

Crystal Structure of *trans*-Polypentenamer

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Synopsis

trans-Polypentenamer, like natural rubber, crystallizes under stretching at room temperature. The x-ray fiber spectra of crystalline *trans*-polypentenamer can be interpreted on the basis of an orthorhombic unit cell whose identity periods in Å. units are: $a = 7.28 \pm 0.10$; $b = 4.97 \pm 0.05$; $c = 11.90 \pm 0.10$ (chain axis); $Z = 4(\text{C}_5\text{H}_8)$; $d_{\text{calc}} = 1.049 \text{ g./cm.}^3$. Probable space groups $C_{2v}^2(Pna2_1)$ or $D_{2h}^{16}(Pnam)$. Atomic positions were deduced by trial and error. The $\text{-(CH=CH-CH}_2\text{-CH}_2\text{-CH}_2\text{)-}$ monomeric units repeat along a twofold helix. The molecular packing in the crystal state is essentially regulated by the H atoms of the CH_2 groups. The packing of the *trans*-polypentenamer molecules is very similar to the packing found for orthorhombic polyethylene.

Research done at our Institute allowed us to synthesize, by cleavage of cyclopentene rings, high polymers deriving from a head-to-tail succession of unsaturated base units $\text{-(CH=CH-CH}_2\text{-CH}_2\text{-CH}_2\text{)-}$, in which almost all the double bonds have a *trans*-configuration.¹ The *trans*-polypentenamer, as natural rubber and *cis*-1,4-polybutadiene,² is practically amorphous or only slightly crystalline at room temperature in the unstretched state, but on cooling or stretching it crystallizes to a considerable extent. Its melting point, determined by dilatometric methods, is $+23^\circ\text{C}$. When thin cylinders of *trans*-polypentenamer are stretched (elongation of 600–700%), the x-ray fiber diffraction patterns show a high degree of crystallinity also at temperatures markedly above room temperature.

The interesting elastomeric properties of *trans*-polypentenamer and of many analogous polymers obtained by polymerization via ring cleavage of other cycloolefins studied in our Institute, prompted us to examine in detail the chain conformations and the crystal structures of these polymers. The new *trans*-polyalkenamers obtained by us, differ from *trans*-1,4-polybutadiene and from *trans*-polypentenamer owing to the different number of CH_2 methylenic groups (up to 10) separating two successive double bonds.

In this paper we describe the crystal structure of *trans*-polypentenamer only. This work is the first of a series of papers which are now being prepared on the crystal structures of a series of new *trans*-polyalkenamers synthesized in our Institute.

Experimental Studies

Narrow ribbons, cut out from a molded sheet of *trans*-polypentenamer, have been examined by x-rays while stretched (600–700%) either at room temperature or at low temperature ($\simeq -40^\circ\text{C}$). The x-ray fiber photographs, taken with a cylindrical camera employing Cu, $K\alpha$, or Fe, $K\alpha$ radiations at either of the above-mentioned temperature conditions, did not differ appreciably.

The chain repeat is 11.90 ± 0.10 Å. All the reflections of the fiber pattern can be interpreted on the basis of an orthorhombic unit cell, whose constants are: $a = 7.28 \pm 0.10$ Å.; $b = 4.97 \pm 0.05$ Å.; $c = 11.90 \pm 0.10$ Å. (chain axis).

The crystalline density when four C_5H_8 units are contained in the unit cell results 1.049 g./cc. This value is slightly higher than that calculated for orthorhombic polyethylene (1.006 g./cc.). We wish to point out that polyethylene crystallizes in a unit cell, the equatorial dimensions of which ($a = 7.40$ Å., $b = 4.93$ Å.) are very close to those found for *trans*-polypentenamer.

The reflections ($h0l$) are absent when $h \neq 2n$ and no reflection ($0kl$) has been observed when $k + l \neq 2n$. When we assume that the missing reflections correspond to systematic absences, the most probable space groups are $C_{2v}^9(Pna2_1)$ or its centrosymmetrical space group D_{2h}^{16} in the *Pnam* orientation.⁴

The intensities of the reflections were measured by visual comparison with calibration spots of known relative exposure. The multiple film method was employed and the corrections for the area of diffraction spots have been made by visual estimation. The observed intensities have been corrected for the Lorentz and polarization factors relative to single crystals and for multiplicity.

Possible Conformations of the Macromolecule of *trans*-Polypentenamer in the Crystalline State

The observed identity period along the chain axis (11.9 Å.) suggests that the fiber repeat comprises two chemical units $\text{-(CH=CH-CH}_2\text{-CH}_2\text{-CH}_2\text{)-}$. The calculated repeat, based on a planar zig-zag chain conformation and the generally accepted bond lengths and angles ($\text{C-C} = 1.54$ Å., $\text{C=C} = 1.34$ Å., $\text{C-C-C} = 109^\circ 28'$, $\text{C=C-C} = 120^\circ$) being *trans* the configurations of the double bonds, is 12.50 Å.

