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Crystal Structure and Melting Entropy of Natural Rubber

Attilio Immirzi,*[,†,‡] Consiglia Tedesco,[†] Guglielmo Monaco,[†] and Alan E. Tonelli[§,||]

Dipartimento di Chimica, Università di Salerno; Via S. Allende, I-84081 Baronissi (SA), Italy, and
Fiber and Polymer Science Program, North Carolina State University, Campus Box 8301,
Raleigh, North Carolina 27695-8301

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ABSTRACT: The constant-volume melting entropy of natural rubber (*cis*-1,4-polyisoprene = c-PIP) is small compared with other linear polymers. With the aim of understanding this behavior a reliable structural model for the crystalline state of c-PIP is needed. To this end the recent study by Takahashi and Kumano (T−K) has been revised, using the same X-ray diffraction measurements published by these authors. The new study has employed different refinement methods and considered several structural models. The chain structure claimed by Nyburg (S T $\bar{S}$ cis $\bar{S}$ T S cis) has been confirmed, but the resulting chain torsion angles are different, both if the glide-plane chain symmetry is assumed (R = 0.079) and if such chain symmetry is waived. (R = 0.067. The chain torsion angles for this model are 86, 171, and −88°, cis, and −120, −170, and 116°, cis.) At the chain packing level, while the disorder claimed by Nyburg and by T−K is not supported by the diffraction data, a different disordered model improves the F_c vs F_o fit giving a good crystal packing. Also the hypothesis of an orthorhombic structure (suggested in the past by Natta and Corradini) has been explored (R = 0.090). The implications of the crystalline structure and its possible conformational disorder on the low melting entropy are discussed.

Introduction

For most semicrystalline polymers it is possible to explain their constant-volume experimental melting entropies using statistical thermodynamics and the rotational isomeric state (RIS) description of their conformations. However, this analysis also requires a reliable description of the conformation(s) of the polymer chains in their crystals. For natural rubber (*cis*-1,4-polyisoprene = c-PIP) the experimental constant-volume melting entropy is very low and about three times smaller than the theoretical value computed from structural models inferred many years ago from X-ray fiber diffraction data.[1−4] To explain such an unusually low value, which seems to play a role in determining natural rubber elastic properties,[5] an accurate structural analysis has been undertaken.

In 1942 Bunn[3] and later in 1954 Nyburg[4] proposed the first models for the crystalline structure of c-PIP: Bunn claimed a structure with 2-fold screw helices packed into a monoclinic unit cell with lattice constants a = 12.46 Å, b = 8.89 Å, c (fiber axis) = 8.10 Å, β = 92°, space group $P2_1/a$ (two C_5H_8 repeat units in the crystallographic asymmetric unit); Nyburg gives a structure, again monoclinic $P2_1/a$, but with β = 90°, containing chains endowed with a glide-plane (again two independent C_5H_8 units). Later Natta and Corradini[6] reinterpreted Nyburg's data and claimed an orthorhombic cell of *Pcab* symmetry (equivalent to the conventional *Pbca*) with the chain crossed by a crystallographic glide plane.

In addition, according to Nyburg, there would be a statistical alternation of chains related to each other by mirror symmetry and a statistical structure with chains of different conformation was also proposed by Benedetti, Corradini, and Pedone.[7] These structural analyses were indeed very coarse, and the fits of observed vs calculated structure factors are not satisfactory.

Very recently, using purified samples,[8] Takahashi and Kumano[9] recorded new X-ray fiber diffraction data for c-PIP fibers, determined that the lattice constants by Bunn are substantially correct (new values are a = 12.41, b = 8.81, c = 8.23 Å, β = 93.1°; the quoted β is indeed ambiguous since it was reported differently in the article), and a new structural chain model is proposed (close to the one previously proposed by Nyburg[4]). They also claim a statistical alternation in the packing of crystalline chains (also proposed by Nyburg), but with unbalanced occupancy factors of $^2/_3$ and $^1/_3$.

The analysis done by Takahashi and Kumano, however, does not seem fully convincing for several reasons: (i) the arguments presented for assigning $\beta \neq 90°$ appear weak (the authors do not publish a full list of measured d spacings), and consequently, the rejection of the orthorhombic unit cell seems too facile and not justified; (ii) the assumed chain statistics (claimed also by Nyburg) appear to be arbitrary, especially for the unbalanced occupation factors; (iii) the refinement procedure they adopted seems incorrect to us, because (a) once the chain is oriented parallel to the c edge, there should only be one chain orientation angle and not three as used by them, and (b) the conditions adopted for chain continuity are not well stated. For these reasons, we have undertaken a new analysis on their experimental measurements but employing different techniques and alternative computer programs.

Structure Description by Means of Internal Coordinates

All structural models considered have been examined using TRY,[10−12] a general purpose program for assigning and refining crystal structures. TRY, especially useful when the data-to-parameter ratio is low, works on the basis of diffraction measurements and potential energy computations (either molecular, or lattice energy is considered). This program, which is *entirely based on internal coordinates*, allows modeling almost any kind

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[†] Università di Salerno.
[‡] E-mail: aimmirzi@unisa.it.
[§] North Carolina State University.
[||] E-mail: alan_tonelli@ncsu.edu.

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Table 1. Internal Coordinates for Natural Rubber at the End of Each Structure Refinement

