Conclusions

The macromolecular conformations in the crystalline state of both II and III correspond to the model shown in Figure 1a, provided the methyl group is properly replaced by an ethyl and an *n*-propyl group, respectively. The actual chain structure of II is given in Figure 5. The reason that the side groups of II and III cannot correspond to a cis arrangement of the $C_3C_2C_1C_5$ sequence, as is the case for I (Figure 1b), is readily understood upon examination of the intramolecular nonbonded interactions. In fact, as is shown in Figure 4 with reference to polyhexadiene, any of the three orientations of the methyl group (C_6) obeying the criterion of the staggered bonds gives rise to C···C contact distances much shorter than 3 Å among atoms separated by four bonds and is therefore unacceptable.

As a last remark, let us recall that, of the two C=C—C—C sequences contained in each monomer unit of isotactic poly(*trans*-1,4-penta-1,3-diene) in the crystalline state, one is in the skew, the other in the cis conformation. Since a reasonable conformation of the macromolecule might also be achieved with both sequences in the skew arrangement, our finding is further proof that the cis and the skew conformations have very close energy contents.

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Single Crystal to Single Crystal Transformation of Perhydrotriphenylene Inclusion Compounds during Canal Polymerization of Butadiene

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ABSTRACT: The PHTP–1,3-butadiene inclusion compound (I, $a = 13.35 \pm 0.05$, $b = 14.72 \pm 0.06$, $c = 4.78 \pm 0.02$ Å, $\gamma = 115.3 \pm 0.5°$, space group $P2_1/m$; $Z_{PHTP} = 2$) undergoes a single crystal–single crystal transformation parallel to the canal polymerization of butadiene to *trans*-1,4-polybutadiene under the action of X or γ rays. The transformation proceeds through an intermediate disordered structure, and has been followed by us by X-ray. The PHTP–polymer inclusion compound (II, $a = b = 14.26 \pm 0.05$, $c = 4.78 \pm 0.02$ Å, $\gamma = 120°$, space group $P6_3/m$, $Z_{PHTP} = 2$) is virtually identical with PHTP–linear hydrocarbon adducts as far as the host molecules are concerned. While the shape of the channels in II is nearly cylindrical, in I it is markedly elongated, in order to accommodate the included butadiene molecules. During the polymerization the infinite stacks of PHTP molecules undergo a simple rearrangement which does not involve any molecular rotation or packing change within the stacks. The results of the X-ray structural determination are reported for both structures I and II. The terminal C atoms of neighboring butadiene molecules in I are only about 3.50 Å apart, which favors 1,4 addition under the radiation.

Many examples of stereospecific polymerization of irradiated monomers included in the crystalline matrix of the fully equatorial isomer of perhydrotriphenylene (PHTP) have already been reported and discussed from several points of view.[1–4] We recall that all PHPT inclusion compounds are channel-like, in analogy with urea and thiourea complexes.[5] In particular, monomers characterized by different degrees of bulkiness, such as 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, may undergo canal 1,4 trans polymerization in PHTP,[1] while this is possible in urea only for the former,[6] and in thiourea only for the latter monomer.[7] The greater range of possible inclusion compounds obtainable with PHTP is connected with both the size and the shape of the channels being adaptable to the included molecules. This in turn is due to the fact that only weak, nondirectional van der Waals forces are responsible for PHTP molecules being held together in the crystalline state, whereas the crystal structure of urea and thiourea results from a three-dimensional network of intermolecular hydrogen bonds.

A remarkable example which illustrates how molecules with quite a different shape may be accommodated in the channels with a change in crystalline packing is given by the transformation which takes place during the radiation polymerization in PHTP of 1,3-butadiene to poly(*trans*-1,4-butadiene). An interesting feature of this transformation is that it entails a single crystal–single crystal structural change, where the two crystals have different symmetry. We have been able to determine the structure of both crystals as well as to follow the transition, which may occur under the X-ray beam. From the geometry of the channels of the two crystals and from analytical data, significant information has been derived which helps in understanding the mechanism of the polymerization.