The difference between the observed (11.90 Å.) and the calculated (12.50 Å.) repeats indicates a shortening of the macromolecule axis. This shortening may be well justified with a distortion of the macromolecule from a planar zig-zag conformation, due to the values assumed by the internal rotation angles occurring on the single bonds adjacent to the double bonds.

In the case of many other crystalline polymers containing double bonds along the main chain, it was actually observed that according to the prin-

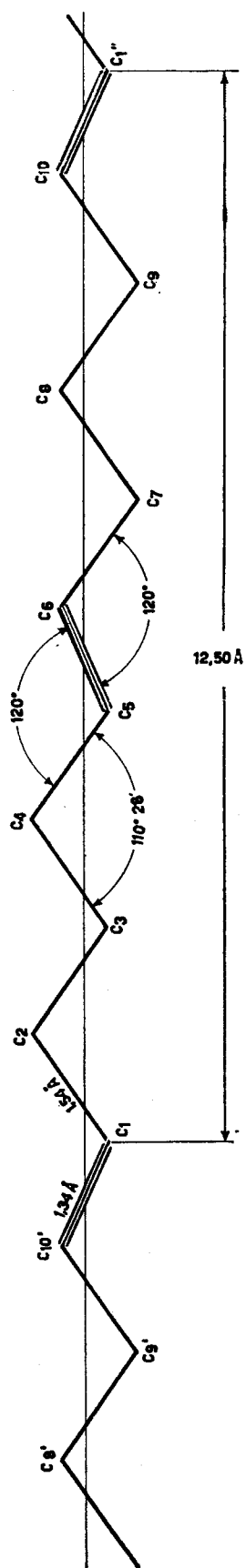


Fig. 1. (left) Model of the macromolecule of *trans*-polyentenamer; all carbon atoms are arbitrarily disposed on a plane.

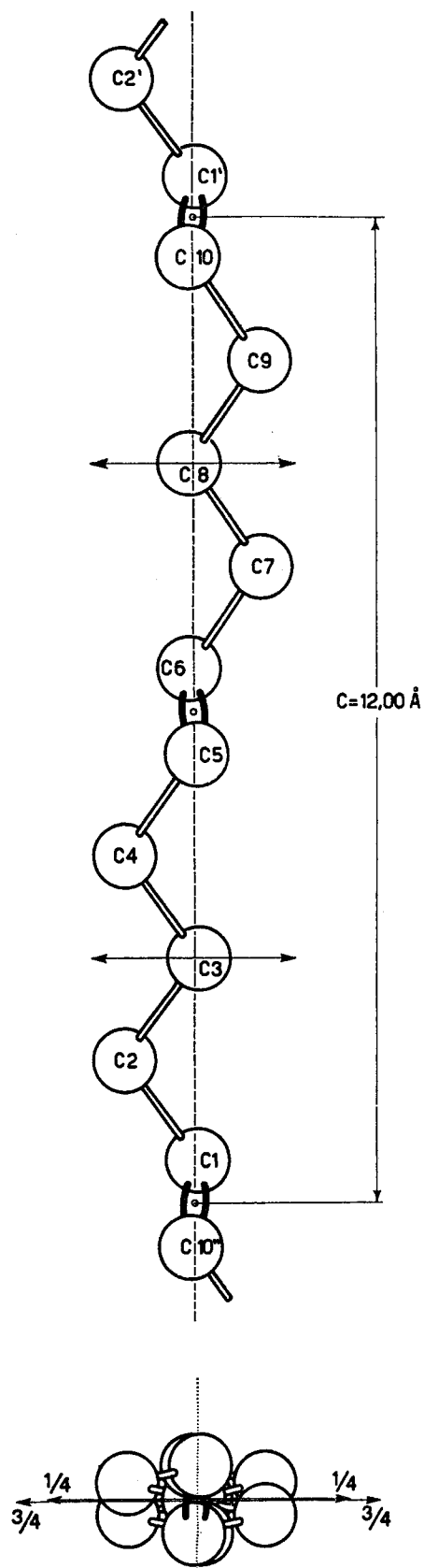


Fig. 2. (right) Model of the macromolecule of *trans*-polyentenamer; the monomeric units repeat by the action of a glide plane (side and end views).

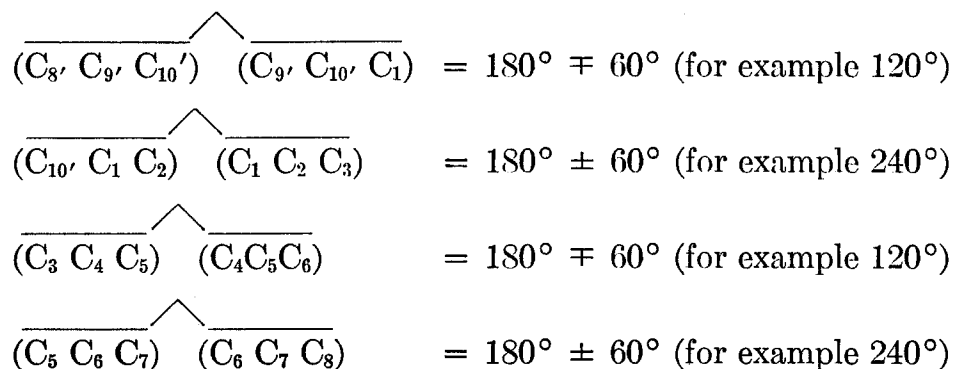
ciple of staggered bonds,⁵ the internal rotation angles occurring on the single bonds adjacent to the double bonds assume the values of $180^\circ \pm 60^\circ$.⁶

