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CRYSTAL AND MOLECULAR STRUCTURE OF *CIS*-TACTIC POLY-1-OCTENYLENE

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Abstract—Fibres of poly-1-octenylene with very high (89%) content of *cis*-tactic configurations were studied by X-ray analysis. The polymer crystallizes in a monoclinic unit cell; $a = 4.58$ Å, $b = 9.50$ Å, $c = 17.11$ Å (fibre axis), $\beta = 98°$; space group C2/*c*. The chain symmetry is *tic*. A strongly anisotropic thermal factor is suggested. A close analogy of the mode of packing of our polymer with *cis*-tactic poly-1-butenylene is pointed out.

The crystal structures of stereoregular hydrocarburic polymers with *cis* double bonds along the chain have been the subject of previous investigations [1,2] from our laboratories. One of us (I.W. Bassi) has also studied the crystal structures of *trans*-tactic poly-1-alkenylenes [3] (called in the paper polyalkenamers according to the older IUPAC nomenclature [4,5]). Depending on the catalysts employed and on the polymerization conditions, it is possible to obtain poly-1-alkenylenes from cycloalkenes [6], having a very high *cis–trans* ratio of configurations. In this paper we refer to the chain conformation and on the mode of packing of *cis*-tactic poly-1-octenylene [7].

EXPERIMENTAL

The polymer which has been studied had a very high (89%) content of *cis*-tactic configurations. A Geiger spectrum (Cuk$_\alpha$) recorded at 0° is shown in Fig. 1.

A film of the polymer was obtained by evaporation of a benzenic solution. X-ray fibre spectra with various exposures were obtained from stripes of the film stretched at 500%, both at low and room temperature (the crystallinity is high under stress even at room temperature).

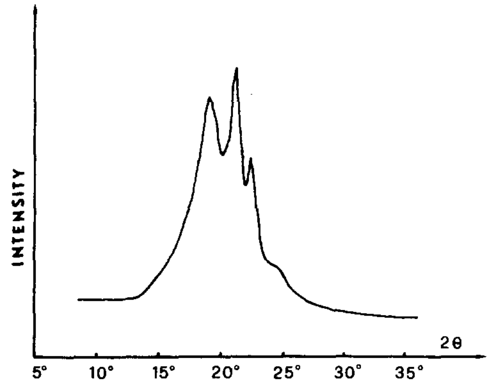

Fig. 1. X-ray diffraction spectrum (Cuk$_\alpha$) registered with a Geiger counter of a sample of highly *cis*-tactic poly-1-octenylene at ~0°.

The high exposure spectra appear very rich in reflections, taking into account the polymeric nature of the product. A low exposure picture is reported in Fig. 2. The identity period along the fiber axis is $c = 17.11 \pm 0.15$ Å.

The equatorial reflections have been indexed on the basis of the reciprocal lattice constants $a^* = 0.220$ Å^{-1}, $b^* = 0.105$ Å^{-1}, $\gamma^* = 90°$.

The reflections ($hk0$) with $h + k = 2n + 1$ are missing. Difficulties in the first steps of the interpretation resulted from the fact that the reflection (020) is not observed. All the non-equatorial reflections may be interpreted assuming $c^* = 0.0583$ Å^{-1}, $\alpha^* = 90°$, $\beta^* = 82°$. The reflections having $h + k + l = 2n + 1$ are systematically absent; possible space groups are C*c* or C2/*c*. With 4 costitutional repeating units (and two chains) per unit cell of axes $a = 4.58$ Å, $b = 9.50$ Å, $c = 17.11$ Å, $\beta = 98°$ the calculated density is 0.98 g/cm^3 in good agreement with the experimental density.

CHAIN CONFORMATION

The chain symmetry has to be at least *tc* [8] if the space group is C/*c*; it must be *tic* if the space group is C2/*c*.

