we shall denote by C_1 and C_2 the carbon atoms CH_2 and CH in the main chain and by C_3 and C_4 the carbon atoms CH and CH_2 of the pending vinyl groups. The general weakness of the $hk0$ reflections with $h = 2n$ affirms the fact that atoms C_1 and C_2 of the main chain are projected along c in the neighborhood of $x = 0, y = 0$ and $x = 1/2, y = 0$. The identity period of 5.1 Å. parallel to the fiber axis coincides with the presence of a plane rigid zigzag paraffin chain with a periodicity represented by four carbon atoms. Since this identity period corresponds to two monomer units, one must conclude that the two vinyl groups alternate in opposite

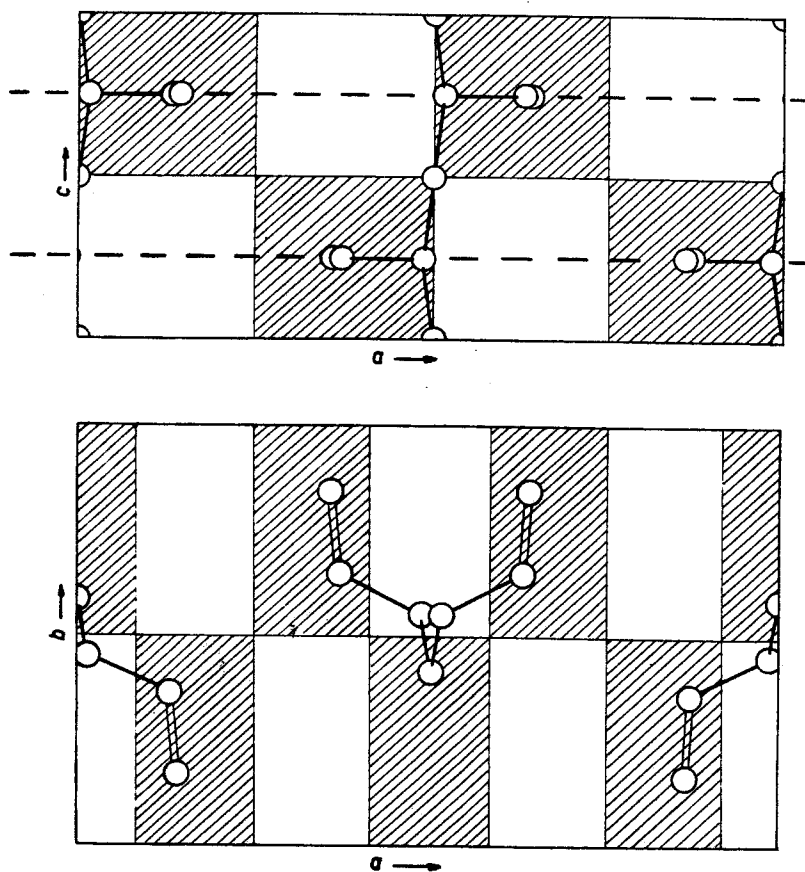


Fig. 8. Negative and positive areas of the structure factors of the reflections (201) and (310).

TABLE II
ATOM FORM FACTORS TAKEN FROM X-RAYS

Indices	nF^2 (first approach)	nF^2 (final approach)	Intensity
010	64	90	<i>s</i>
110, 200	136	87	<i>s</i>
210	116	116	<i>s</i>
020	5	6	—
310	50	67	<i>ms</i>
120	12	1	—
220	26	42	<i>mw</i>
400	—	0	—
410	65	46	<i>m</i>
320	4	2	—
030	1	4	—
130	0	0	—
420, 510	96	58	<i>m</i>
230	1	3	—
330	6	6	—
600	12	49	<i>w</i>
520	3	4	—
610	34	27	<i>w</i>
111, 201	96	131	<i>s</i>
211	0	2	—
311	39	19	<i>w</i>
121	0	0	—
221	7	4	—
401	1	1	—
411	1	3	—
321	0	2	—
131	2	3	—
421	0	3	—
511	8	24	<i>w</i>
231	0	0	—
331	3	3	—
002	20	20	<i>mw</i> (x-ray)
012	0	1	—
112, 202	72	59	<i>ms</i>
212	0	0	—
022	0	1	—
312	0	3	—
122	23	30	<i>mw</i>
222	4	2	—
402	25	22	<i>ww</i>
412	1	0	—
322	21	24	<i>w</i>
032	5	2	—
132, 422	52	52	<i>mw</i>
512	3	1	—
232	8	2	—

