tion effect on shifting the T_g's inward is greater than the density effect on T_g.

In summary, the density and glass transition behavior agree with the electron microscopy[2a,3] and indicate that the phase separation is not complete, with "permanent" interpenetration being responsible for increased interaction between the phases (smaller domain sizes). Studies on the viscoelastic properties of these IPN's (which will be reported later) support these results.

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Structures of Two Crystalline Forms of Poly(butylene terephthalate) and Reversible Transition between Them by Mechanical Deformation

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ABSTRACT: For poly(butylene terephthalate) ([-O(CH$_2$)$_4$OCOPhCO-]$_n$) two crystal modifications (α and β forms) were found and their crystal structures were analyzed by x-ray diffraction. The transition between two modifications takes place reversibly by mechanical deformation: from the α form to the β form by elongation and inversely by relaxation. Two modifications belong to the triclinic system with the space group $P\bar{1}$-C_i^1. Each unit cell contains one molecular chain; the cell dimensions are a = 4.83 Å, b = 5.94 Å, c (fiber axis) = 11.59 Å, α = 99.7°, β = 115.2°, and γ = 110.8° for the α form; and a = 4.95 Å, b = 5.67 Å, c (fiber axis) = 12.95 Å, α = 101.7°, β = 121.8°, and γ = 99.9° for the β form. Several plausible molecular models obtained by the intramolecular potential energy calculation were examined by x-ray analysis, and finally the refinement of the proper models was carried out by the constrained least-squares method. The difference in fiber periods of two crystalline forms is ascribed majorly to a conformational change of a four-methylene group sequence in both forms: approximately $\bar{G}\bar{G}$TGG for the α form and TST$\bar{S}$T for the β form. The phenomena of the double orientation and tilting were observed as in the case of poly(ethylene terephthalate) and discussed in connection with the crystal structures.

Among the polyesters of the type [-O(CH$_2$)$_m$OCOPhCO-]$_n$, crystal structure of poly(ethylene terephthalate) [PET] (m = 2) was determined,[2] but for other members (m = 3-10), only the lattice dimensions or the fiber identity periods have been reported.[3-5] The present paper deals with poly(butylene terephthalate) [PBT] [-O(CH$_2$)$_4$OCO-PhCO-]$_n$ (m = 4). We have found two crystal modifications, the α and β forms; the latter form exists only under tension and consists of more extended molecular chains. The transition between the α form and β form takes place reversibly by stretching and relaxation. The crystal structures of both forms were determined by x-ray analysis with the help of conformation energy calculation. Moreover, the phenomena of double orientation and tilting were observed as in the case of PET and will be discussed later, being correlated to the crystal structures.

After almost completion of the present study, the authors were informed the investigation of Professor Ward's group[6,7] had found the existence of two modifications in PBT and discussed the crystal deformation due to the transition.

Experimental Section

Samples. The preparation methods of the samples are summarized in Figure 1. The white opaque polymer was heated to become a transparent molten sample (mp 224 °C). The molten sample was drawn quickly soon after quenching in ice-water giving amorphous sample (observed density, 1.30 g/cm^3). Then the sample was further elongated at room temperature and was subjected to heat treatment at 200 °C in vacuo for 2 h under tension. The crystal form thus obtained in the uniaxially oriented fiber was named the β form. It was found that this modification exists only under tension and is transformed into another highly crystalline modification, the α form, by removing the tension. When the sample of the α form is again stretched about 12%, a pure β form is obtained. When the elongation is less than 12%, both modifications coexist. A doubly oriented specimen of the α form was prepared by rolling the uniaxially oriented α form fiber along the drawn direction. As to the β form, no doubly oriented specimen could be obtained.

Measurements. X-ray photographs were taken by using nickel-

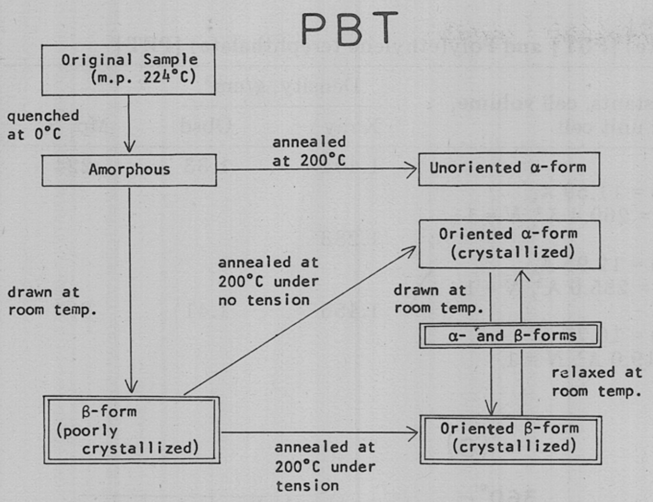


Figure 1. Formation of two crystal modifications (α and β forms) of poly(butylene terephthalate). Double frames indicate the states "under tension".

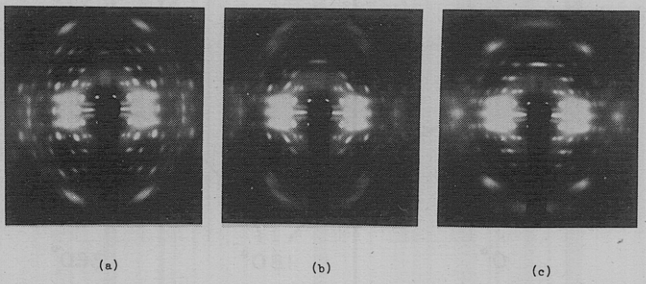


Figure 2. X-ray fiber patterns of the modifications of poly(butylene terephthalate): (a) α form, (b) mixture of α and β forms, and (c) β form.

filtered Cu Kα radiation. The x-ray photographs of the α form, the mixture of the α and β forms, and the β form of PBT are shown in Figures 2a, b, and c, respectively. The reflections near the meridian were measured on the photographs using a Weissenberg camera, where the sample was oscillated about an axis perpendicular to the fiber axis. The equatorial reflections of the doubly oriented sample of the α form were photographed by the usual procedure of a Weissenberg camera as shown in Figure 3. From the photographs in Figures 2a and c, 53 and 28 independent reflections were observed for the α and β forms, respectively. The d spacings were corrected with those of aluminum powder. The intensities of the fiber diagrams obtained by the multiple-film method were measured by using a microphotometer (Rigaku Denki Co. MP-3). The corrections for Lorentz-polarization factor and the obliquity effect in the fiber diagram were made.