For the *tic* symmetry the succession of the dihedral angles along the chain has to be: 0° (for the *cis* double bond), σ_1, σ_2, σ_3, 180°, $-\sigma_3$, $-\sigma_2$, $-\sigma_1$, 0° (again, for the *cis* double bond), $-\sigma_1$, $-\sigma_2$, $-\sigma_3$, 180°, σ_3, σ_2, σ_1, with twofold axes perpendicular to the chain axis through the centre of the double bonds and centres of symmetry on the central CH_2—CH_2 bonds.

According to well known results of the conformational analysis of hydrocarbons [9], the minimum energy values for the internal rotation angles along the chain may be assumed to be: $\sigma_1 = \pm 120°$, $\sigma_2 = \pm 60°$ or 180°, $\sigma_3 = 180°$.

While a gauche conformation for σ_2 can be excluded on the basis of the known length of the identity period, the observed identity period can be reproduced very well with the assumption of a *tic* chain symmetry and the following reasonable set of internal coordinates: bond lengths C—C = 1.54 Å, C=C = 1.34 Å; bond angles: $\widehat{\mathrm{C{-}C{-}C}} = 112°$, $\widehat{\mathrm{C{-}C{=}C}} = 126°$; internal rotation angles: $\sigma_1 = \pm 120°$, $\sigma_2 =$

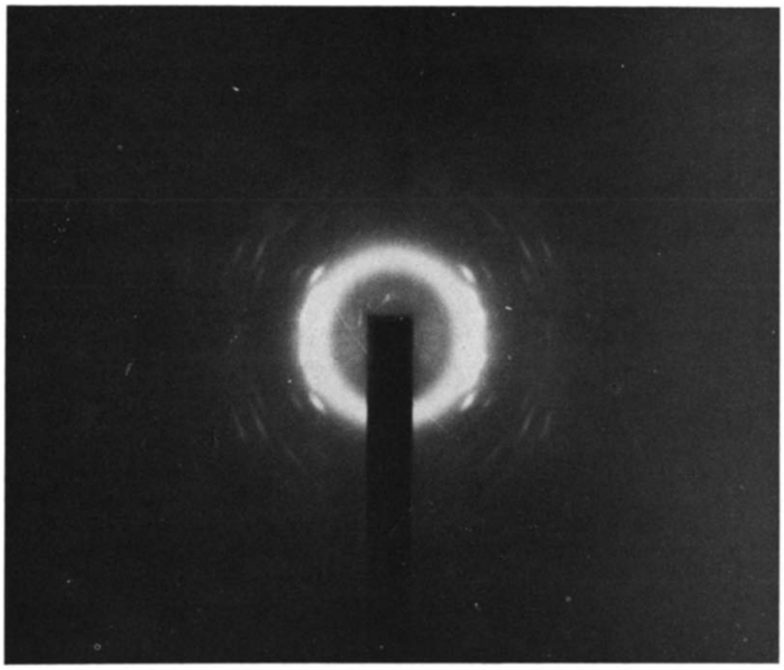

Fig. 2. X-ray (Cuk$_\alpha$) fibre photograph of a drawn fibre of poly-1-octenylene (89% *cis*).

180°, $\sigma_3 = 180°$. The validity of the assumption of a *tic* symmetry, and therefore of the C2/*c* space group, has been confirmed also by the later structure factor calculations.

DETERMINATION OF THE STRUCTURE

Since all the symmetry elements of the isolated chain are maintained in the crystals if the space group is C2/*c*, there are only two ways to insert the described model of the chain in the unit cell (Fig. 3, A and B). On close inspection, the situation A shows a better distribution of interatomic contacts, while the relative orientations of the double bonds and of the paraffinic sections of the chain appear to be analogous to those observed in *cis*-tactic poly-1-butenylene (Fig. 3, C). Also the results of the structure factor calculations show clearly that the correct model of the structure corresponds to A. The fractional coordinates of the atoms of model A are reported in Table 1 corresponding to the internal coordinates previously reported; the hydrogen atoms, not reported in Fig. 2, were inserted in stereochemical positions.

The results of the calculations with an isotropic thermal factor B = 6 Å^2, are reported in Table 2 ($I_c(1)$).