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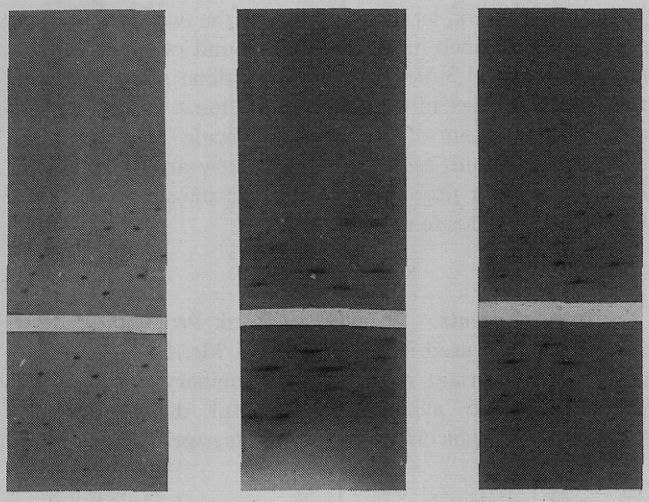

Figure 1. Equatorial Weissenberg spectra taken from the same crystal along the c axis during the transformation from I to II. Spectra a, b, and c correspond to I, to a disordered structure intermediate between I and II, and to II, respectively. The three spectra correspond to the same angular interval; exposure time for each spectrum is about 5 min. From the end of each spectrum to the beginning of the next the crystal irradiation lasted about 20 min (Cu Kα, normal focus, 35 kV, 15 mA).

Experimental Section

Crystals of the PHTP–1,3-butadiene inclusion compound were obtained from a solution of PHTP in butadiene at about $-10°$C. Several crystals were sealed in a thin-walled glass tube of about 0.3 mm internal diameter; their shapes were approximately cylindrical, their axes being parallel to the c axis of the unit cell. X-Ray photographs were taken with both the rotating crystal and Weissenberg techniques. The crystal to crystal transformation, which proceeds parallel to the canal polymerization, was obtained under the X-ray beam (Cu Kα) and followed with Weissenberg spectra taken at different times. Under the conditions employed in our laboratory (Philips generator with normal-focus X-ray tube, 35 kV, 15 mA), the transformation was complete in about 50 min. As a check that butadiene has polymerized to substantial completion, we determined the melting point of the crystal after a long irradiation (~2 hr); the melting point was found to be close to 182°, which is the figure already obtained in several cases for PHTP inclusion compounds containing linear polymers with high molecular weights.[1]

Structural Results

Figure 1 shows a portion of the zero-layer Weissenberg spectra taken on the same crystal at three different degrees of transformation. The large amount of diffuse intensity observable on the spectrum of Figure 1b shows that the polymerization tends to start in different points uniformly distributed all over the crystal, thus giving rise to disordered regions where the molecular packings corresponding to the two ordered structures are mixed at random.

The unit cell dimensions of the inclusion compound with the monomer (I) and with the polymer (II) are reported in Table I. From inspection of the photographs it is apparent that structure II is substantially identical with that found for the PHTP–linear hydrocarbons inclusion compounds.[5,8] Hence the space group is $P6_3/m$. I is monoclinic, the only observed systematic absences being (00l) with l odd; therefore, possible space groups are $P2_1$ and $P2_1/m$. However,

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TABLE I
CRYSTAL DATA

I	II
$a = 13.35 \pm 0.05$ Å	$a = b = 14.26 \pm 0.05$ Å
$b = 14.72 \pm 0.06$ Å	
$c = 4.78 \pm 0.02$ Å	$c = 4.78 \pm 0.02$ Å
$\gamma = 115.3 \pm 0.5°$	$\gamma = 120°$
$V = 849.3 \pm 8$ Å^3	$V = 841.3 \pm 8$ Å
$Z_{PHTP} = 2$	$Z_{PHTP} = 2$
$D_{exptl} = 1.05 \pm 0.1$ g/cm^3	$D_{exptl} = 1.07 \pm 0.1$ g/cm^3
$D_{calcd} = 1.07 \pm 0.03$ g/cm^3	$D_{calcd} = 1.08 \pm 0.3$ g/cm^3
Absent reflections (00l) with l odd	Absent reflections (00l) with l odd
Space group $P2_1/m$	Space group $P6_3/m$

starting from the packing of PHTP molecules which corresponds to the $P6_3/m$ space group—which implies a statistical coexistence of d and l molecules in the same crystalline sites[9]—only the $P2_1/m$ space group may be obtained. The axis has the same value for both structures ($c = 4.78 \pm 0.02$ Å) and maintains the same orientation, coincident with the rotation axis of the crystal. This means that the rows of PHTP molecules are stacked along c in the same way and only the packing among the rows is different in the two cases. As Table I shows, the angle between a and b in I is close to 120° ($\gamma = 115.3°$). From the Weissenberg spectra we observe that the b direction in I nearly coincides with the b direction in II, after the transformation, while the a axis rotates about 5°, in order to bring the angle to the hexagonal value ($\gamma = 120°$).