All measurements of the β form were carried out under tension.

Analyses and Results

Unit Cells and Space Groups. From the fiber photographs of the α and β forms, it is obviously seen that the diffraction spots on each layer line are displaced, some up and some down, from the positions in which they should appear as a straight line in the case of uniaxial orientation. This phenomenon is known as tilting. The magnitude of the tilt displacements is available in the determination of the reflection indices. The observed reflections could be indexed by triclinic cells for both cases of the α and β forms, the cell dimensions of which are given in Table I, where those of PET[2] are also listed for comparison. Here the method, as applied to PET by Daubeny et al,[2] was utilized as shown in Figures 4a and b, which represent the c-axis projection of the reciprocal lattice nets for the α and β forms, respectively. The symbol O_j ($j = 0, 1, \ldots, 5$) indicates the origin of the reciprocal lattice projected to the jth layer plane. The lattice is tilted about the line T_jT_j: all hk reciprocal lattice points on the jth layer line on the right-hand side of T_jT_j are displaced downwards, and the rest upwards. The angles of tilt in the α and β forms, ϕ_α and ϕ_β, were found to be both about 1°, and the azimuthal angles χ_α and χ_β 38 and 19°, respectively, where ϕ is defined as an angle between the fiber axis and the tilted c axis, and χ as an angle between the tilt line and the b^* axis as shown in Figure 4.

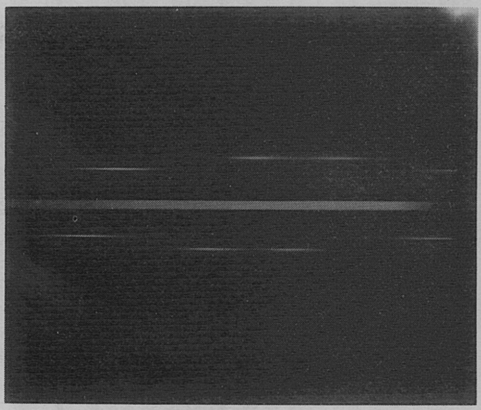
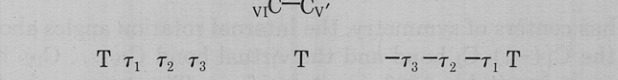


Figure 3. Weissenberg photograph of the equatorial reflections of the α form of poly(butylene terephthalate).

The density of the α form, calculated by assuming one monomer unit in the unit cell, is 1.404 g/cm^3, which is reasonable compared with the observed density measured by flotation method, 1.33 g/cm^3. On the other hand, it was difficult to measure the density of the β form, because the β form is stable only under tension. But when it is assumed that one monomer unit is in the unit cell, the density is calculated as 1.283 g/cm^3.

The space groups for both modifications are either $P1\text{-}C_1{}^1$ or $P\bar{1}\text{-}C_i{}^1$. If the molecule possesses centers of symmetry in the crystal, the space group becomes $P\bar{1}\text{-}C_i{}^1$. Here we can utilize the mutual exclusion rule found in the infrared and Raman spectra for both the α and β forms. Therefore the space groups of two modifications of PBT are both assumed to be $P\bar{1}\text{-}C_i{}^1$.

Molecular Models. The conformational energies were calculated for the possible molecular models with the centers of symmetry and the fiber identity periods 11.59 and 12.95 Å for the α and β forms, respectively. The numbering of the atoms and internal rotation angles, and the fixed bond lengths and bond angles used are as follows;



$C_{I'}(-1)–C_I = C_I–C_{II} = 1.54$ Å, $C_{II}–O_I = 1.43$ Å, $O_I–C_{III} = 1.36$ Å, $C_{III}–O_{II} = 1.23$ Å, $C_{III}–C_{IV} = 1.49$ Å, $C_{IV}–C_V = C_{IV}–C_{VI} = C_V–C_{VI'} = 1.395$ Å, $\angle C_{I'}(-1)–C_I–C_{II} = \angle C_I–C_{II}–O_I = 110°$, $\angle C_{II}–O_I–C_{III} = 111°$, $\angle O_I–C_{III}–C_{IV} = 114°$, $\angle O_I–C_{III}–O_{II} = \angle O_{II}–C_{III}–C_{IV} = 123°$, $\angle C_{III}–C_{IV}–C_V = \angle C_{III}–C_{IV}–C_{VI} = \angle C_{IV}–C_V–C_{VI'} = 120°$. The bond lengths and angles including the hydrogen atoms were assumed as usual. The angle ω is defined as an internal rotation angle about the sequence $O_I–C_{III}–C_{IV}–C_{VI}$, which corresponds to the angle between the benzene ring and the plane determined by $O_I–C_{III} \ldots C_{III'}–O_{I'}$. Since the molecular chain

Table I
Crystallographic Data for Poly(butylene terephthalate) [PBT] and Poly(ethylene terephthalate) [PET]

Sample	Crystal system, space group, lattice constants, cell volume, and no. of monomer units per unit cell	Density, g/cm^3 X ray	Density, g/cm^3 Obsd	Mp, °C
PBT (α form)	Triclinic, $P\bar{1}$-C_i^1, a = 4.83 Å, b = 5.94 Å, c (fiber axis) = 11.59 Å, α = 99.7°, β = 115.2°, γ = 110.8°, V = 260.4 Å^3, N = 1	1.404	1.33	224
PBT (β form)	Triclinic, $P\bar{1}$-C_i^1, a = 4.95 Å, b = 5.67 Å, c (fiber axis) = 12.95 Å, α = 101.7°, β = 121.8°, γ = 99.9°, V = 285.0 Å^3, N = 1	1.283		
PET[2]	Triclinic, $P\bar{1}$-C_i^1, a = 4.56 Å, b = 5.94 Å, c (fiber axis) = 10.75 Å, α = 98.5°, β = 118°, γ = 112°, V = 219.0 Å^3, N = 1	1.455	1.41	264