Starting from the planar zig-zag conformation of *trans*-polypentenamer shown in Figure 1, and considering as satisfied the equivalence postulate of the monomeric units,⁷ the repetition after two monomeric units is possible only if the internal rotation angles occurring on the single bonds adjacent to the same double bond assume the values of $180^\circ \pm 60^\circ$ and $180^\circ \mp 60^\circ$, respectively.

Two alternatives are still possible: the monomeric units can repeat along the chain axis either by the action of a glide plane (1) or by means of a two-fold screw axis (2).

In the first case the succession of these internal rotation angles is $180^\circ \pm 60^\circ$, $180^\circ \mp 60^\circ$; $180^\circ \mp 60^\circ$, $180^\circ \pm 60^\circ$; $180^\circ \pm 60^\circ$, $180^\circ \mp 60^\circ$; the calculated repeat is of 12.00 Å. and model (1) of the macromolecule, shown in Figure 2, has intrinsically *tic* symmetry.⁸ In fact, besides the glide plane, there are symmetry centers on the double bonds and binary axis perpendicularly to the glide plane and passing through C₃, C₈, etc.

If the monomeric units are connected by a twofold screw axis, the succession of these internal rotation angles is:



Evidently, as in the former case, all the other internal rotation angles assume the value of 180° . The repeat calculated for this model is 11.85 Å. Model (2) of the macromolecule shown in Figure 3 has intrinsically symmetry $S(2/1)m$.⁸ In fact, besides the twofold screw axis, there are symmetry planes passing through C₃, C₈, and symmetry centers on the double bonds.

A choice between these two models is impossible on the basis of the chain repeat and does not seem possible, even considering the intramolecular contact distances which are satisfactory for both alternatives. Taking into account the intrinsic symmetry elements of the two models, in order to realize a good space filling under the conditions imposed by the unit cell dimensions and by the C_{2v}^9 and D_{2h}^{16} space groups, it is possible to reject, in our case, the model characterized by the glide plane [model (1)].

The general positions foreseen by the $Pnam$ space group are 8; since two portions of macromolecules, each consisting of two C₅H₈ monomeric units, are contained in the unit cell, the asymmetric unit must be one half of the

C_5H_8 chemical unit. Evidently this is possible only if all the intrinsic symmetry elements of the macromolecule are consistent with the symmetry elements of the *Pnam* space group. Unlike model (2) [symmetry $S(2/1)m$] that satisfies this requisite, model (1) (symmetry *tic*) cannot be arranged in the D_{2h}^{16} space group, because this space group does not allow the presence of binary axes. Moreover, model (1) cannot be arranged in the $Pna2_1$ space group either since, as in the *Pnam* one, the systematic absences found do not foresee the existence of a glide plane parallel to the chain axis. All these considerations sufficiently prove model (2), which fully satisfies the experimental findings considered so far.

Structure Determination

We have thought it reasonable to perform the crystal structure determination of *trans*-polypentenamer on the basis of the *Pnam* space groups so that all the intrinsic symmetry elements of the macromolecule can find correspondence in the symmetry elements of the space group.

Due to the limiting conditions imposed by the *Pnam* space group, the *Z* coordinates of the macromolecule atoms are automatically fixed. We have only to define the atomic coordinates with respect to the *a* and *b* axes of the unit cell.

Following a criterion adopted in many analogous cases,¹⁰ we tried to define the position of the macromolecules in the equatorial plane on the basis of intermolecular Van der Waals distances. The best intermolecular contact distances are reached when the φ angle formed by the direction of the *b* axis of the unit cell and by the planes on which the C atoms of the macromolecules are situated (Fig. 3) amounts to about 40° (Figs. 5, 6). At this point we performed some calculations of the structure factors, in which the contribution of the hydrogen atoms was also taken into account, for several different orientations of the macromolecule in the range of φ

comprised between 35° and 45° ($C-H = 1.08$ A., $C-C-H = 109^\circ 98'$).

The comparison between the observed structure factors and those calculated for the different positions of the macromolecule has shown the substantial correctness of the postulated structure; however, it has also pointed out some discrepancies for some of the weakest reflections of the diffraction photographs. Since the disagreement could not be overcome by rotation of the molecule around its twofold screw axis, we have supposed that the macromolecule model had to be slightly modified. A projection of the electron density on the (001) plane performed with the (*hk*0) reflections seemed to support this occurrence, although it did not lead to a good resolution of the atomic positions.

The simplest deformation to be done on the model seemed that of a change in the values of the internal rotation angles on the single bonds adjacent to the double bonds. Keeping the model symmetry always $S(2/1)m$, we have turned these angles from 180 ± 60 and $180^\circ \mp 60^\circ$ to $180^\circ \pm 50^\circ$ and $180^\circ \mp 50^\circ$, respectively. All the other parameters of the starting model were retained. The calculated chain repeat (11.97 A.)