One butadiene molecule and one monomer unit are contained in the unit cells of I and II, respectively. In fact, in neither case were continuous streaks between the layer lines observed in the rotating crystal photographs performed along c, contrary to the case of the PHTP–linear molecule inclusion compounds.[5,8] This may only be explained by the assumption that the repeat distance between consecutive units in the channels is identical with that between PHTP molecules (*i.e.*, 4.78 Å). In fact, with this hypothesis we are left with two possibilities: either the arrangement of the included molecules, or monomers units, is coherent with that of the host molecules, and then their diffraction effect consists of contributing to the total diffracted amplitude of all the (*hkl*) reflections, or they are arranged incoherently in the different channels, and their diffracted streaks coincide with the PHTP layer lines, being therefore unobservable. Another piece of evidence confirming the presence of one butadiene molecule in the unit cell of I, *i.e.*, per two PHTP molecules, is given by the PHTP:butadiene molar ratio obtained from thermogravimetric analysis, which is 1.93 ± 0.1.[10] As for II, it is no wonder that the repeat distance among consecutive monomer units of poly(*trans*-1,4-butadiene) is 4.78 Å in the present case, since the value observed in the crystalline polymer is very slightly different (4.85 Å) [11] and the corresponding conformation appears to be quite suitable for inclusion in the channels (see Figure 5b).

In spite of the rather quick transformation that I undergoes under X-rays, we have been able to derive its fundamental features from analysis of the structural projection along c. A

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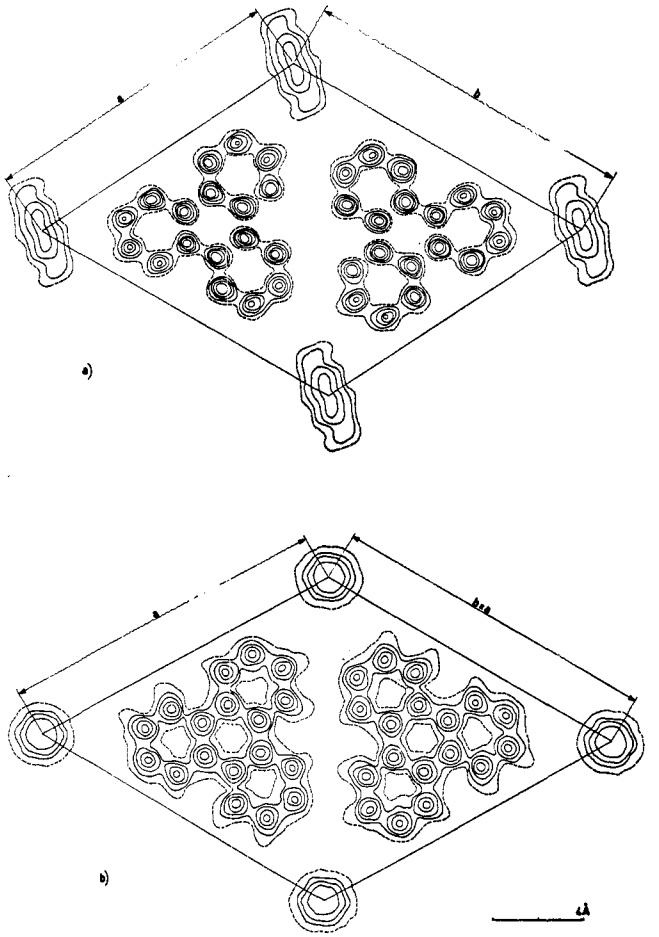

Figure 2. Electron density projections for I (a) and II (b) along the c axis. Contours are drawn at 2 (– – –), 3, 4, ... e/Å^2. Atomic peaks of I appear to be sharper than those of II because of the lower average B value (2.5–3 Å^2 *vs.* 4–5 Å^2).

single Weissenberg ($hk0$) photograph, obtained with a total exposure time of only 15 min, allowed us to estimate visually 83 independent nonzero intensities from a total number of 236 measurable reflections. The value of the repeat distance along c guarantees that the threefold axis of the PHTP molecules is parallel to this direction; therefore, the molecule which constitutes the asymmetric unit possesses only three degrees of freedom in the ab projection if its conformation is assumed to be identical with that found in other inclusion compounds. The angle of rotation with respect to the unit cell axes was easily derived from inspection of the intensity distribution, while the (x, y) coordinates of the molecular center were determined with packing criteria. These three parameters were then refined with the aid of a Fourier projection (Figure 2a). Then structure factor calculations were performed with isotropic thermal factors, giving thermal parameters identical with those of C atoms related by intramolecular symmetry D_3, the larger their values the greater their distances from the center of the molecule. Hydrogen atoms were also introduced in the expected positions (d_{C-H} = 1.1 Å) with identical isotropic thermal parameters. The Fourier projection showed a rough image of the included molecule (see Figure 2a) which appears as clearly elongated, contrary to the quasicircular symmetry shown by the image of most PHTP-included molecules (see, *e.g.*, Figure 2b). From this image, as well as from packing considerations, assuming the molecular geometry derived from electron diffraction data,[12] we have obtained the coordinates of the butadiene atoms, which have been also introduced into the structure factor calculations with uniform isotropic thermal parameters. The best agreement between calculated and observed structure factors was obtained with the atomic parameters reported in Table II. The comparison between $F_c(hk0)$ and $|F_o(hk0)|$ is reported in Table III: the $R = \Sigma||F_c| - |F_o||/\Sigma|F_o|$ disagreement factor is 0.19 for the 83 observed reflections.