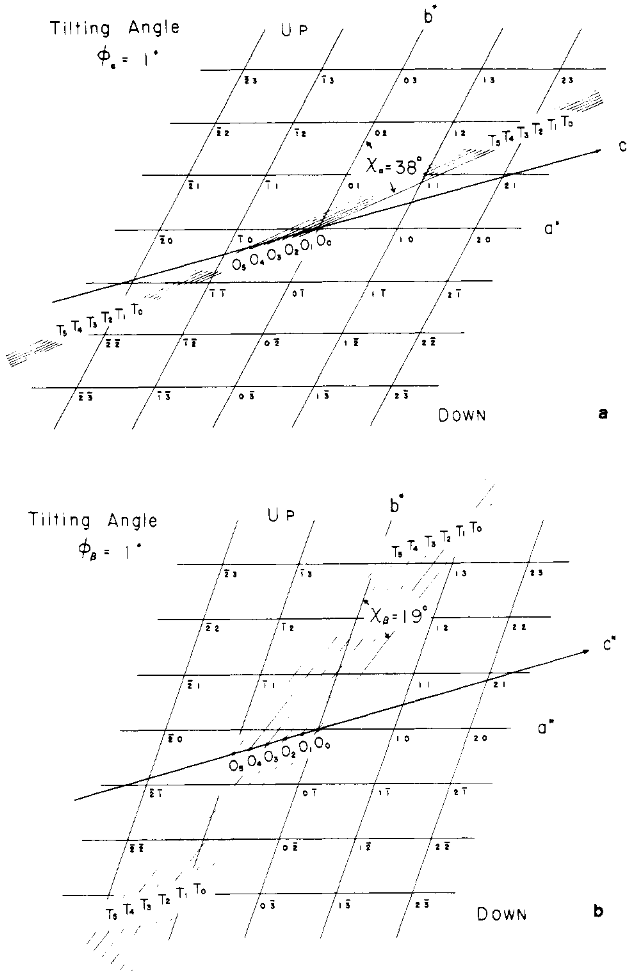


Figure 4. Reciprocal lattice nets for c projection of poly(butylene terephthalate): (a) α form and (b) β form. ϕ is a tilting angle and χ is an angle between the tilt line and the b* axis.

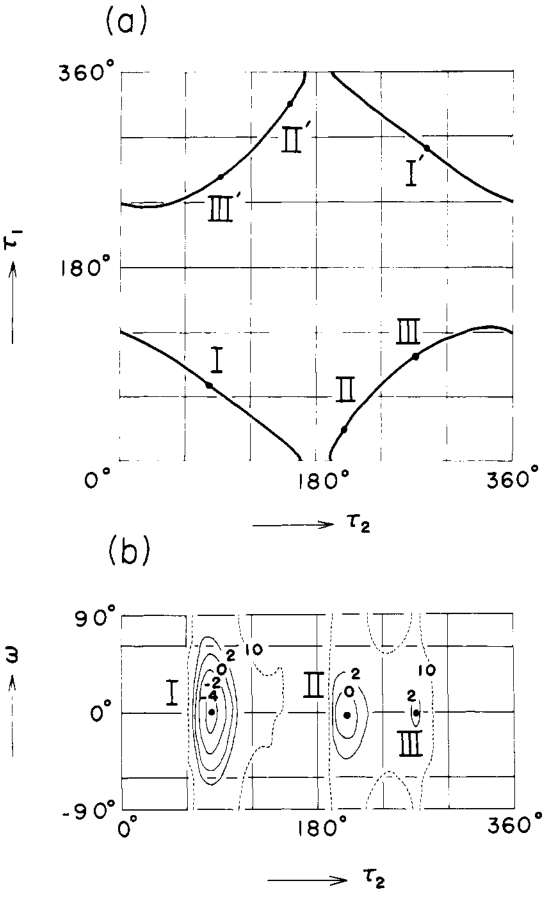


Figure 5. (a) Curves showing the relationship between τ_1 and τ_2 of the α form of poly(butylene terephthalate) with the centers of symmetry and the fiber identity period 11.59 Å. (b) Conformational energy contour map on the τ_2–ω plane for the lower part of the curves shown in (a).

has centers of symmetry, the internal rotation angles about the $C_{I'}(-1)$–C_I bond and the virtual bond $C_{IV} \ldots C_{IV'}$ become inevitably 180°, i.e., trans form. The energy calculations were made according to the method reported in the previous papers.[8,9] For the carbon atoms of the benzene ring it was assumed that the polarizability α is 1.13 Å^3, the effective number of outer shell electrons N_{eff} is 5.0, and the van der Waals radius is 1.8 Å.[10] The rotational barrier V_0 about the angle ω was assumed to be 5 kcal/mol.[11] Referring to the structures of polyesters analyzed so far, the internal rotation angle τ_3 of the ester group is reasonably taken as 180°. For the α form of PBT, the sets of the internal rotation angles, τ_1 and τ_2, are on the curves shown in Figure 5a. Since the angle ω is independent of the conformation of the main chain, there is another degree of freedom: ω being varied from −90 to 90° on the curves. The energy map in the τ_2–ω plane of the lower part of the curves is shown in Figure 5b. From these calculations, three minima were found. The internal rotation angles (τ_1, τ_2, and ω) and the conformational energy E (kcal/mol per monomer unit) are listed in Table II. The molecular models I′, II′, and III′ in Figure 5a correspond to the mirror images of I, II, and III. For the β form, similar calculations were made, where the different point is only that the fiber identity period of the β form is 12.95 Å. The results were shown in Figures 6a and b, and we obtained three molecular models and their mirror images (Table II).