param	model A	model B	model C	model D	model E
b_1 (Å)	1.54	1.54	1.54	1.54	1.54
b_2 (Å)	1.34	1.34	1.34	1.34	1.34
b_3 (Å)	1.50	1.50	1.50	1.50	1.50
τ_4 (deg)	111.0	108.7(4)	107.8(5)	108.9	111.7(10)
τ_5 (deg)	122.1	127.3(8)	137.1(10)	130.6	129.5(14)
ϑ_6 (deg)	138.3	112.5(25)	116.0(28)	101.7	103.6(34)
ϑ_7 (deg)	−136.8	113.2(22)	85.7(42)	102.3	$=\vartheta_6$
ϑ_8 (deg)	180.0	163.6(15)	170.8(9)	176.0	
ϑ_9 (deg)	$=\vartheta_6$	$=-\vartheta_6$	−87.7(40)	$=-\vartheta_6$	
$-\vartheta_{10}$ (deg)	$=\vartheta_7$	$=-\vartheta_7$	−120.4*	$=-\vartheta_7$	
ϑ_{11} (deg)	$=\vartheta_8$	$=-\vartheta_8$	−169.6*	$=-\vartheta_8$	
Φ (deg)	5.8	4.7(11)	−0.7(10)	−0.7	
x_0 (Å)	3.18	3.31(4)	3.07(4)	3.21	*a*/4
y_0 (Å)	0.55	0.79(3)	0.45(21)	0.93	3.94(3)
z_0 (Å)	2.25	2.15(5)	2.05(3)	7.18	0.35(4)
ndf	7	7	8	8	4
B_{iso} (Å^2)	4.0	6.0	5.0	3.7	7.5
R_1 index	0.093	0.079	0.067	0.071	0.090
short C···C (Å)	3.57, 3.60, 3.64, 3.77.	3.59, 3.67, 3.81, 3.88.	3.57, 3.65, 3.75, 3.77.	3.34, 3.36, 3.50, 3.52.	3.74, 3.87, 3.90, 3.85.

[a] A = Bunn model with geometrically equivalent units, B = Nyburg model with equivalent units, C = Nyburg model with non equivalent units, D = model with statistical chains, E = Natta−Corradini model. In cases B, C, and E, the values given are those obtained by a least-squares procedure (standard errors are given in parentheses); in cases A and D, the values were obtained by trial optimization (least-squares procedure fails). The chain internal parameters are defined in Figure 1. Parameters in italics were not refined. Values marked with an asterisk are not refined but computed a posteriori from the refined quantities.

of molecular or polymer crystal thanks to a special "symbolic language" used in performing almost any kind of geometrical construction. The least-squares process is straightforward and applicable also to coarse models provided that internal coordinates are few.

Special attention has been dedicated to polymeric structures by adequately considering the chain symmetry (helix or glide-plane chains); the chain continuity requirements are treated *exactly*. To this purpose appropriate "constraints" must be imposed *on the internal parameters*; and this is done using the Lagrange's multipliers method. Recent X-ray structures established and refined using TRY are those of refs 11 and 12.

As the asymmetric unit consists of two repeating units $-CH_2-C(CH_3)=CH-CH_2-$, the description of the chain structure by internal coordinates, should require eight bond angles and six torsion angles (two are fixed to 0° because the two chain double bonds are fixed in the cis configuration). This high number of degrees of freedom (ndf) can be lowered if more symmetrical chain models are adopted (see later).

The chain models considered in this analysis are those by Bunn[4] and Nyburg,[4] with the following succession of conformations: (S = skew, T = trans; note that the chain repeat 8.23 Å, is fulfilled, in both cases, using almost canonical values: S, $\bar{S}$ = ±120 °, T = 180 °):

Bunn: ...ST$\bar{S}$ cis ST$\bar{S}$ cis... (internal 2_1 helix)

Nyburg: ...ST$\bar{S}$ cis $\bar{S}$TS cis... (internal glide plane)

The chain building is performed by TRY considering the parameters listed in Table 1 and defined in Figure 1. Starting from the moiety C1−C2−C3, further backbone atoms are added using the appropriate bond lengths (b_1, b_2, b_3), bond valence angles (τ_4, τ_5), and torsion angles (ϑ_6, ..., ϑ_{11}). It is also necessary (see later) to compute three more atomic positions: C1′, C9″, and C8″ (see Figure 1). The chain must be oriented with its axis parallel to the *c* edge and then rotated by the angle Φ and translated by x_0, y_0, z_0.

If all six variable torsion angles are used in chain building, to account for the chain continuity, one should impose four Lagrange's conditions: one is that the C1−C1′ distance be equal to the *c* edge, and the other three are derived from the condition that any three consecutive chain atoms, e.g., C9″−C1−C2 (see Figure 1) must superpose the repeated C9−C1′−C2′ *by simple translation*. This condition implies that the vector products $v_{(9''-1)} \times v_{(1-2)}$ and $v_{(9-1')} \times v_{(1'-2')}$ must give, by vector multiplication, the null vector.

As discussed in ref 10, to avoid ill conditioned matrices in the least-squares refinement, it is more practical to perform chain building using two fewer chain torsion angles and therefore two fewer constraints (this leaves unaltered the number of degrees of freedom). In detail the chain from C1 to C9 was built-up using only the torsion angles ϑ_7, ϑ_8, and ϑ_9, and the angle ϑ_6 was used for building C9″; then the vector C9″−C1 is translated onto C9 to obtain C1′. Lagrange's conditions used are as follows: (i) C1−C1′, distance = c; (ii) C8−C9−C1′, angle = τ_4. Indeed the torsion angles ϑ_{10} and ϑ_{11} are used in chain building, and are computed a posteriori from the chain coordinates by obeying *the continuity conditions*.

The whole analysis has been done assuming that (i) the bond-lengths are known, (ii) all C−C−C chain angles are equal (τ_4) as well as all C−C=C chain angles (τ_5), (iii) the hydrogen atom positions are computed from the carbon atom positions, and (iv) all atoms have the same isotropic thermal vibration parameter (adjusted by trial). Considering the four rotation/translation parameters Φ, x_0, y_0, z_0, there are, for the unsymmetrical case, 2 + 4 + 4 variables and fewer for the symmetrical ones. The ndf is, in the unsymmetrical case, 10 − 2 = 8. Of course *if symmetry restrictions are imposed on the chain, ndf* is lower.