No measurement of the X-ray intensities was undertaken for II. Both the unit cell dimensions and the intensity

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TABLE II
ATOMIC FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS (Å^2) FOR THE PHTP–1,3-BUTADIENE INCLUSION COMPOUND (I)

	x/a	y/b	z/c	B
C(1)	0.1521	0.4069	0.1963	3.11
C(2)	0.1397	0.5000	0.3037	2.61
C(3)	0.2363	0.5954	0.1963	2.11
C(4)	0.2236	0.6882	0.3037	2.11
C(5)	0.1142	0.6844	0.1963	2.61
C(6)	0.1015	0.7779	0.3037	3.11
C(7)	0.1985	0.8726	0.1963	3.11
C(8)	0.3082	0.8750	0.3037	2.61
C(9)	0.3210	0.7829	0.1963	2.11
C(10)	0.4307	0.7863	0.3037	2.11
C(11)	0.5262	0.8801	0.1963	2.61
C(12)	0.6371	0.8821	0.3037	3.11
C(13)	0.6498	0.7911	0.1963	3.11
C(14)	0.5543	0.6953	0.3037	2.61
C(15)	0.4434	0.6926	0.1963	2.11
C(16)	0.3464	0.5978	0.3037	2.11
C(17)	0.3584	0.5034	0.1963	2.61
C(18)	0.2622	0.4100	0.3037	3.11
C(19)	0.0524	0.0414	0.0289	3.00
C(20)	0.0704	0.0982	0.2687	3.00
H(1)	0.084	0.340	0.272	3.0
H(1)′	0.152	0.407	−0.028	3.0
H(2)	0.063	0.498	0.230	3.0
H(2)′	0.140	0.500	0.528	3.0
H(3)	0.236	0.595	−0.028	3.0
H(4)	0.224	0.688	0.528	3.0
H(5)	0.114	0.684	−0.028	3.0
H(5)′	0.047	0.618	0.272	3.0
H(6)	0.025	0.776	0.228	3.0
H(6)′	0.101	0.778	0.528	3.0
H(7)	0.198	0.872	−0.028	3.0
H(7)′	0.190	0.938	0.270	3.0
H(8)	0.376	0.942	0.230	3.0
H(8)′	0.308	0.875	0.528	3.0
H(9)	0.321	0.783	−0.028	3.0
H(10)	0.431	0.787	0.528	3.0
H(11)	0.526	0.880	−0.028	3.0
H(11)′	0.518	0.945	0.271	3.0
H(12)	0.705	0.949	0.230	3.0
H(12)′	0.637	0.881	0.528	3.0
H(13)	0.649	0.791	−0.028	3.0
H(13)′	0.727	0.793	0.269	3.0
H(14)	0.564	0.631	0.228	3.0
H(14)′	0.555	0.695	0.528	3.0
H(15)	0.443	0.692	−0.028	3.0
H(16)	0.347	0.598	0.528	3.0
H(17)	0.358	0.503	−0.028	3.0
H(17)′	0.435	0.505	0.271	3.0
H(18)	0.262	0.411	0.528	3.0
H(18)′	0.271	0.345	0.231	3.0
H(19)	0.114	0.055	−0.132	3.0
H(20)	0.148	0.160	0.320	3.0
H(20)′	0.011	0.088	0.428	3.0

TABLE III
PHTP–1,3-BUTADIENE INCLUSION COMPOUND (I). COMPARISON BETWEEN THE OBSERVED AND CALCULATED STRUCTURE FACTORS OF THE (*hk*0) REFLECTIONS