Thus, we selected six models for each modification from a large number of molecular models, but we could not con-

Table II
Energetically Stable Molecular Models for the α and β Forms of Poly(butylene terephthalate) [PBT]^c

		τ_1, deg	τ_2, deg	ω, deg	E^a	R, %
PBT (α form)	Model I	71	81	1	−4.6	25.3
Fiber identity period = 11.59 Å	Model II	29	−152	−3	−0.9	50.3
	Model III	95	−91	0	1.7	55.1
	Model I'^{b}	−71	−81	−1	−4.6	50.6
	Model II'	−29	152	3	−0.9	36.9
	Model III'	−95	91	0	1.7	51.6
PBT (β form)	Model I	112	−178	0	−1.2	38.1
Fiber identity period = 12.95 Å	Model II	164	93	−3	1.1	41.5
	Model III	162	−108	−1	6.3	48.4
	Model I'	−112	178	0	−1.2	26.1
	Model II'	−164	−93	3	1.1	49.5
	Model III'	−162	108	1	6.3	43.7

^{a} kcal/mol per monomer unit. ^{b} (') shows the mirror image molecular model. ^{c} The independent internal rotation angles (τ_1, τ_2, and ω), conformational energy E, and the discrepancy factor R.

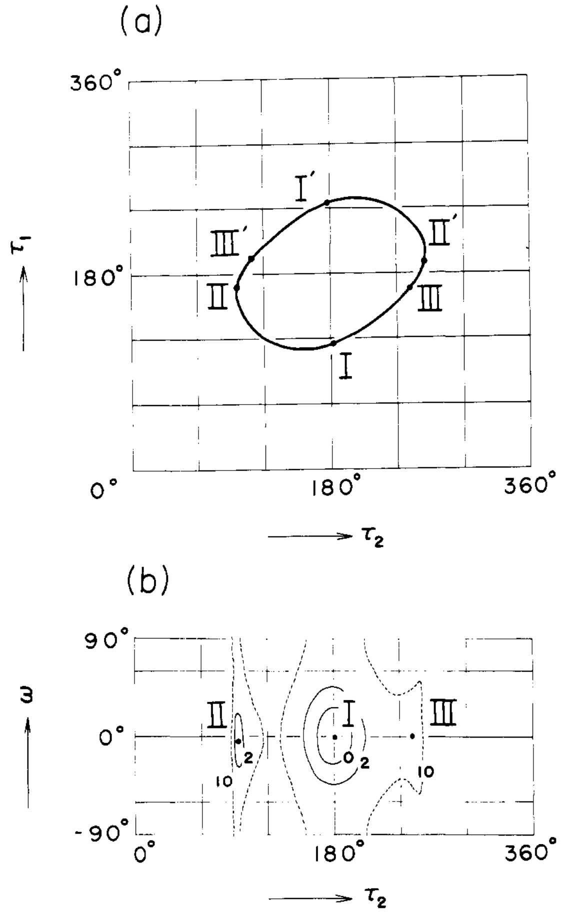


Figure 6. (a) Closed curve showing the relationship between τ_1 and τ_2 of the β form of poly(butylene terephthalate) with the centers of symmetry and the fiber identity period 12.95 Å. (b) Conformational energy contour map on the τ_2–ω plane for the lower part of the closed curve shown in (a).

clude which is the most acceptable one from the result of the energy calculation alone.

Structure Factor Calculations. In the triclinic system, if the cell dimensions are fixed, the crystal model, including molecular model A for example, can never become identical with the crystal model including the mirror image of molecular model A, even if molecular model A has no asymmetric atoms. Therefore, for the determination of the crystal structure, the mirror images of the molecular models obtained from the energy calculation must also be taken into

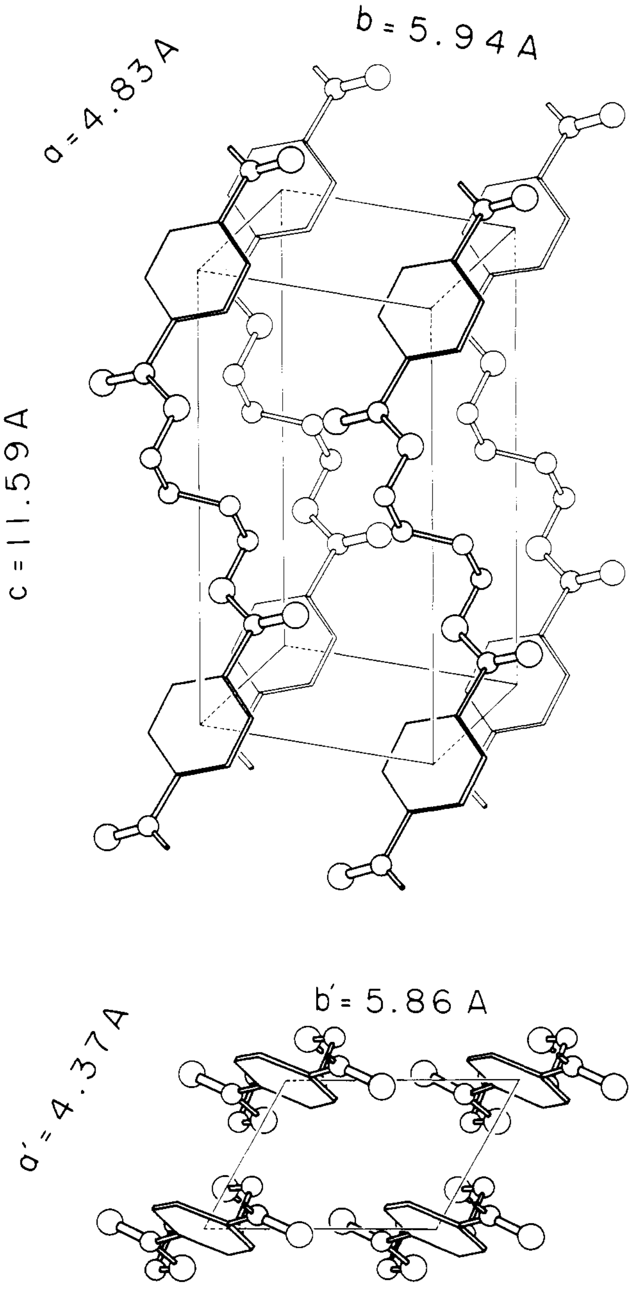


Figure 7. Arrangement of molecules in crystal of the α form of poly(butylene terephthalate): above, projection normal to the 010 plane; below, projection along c axis.