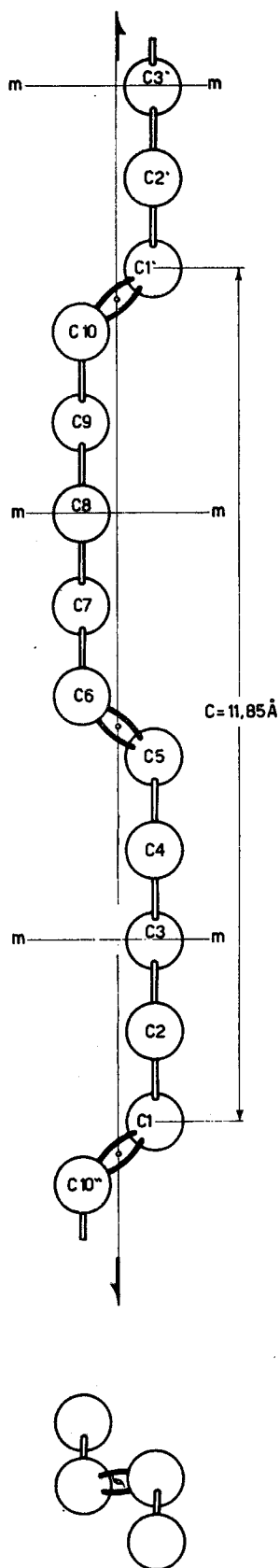


Fig. 3. (left) Model of the macromolecule of *trans*-poly(pentenamer); the monomeric units repeat by the action of a twofold screw axis (side and end views).

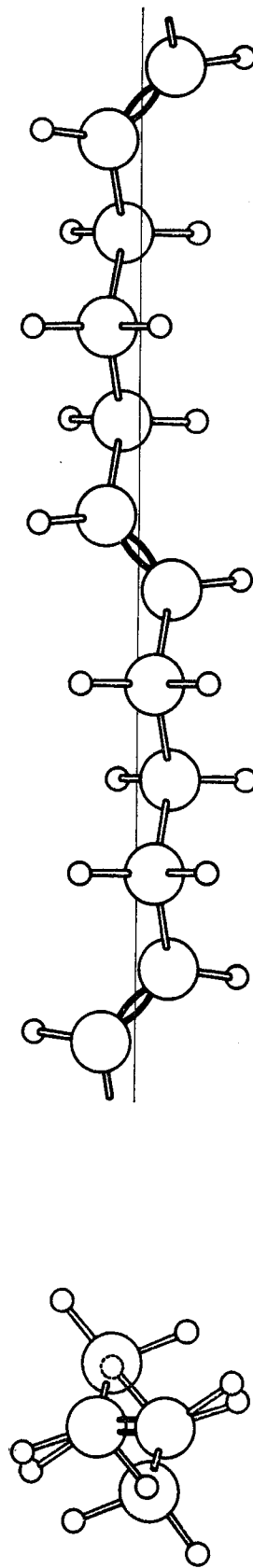


Fig. 4. (right) Model of the macromolecule of *trans*-poly(pentenamer) in the crystalline state (side and end views).

TABLE I
Coordinates of the Asymmetric Unit of Crystalline *trans*-Polypentenamer
(Space Group: *Pnam*)^a

	x/a	y/b	z/c
C ₁	0.039	0.075	0.040
C ₂	0.118	0.942	0.145
C ₃	0.039	0.075	0.250
H ₁	0.045	0.289	0.033
H ₂	0.089	0.726	0.145
H' ₂	0.270	0.965	0.145
H ₃	0.077	0.287	0.250
H' ₃	0.896	0.048	0.250

* The marks attributed to the hydrogen atoms indicate the carbon atom to which they are bound.

always agrees well with the experimental one (11.90 ± 0.10 Å). On the basis of this model, shown in Figure 4, we have performed the calculation of the structure factors for some orientations of the macromolecule, with respect of the equatorial axes of the unit cell, with $\varphi \simeq 40^\circ$. The best agreement between observed and calculated structure factors was obtained when $\varphi = 40.8^\circ$. In Table I are reported the atomic coordinates corresponding to this position of the macromolecule.

The comparison between the observed and calculated structure factors is reported in Table II; the isotropic temperature factor used corresponds to $B = 3.9 \text{ \AA}^2$.