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
0	0	0	0	3060	7	3	0	<78	64	1	6	0	<60	−101	2	9	0	<82	48
2	0	0	201	−181	8	3	0	<83	−56	2	6	0	<64	−47	3	9	0	<85	−18
3	0	0	<39	16	9	3	0	<87	34	3	6	0	<69	48	4	9	0	<87	20
4	0	0	238	−245	−1	3	0	267	324	4	6	0	<74	−73	5	9	0	<88	−85
5	0	0	131	−143	−2	3	0	326	425	5	6	0	<79	49	−1	9	0	<73	−60
6	0	0	<60	−10	−3	3	0	190	170	6	6	0	<84	−37	−2	9	0	<71	30
7	0	0	<68	−94	−4	3	0	351	337	7	6	0	<87	28	−3	9	0	141	77
8	0	0	<74	−43	−5	3	0	322	254	−1	6	0	121	32	−4	9	0	<71	−38
9	0	0	229	185	−6	3	0	451	−463	−2	6	0	346	274	−5	9	0	<72	−16
10	0	0	210	−165	−7	3	0	<63	39	−3	6	0	388	−335	−6	9	0	<74	−3
11	0	0	<88	11	−8	3	0	<70	38	−4	6	0	136	−88	−7	9	0	<76	−84
1	1	0	260	370	−9	3	0	<76	59	−5	6	0	<58	17	−8	9	0	275	−202
2	1	0	329	416	−10	3	0	<82	−77	−6	6	0	<62	91	−9	9	0	234	135
3	1	0	177	90	−11	3	0	<86	−33	−7	6	0	<67	80	−10	9	0	192	224
4	1	0	141	63	−12	3	0	<88	−45	−8	6	0	<72	72	−11	9	0	<88	45
5	1	0	<56	−25	0	4	0	233	−215	−9	6	0	<77	42	0	10	0	363	353
6	1	0	<63	−16	1	4	0	143	71	−10	6	0	<82	46	1	10	0	<84	−1
7	1	0	<70	−140	2	4	0	346	278	−11	6	0	<86	37	2	10	0	<86	−2
8	1	0	218	−239	3	4	0	<58	−113	−12	6	0	<88	−114	3	10	0	<88	−22
9	1	0	203	−205	4	4	0	260	−273	0	7	0	<63	−51	−1	10	0	224	−189
10	1	0	301	284	5	4	0	<69	−97	1	7	0	<66	−35	−2	10	0	173	−110
−2	1	0	201	219	6	4	0	<76	−47	2	7	0	<70	−21	−3	10	0	<76	6
−3	1	0	272	259	7	4	0	<81	2	3	7	0	<75	−47	−4	10	0	<76	−88
−4	1	0	219	157	8	4	0	<86	14	4	7	0	<80	77	−5	10	0	<77	−24
−5	1	0	126	−103	9	4	0	<88	85	5	7	0	<84	53	−6	10	0	<78	53
−6	1	0	154	95	−1	4	0	<42	10	6	7	0	<87	−60	−7	10	0	<80	2
−7	1	0	<65	−88	−2	4	0	111	102	7	7	0	<88	−37	−8	10	0	<83	88
−8	1	0	<72	−89	−3	4	0	306	298	−1	7	0	86	−78	−9	10	0	225	309
−9	1	0	<79	74	−4	4	0	179	−79	−2	7	0	187	−178	−10	10	0	230	−317
−10	1	0	<84	−64	−5	4	0	166	138	−3	7	0	251	−264	−11	10	0	<88	−10
−11	1	0	<88	−43	−6	4	0	<58	−7	−4	7	0	361	375	0	11	0	383	−368
0	2	0	200	−179	−7	4	0	211	229	−5	7	0	<62	73	1	11	0	<87	81
1	2	0	253	237	−8	4	0	<70	−42	−6	7	0	<66	53	2	11	0	<88	72
2	2	0	<41	−13	−9	4	0	<76	−16	−7	7	0	<69	113	−1	11	0	<84	−21
3	2	0	134	−167	−10	4	0	<82	−19	−8	7	0	<74	4	−2	11	0	<83	85
4	2	0	<54	−112	−11	4	0	<86	−64	−9	7	0	111	−86	−3	11	0	<82	83
5	2	0	<60	−8	−12	4	0	<88	−22	−10	7	0	<83	68	−4	11	0	<81	67
6	2	0	<67	−59	0	5	0	174	−165	−11	7	0	<86	2	−5	11	0	<82	12
7	2	0	<74	−15	1	5	0	<54	−24	−12	7	0	<88	−37	−6	11	0	<83	21
8	2	0	340	267	2	5	0	266	−306	0	8	0	138	38	−7	11	0	<84	6
9	2	0	319	−299	3	5	0	260	236	1	8	0	<72	−40	−8	11	0	<85	−39
10	2	0	<88	−47	4	5	0	<69	−15	2	8	0	170	−117	−9	11	0	<87	−39
−1	2	0	236	365	5	5	0	<74	−39	3	8	0	<80	5	−10	11	0	<88	−11
−2	2	0	264	−213	6	5	0	<80	−30	4	8	0	<84	−34	0	12	0	<88	−78
−3	2	0	310	362	7	5	0	<85	0	5	8	0	<87	−42	−1	12	0	<87	205
−4	2	0	160	138	8	5	0	<88	−4	6	8	0	197	186	−2	12	0	<86	−70
−5	2	0	208	101	−1	5	0	145	140	−1	8	0	<67	20	−3	12	0	<86	12
−6	2	0	379	327	−2	5	0	117	−101	−2	8	0	<65	14	−4	12	0	<86	9
−7	2	0	128	−145	−3	5	0	169	128	−3	8	0	172	150	−5	12	0	<86	30
−8	2	0	<71	−95	−4	5	0	115	89	−4	8	0	146	−119	−6	12	0	<86	13
−9	2	0	<77	−54	−5	5	0	<55	24	−5	8	0	<67	6	−7	12	0	<87	−1
−10	2	0	<83	−96	−6	5	0	<59	72	−6	8	0	<69	18	−8	12	0	<87	13
−11	2	0	<87	−51	−7	5	0	<65	84	−7	8	0	<73	−77	−9	12	0	<88	−63
0	3	0	205	−233	−8	5	0	141	106	−8	8	0	171	186	−2	13	0	<88	66
1	3	0	<41	−23	−9	5	0	<76	−69	−9	8	0	228	−166	−3	13	0	<88	−39
2	3	0	<46	−91	−10	5	0	<82	−22	−10	8	0	<84	79	−4	13	0	<88	22
3	3	0	397	−468	−11	5	0	<86	−31	−11	8	0	<87	20	−5	13	0	<88	37
4	3	0	273	161	−12	5	0	<88	133	0	9	0	131	106	−6	13	0	<88	−148
5	3	0	<64	−76	0	6	0	<56	−75	1	9	0	157	−69	−7	13	0	<88	91
6	3	0	<71	−59															