Table III
Fractional Atomic Coordinates of the α and β Forms of Poly(butylene terephthalate) [PBT][a]

	α form			β form		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C_I	−0.026	−0.136	0.499	0.145	−0.009	0.564
C_{II}	0.281	−0.105	0.632	0.007	−0.202	0.607
C_{III}	0.067	−0.189	0.772	−0.070	−0.238	0.764
C_{IV}	0.032	−0.092	0.890	−0.033	−0.115	0.886
C_V	−0.139	−0.267	0.934	−0.148	−0.265	0.938
C_{VI}	0.170	0.175	0.956	0.116	0.149	0.949
O_I	0.268	0.002	0.749	0.055	−0.072	0.725
O_{II}	−0.044	−0.422	0.712	−0.210	−0.469	0.702

[a] The overall temperature coefficients *B* are 6.9 and 5.6 Å^2 for the α and β forms, respectively.

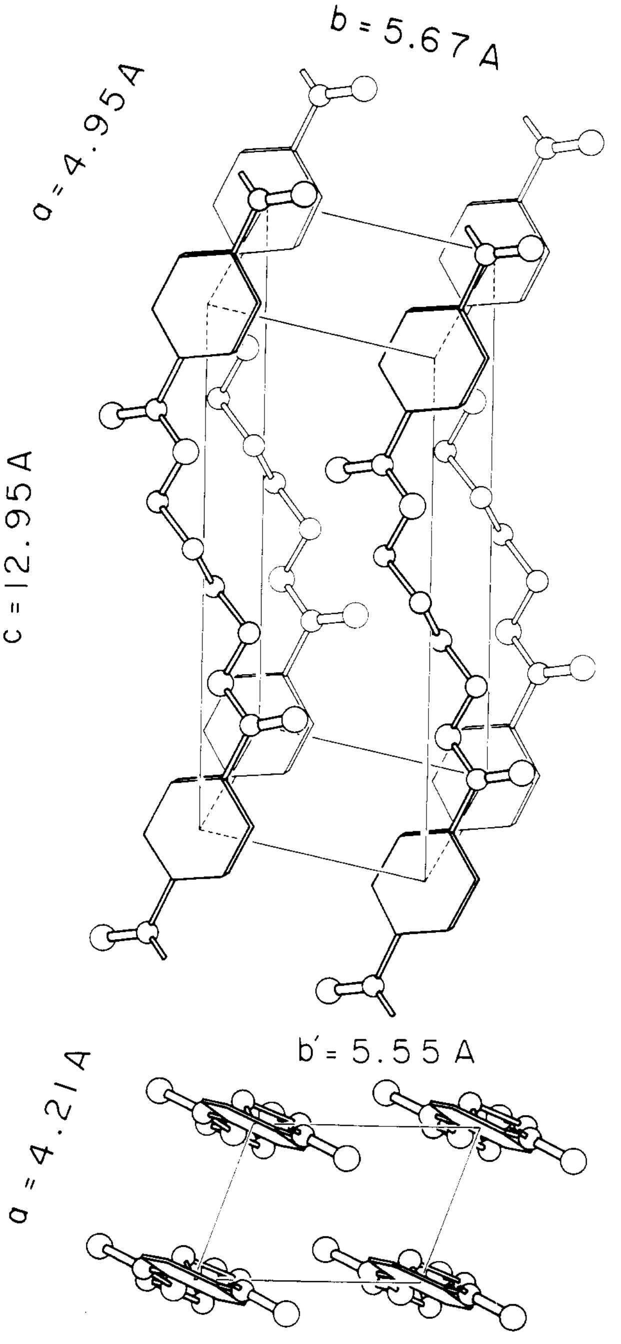
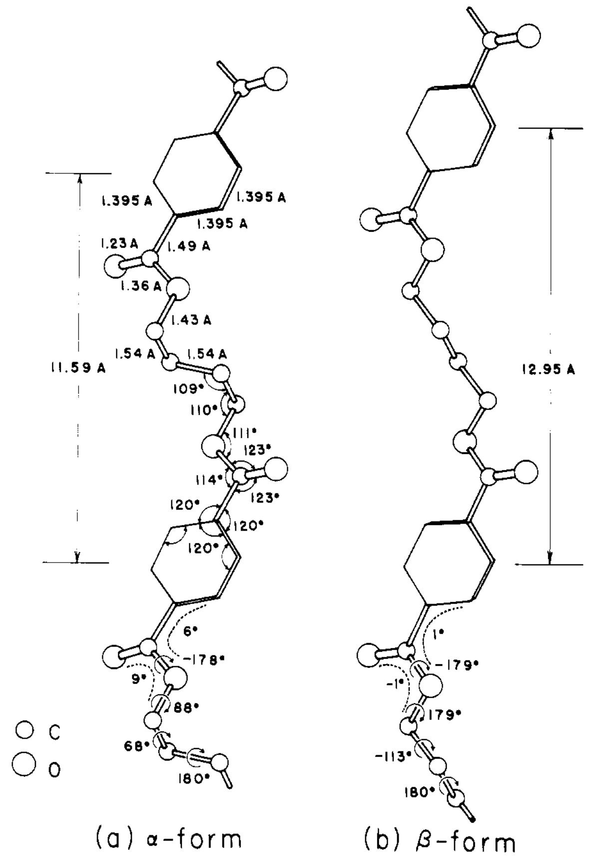


Figure 8. Arrangement of molecules in crystal of the β form of poly(butylene terephthalate): above, projection normal to the 010 plane; below, projection along *c* axis.