The absence in the spectra of the reflection (020) is completely justified and the general agreement appears to be satisfactory. However, a general trend is that the intensities calculated for the reflections which correspond to reciprocal lattice vectors with a direction near to $\vec{a}*$ are generally higher than observed values, while the calculated intensities of the reflections which correspond to reciprocal lattice vectors with directions nearly perpendicular to $\vec{a}*$ are generally lower than those observed.

This observation is an indication that the thermal factor is strongly anisotropic. Strongly anisotropic thermal factors have been suggested also for other polymers [10].

Possible improvement of the agreement between calculated and observed reflections under the assumption that $B_{11} = 12$ Å^2; $B_{22} = 4$ Å^2; $B_{33} = 4$ Å^2;

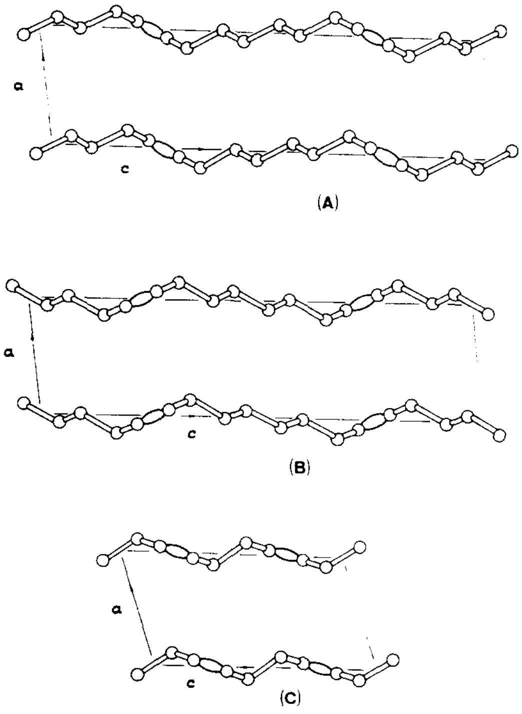

Fig. 3. Comparison between the two possible modes of packing of chains of *cis*-tactic poly-1-octenylene (models A and B) having *tic* symmetry in the unit cell experimentally determined and that of *cis*-tactic poly-1-butenylene (model C) experimentally observed. Model A has been established as correct through structure factor calculations.

Table 1. Atomic fractional coordinates of the independent structural unit

	x/a	y/b	z/c
C1	0.079	−0.002	0.043
C2	−0.008	−0.134	0.087
C3	0.150	−0.139	0.173
C4	0.064	−0.270	0.217
H1(C1)	0.314	−0.003	0.042
H2(C1)	0.024	0.091	0.074
H1(C2)	−0.243	−0.133	0.088
H2(C2)	0.048	−0.227	0.056
H1(C3)	0.386	−0.139	0.172
H2(C3)	0.095	−0.045	0.204
H(C4)	0.111	−0.371	0.193

Table 2. Comparison between the observed and calculated intensities with an isotropic thermal factor B = 6 Å^2 ($I_c(1)$) and with anisotropic thermal factors B_{11} = 12 Å^2, B_{22} = 4 Å^2, B_{33} = 4 Å^2, $B_{12} = B_{13} = B_{23} = 0$ ($I_c(2)$) according to the C2/*c* space group