For the building of lateral CH_3 groups we have considered the statistical geometry for the $C-C(CH_3)=C$ moiety inferred from the Cambridge Structural Database[13] (~3800 observations): the average $C-C-CH_3$ angle is 119° and the average $C=C-CH_3$ angle is 125°. We have, thus, used the procedure of positioning

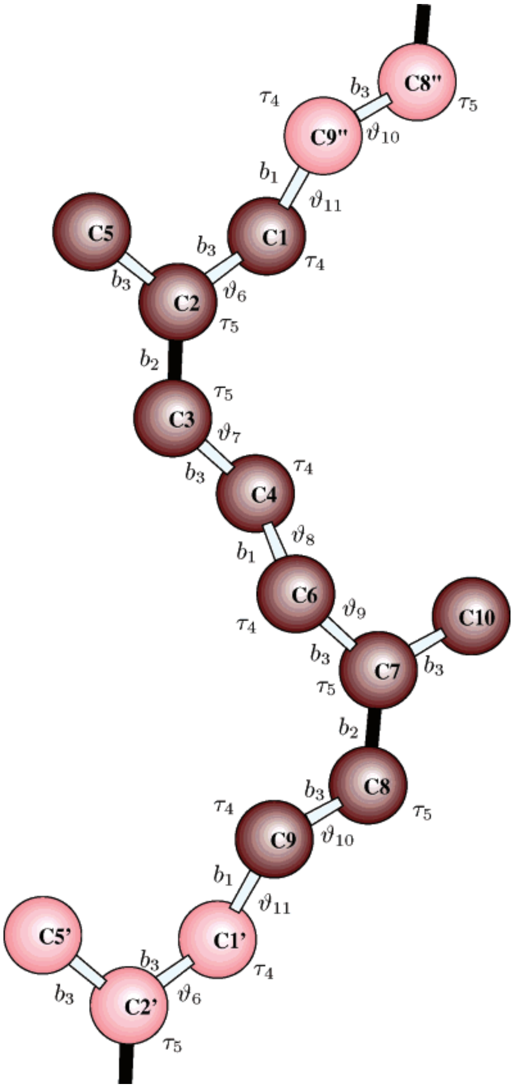

Figure 1. Chain model for the natural rubber. The asymmetric unit for the natural rubber, extended by some atoms, is given with the definition of the chain internal coordinates: b_1, b_2, b_3 (bond lengths), τ_4,τ_5 (bond angles), and $\vartheta_6 \cdots \vartheta_{11}$ (torsion angles). Other internal coordinates (not shown) are the overall rotation angle for the chain Φ and the overall translations x_0, y_0, z_0 (reference atom is C5, except in case E where the reference atom is C4).

lateral CH_3 groups according to the trigonal planar geometry of the sp^2 carbon atoms imposing that the above angles differ by $125° - 119° = 6°$.

In all cases the initial structure modeling, based on the reproduction of the chain repeat and on packing consideration, is very simple (the best packing parameters according to ref 14 can be found by systematic variable-space search with TRY). Models were subsequently optimized using the least-squares procedure. This has been performed following two schemes: the first based on the assumption that the two isoprene units are geometrically equivalent (considering both Bunn's[3] and Nyburg's[4] models), the second considering two independent repeat units (applied only to Nyburg's model).

Least-Squares Refinement

TRY performs structure refinement using the least-squares procedure, with the refined variables being the internal coordinates themselves. In addition, *rigid constraints among the internal coordinates* can be imposed, by means of the Lagrange's multipliers method.

The minimized quantity is $\chi^2 = \sum w_i(F_{o,i}{}^2 - F_{c,i}{}^2)^2$. Lacking information about the standard errors of the measurements, unitary w_i values were used. Initially only the observed reflections were included; subsequently, also the unobserved reflections (u) were also added attributing to them the weight $w_u = 0.50$ and the conventional $F_{obs}{}^2$ set to $F_u{}^2 = 10$ (half of the average $\langle F^2{}_{calcd}{}^2\rangle$ for unobserved); the choice of w_u and $F_u{}^2$ is rather arbitrary, but it turns out to be irrelevant to the final results.

The least-squares procedure runs satisfactorily except for z_0 to which χ^2 is relatively insensitive; a reasonable explanation is the limited resolution of the diffraction intensities along the fiber axis. The z_0 parameter was therefore adjusted by trial based on packing considerations. In all cases the resulting angular values are realistic and the crystal packing is acceptable considering the uncertainty in z_0.

Chains Obeying the Rule of Geometrical Equivalence of the Isoprene Units. It is well-known that polymers lacking crystallographic symmetry within their chain frequently obey the rule that repeating units are geometrically equivalent.[15] Helical polymer chains are good examples.

Adherence to the above rule implies, if the glide-plane model applies (Nyburg), $\vartheta_9 = -\vartheta_6$, $\vartheta_{10} = -\vartheta_7$, $\vartheta_{11} = -\vartheta_8$. If the screw model applies (Bunn) then $\vartheta_9 = \vartheta_6$, $\vartheta_{10} = \vartheta_7$, $\vartheta_{11} = \vartheta_8$. Following these two models in turn, one obtains easily, after adjustment by trial based on packing inspection, a good R index ($<15\%$) in both cases. The least-squares procedure was then attempted: the refinement of the Bunn model fails (the values listed in Table 1, column A, are merely the result of a trial optimization done considering each variable in turn, and imposing 180° to T angles and an unique S angle); the Nyburg model, instead, gives good convergence to the values listed in Table 1, column B. The final C−C−C bond angle (sp^3 carbon) is realistic; the C−C=C bond angle (sp^2 carbon) is instead rather large; skew torsion angles differ slightly from the idealized values (±120°).

Also examination of the F_o vs F_c list (see Table 3) leads to the conclusion that the Bunn model must be abandoned; there are indeed in the Bunn case numerous unobserved reflections for which the calculated structure factor F_B is too high.

The Unsymmetrical Chain. If the chain is treated as unsymmetrical there are altogether 10 variables which must obey two constraints. The performed refinement has shown that convergence takes place as in the previous case (see results in Table 1). The R index (0.067) is improved significantly on the basis of the Hamilton test.[16] The ratio $R_1(B)/R_1(C) = 1.179$ is greater than the one calculated by Hamilton at a significance level of 0.05, considering that $N_{observation} - N_{parameters} = 34$ and that there is in the B case one more parameter.

While chain bond angles are only moderately modified with respect to case B, two skew torsion angles, viz. ϑ_7 and ϑ_9, are markedly different and rather far from 120° (+86 and −88°). The other torsion angles are close to their canonical values.

The atomic coordinates for model C are also listed in Table 2; the final F_o, F_c values are listed in Table 3, and the crystal packing remains acceptable.