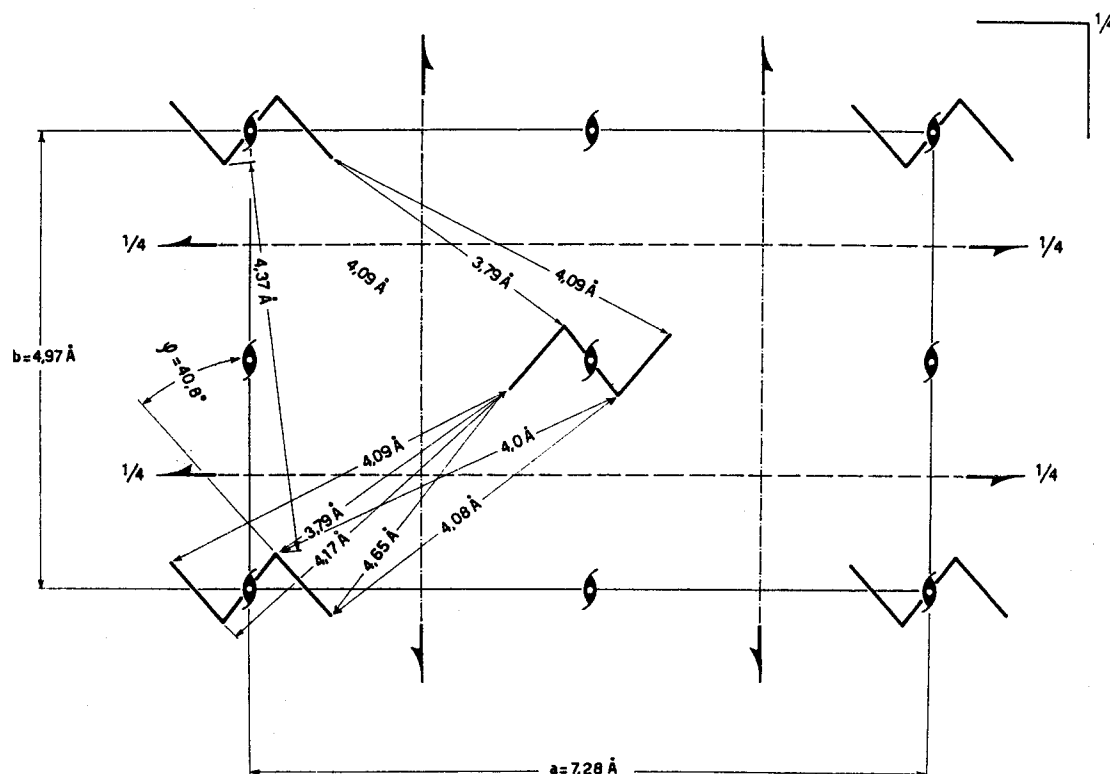


Fig. 5. Projection on the (001) plane of the structure of *trans*-polypentenamer. The shortest C—C intermolecular contact distances are indicated.

TABLE II
Comparison Between Calculated and Observed Structure Factors of *trans*-Polypentenamer^a

<i>h</i>	<i>k</i>	<i>l</i>	$(\sin \theta / \lambda)^2$	F_c	F_0	<i>h</i>	<i>k</i>	<i>l</i>	$(\sin \theta / \lambda)^2$	F_c	F_0
1	1	0	0.0148	71.4	79.3	4	1	2	0.0926	3.1	(2.7)
2	0	0	0.0188	51.5	47.4	1	3	2	0.1028	0.4	(2.9)
2	1	0	0.0289	1.6	(1.9)	0	1	3	0.0259	4.2	4.3
0	2	0	0.0404	37.0	45.4	1	1	3	0.0307	11.0	12.6
1	2	0	0.0452	5.6	5.4	2	0	3	0.0347	15.2	19.0
3	1	0	0.0525	9.0	6.5	2	1	3	0.0448	1.6	(1.9)
2	2	0	0.0593	11.4	12.9	1	2	3	0.0610	1.3	(2.2)
4	0	0	0.0755	2.4	(3.7)	3	1	3	0.0684	7.2	6.8
3	2	0	0.0829	4.0	(2.7)	2	2	3	0.0752	5.7	5.2
4	1	0	0.0856	7.6	8.1	4	0	3	0.0913	4.4	(3.7)
1	3	0	0.0958	9.4	13.7	3	2	3	0.0988	3.4	(2.7)
2	3	0	0.1099	2.4	(3.0)	4	1	3	0.1015	3.3	(2.8)
4	2	0	0.1159	2.1	(3.1)	1	1	4	0.0430	7.9	8.1
5	1	0	0.1281	4.3	(3.2)	2	0	4	0.0471	22.4	22.1
3	3	0	0.1335	0.5	(3.2)	2	1	4	0.0572	13.6	14.4
5	2	0	0.1584	12.5	11.4	0	2	4	0.0687	2.0	(3.0)
0	4	0	0.1619	1.6	(4.8)	1	2	4	0.0734	9.7	8.6
1	4	0	0.1666	3.2		3	1	4	0.0808	17.1	15.9
				8.9	11.8	2	2	4	0.0875	7.5	9.2
4	3	0	0.1666	8.3		4	0	4	0.1037	17.8	14.4
6	0	0	0.1699	2.2	(4.8)	3	2	4	0.1111	10.8	
6	1	0	0.1800	8.4						12.9	10.6
				8.8	10.3	4	1	4	0.1138	7.0	
2	4	0	0.1808	2.8		1	3	4	0.1240	0.8	(2.8)