distribution derived from inspection of the photographs are so similar to those of the PHTP–linear hydrocarbons inclusion compounds that we have concluded that they are substantially identical. Figure 2b shows the *ab* electron density projection for PHTP–*n*-heptane.[5,8]

Figure 3 shows the packing among the PHTP molecules for both structures. As may be observed, the fact that the *b* direction for either structure does not change during the transformation from I to II implies that the stacks of PHTP molecules undergo a simple (and small) translational shift,

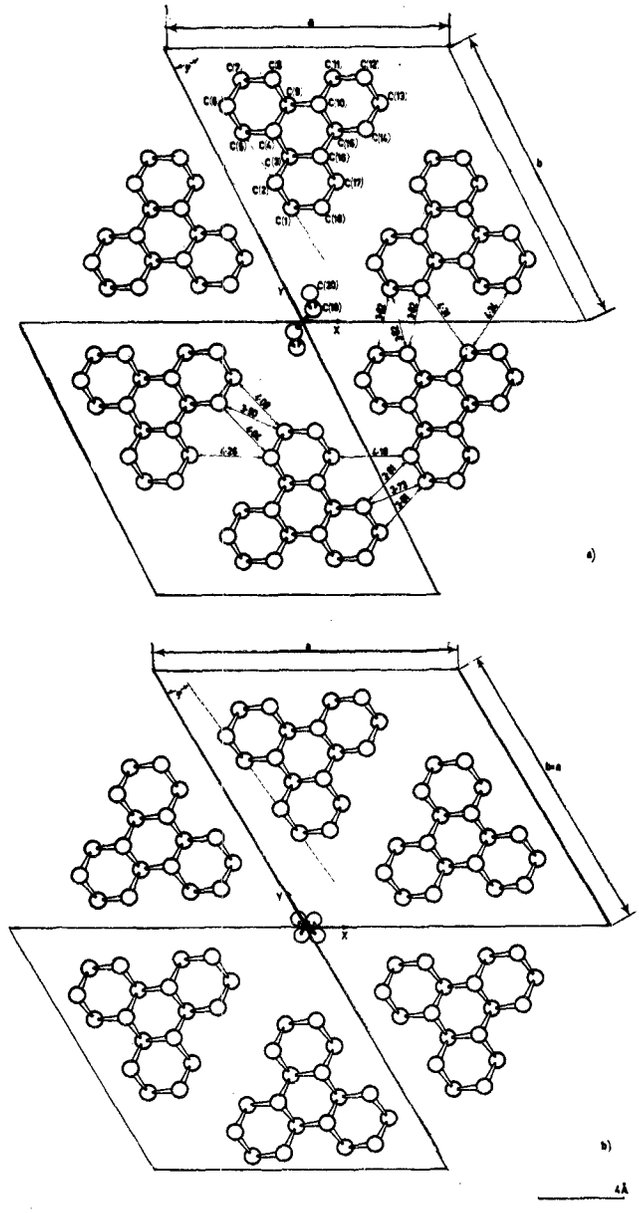

Figure 3. Molecular packing of I (a) and II (b). The closest C···C intermolecular distances are indicated. (II has already been described elsewhere.[5])