Models with Disorder. Although the excellent fit of observed vs calculated structure factors makes it

Table 2. Atomic Fractional Coordinates for Models B, C, and D

	model B			model C			model D		
atom	*x*/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*
C1	0.2675	0.0897	0.3487	0.2482	0.0508	0.3220	0.2606	0.0393	0.3321
C2	0.3357	0.1296	0.2384	0.3438	0.0825	0.2153	0.3530	0.0647	0.2251
C3	0.3445	0.1795	0.0848	0.3469	0.1382	0.0640	0.3544	0.1175	0.0725
C4	0.2412	0.2082	−0.0134	0.2582	0.1892	−0.0546	0.2641	0.1691	−0.0429
C5	0.4712	0.1131	0.2997	0.4549	0.0473	0.2862	0.4643	0.0269	0.2933
C6	0.2319	0.0929	−0.1542	0.2157	0.0485	−0.1488	0.2388	0.0425	−0.1683
C7	0.1480	0.1479	−0.2785	0.1383	0.1037	−0.2890	0.1517	0.0998	−0.2940
C8	0.1469	0.1957	−0.4300	0.1569	0.1466	−0.4412	0.1601	0.1514	−0.4460
C9	0.2686	0.2057	−0.5112	0.2597	0.1559	−0.5286	0.2571	0.1708	−0.5450
C10	0.0320	0.1526	−0.2361	0.0207	0.1136	−0.2571	0.0369	0.1007	−0.2454

unnecessary to postulate structural models with disorder, there is clear evidence that the chain structure of c-PIP is compatible with disorder. We have thus tested a number of such models, starting from the model B ($R = 0.079$). These disordered models turn out to be not refinable by the least-squares procedure and were adjusted by trial. Both the case of irregularly conformed chains and the case of disordered packing of identical (or enantiomeric) chains were considered. In the first category of models (including, incidentally, the model proposed by Benedetti et al.[4]), none give an R improvement. In the second category (including just the model proposed in the past by Nyburg and recently by T−K[5]) there are models that moderately improve R. Only in one case did we find an R improvement (0.071) and also a good packing (C···C distances > 3.3 Å): a statistical alternance of two identical chains related to each other through a 2-fold screw axis running along the chain axis (this is not a crystallographic operator!). Nyburg's and T−K's disordered models (which appear rather arbitrary) give poor packing and a worsening of R. Internal parameters obtained in this case are listed in Table 1, column D. There are appreciable variations in bond and torsion angles, with respect to the B case, which are however of uncertain significance.

In conclusion, the above trials demonstrate that the existence of some disorder in the solid state is not clearly supported by the X-ray diffraction data, but it cannot be excluded. It may be that such disorder exists and plays a role in determining the low melting entropy of natural rubber (see later). The calculated structure factors for the above disordered model are given in Table 3.

The Natta—Corradini Model. Examination of the B model (see Figure 2 and the atomic coordinates in Table 3) clearly shows that the chain glide plane *is close to a crystallographic position*. Considering that Nyburg himself claimed a β angle of 90°, we were, thus, also persuaded that the structure proposed by Natta and Corradini[6] must be reconsidered for a more complete analysis.

Indeed, by changing β to 90°, adopting *Pcab* symmetry, building up a chain lying on the *c* glide-plane at $x = 1\ 4$ (one isoprene unit per asymmetric unit), and computing structure factors *from the same hkl* list by Takahashi and Kumano, one obtains immediately an excellent R index (~0.11)! Also refinement of the model has been done and the R index lowered to 0.090.

To test the Natta−Corradini model carefully, it would be necessary to perform again the Bragg reflection indexing, but this is impossible for us since observed d spacings were not published. The idea that the true crystalline structure of c-PIP could be more symmetrical remains however a stimulating one. For a definitive answer it is desirable to record the fiber spectrum again with the highest possible resolution, also using advanced techniques like neutron diffraction and/or synchrotron radiation.

Melting Entropy of Semicrystalline Polymers

The melting of the crystalline regions in semicrystalline polymers is well documented[17] to be a first-order phase transition between two polymeric states in equilibrium: the solid crystalline and molten amorphous, or liquid states. Consequently, the melting temperature T_m is well-defined and given by $T_m = \Delta H_m/\Delta S_m$, where ΔH_m and ΔS_m are the differences between the enthalpy and entropy, respectively, of the crystalline and molten polymer phases in equilibrium at T_m. Thus, the fusion process affords an opportunity for studying the effects of polymer molecular structure on the melting temperature and, more importantly, upon both components of the ratio $\Delta H_m/\Delta S_m$ which determines T_m.

Knowledge of the state or conformation(s) of the polymer chains in either the crystalline or molten phases, together with T_m, ΔH_m, and ΔS_m, permits certain deductions to be made concerning the state of the polymer chains in the phase for which information is lacking. Crystallized polymer chains[17] generally adopt single conformations or a few regular repeating and extended conformations with low intramolecular energies and so are generally in a state of low entropy. In the molten phase, on the other hand, it is apparent[18] that each polymer chain is free to adopt a myriad of different conformations because of the absence of intra- and interchain excluded volume effects.[19] Each chain in the molten bulk may assume any of the conformations available to the same chain in dilute solution at its Θ-temperature.[19] In contrast to the crystalline phase, molten polymer chains are not conformationally restricted by interchain interactions and therefore usually possess a significant conformational entropy.

In an attempt to obtain information concerning bulk polymer chain conformations and interactions from the fusion process it has been assumed to be separable into two independent contributions: (i) volume expansion and (ii) constant-volume conformational contributions. As a result, $\Delta H_m = \Delta H_V + (\Delta H_m)_V$ [or approximately, $\Delta H_m \sim \Delta E_V + (\Delta E_m)_V$] and $\Delta S_m = \Delta S_V + (\Delta S_m)_V$, where ΔE_V and ΔS_V correspond to the changes in energy and entropy accompanying expansion of the crystal to the volume and density of the melt, but without conformational disordering of the chains. These volume expansion contributions to melting consist of the increases in energy and entropy attendant upon the increase in the average separation between polymer chains and is clearly an intermolecular process. In addition, ΔS_V can be obtained experimentally[2−22] from $\Delta S_V = \Delta V_m(\partial P/\partial T)_V$