3	4	0	0.2044	1.4	(3.5)	2	3	4	0.1381	11.0	10.4
5	3	0	0.2090	2.5		4	2	4	0.1442	8.2	7.2
				2.6	4.9	5	1	4	0.1563	8.8	6.3
6	2	0	0.2103	0.5		3	3	4	0.1617	3.1	(3.1)
4	4	0	0.2374	2.1	(3.5)	5	2	4	0.1866	3.3	(3.2)
7	1	0	0.2413	1.6	(3.5)	0	4	4	0.1901	3.2	
1	5	0	0.2577	6.5		1	4	4	0.1948	6.3	8.9
				13.5	11.8	4	3	4	0.1948	6.5	
6	3	0	0.2609	11.8		6	0	4	0.1981	2.4	(4.7)
7	2	0	0.2717	8.5		6	1	4	0.2082	1.7	
2	5	0	0.2718	2.3	11.1					2.1	(4.7)
5	4	0	0.2799	8.7		2	4	4	0.2090	1.2	
3	5	0	0.2954	2.8	(3.2)	3	4	4	0.2326	7.9	6.5
8	0	0	0.3020	1.4	(4.4)	5	3	4	0.2372	2.4	
8	1	0	0.3121	3.1	(3.0)					2.7	(4.5)
0	1	1	0.0118	1.3	(2.0)	6	2	4	0.2386	1.3	
1	1	1	0.0166	25.1	26.8	0	1	5	0.0542	27.1	20.1
2	0	1	0.0206	40.0	40.8	1	1	5	0.0589	8.9	8.5
2	1	1	0.0307	8.8	10.1	2	0	5	0.0629	6.1	5.5
1	2	1	0.0469	4.8	3.7	2	1	5	0.0730	12.3	12.1
3	1	1	0.0543	17.4	19.7	1	2	5	0.0893	21.6	17.4
2	2	1	0.0611	11.2	13.2	3	1	5	0.0966	2.2	(2.2)
4	0	1	0.0772	14.6	12.6	2	2	5	0.1034	4.3	(2.4)
3	2	1	0.0847	10.9	9.3	4	0	5	0.1196	11.0	12.4
4	1	1	0.0873	6.9	4.7	3	2	5	0.1270	4.8	
0	3	1	0.0928	0.9	(3.4)					4.8	(2.7)
1	3	1	0.0975	4.5	4.8	4	1	5	0.1297	0.2	
2	3	1	0.1117	7.6	5.1	0	3	5	0.1351	22.4	22.8
4	2	1	0.1177	4.4	VW	1	3	5	0.1399	3.0	(2.8)

(continued)

TABLE II (continued)

h	k	l	$(\sin \theta/\lambda)^2$	F_c	F_0	h	k	l	$(\sin \theta/\lambda)^2$	F_c	F_0
5	1	1	0.1298	2.7	(3.2)	2	3	5	0.1540	10.8	8.2
3	3	1	0.1353	3.6	(3.2)	4	2	5	0.1600	4.3	(2.9)
5	2	1	0.1602	5.5	8.2	5	1	5	0.1722	13.2	12.6
1	4	1	0.1684	1.2		3	3	5	0.1776	1.2	(3.0)
4	3	1	0.1684	8.4	8.5	5	2	5	0.2025	1.2	(3.0)
6	0	1	0.1716	0.2		1	4	5	0.2107	13.9	
6	1	1	0.1817	0.2		4	3	5	0.2107	0.2	21.3
					(4.9)	6	0	5	0.2140	16.1	17.1
2	4	1	0.1825	0.1		2	4	5	0.2249	2.0	(3.2)
3	4	1	0.2061	7.8	vw						
5	3	1	0.2108	0.1							
					(4.9)						
6	2	1	0.2121	1.0							
1	1	2	0.0218	2.9	3.4						
2	0	2	0.0259	11.4	10.7						
2	1	2	0.0360	6.0	8.5						
0	2	2	0.0475	1.3	(3.0)						
1	2	2	0.0522	4.5	4.9						
3	1	2	0.0596	7.3	7.8						
2	2	2	0.0664	2.8	(2.4)						
4	0	2	0.0825	8.4	7.4						
3	2	2	0.0900	4.8	4.6						

^a The F_0 figures in brackets correspond to half the minimum observable intensity on each layer ($B = 3.9 \text{ \AA}^2$).