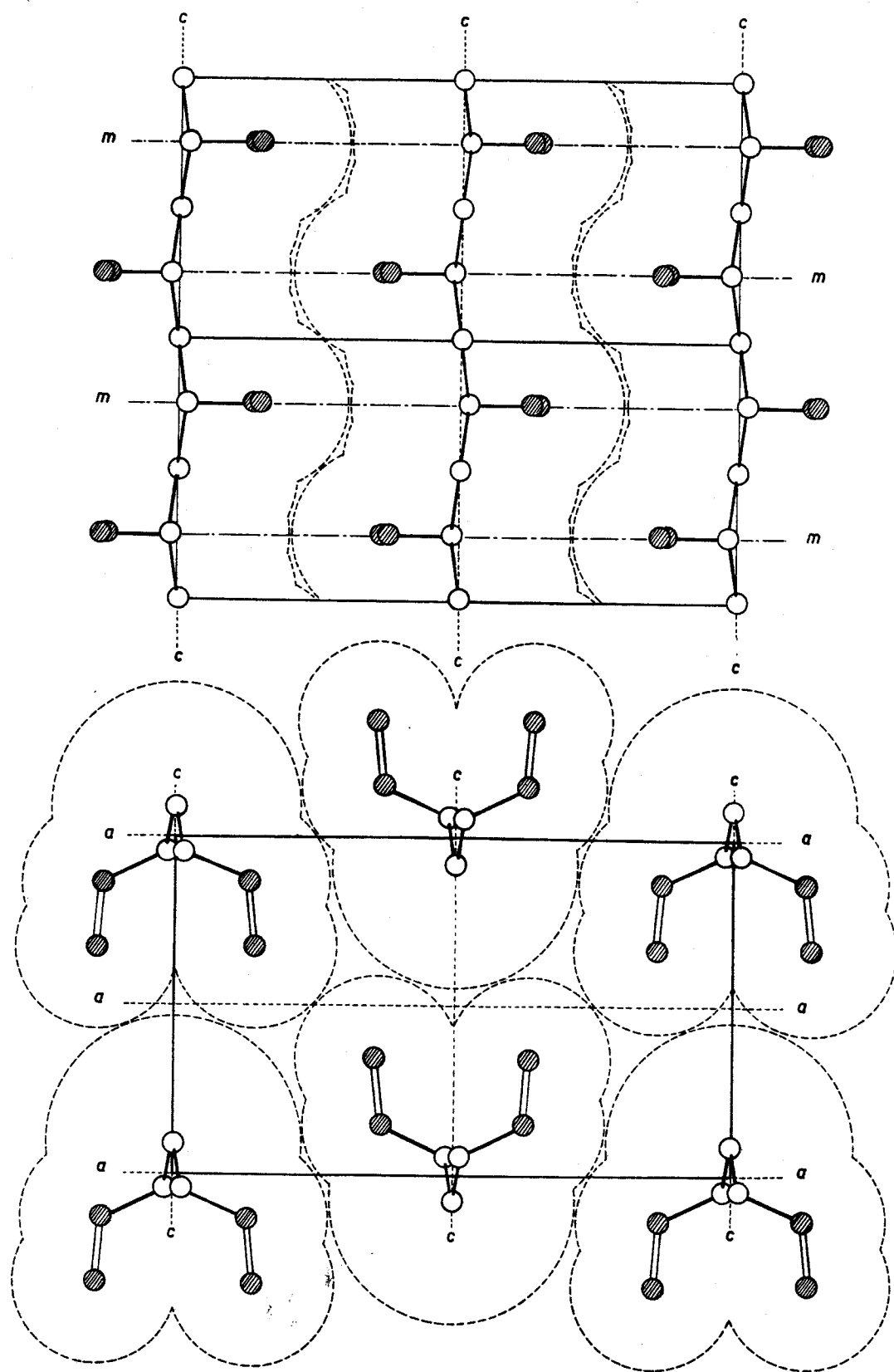


Fig. 9. Model of the structure of 1,2-polybutadiene.

positions, as if they were attached to two asymmetric carbon atoms that have the L- and D-configuration, respectively. Such a distribution has been proposed to explain the diffuse scattering of polyvinyl chloride, although the diagrams of this material reveal a much lower degree of order than in the present case.