Table 3. Observed and Calculated Structure Factors for the Four Models Considered

h	k	l	d_{calcd}	F_{obsd}	F_A	F_B	F_C	F_S
2	0	0	6.20	1262	1150	1212	1204	1275
1	1	0	7.22	–	460	232	32	483
2	1	0	5.08	–	239	32	32	122
0	2	0	4.40	2847	2851	2849	2850	2850
1	2	0	4.15					
3	1	0	3.74	–	182	32	148	0
2	2	0	3.59	–	32	437	207	152
4	0	0	3.10	682	677	776	709	784
3	2	0	3.02					
4	1	0	2.92	–	89	55	122	276
1	3	0	2.86	–	632	89	389	502
2	3	0	2.65	–	506	210	0	192
4	2	0	2.54	–	32	105	164	110
3	3	0	2.39	–	407	77	344	0
5	1	0	2.39	–	95	0	207	63
0	4	0	2.20	602	808	586	573	506
1	4	0	2.17	333	311	577	200	210
5	2	0	2.16					
4	3	0	2.13	214	84	32	138	100
2	4	0	2.08	–	32	118	45	63
6	0	0	2.07	–	105	207	170	45
6	1	0	2.01	–	126	32	114	32
3	4	0	1.94	–	122	145	182	179
5	3	0	1.89	–	0	63	122	0
6	2	0	1.87	–	45	126	84	63
4	4	0	1.79	–	71	32	366	358
1	5	0	1.74	–	290	205	179	45
7	1	0	1.74	–	71	55	55	55
2	5	0	1.70	–	628	0	100	245
6	3	0	1.69	–	138	0	77	141
5	4	0	1.65	–	0	290	0	212
7	2	0	1.64	–	0	170	89	89
3	5	0	1.62	–	167	45	179	55
8	0	0	1.55	602	608	322	468	508
4	5	0	1.53					
8	1	0	1.53					
7	3	0	1.52					
6	4	0	1.51	–	167	210	385	390
0	6	0	1.47	–	32	100	0	89
8	2	0	1.46	–	141	71	71	221
1	6	0	1.46	–	118	105	32	170
5	5	0	1.44	–	0	55	55	141
2	6	0	1.43	–	141	138	145	247
3	6	0	1.38	–	276	217	247	295
7	4	0	1.38	–	45	138	184	32
8	3	0	1.37	–	118	118	155	0
9	1	0	1.36	–	249	0	239	274
6	5	0	1.34	663	713	535	539	679
4	6	0	1.33					
9	2	0	1.31					
8	4	0	1.27	–	32	84	170	32
5	6	0	1.26	–	89	32	377	356
1	7	0	1.25		367	0	45	32
7	5	0	1.25	459	666	321	407	617
9	3	0	1.25					
10	0	0	1.24					
2	7	0	1.23					
0	0	1	8.22	–	148	130	77	130
0	1	1	6.02	–	367	105	272	245
−1	1	1	5.49	322	454	89	329	375
1	1	1	5.33					
−2	0	1	5.08	1591	1021	1243	1187	1235
2	0	1	4.83					
−2	1	1	4.40	536	561	465	718	544
2	1	1	4.23					
0	2	1	3.88	–	560	32	77	89
−1	2	1	3.74	1366	1350	1528	1365	1373
1	2	1	3.68					
−3	1	1	3.47	425	815	285	557	746
3	1	1	3.34					
−2	2	1	3.33					
2	2	1	3.25	–	200	243	344	148
−4	0	1	2.95	–	184	114	0	63
−3	2	1	2.87	–	0	155	195	190
4	0	1	2.85	–	77	167	105	71
−4	1	1	2.80	–	243	126	261	221
3	2	1	2.80	–	55	155	237	274
0	3	1	2.77	–	513	221	77	195
−1	3	1	2.71	–	612	205	465	319
4	1	1	2.71	–	141	0	32	134
1	3	1	2.69	–	327	122	184	77
−2	3	1	2.54	452	375	212	355	519
2	3	1	2.51					
−4	2	1	2.45	–	63	100	130	84
4	2	1	2.39	–	71	0	84	152
−5	1	1	2.32	–	84	170	293	55
−3	3	1	2.32	–	192	235	187	0
3	3	1	2.28	–	184	297	451	263
5	1	1	2.26	–	148	182	55	141
0	4	1	2.13	–	161	0	155	89
−5	2	1	2.11	–	71	251	179	228
−1	4	1	2.10	–	572	192	300	253
1	4	1	2.09	385	363	409	399	367
−4	3	1	2.08					
5	2	1	2.07					
−6	0	1	2.03					
4	3	1	2.04					
−2	4	1	2.02	456	381	490	470	452
2	4	1	2.00					
−6	1	1	1.98	434	230	351	241	130
6	0	1	1.98	–	77	71	122	0
6	1	1	1.93	–	224	307	95	158
−3	4	1	1.90	–	71	77	45	55
3	4	1	1.88	–	32	122	77	118
−5	3	1	1.86	–	0	0	179	71
−6	2	1	1.84	–	0	0	55	45
5	3	1	1.83	–	0	95	110	0
6	2	1	1.80	–	32	126	251	32
−4	4	1	1.77	–	63	32	0	118
4	4	1	1.74	–	63	55	170	89
0	5	1	1.72	–	516	32	200	243
−7	1	1	1.72	396	370	235	230	272
−1	5	1	1.71					
1	5	1	1.70					
−6	3	1	1.67	–	114	55	241	118
7	1	1	1.68	–	89	152	243	126
−2	5	1	1.66	–	158	45	167	0
2	5	1	1.65	–	45	89	272	63
6	3	1	1.64	–	176	55	63	155
−7	2	1	1.63	329	348	283	389	423
−5	4	1	1.63					
5	4	1	1.60					
−3	5	1	1.60					
7	2	1	1.60					
3	5	1	1.58	–	45	152	197	122
−8	0	1	1.54	192	283	315	300	298
−8	1	1	1.51					
−4	5	1	1.51					
−7	3	1	1.50	–	148	210	134	176
8	0	1	1.51	–	313	205	179	303
−6	4	1	1.49	–	77	32	118	32
4	5	1	1.50	–	71	45	71	55
0	0	2	4.11	–	321	249	316	355
0	1	2	3.73	440	411	324	354	303
−1	1	2	3.62					
1	1	2	3.52	921	594	961	928	897
−2	0	2	3.51					
2	0	2	3.34					
−2	1	2	3.26					
2	1	2	3.13	762	239	773	995	226
0	2	2	3.00					
−1	2	2	2.95					
1	2	2	2.89	667	375	381	559	596
−3	1	2	2.84					
−2	2	2	2.75	613	472	624	494	535
3	1	2	2.70					
2	2	2	2.66	–	145	500	418	0
−4	0	2	2.54	130	221	77	71	179
−3	2	2	2.48	286	176	379	467	202