(a) α-form (b) β-form

Figure 9. Molecular dimensions of poly(butylene terephthalate): (a) α form and (b) β form.

consideration. We tried to calculate the crystal structure factors by using six molecular models (I, II, III, I′, II′, and III′) of the α and β forms, respectively. For both modifications, the centers of symmetry of the molecular chain (the center of the benzene ring and the midpoint of the bond $C_{I'}$–C_I) are located so as to coincide with the centers of symmetry, (0, 0, 0) and (0, 0, ½), in the crystal lattice of $P\bar{1}$-C_i^1. There still remains one variable parameter, i.e., the rotation about the molecular chain axis (*c* axis). Then, the suitable position of the molecular chain was determined by rotating each molecular model about the *c* axis, so that close agreement between the observed and calculated structure factors could be obtained. In Table II are listed the values of the discrepancy factor R $(=\Sigma|(I_o)^{1/2} - (I_c)^{1/2}|/\Sigma(I_o)^{1/2})$ in which nonobserved reflections within the highest observed diffraction angle were taken into account, nonobserved reflections being assumed to have half of the most weakly observed intensity. From the *R* values and the conformational energies, model I and model I′ were considered to be the most probable for the cases of the α and β forms, respectively, and here the other models were excluded. Then the atomic coordinates and the overall temperature factor *B* were refined by the constrained least-squares method,[12,13] where the bond lengths and bond angles were held fixed and all the internal rotation angles were varied. At this stage, nonobserved reflections were not taken into consideration. The *R* factors were reduced to 14.4 and 19.1% for the α and β forms, respectively. Table III lists the final atomic parameters. The crystal structures of the α and β forms are shown in Figures 7 and 8, respectively. Figure 9 shows the molecular dimensions for both modifications. The conformation of the four-methylene group sequence is as follows: the α form, approximately $\bar{G}\bar{G}TGG$ (−88°,

Table IV

Comparison of Observed and Calculated Spacings (in Å) and Structure Factors for the α- and β-forms of Poly(butylene Terephthalate) [PBT].