From the space group *Pacm* it follows that the molecule itself has a plane of symmetry with a translation period of $1/2$ along *c*. The plane paraffin chains therefore lie in the planes $(0, y, z)$. Assuming now a certain chain model in concordance with these conditions, it is possible to localize the molecules in the cell and to calculate the structure factors with only one variable parameter along direction *b*. In order to localize the vinyl groups in a tentative fashion, one is guided by the exceptional intensity of the (201) reflection, which indicates that these groups alternate in the D- and L-configuration, changing from one into the other in respect to the adjacent molecules as one proceeds one-half of the identity period along *c* (see Fig. 8). Equally important is the high intensity of (310) independent of the reflectivity of the chain carbon atoms because $h = 3$ and therefore probably mainly caused by the arrangements of the vinyl groups (see Fig. 8).

In the calculation of the structure factors we have assumed the atomic distances and valence angles as generally accepted and found that a model with a planar paraffin chain parallel to $(0, y, z)$ and with the coordinates:

	<i>x</i>	<i>y</i>	<i>z</i>
C ₁	0	0.896	0
C ₂	0	0.030	0.250
C ₃	0.117	0.164	0.250
C ₄	0.117	0.364	0.250

gave the best agreement between experimental and calculated intensities (see Table II). This model, as any other model in which the chains are planar, leads, however, to a crowding of the atoms C₁ and C₄ (3.9 Å.) and also to a rather close approach of the C₄ atoms of the same chain, which appears to be excessive in view of the distances between the other carbon atoms (*ca.* 4.2 Å.) of the model.

We have, therefore, examined other models in the same space groups by making slight adjustments of the above coordinates, abandoning the complete planarity of the backbone chain. One arrives at a better agreement and at a better packing of the molecules by a model not much different from the above, in which the chains are somewhat nonplanar. It is shown in Figure 9 and its coordinates are:

	<i>x</i>	<i>y</i>	<i>z</i>
C ₁	0	0.916	0
C ₂	0.014	0.050	0.250
C ₃	0.136	0.143	0.250
C ₄	0.143	0.342	0.250

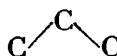
In Table II a comparison is given of the experimental intensities with the F^2 -values computed for the two models. The van der Waals' distances between carbon atoms of different chains corresponding to the second model are all equal to or larger than 4.0 Å. and are given in Table III.

TABLE III
VAN DER WAALS' DISTANCES BETWEEN C-ATOMS OF DIFFERENT CHAINS
FOR THE SECOND MODEL

$C_4 \dots C_4$	4.0 Å.
$C_4 \dots C_1$	4.3-4.4 Å.
$C_3 \dots C_3$	4.0 Å.
$C_3 \dots C_1$	4.2 Å.
$C_4 \dots C_4$ (same chain)	4.0 Å.

The calculated structure factors favor to a slight extent the second model, but only a more detailed structure investigation (probably only with the aid of better x-ray diagrams) can finally settle this question.

The valence angles:



in the main chains are 113° , in good agreement with other reported values,⁴ such as polyethylene (111°), polypropylene (114°), polyisobutylene (114°), and polystyrene (116°).

VI. DEFINITION OF "SYNDYOTACTIC" POLYMERS

The structure of 1,2-polybutadiene as described in the preceding paragraph merits a special discussion of its characteristics. It is the first case of a polyvinyl derivative in which a regular alternation of the D- and L-configuration of the substituents has been established and also the first case of a polyhydrocarbon of high molecular weight combining asymmetric carbon atoms with a relatively large substituent which is crystalline, and the chain of which is essentially planar. It may therefore be interesting to compare this structure with that of crystalline polyolefins which show simply a regular succession of tertiary carbon atoms with the same steric configuration alternating with CH_2 groups in the main chains.

In a paper presented to the Accademia dei Lincei² in December, 1954, we defined as isotactic polymers those linear crystallizable polymers of alpha olefins of head-to-tail structure in which, over a certain chain length, the asymmetric carbon atoms display the same steric configuration. These materials have high melting points and possess in the crystalline state helicoid chains that are quite different from those found in 1,2-polybutadiene (lower structure in Fig. 10). This structure differs rather noticeably from that of an isotactic polymer such as, for instance, poly- α -butylene, in that, if the main chain of the latter were completely accommodated in one

plane, the substituents R would be all above or all below that plane (upper structure in Fig. 10).