Table 3. (Continued)

h	k	l	d_{calcd}	F_{obsd}	F_A	F_B	F_C	F_S
−4	1	2	2.44	638	871	1070	986	943
0	3	2	2.39					
4	0	2	2.41					
−1	3	2	2.36					
3	2	2	2.39					
1	3	2	2.33					
4	1	2	2.33					
−2	3	2	2.25	–	45	190	55	105
−4	2	2	2.20	–	114	167	32	134
2	3	2	2.21	–	0	270	63	32
−5	1	2	2.11	841	701	550	837	778
−3	3	2	2.10					
4	2	2	2.11					
3	3	2	2.04	–	179	63	141	130
5	1	2	2.02	–	679	418	529	725
−5	2	2	1.95	954	709	998	1058	662
0	4	2	1.94					
−4	3	2	1.92					
−1	4	2	1.93					
1	4	2	1.91					
−6	0	2	1.89					
−2	4	2	1.87					
2	4	2	1.84					
−6	1	2	1.84					
5	2	2	1.88	–	32	55	32	197
4	3	2	1.86	–	318	167	251	322
0	0	3	2.74	–	63	77	77	89
0	1	3	2.62	400	424	173	239	182
−1	1	3	2.59					
−2	0	3	2.56	241	214	200	226	230
1	1	3	2.53					
2	0	3	2.46	–	45	45	161	32
2	1	3	2.37	–	114	89	207	45
0	2	3	2.33	390	545	293	300	214
−1	2	3	2.31					
−3	1	3	2.26	122	205	351	148	232
1	2	3	2.27					
−2	2	3	2.21	–	277	152	226	63
−4	0	3	2.11	–	205	281	257	268
3	1	3	2.16	–	330	134	161	179
2	2	3	2.15	–	310	77	89	77
−3	2	3	2.07	480	362	230	141	192
−4	1	3	2.05					
0	3	3	2.00	–	167	32	0	45
−1	3	3	1.99	–	268	32	55	63
4	0	3	2.00	–	71	167	167	114
3	2	3	1.99	–	232	207	385	176
1	3	3	1.97	–	351	45	63	0
4	1	3	1.95	–	77	161	77	63
−4	2	3	1.90	–	292	77	118	45
2	3	3	1.88	–	71	71	100	0
−5	1	3	1.85	–	77	114	110	77
−3	3	3	1.83	–	2.19	55	145	63
4	2	3	1.82	–	367	95	0	32
3	3	3	1.78	–	89	192	63	71
−5	2	3	1.74	–	0	45	0	45
5	1	3	1.75	–	32	173	45	155
−4	3	3	1.71	–	63	45	45	32
0	4	3	1.72	–	0	77	45	0
−6	0	3	1.69	359	571	333	321	239
−1	4	3	1.71					
1	4	3	1.69					
−6	1	3	1.66					
−2	4	3	1.67					
5	2	3	1.66					
4	3	3	1.65					
2	4	3	1.64					
0	0	4	2.05	–	404	263	330	321
−1	1	4	1.99	414	167	369	126	167
0	1	4	2.00					
−2	0	4	1.98	–	148	0	100	55
1	1	4	1.96	–	32	155	176	89
−2	1	4	1.93	–	0	45	89	45
2	0	4	1.92	–	32	100	161	170
0	2	4	1.86	618	491	369	377	361
2	1	4	1.88					
−1	2	4	1.85					
−3	1	4	1.84	–	190	0	32	114
1	2	4	1.83	–	245	0	100	141
−2	2	4	1.81	–	55	228	145	55
−4	0	4	1.76	–	71	55	145	110
2	2	4	1.76	–	32	251	200	63
3	1	4	1.76	–	32	95	145	95
−3	2	4	1.73	–	63	176	202	148
−4	1	4	1.72	–	0	63	219	0
0	3	4	1.68	436	308	302	355	214
−1	3	4	1.68					
1	3	4	1.66					
−2	3	4	1.67					
3	2	4	1.67					
4	0	4	1.67					
−4	2	4	1.63	–	55	210	190	77
0	0	5	1.64	–	84	77	217	105
−2	0	5	1.61	344	173	247	195	272
−1	1	5	1.61					
0	1	5	1.62					
−2	1	5	1.58					
1	1	5	1.59					
2	0	5	1.57	–	200	145	197	272
−3	1	5	1.53	522	394	277	407	383
−1	2	5	1.54					
0	2	5	1.54					
2	1	5	1.54					
−2	2	5	1.51					
1	2	5	1.52					
2	3	6	1.21	754	550	184	346	448
−5	1	6	1.22					
−3	3	6	1.21					
4	1	6	1.22					
3	3	6	1.17	–	100	63	164	0
5	1	6	1.16	482	456	288	332	387
0	4	6	1.16					
−1	4	6	1.16					
−6	1	6	1.16					
−6	0	6	1.17					

[a] F_A, F_B, F_C, are the calculated structure factors for A, B, and C models (see Table 1). F_S are the structure factors for the statistical structure (see text). Reflections are ordered by layers and by decreasing d_{cal} (Å) within each layer. Unobserved reflections are flagged—under F_{obs}. For clusters of overlapped reflections (enclosed in braces) $F = (\sum m_k F_k^2)^{1/2}$.

$= (\alpha/\beta)\ \Delta V_m$, where α, β, and ΔV_m are the thermal expansion coefficient at T_m, the compressibility at T_m (both measured on the melt just above T_m), and the volume change observed on melting.

Presumably the constant volume contribution to the fusion process is attributable to the conformational changes in the polymer chains (increased conformational freedom), which accompany their melting, and is an intramolecular process. So we write $(\Delta E_m)_V = \Delta E_{conf} = E_a - E_c$ and $(\Delta S_m)_V = \Delta S_{conf} = S_a - S_c$, where the subscripts a and c denote the molten amorphous and crystalline phases, respectively.