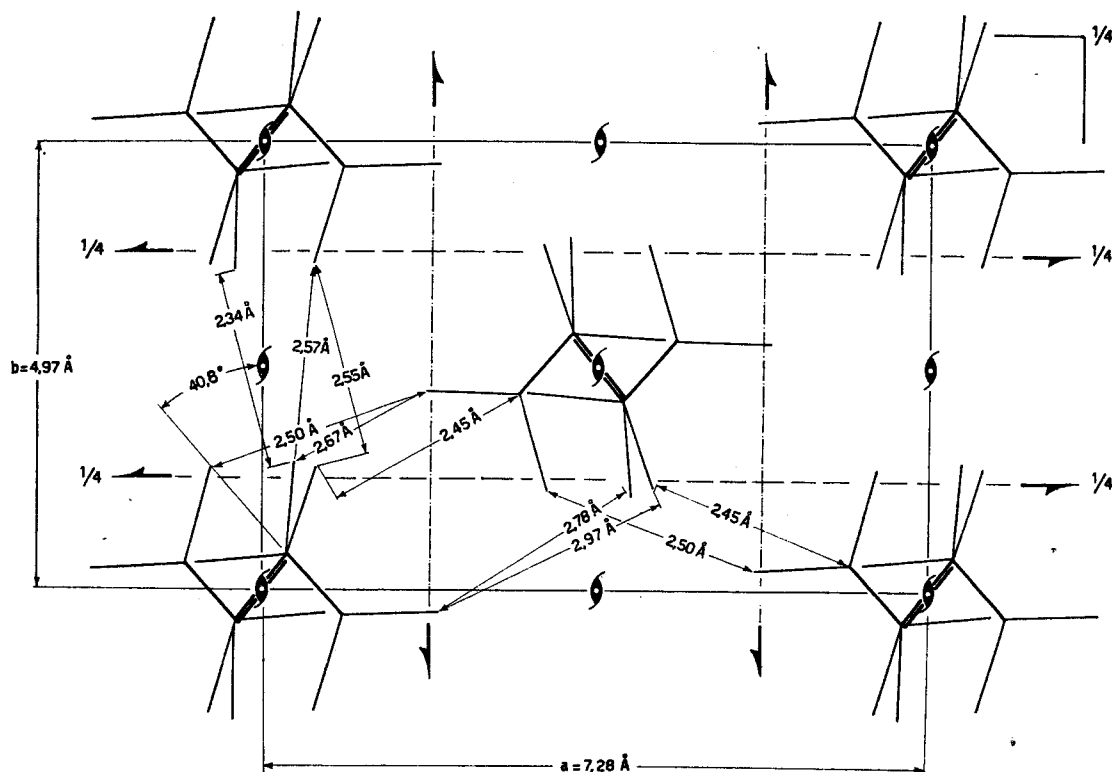


Fig. 6. Projection on the (001) plane of the structure of *trans*-polypentenamer; the shortest H—H Van der Waals distances are indicated.

The reliability factor calculated from the expression

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

corresponds to 20% and may be considered quite satisfactory for a polymer structure. In evaluating R we have also taken into account the reflections that are not observed and assumed for them an intensity value corresponding to half the minimum observable intensity in correspondence of each layer line. Figures 5 and 6 show the arrangement of the molecules viewed down the chain axis and Figure 7 shows the unit cell of *trans*-polypentenamer. As we can see from Figure 5, the Van der Waals distances between carbon atoms are quite satisfactory.

Discussion of the Structure

We think it is of interest to compare the crystal structure found for *trans*-polypentenamer with that found by Bunn for orthorhombic polyethylene. As already pointed out in the previous sections, the equatorial axes of the unit cell of the two polymers are strictly similar. Moreover the packing conditions are quite the same, the space group for both polymers being $Pnam$. These analogies also influence the orientation of the macromolecules of both polymers, with regard to the a - b planes of the unit cells. In the case of polyethylene, the angle formed by the plane on which the main chain carbon atoms lie and the b axis, is of 41.2° .³ For *trans*-

polypentenamer, the angle formed by the direction of the b axis of the unit cell and the two planes on which the main chain carbon atoms are disposed five by five (Fig. 5) is 40.8° . The equatorial dimensions and the symmetry of the unit cell of *trans*-polypentenamer are evidently determined by the planar part of the chain; the double bonds and the chain distortion do not appreciably distort the unit cell, in comparison with those found for orthorhombic polyethylene, and for one of the crystalline modifications