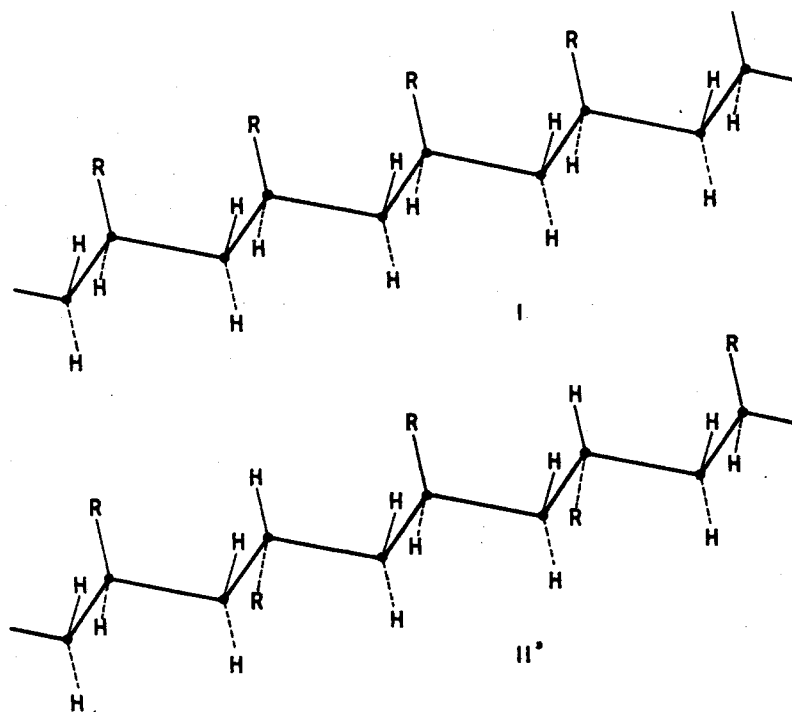


Fig. 10. Models of isotactic (I) and syndiotactic (II) structure with planar chains.

In reality, because of the steric interference of the C_2H_5 groups with each other the main chain of poly- α -butylene cannot possess a planar structure and does assume the helicoid configuration described in an earlier paper, whereas in the 1,2-polybutadiene a certain degree of planarity is possible for the main chain because of the more favorable arrangement of the vinyl groups. The difference between the two structures becomes more evident if one examines the projections of the main chains on two planes—one perpendicular to and one parallel with the axis of the molecule (Fig. 11). Both types of chains represent a high regularity but, whereas isotactic chains have—over a certain length—all asymmetric carbon atoms in the same configuration, the chains of 1,2-polybutadiene are characterized by a regular alternation of D- and L-configurations along the length of the chains.

We propose to call all vinyl polymers with alternating D- and L-configurations of their substituents (like 1,2-polybutadiene) "syndiotactic" polymers, using the Greek words *tatta* ("put in order") and *syndyo* ("every two").

VII. STRUCTURE OF POLYVINYL CHLORIDE

In connection with our results on the structure of 1,2-polybutadiene we have resumed the study of the x-ray diagrams given by other polyvinyl compounds of equal identity period, such as polyvinyl chloride, in order to find out whether they also possess a syndiotactic structure. Previously