It is apparent that from knowledge of the polymer chain conformation in the crystal we can deduce information, such as the conformational energy and entropy, about the molten amorphous chains if we know ΔH_m, T_m, α, β, and ΔV_m. Furthermore, if we can calculate ΔE_{conf} and ΔS_{conf}, then it becomes possible, by comparison with the experimental values, to learn something about the conformations and the interactions between

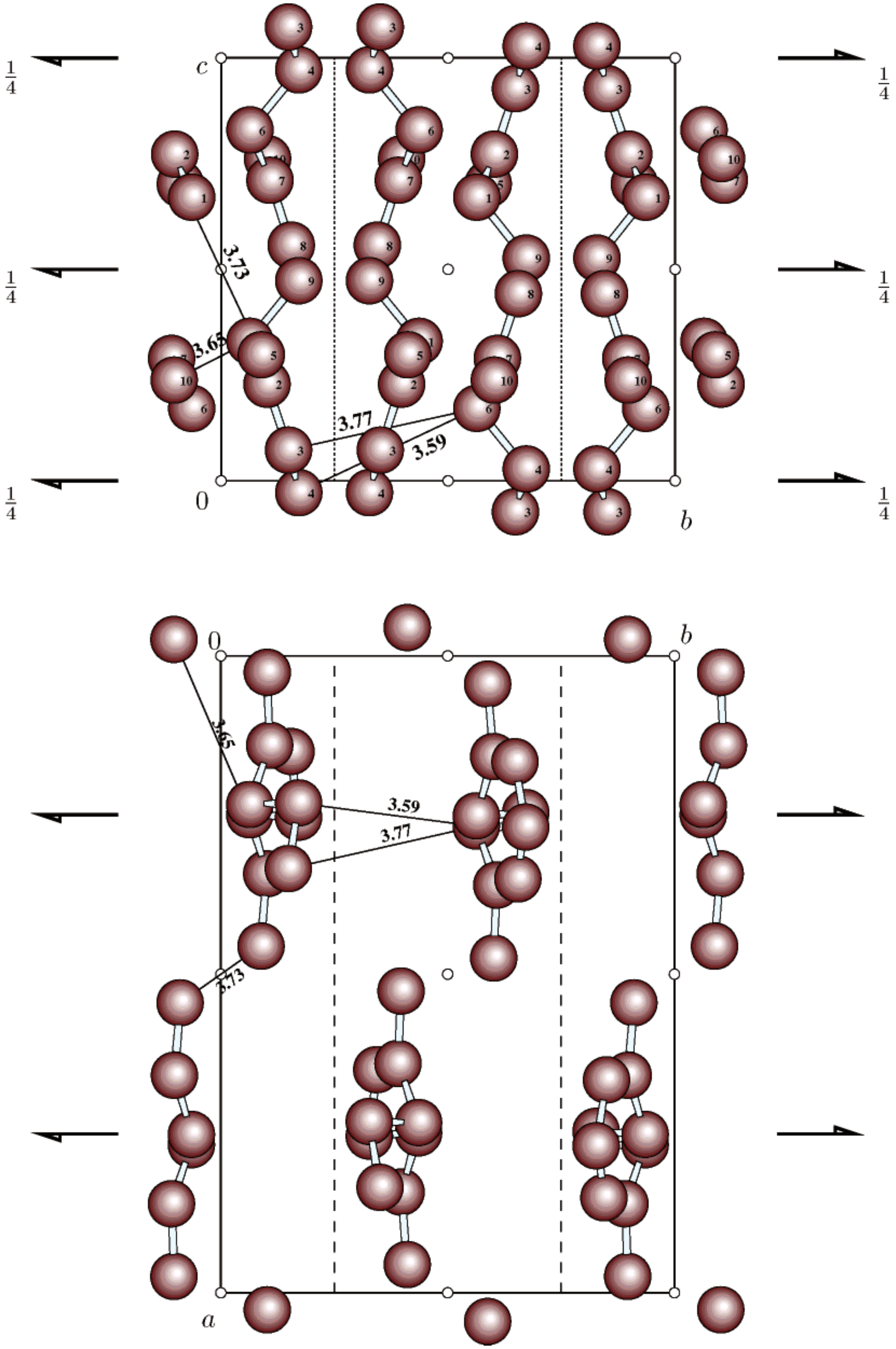

Figure 2. Crystal packing for natural rubber (C model). Crystal structure of natural rubber in $P2_1/a$ projected along a edge (up) and c edge (down); the shortest C⋯C distances (Å) are shown. Hydrogen atoms are omitted.

polymer chains both in the melt and in the crystal. $\Delta E_{\mathrm{conf}} = E_a - E_c$ and $\Delta S_{\mathrm{conf}} = S_a - S_c$, and their intramolecular or conformational components in the molten amorphous states at T_m can be obtained from the usual statistical thermodynamic relations[23] $E_a = (RT^2/Z)\ \mathrm{d}Z/\mathrm{d}T$ and $S_a = R \ln Z + (RT/Z)\ \mathrm{d}Z/\mathrm{d}T$, providing the configurational partition function, Z, for the polymer chain and its temperature coefficient are known.

In fact, the configurational partition function and its temperature coefficient can be evaluated by adopting the rotational isomeric state (RIS) model[24] of polymer chain conformations and utilizing the matrix multiplication methods of Flory and Jernigan.[18,25] Table 4

Table 4. Entropies of Fusion for Some Semicrystalline Polymers

polymer	T_m °C	ΔS_m[a]	ΔS_V	$(\Delta S_m)_V$	ΔS_{conf}
polyethylene	140	2.29−2.34	0.46−0.52	1.77−1.84	1.76
isotacticpolypropylene	208	1.50	0.44−0.65	0.85−1.09	0.96
cis−1, 4-polyisoprene	28	0.87	0.45	0.43	1.34
trans−1, 4-polyisoprene	74	2.19	0.91	1.28	1.37
polyoxymethylene	183	1.75	0.35	1.40	1.50
polyoxyethylene	66	1.78	0.37	1.41	1.70
poly(ethylene terephthalate)[b]	267	1.46	0.29	1.17	1.07
poly(tetrafluoroethylene)	327	1.97	0.52	1.45	1.60
cis−1, 4-polybutadiene	5	1.92	0.43	1.49	1.38
polyethyleneadipate	65	1.48	0.38	1.10	1.04
polyethylenesuberate	75	1.50	0.38	1.12	1.16
polyethylenesebacate	83	1.54	0.38	1.16	1.24