h	k	l	d_o	d_c	$\sqrt{I_o}$	$\sqrt{I_c}$
The α-form						
0	1	0	5.13	5.13	42	43
-1	1	0	4.20	4.28	18	15
1	0	0	3.79	3.83	56	59
-1	2	0	2.86	2.86	17	16
0	2	0	-	2.57	-	6
1	1	0	-	2.54	4	4
2	-1	0	-	2.17	-	3
-2	2	0	2.09	2.09	8	7
-1	3	0	1.95	1.95	20	19
2	0	0		1.92		
1	2	0	1.77	1.78	10	10
-2	3	0		1.76		
0	3	0	1.71	1.71	7	6
2	1	0	1.57	1.57	7	13
0	-1	1	5.46	5.48	31	26
-1	0	1	4.32	4.46	25	26
-1	1	1		4.27		
0	1	1	3.94	3.96	25	20
1	-1	1	3.49	3.51	48	53
1	0	1	3.05	3.06	20	21
-1	-1	1	2.88	2.87	11	12
1	-2	1	-	2.76	11	8
0	-2	1	2.75	2.75	11	7
-1	2	1	-	2.72	-	5
-2	1	1	2.28	2.35	13	9
0	2	1		2.28		
1	1	1	-	2.19	-	0
-2	2	1	2.17	2.16	9	10
-2	0	1		2.10		
1	-3	1	1.94	1.97	20	20
2	-1	1		1.94		
2	-2	1		1.94		
-1	-2	1		1.85		
-1	3	1	1.86	1.85	9	8
0	0	2	4.87	4.85	10	10
0	-1	2	4.43	4.47	11	8
-1	0	2		4.31		
-1	1	2	3.68	3.69	31	25
-1	-1	2	3.02	3.02	11	12
0	1	2	-	3.00	-	2
1	-1	2	2.77	2.82	30	29
0	-2	2		2.74		
1	-2	2	-	2.49	9	12
1	0	2	-	2.45	-	3
-1	2	2	2.43	2.43	16	17
-2	1	2		2.41		
-2	0	2	-	2.23	6	3
-2	2	2		2.14		
-1	-2	2	-	2.03	-	2
0	2	2	1.99	1.98	17	12
1	-3	2	-	1.92	-	6
1	1	2	-	1.88	-	2
0	-3	2	1.85	1.85	8	12
-2	-1	2	-	1.81	-	6
2	-2	2	1.75	1.76	20	21
2	-1	2	1.72	1.72	22	19
0	-1	3	3.37	3.37	14	10
0	0	3	3.23	3.23	8	7
-1	1	3	-	2.97	-	0
-1	-1	3	2.90	2.89	18	14
0	-2	3	2.52	2.53	7	7
0	1	3	-	2.36	-	5
-2	1	3	-	2.33	-	2
1	-1	3	2.28	2.28	19	16
-2	0	3	-	2.25	-	10
1	-2	3	-	2.17	-	1
-1	2	3	-	2.11	-	1
-1	-2	3	-	2.06	-	9
-2	2	3	-	2.02	-	7
1	0	3	-	2.01	-	6
-2	-1	3	1.87	1.87	16	17
0	-3	3	-	1.83	-	0
1	-3	3	1.80	1.81	9	10
0	2	3	-	1.72	-	2
1	1	3	1.62	1.62	12	8
-3	1	3		1.60		
-2	3	3	-	1.61	-	6
2	-2	3	-	1.57	-	9
-3	2	3	1.57	1.57	17	13
-1	3	3		1.56		
0	-1	4	2.58	2.61	11	12
-1	-1	4		2.58		
0	0	4	2.42	2.43	16	16
-1	1	4		2.39		
0	-2	4	-	2.24	-	6
-2	0	4	2.15	2.16	22	15
-2	1	4		2.15		
-1	-2	4	2.00	1.99	11	15
0	1	4	-	1.93	-	1
1	-1	4	-	1.89	-	7
1	-2	4	-	1.88	-	3
-2	-1	4	1.86	1.86	15	11
-2	2	4		1.84		
-1	2	4		1.82		
0	-3	4	-	1.74	-	4
1	0	4	-	1.69	-	5
1	-3	4	-	1.66	-	0
-3	1	4	-	1.59	7	6
-3	2	4		1.54		
-1	-3	4	-	1.53	-	3
-2	-2	4	-	1.51	-	5
-3	0	4	1.51	1.50	10	8
0	2	4		1.50		
-2	0	5	1.98	1.98	17	18
-1	1	5		1.97		
0	-2	5	-	1.94	-	12
0	0	5	1.93	1.94	18	16
-2	1	5		1.92		
-1	-2	5	1.86	1.86	11	11
-2	-1	5		1.79		
The β-form						
0	1	0	5.19	5.23	44	35
1	0	0	3.71	3.96	90	99
-1	1	0		3.84		
1	1	0	-	2.75	-	10
-1	2	0	-	2.62	-	8
0	2	0	-	2.62	-	4
-2	1	0	2.00	2.10	16	37
2	0	0	-	1.93	16	16
-2	2	0		1.92		
1	2	0	1.85	1.91	12	11
-1	3	0		1.84		
0	-1	1	5.55	5.51	44	32
-1	0	1	4.00	4.74	46	41
0	1	1		4.12		
-1	1	1		4.02		
1	-1	1	3.30	3.28	37	48
-1	-1	1	-	3.16	9	9
1	0	1		3.14		
0	-2	1	-	2.78	-	4
-1	2	1	2.76	2.56	10	10
1	-2	1	2.57	2.52	12	11
1	1	1	-	2.34	-	9
0	2	1	2.21	2.35	16	21
-2	1	1		2.28		
0	0	2	5.11	5.15	11	9
-1	0	2	-	4.75	-	2
0	-1	2	4.62	4.56	12	8
-1	1	2	3.64	3.66	18	18
-1	-1	2	-	3.39	-	4
0	1	2	3.11	3.16	9	10
0	-2	2	2.76	2.75	16	15
1	-1	2		2.71		
1	0	2	2.38	2.51	7	8
-2	1	2		2.38		
-1	2	2		2.37		
-2	0	2		2.37		
1	-2	2	-	2.31	-	4
-1	-2	2	-	2.22	11	15
0	2	2	-	2.06	-	6
1	1	2	-	1.99	-	8
-2	2	2	1.99	2.01	12	14
-2	-1	2		1.99		
0	-1	3	-	3.49	-	7
0	0	3	3.43	3.44	11	16
-1	-1	3	3.07	3.28	10	6
-1	1	3		3.07		
0	-2	3	-	2.56	-	1
0	1	3	-	2.50	-	5
-2	0	3	2.27	2.44	12	15
-2	1	3		2.36		
-1	2	3		2.12		
-1	-2	3	-	2.26	-	7
1	-1	3	-	2.24	-	1
-2	-1	3	-	2.08	-	6
1	0	3	-	2.07	-	11
1	-2	3	-	2.05	-	2
-2	2	3	-	1.95	-	6
0	-3	3	1.84	1.84	10	13
-1	-1	4	2.86	2.92	12	11
0	-1	4		2.72		
0	0	4	2.53	2.58	8	8
-1	1	4		2.53		
-1	1	5	2.11	2.11	16	19
0	0	5		2.06		
-1	-2	5	2.01	2.05	39	39
-2	-1	5		2.04		
-2	1	5		2.03		
0	-2	5		1.99		