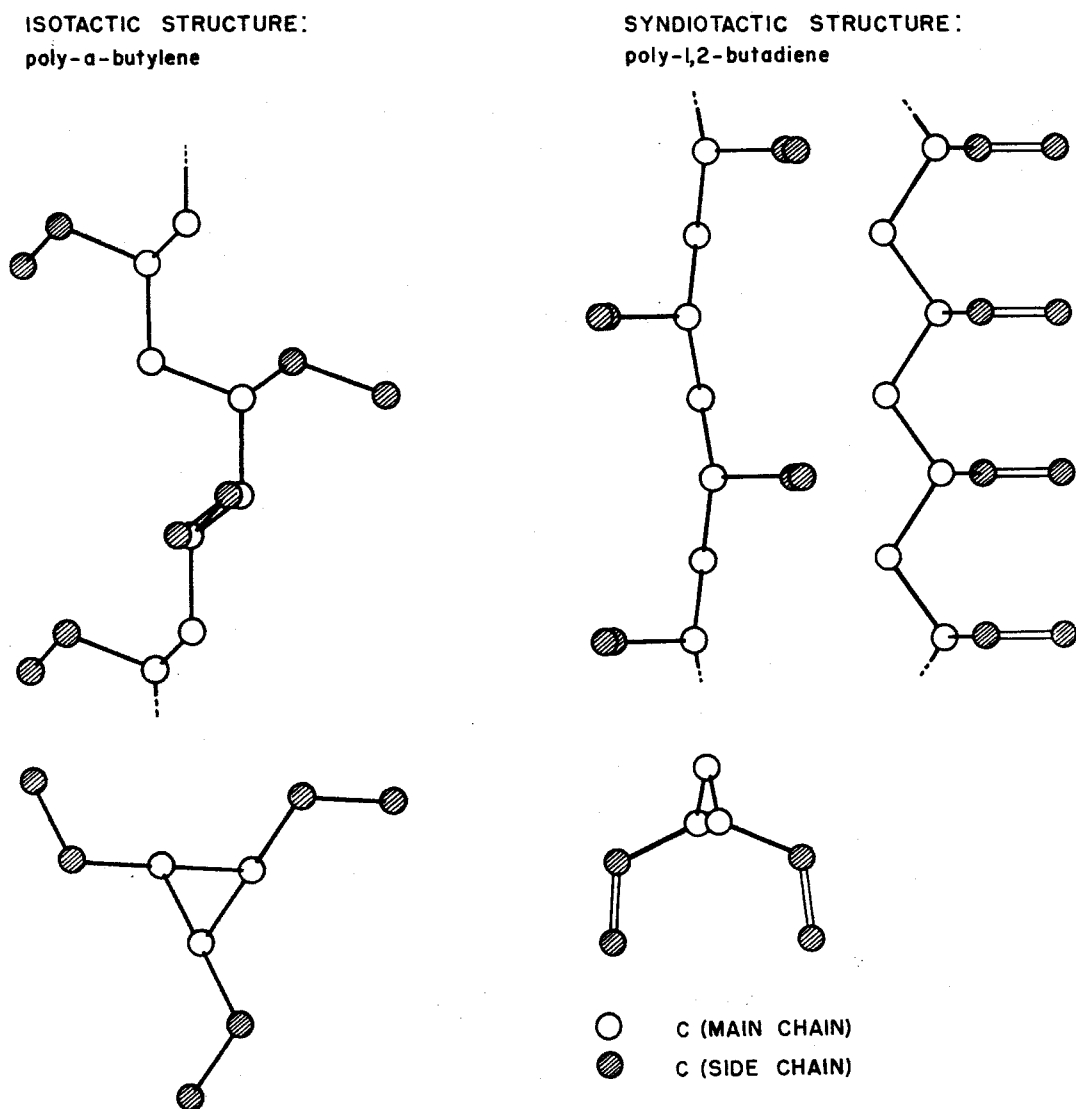


Fig. 11. Models of 1,2-polybutadiene and poly- α -butylene.

their imperfect crystallinity did not permit a sufficiently thorough investigation.

Oriented fibers of polyvinyl chloride, prepared with the aid of free radical catalysts, give an x-ray diagram with imperfect layer lines, indicating the existence of laterally ordered domains (about 50 Å. wide) with a rather poor order along the length of the chains. The diagram reveals equatorial reflections with $d = 5.39, 4.78, 3.74,$ and 2.94 Å. These values, observed by us, are in agreement with those reported in literature.³ The first, very diffuse, layer line has a maximum at $d_{\text{eq}} = 5.3$ Å.; the identity along the fiber axis is 5.1 ± 0.1 Å.

Assuming that polyvinyl chloride crystallizes in the orthorhombic space group *Pacm* and that the arrangement of the macromolecules is similar to that of 1,2-polybutadiene, one can interpret all equatorial reflections by an orthorhombic cell with the axes $a = 10.6 \pm 0.1, b = 5.4 \pm 0.1$ Å.

In Table IV the experimental and theoretical spacings of five planes are compared.

TABLE IV
LATTICE SPACINGS OF POLYVINYL CHLORIDE

Indices	$d(\text{experimental}), \text{A.}$	$d(\text{theoretical}), \text{A.}$
200 } 010 }	5.39	5.4 5.3
110	4.78	4.79
210	3.74	3.76
310	2.94	2.95

The four strongest reflections of 1,2-polybutadiene have the same indices: 010, 200 + 110, 210, and 310.