[a] All entropies are given in eu/mol of backbone bonds. [b] The benzene ring is treated as a single bond, because it is conformationally rigid.

presents a comparison[26,27] of the experimental entropies of fusion ΔS_m, ΔS_V, and $(\Delta S_m)_V$ with ΔS_{conf}, the calculated difference between the conformational entropies of the molten amorphous and crystalline chains, S_a and S_c, where S_c is assumed to be 0, because polymers generally crystallize by adopting a single conformation of low intramolecular energy.[17]

If one disregards c-PIP, there is an excellent agreement between the experimental and computed values and this serves as a validation of the correctness of the RIS approach in computing partition functions of molten polymers, as well as of the specific RIS models adopted.

Melting Entropy of Natural Rubber

The disagreement between the observed and expected melting entropy of c-PIP remains to be explained and could be due to many factors such as (1) a higher conformational disorder of the crystalline phase, (2) a lower conformational entropy of the molten state than that expected from the RIS model adopted,[18,28] or (3) a breakdown of the RIS approach. Because detailed investigation of any of these factors would require a separate study, here we will only discuss some relevant aspects. As has been pointed out, the diffraction analysis of crystalline natural rubber has not afforded a unique disordered model but only an indication that disorder seems reasonable. The evaluation of the entropy of a disordered crystalline phase involves the relative energies of the conformations existing in the crystalline state. However, lacking this energy information, its upper bound can be computed assuming that each conformer is equally populated. For the disordered model of Benedetti et al. this corresponds to a statistical alternation of two conformational units along the main chain (conformations cis S T $\bar{S}$ cis and cis $\bar{S}$ T S cis) leading to $S_c = (R \ln 2)/4 = 0.34$ eu/mol of main-chain bonds for the conformational entropy. Using this crystalline conformational entropy value $\Delta S_{conf} = S_a - S_c = 1.34 - 0.34 = 1.00$, which is still more than twice the experimental value. Thus, the adoption of the disordered model of Benedetti et al. is insufficient to fill the gap between experimental and calculated values. The investigation both of solid-state models more disordered than the one just considered and of possible changes in the RIS model for the melt could best be guided by computations of energies and geometries of accessible conformations.[29] As a starting point we built up octamers of c-PIP and we studied the conformations of Nyburg and Bunn chains. To our surprise, energy minimization adopting the Merck force field[14] led to dihedral angles so different from the canonical skew values that they led to chain periodicities of 7.79 and 7.32 Å for Nyburg and Bunn chains, respectively, very far from crystalline chain periodicity (8.23 Å). The main difference among these dihedral angles is found in the dihedral −C═C−C(Me)−C− which is between 90 and 100°. To be more confident of the deviation of the dihedral angle we also performed DFT[30] calculations on smaller models (3-methyl-3-hexene, and a trimer of c-PIP) obtaining in all cases dihedrals in the 90−100° range. In effect, an alteration of that torsion angle from the ±120° value was already anticipated by Flory, who assigned it to 110° in his later RIS model.[31] As a consequence of this distortion, the chain is more wrinkled than usual for crystallization, and the chain in the crystal can be anticipated to have a considerably higher conformational energy than the free chain; molecular mechanics calculations done on the same models but constraining the central unit to have the correct periodicity suggest a strain energy of 1−2 kcal/mol (see Table 5). To obtain a good packing, the chain is stretched, with a small but appreciable increase of energy. This notable effect can be considered an exception in polymers, where the basic assumption that the minimum energy conformation for the isolated chain is found practically unchanged also in the crystalline state generally holds.[15,17] Beyond the crystallographic interest of this finding, the observation that one of the torsion angles is notably different from the values considered in published RIS models lead us to suspect that the value computed for S_a could be in error, although it should be mentioned that the RIS model adopted allows a good reproduction of other molecular properties, such as the chain dimensions. As for the possibility of a higher conformational disorder in the solid state, Monte Carlo calculations[32] on the free chain did not allow to find conformations suitable to crystallize beyond those considered above; indeed all other conformations have a shorter repeat. Thus, if the Flory RIS model is not questioned, we are left with the hypothesis of a breakdown of the RIS approach, which could mean that the vibrational partition functions of chains embedded in the crystal and in the melt are significantly different, which is at odds with what happens in most polymers.

Table 5. Computed Energies of Octamers of c-PIP with and without Constraints[a]

model	E (kcal/mol)	periodicity (Å)	$E_{8.23}$ (kcal/mol)
Nyburg	0.00	7.79	0.84
Bunn	0.86	7.32	2.62

[a] Two methylene−methylene distances in the central part of the octamer (monomers **3**−**5** and monomers **4**−**6** of the octamer) were constrained at 8.23 Å.

This could be related to the fact that the chains in the crystal adopt a conformation that is higher in energy than the lowest energy conformation in the melt. However investigation of this point certainly needs a more extensive and dedicated study.

Conclusions

A new analysis of the fiber X-ray diffraction spectrum of natural rubber allowed us to assign and refine a structure model, within the monoclinic cell assigned by Takahashi and Kumano, which seems to us quite reliable and convincing, despite the modest number of reflections observed. The chain torsion angles resulting differ significantly from the ones found by Takahashi and Kumano. In particular the T chain torsion angle deviates only modestly from 180°.

The resulting pseudo-orthorhombic symmetry also gives credibility to the more symmetrical orthorhombic model proposed by Natta and Corradini (on the basis of Nyburg's measurements). A definite choice between monoclinic and orthorhombic models, however should require a new accurate indexing of the Bragg reflections. An improvement in resolution is also desirable.

We have shown that structure refinement of fibrous polymers is a realistic goal *even with few data* provided that (i) structures are described by internal coordinates, (ii) models with *few* internal coordinates are chosen, and (iii) the appropriate constraints are imposed. Finally the novel program TRY, already successfully used in resolving arduous polymeric problems, has again confirmed its utility.

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