without any rotation involved. In fact, the φ angle (see Figures 3a and 3b) which characterizes the molecular rotations with reference to b is virtually identical for the two structures. In Figure 4 the change of packing which takes place during the transformation is emphasized with a congruent superposition of the two images reported in Figure 3.

Figure 5 shows the fitting of the van der Waals envelope of the included molecules in the channel whose contours correspond to the envelope of the van der Waals spheres of hypothetical hydrogen atoms contacting the PHTP molecules. Figure 5a shows this fitting for structure I at three different sections of the channel. The center of the butadiene molecule has been put at $z = {}^1/_2c$, although, for space group requirements, a molecule placed at $z = 0$ is also statistically present in the unit cell, with the same probability. This statistical coexistence may be achieved through some disorder in the sequence of the included molecules in the channel, through lack of correlation among sequences in different channels, or both. Figure 5b shows the projection of the van der Waals envelope of the polymer inside the narrowest section of the

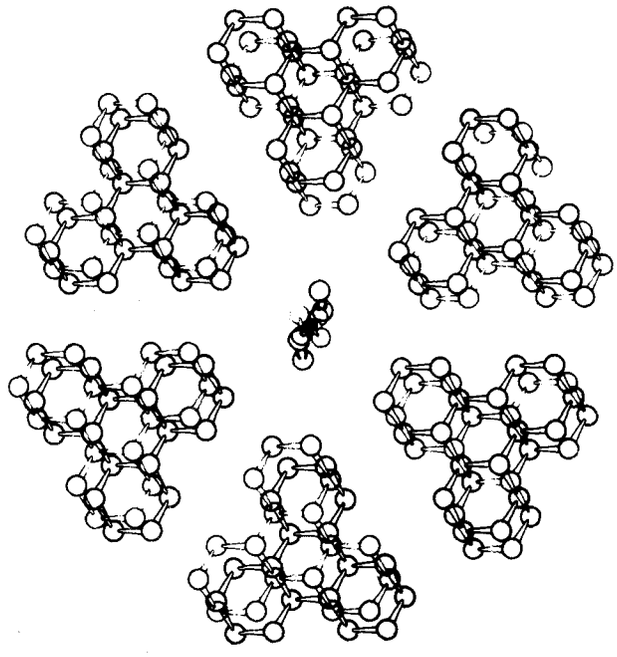

Figure 4. Superposition of the crystalline packing of I and II (see Figure 3) showing the molecular shifts which take place during the transformation. Structure I is drawn in heavier lines than structure II. The same molecular orientation with respect to the crystal has been maintained in the two cases.

channel (at $z = {}^1/_4c$ or ${}^3/_4c$). As may be seen, the fitting is satisfactory, so any value of the z coordinate may be attained in principle by any atom of the monomer unit within the unit cell, as happens with the PHTP-*n*-hydrocarbon inclusion compounds.

Although no detailed structure factor calculation has been done by us on II, we believe that the strong resemblance shown by the intensity distribution of II with the case of PHTP-*n*-heptane justifies the hypothesis that no precise z coordinates may be assigned to the polymer atoms.

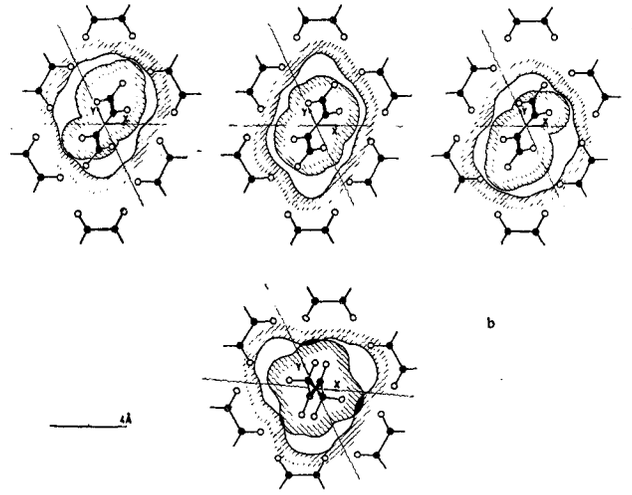

Figure 5. (a) Three sections (at $z/c = {}^1/_4$, ${}^1/_2$, and ${}^3/_4$) of the van der Waals limiting surface of the butadiene molecules included in the PHTP channels. Internal contours of the channel correspond to sections of the van der Waals envelope of hypothetical hydrogen atoms contacting the PHTP molecules (structure I). (b) A projection of the van der Waals limiting surface for the polymer chain along c for II; the van der Waals contour of the channel is a section at $z = {}^1/_4c$.