h	k	l	$(\sin \theta/\lambda)^2$	$nI_c(1)$	$nI_c(2)$	I_{obs}
0	2	0	0.0110	4	4	—
1	1	0	0.0149	2206	1928	vvvs
1	3	0	0.0371	—	—	—
0	4	0	0.0443	3	3	—
2	0	0	0.0486	198	111	w
2	2	0	0.0597	2	1	—
1	5	0	0.0814	2	2	—
2	4	0	0.0929	2	2	—
0	6	0	0.0997	10	15	—
3	1	0	0.1121	5	1	—
3	3	0	0.1343	—	—	—
1	7	0	0.1479	40	60	vw
2	6	0	0.1484	—	—	—
0	8	0	0.1774	16	33	vvw
0	2	1	0.0119	669	701	s
$\bar{1}$	1	1	0.0148	622	539	mw
1	1	1	0.0166	1221	1081	s
$\bar{1}$	3	1	0.0370	9	8	—
1	3	1	0.0388	3	3	—
0	4	1	0.0452	—	—	—
$\bar{2}$	2	1	0.0587	2	1	—
2	2	1	0.0623	2	1	—
$\bar{1}$	5	1	0.0814	—	—	—
$\bar{2}$	4	1	0.0920	1	—	—
2	4	1	0.0956	—	—	—
0	6	1	0.1006	26	39	vw
0	2	2	0.0144	1141	1206	vvs
$\bar{1}$	1	2	0.0165	880	762	ms
1	1	2	0.0201	24	22	—
$\bar{1}$	3	2	0.0387	—	—	—
1	3	2	0.0422	2	2	—
0	4	2	0.0477	6	7	—
$\bar{2}$	0	2	0.0484	92	50	vw
2	0	2	0.0555	42	25	—
$\bar{2}$	2	2	0.0595	25	14	—
2	2	2	0.0666	18	11	—
$\bar{1}$	5	2	0.0830	16	18	—
1	5	2	0.0866	12	14	—
$\bar{2}$	4	2	0.0927	4	3	—
2	4	2	0.0999	5 }	3 }	vw
0	6	2	0.1031	14 }	22 }	
$\bar{3}$	1	2	0.1101	14	4	—
0	2	3	0.0187	424 }	456 }	s
$\bar{1}$	1	3	0.0198	236 }	205 }	
1	1	3	0.0252	190	177	mw
$\bar{1}$	3	3	0.0420	122	116	mw
1	3	3	0.0474	25	26	—
0	4	3	0.0519	27	34	vvvw
$\bar{2}$	2	3	0.0619	78	44	vvw
2	2	3	0.0727	2	2	—
$\bar{1}$	5	3	0.0864	54	61	vw
$\bar{3}$	1	3	0.1117	12	1	—
0	2	4	0.0246		—	—
$\bar{1}$	1	4	0.0249	15	13	—
1	1	4	0.0320	2	2	—
$\bar{1}$	3	4	0.0470	371	356	ms
1	3	4	0.0542	1	1	—
$\bar{2}$	0	4	0.0550	13	7	—
0	4	4	0.0579	185	232	m
$\bar{2}$	2	4	0.0661	27	15	—
2	0	4	0.0693	32	20	—
2	2	4	0.0804	33	22	vvvw
$\bar{1}$	5	4	0.0914	23	26	vw
1	5	4	0.0986	3	3	—
$\bar{2}$	4	4	0.0993	45	29	vw
$\bar{1}$	1	5	0.0316	41 }	37 }	w
0	2	5	0.0322	51 }	58 }	
1	1	5	0.0406	251	250	m
$\bar{1}$	3	5	0.0538	30	30	vw
2	2	5	0.0898	11	—	—
3	1	5	0.1467	13	—	—
$\bar{1}$	1	6	0.0401	10	10	—
0	2	6	0.0416	9	10	—
1	1	6	0.0508	111	116	w
$\bar{1}$	3	6	0.0622	37	37	vvw
$\bar{2}$	0	6	0.0684	4	2	—
1	3	6	0.0730	2	2	—
0	4	6	0.0748	2	3	—
$\bar{2}$	2	6	0.0795	4	3	—
2	0	6	0.0898	85	60	vw
2	2	6	0.1009	—	—	—
$\bar{1}$	5	6	0.1066	6	7	—
$\bar{2}$	4	6	0.1127	32	21	vvvw
$\bar{3}$	3	6	0.1487	23	6	—
3	1	6	0.1587	12	4	—

For each layer, after the last observed reflection, we report only the reflections with calculated intensity higher than 10.

$B_{12} = B_{13} = B_{23} = 0$ is reported as an example in Table 2 [$I_c(2)$].