The x-ray density of polyvinyl chloride is calculated to be 1.44, which is in good agreement with the experimental values (1.39–1.41).

Calculating the structure factor with the coordinates:

	x	y	z
C(H ₂).....	0.25	0.107	0
C(H).....	0.25	0.066	0.25
Cl.....	0.134	0.25	0.25

one arrives at good agreement with the experimental intensities if one uses a temperature factor $B = 20 \times 10^{-16} \text{ cm.}^2$, which one might better call here a factor of lateral disorder. Table V gives the results of this calculation.

TABLE V
EXPERIMENTAL AND THEORETICAL INTENSITIES OF POLYVINYLCHLORIDE

Indices	$d, \text{A.}$	Intensity (measured)	F^2 (calculated)
200	5.39	m	60
010	—	—	—
110	4.74	m	55
210	3.74	w	21
310	2.94	w	18
All other intensities.....			$\ll 10$

The model represented in Figure 12 corresponds to a planar chain. Any deviation from planarity greater than 5° of the type found in the polybutadiene would lead to a discrepancy between observed and calculated intensities.

The arrangement of the molecules parallel to a leads to a close packing of the Cl atoms of 4.4 A., in agreement with the minimum distances of 4.2 to 4.3 A. found in other organic structures; the distribution along b is determined by an approach between Cl and CH₂ of 3.93 A. in accord with corresponding minimum values of 3.65 in other organic structures (see Fig. 12). Also, the intensities along the layer lines are in agreement with the postulated structure; the maximum on the first layer line corresponds to (201), which is an intense reflection in the pattern of 1,2-polybutadiene. The lack of order along the c -axis can be attributed to imperfections in the