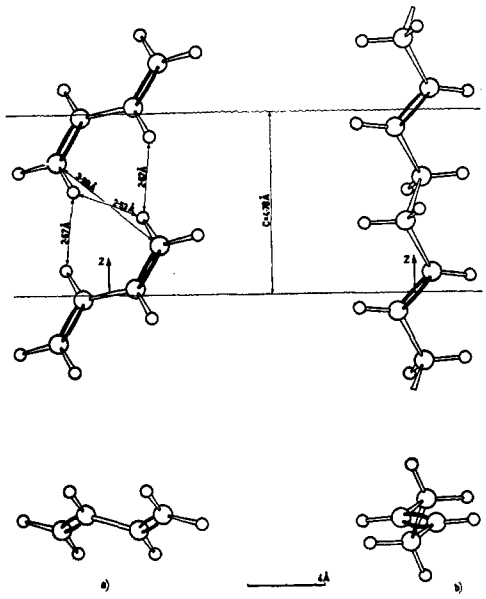

Figure 6. (a) Relative orientation of successive butadiene molecules within the channels of I, in a view at right angles to the c axis (above) and along the axis (below). (b) The corresponding views of the included polymer.

Figure 6a shows the arrangement of the butadiene molecules within the rows, arrived at on the basis both of the Fourier image reported in Figure 2a and of packing criteria. It is interesting to point out that the distance between terminal C atoms of neighboring molecules (~3.50 Å) is very close to the van der Waals value, which certainly favors the 1,4 addition that takes place under γ or X radiation. Figure 6b shows the chain model of poly(*trans*-1,4-butadiene), as derived from X-ray investigations on the crystalline polymer, with only a slight change in the torsional angles (2–4°) to bring the repeat distance from 4.85 to 4.78 Å, as it is in the inclusion compound.

Final Remarks

Very few cases of single crystal to single crystal transformation during a solid-state reaction have been reported hitherto, and we wish to recall in this context the radiation polymerization of trioxane,[13] tritiane,[14] triselenane,[15] and vinyl stearate.[16] However, the polymerization of butadiene included in PHTP is peculiar insofar as a chemical transformation involving the guest molecules is able to determine a packing rearrangement of the host molecules which extends throughout the crystal with three-dimensional order. We believe that the circumstance that the initial monomer:PHTP molar ratio is identical with the (monomer units):PHTP ratio after the polymerization is very favorable to the regularity of the crystalline rearrangement, insofar as it does not require any long-range shift of included molecules within the channels during the polymerization process, thus presumably minimizing the strain within the crystals.

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Nuclear Magnetic Relaxation in Polytetrafluoroethylene Fibers

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ABSTRACT: Nmr relaxation studies have been carried out on fibers of polytetrafluoroethylene (PTFE). Spin–spin relaxation time, T_2, orientation dependences provide confirmation of the onset of chain rotation at the 20° crystalline transition and support the view that longitudinal chain translation sets in at the ~35° transition. The amorphous regions evidence no apparent orientation.

Molecular relaxation processes in polytetrafluoroethylene (PTFE) have been studied extensively by ^{19}F nmr, both in the bulk[1,2] and in the oriented fiber form.[3–6] The use of oriented fiber samples has facilitated the interpretation of the relaxation processes because of the additional information contained in the anisotropy of the nmr absorption signal as a function of the direction of the applied magnetic field.

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PTFE is a partially crystalline polymer with crystalline and amorphous phases. Consequently, the recorded nuclear signal is a superposition of two decay curves. Although Hyndman and Origlio[4] have reported second-moment data for the ^{19}F resonance in PTFE fibers, their calculations refer only to the composite signal. Here we report spin–spin relaxation data which have been analyzed in terms of two distinct relaxation times with the result that more precise comparisons between theoretical predictions and experimental data can be made.

Spin–lattice (T_1) and rotating-frame ($T_{1\rho}$) data have also been recorded. However, T_1 measurements provide no further information in addition to that reported for the bulk polymer.[1] The rotating-frame data are too complicated to extract any useful information at this point.

The spectrometer was operated at a frequency of 30 Mcps