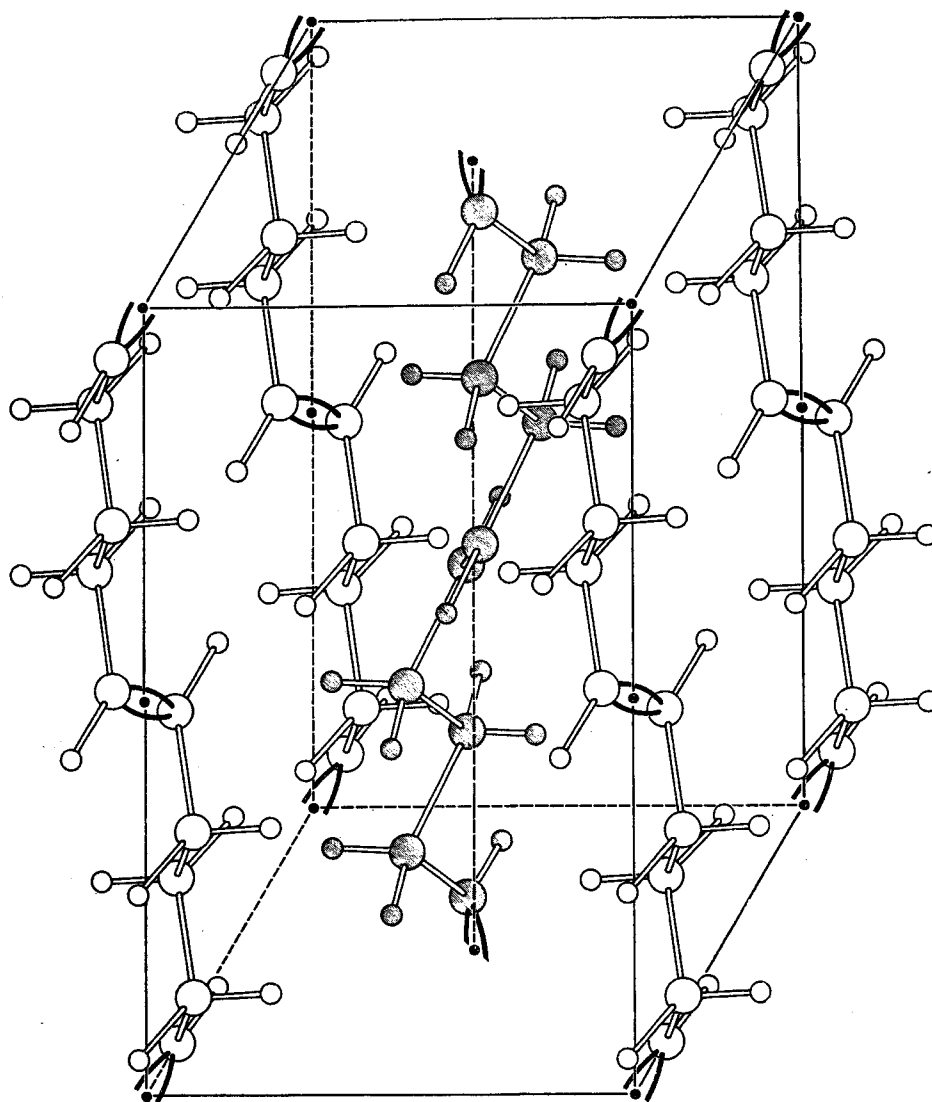


Fig. 7. Unit cell of *trans*-polypentenamer.

in which odd n -alkanes crystallize.³ The macromolecules of *trans*-polypentenamer pack themselves in the unit cell in such a way that the values of the intermolecular H—H distances (Fig. 6) are quite analogous to those occurring for the macromolecules of orthorhombic polyethylene. We think that this is the main argument we can advance to explain the similarity between the crystal structures of these polymers.

The arrangement of the chains side by side and the equatorial dimensions of the unit cell (very similar to those of polyethylene) are determined by the hydrocarbon planar part of the chain, also in the case of polyesters,¹⁰

in spite of the chemical differences and of the very different steric hindrances of the ester groups with respect to the $-\text{CH}=\text{CH}-$ group of *trans*-polypentenamer.

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Résumé

Le *trans*-polypenténamère, de même que le caoutchouc naturel, cristallise sous tension à température de chambre. Les spectres des fibres aux rayons-X du polypenténamère-*trans* cristallin peuvent être interprétés sur la base d'une cellule unitaire orthorhombique dont les périodes d'identité en Å sont: $a = 7.28 \pm 0.10$; $b = 4.97 \pm 0.05$; $c = 11.90 \pm 0.10$; $Z = 4(\text{C}_5\text{H}_8)$ et $d_{\text{calc}} = 1.049 \text{ g/cm}^3$. Les groupes spaciaux probables sont C_{2h}^2 ($Pna2_1$) ou D_{2h}^{16} ($Pnam$). Les positions atomiques ont été déduites par essai et par erreur. Les unités monomériques ($-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) se répètent le long de l'hélice double. L'empaquettement moléculaire à l'état cristallin est essentiellement régulier en ce qui concerne les atomes d'hydrogène des groupes CH_2 . L'empaquettement des molécules de *trans*-polypenténamère est très semblable à celui trouvé pour le polyéthylène orthorhombique.

Zusammenfassung

trans-Polypentenamer kristallisiert, so wie Naturkautschuk, bei der Dehnung bei Raumtemperatur. Das Röntgen-Faserspektrum von kristallinem *trans*-Polypentenamer lässt sich durch eine orthorhombische Elementarzelle mit folgenden Identitätsperioden (in Å-Einheiten) darstellen: $a = 7,28 \pm 0,10$; $b = 4,97 \pm 0,05$; $c = 11,90 \pm 0,10$

(Kettenachse); weiters ist $Z = 4(\text{C}_5\text{H}_8)$ und $d_{\text{ber.}} = 1,049 \text{ g/cm}^3$. Wahrscheinliche Raumgruppe C_{2v}^2 ($Pna2_1$) oder D_{2h}^{16} ($Pnam$). Die Atomlagen wurden durch Probieren abgeleitet. Die $(-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-)$ -Monomereinheiten wiederholen sich längs einer zweifachen Helix. Die Molekülpackung im Kristall wird im wesentlichen durch die H-Atome der CH_2 -Gruppen bestimmt. Die Packung der *trans*-Polypentenamer-moleküle ist der bei orthorhombischen Polyäthylen gefundenen Packung sehr ähnlich.