Coherently, an examination of the model shows that libration around the internal rotation angles causes much higher displacements in the direction perpendicular to the *bc* plane (i.e. in the direction of $\vec{a}*$) than in the other directions.

The complete mode of packing, according to the results of the work performed, is reported in Fig. 4.

Finally, it may be of interest to point out once more the close analogy of the mode of packing of *cis*-tactic poly-1-butenylene and *cis*-tactic poly-1-octenylene (Fig. 3, A and C), as evidenced by the chain symmetry (*tic*, maintained in the lattice in both cases) and the similarity in the interchain distances perpendicular to the plane *bc* (4.35 Å for *cis*-tactic poly-1-butenylene, 4.53 Å for *cis*-tactic poly-1-octenylene).

One of us pointed out that, in the case of the various modifications of *trans*-tactic polyalkenylenes [3], the paraffinic chains tend to realize locally dense packings similar to those foreseen by Kitaigorodsky on the basis of close packing considerations [11]. In

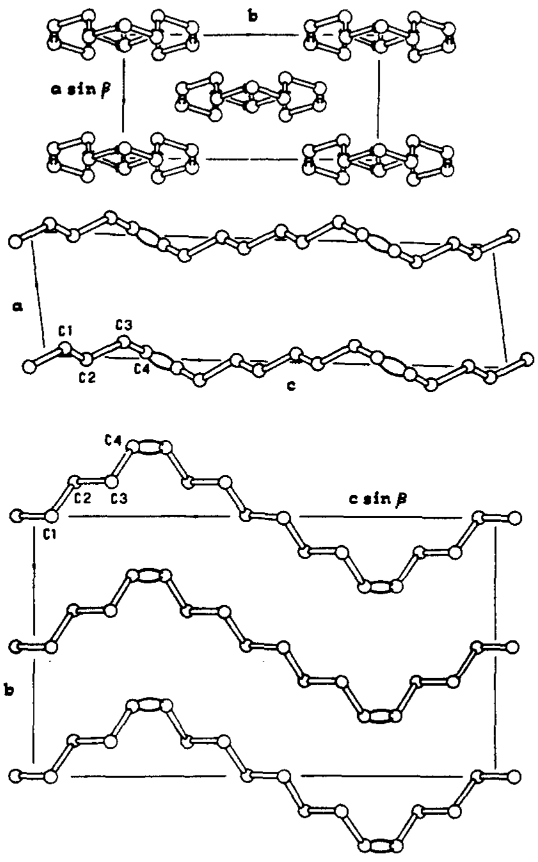

Fig. 4. Three views of the structure of *cis*-tactic poly-1-octenylene along the *a*, *b* and *c* directions.

our case, the sublattice which describes the mode of packing of the parafffinic sections of our chains has constants

$$a = 4.58\ \text{Å},\ b = 4.70\ \text{Å},\ c = 2.54\ \text{Å},$$
$$\alpha = 92^\circ,\ \beta = 90^\circ,\ \gamma = 119^\circ$$
$$\text{(packing density} = 0.68)$$

and does not differ very much from the monoclinic sublattice described by Kitaigorodsky with constants

$$a = 4.26\ \text{Å},\ b = 4.53\ \text{Å},\ c = 2.54\ \text{Å}$$
$$\gamma = 111^\circ\ \text{(packing density} = 0.71).$$

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Riassunto—Sono state studiate ai raggi X fibre di poli-1-ottenilene con un contenuto molto alto (89%) di configurazioni *cis*. Il polimero cristallizza nel sistema monoclino con cella unitaria di assi $a = 4{,}58$ Å, $b = 9{,}50$ Å, $c = 17{,}11$ Å (asse di fibra), $\beta = 98°$; il gruppo spaziale è $C2/c$. La simmetria della catena à *tic*. E' suggerito un fattore termico fortemente anisotropo. Si sottolinea una stretta analogia nell'impacchettamento fra il nostro polimero ed il poli-1-butenilene.