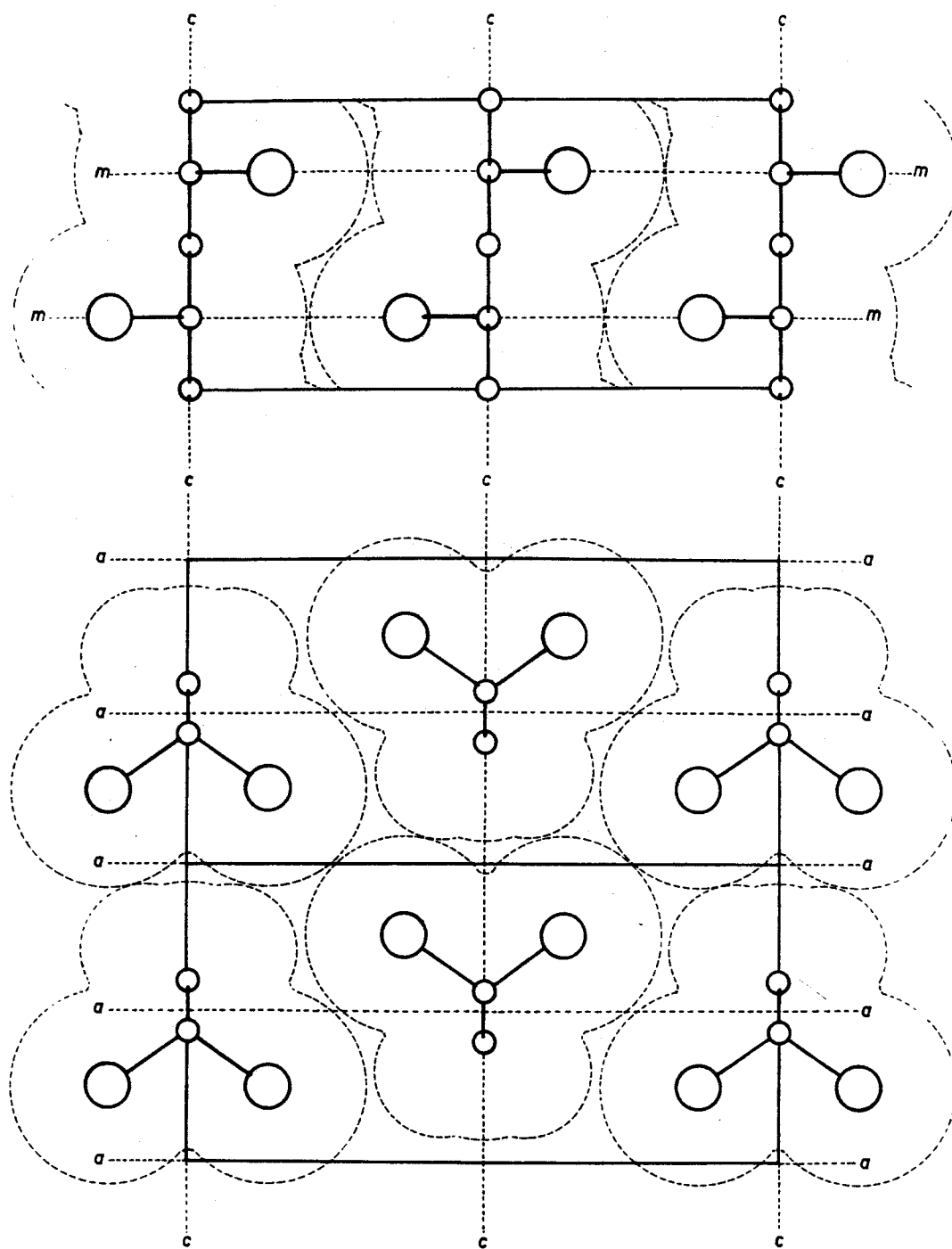


Fig. 12. Model of the structure of polyvinyl chloride.

syndiotactic arrangement of the Cl atoms. The syndiotactic segments of the chains arrange themselves through orientation in crystalline areas that are relatively extended along a and b but are only rather short in parallel to the c -axis.

These imperfections must be caused by the fact that the investigated polyvinyl chloride samples were prepared with free radical initiators and hence by a less regular polymerization process which is exposed to perturbations by chain transfer and by head-to-tail *versus* head-to-head addition. It is also possible that during the addition of any individual monomer to the

growing chain the two possible configurations, D and L, alternate with each other in a statistical manner. Whatever the reason for the imperfections may be, it is justified to assume also in this case the existence of short segments with syndiotactic structure.

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Synopsis

With the aid of anionic polymerization catalysts, 1,2-polybutadiene of high molecular weight has been synthesized. It is a crystalline material with a melting point above 150°C. Electron and x-ray diffraction studies with oriented films permitted determination of the elementary cell, the space group, and the coordinates of the individual carbon atoms in the cell. The chains deviate slightly from the conventional planar zig-zag structure, the vinyl group substituents are arranged in the 1-3 sequence with alternating D and L configurations. It is proposed to call this type of spatial arrangement in head-to-tail vinyl polymers a syndiotactic arrangement. Also polyvinyl chloride, obtained with free radical catalysts, contains small ordered regions, with a structure similar to syndiotactic 1,2-polybutadiene.

Résumé

On a synthétisé du polybutadiène de structure 1-2 de poids moléculaire élevé en présence de catalyseurs de polymérisation anioniques. Ce matériau est cristallin et fond au delà de 150°C. Des études de diffraction aux électrons et aux rayons-X sur des films orientés permettent de déterminer la cellule périodique, le groupe spatial, et les coordonnées des atomes de carbone individuels au sein de la cellule. Les chaînes s'écartent légèrement de la structure en zig-zag conventionnelle, et les groupes vinyliques substituants sont répartis en séquence 1-3 avec des configurations alternativement D et L. On propose d'appeler un tel type d'arrangement spatial au sein de polymères vinyliques alternés un arrangement syndiotactique.

Zusammenfassung

1,2-Polybutadien von hohem Molekulargewicht wurde mit Hilfe von anionischen Polymerisationskatalysatoren synthetisiert. Es ist eine kristalline Substanz mit einem Schmelzpunkt oberhalb 150°C. Elektronen- und Röntgenstrahlen-Diffraktions-Untersuchungen mit orientierten Filmen erlaubten die Bestimmung der elementaren Zelle, der Raumgruppe, und der Koordinaten der individuellen Kohlenstoffatome in der Zelle. Die Ketten weichen leicht von der konventionellen planaren Zickzack-Struktur ab, die Vinylgruppen-Substituenten sind in der 1-3-Folge mit wechselnden D und L Konfigurationen angeordnet. Es wird vorgeschlagen, diese Art der Raumanordnung in Kopf-zu-Schwanz-Vinylpolymeren eine syndiotaktische Anordnung zu nennen. Auch Polyvinylchlorid, welches mit Freiradikal-Katalysatoren erhalten wurde, enthält kleine geordnete Bereiche, die eine Struktur ähnlich der von syndiotaktischem 1,2-Polyvinylbutadien haben.

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