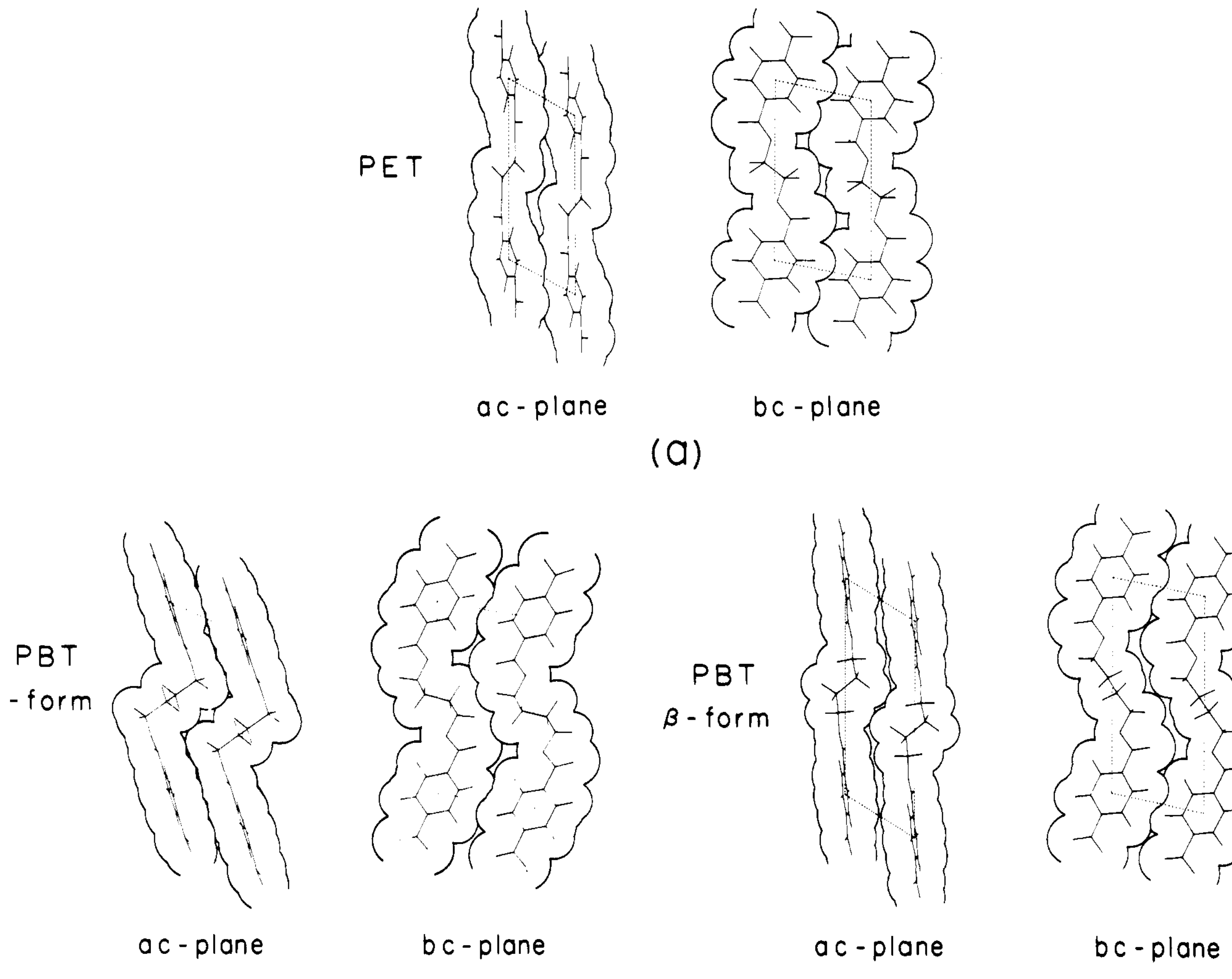


Figure 10. Packing modes of polymer chains projected along the *b* and *a* axes: (a) poly(ethylene terephthalate), (b) and (c) the α and β forms of poly(butylene terephthalate), respectively.

−68°, 180°, 68°, 88°); the β form, approximately TSTS̄T (−179°, 113°, 180°, −113°, 179°). The comparison between the observed and calculated intensities is given in Table IV (miniprint).

Discussion

Crystal and Molecular Structures. As shown in Table I, the lattice dimensions of the α and β forms are very similar except for the fiber identity periods. The molecular

Table V
Intra- and Intermolecular Potential Energy of the α and β Forms of Poly(butylene terephthalate) (kcal/mol per monomer unit)

Form	α	β
Intramolecular interaction	−1.58	−0.29
(Rotation barrier)	(1.16)	(4.44)
(van der Waals)	(−2.77)	(−4.74)
(Electrostatic)	(0.02)	(0.02)
Intermolecular interaction	−28.91	−24.33
(van der Waals)	(−28.82)	(−24.26)
(Electrostatic)	(−0.09)	(−0.07)
Total	−30.49	−24.62

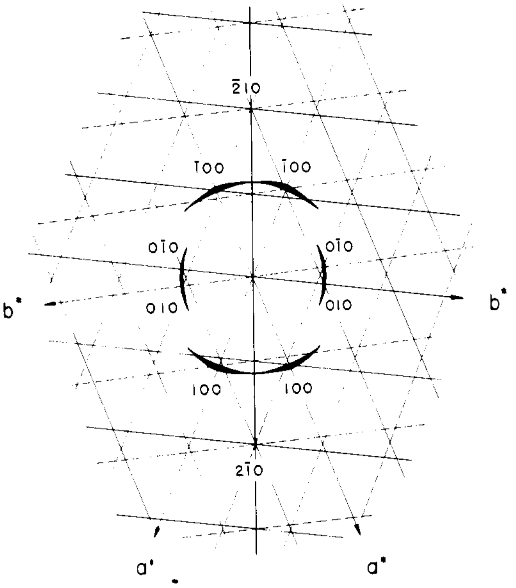


Figure 11. Equatorial reciprocal lattice net for the doubly oriented sample of the α form of poly(butylene terephthalate). The net forms into a twin by the bold line.

packings of both modifications are also quite similar (Figures 7 and 8), and the differences are mainly due to the molecular conformations. The virtual bond C_{III}–C_{IV}···$C_{IV'}$–$C_{III'}$ is commonly inclined by 26° to the fiber axis in both forms. Consequently the contribution to the difference of the fiber identity period is found in the conformations of the four-methylene group sequence [–CH_2–CH_2–CH_2–CH_2–]: $\bar{G}\bar{G}TGG$ for the α form and $TST\bar{S}T$ for the β form (Figure 9). This difference is reflected in the infrared and Raman spectra, the details of which will be reported elsewhere soon.

In Figure 10, the packing modes of polymer chains for PET[14] and the α and β forms of PBT are shown. Too close interchain atomic distances are not found and the molecular chain arrangements in the crystal lattice are very reasonable. The crystallite consists of the alternate sequences of two kinds of parts, a hard one of benzene rings and a soft one of methylene group sequences, along the fiber axis. The arrangements of benzene rings in the hard part are similar in the three cases. The soft part in the case of PBT consists of a four-methylene group sequence and has more flexibility than in the case of PET. In the transition from the α form to the β form, the methylene part is extended with the variation of conformation from $\bar{G}\bar{G}TGG$ to $TST\bar{S}T$, and the density of this part may decrease relatively. This reflects on the coefficients of crystalline packing density:[15] K_c(PET) = 0.73, K_c(PBT-α) = 0.74, and K_c(PBT-β) = 0.68. The smallest value of K_c(PBT-β) corresponds to the poor packing of the β form, and may associate with the existence of this form only under tension. The potential energies of the α and β forms were calculated by using the atomic coordinates determined by x-ray diffraction in the present study, taking into account also the intermolecular interactions. The results are given in Table V. The values given in parentheses are the components of intra- and intermolecular interactions, the rotation barriers, and the van der Waals and electrostatic interactions. As a total, the potential energy of the β form is higher by about 6 kcal/mol per monomer unit than that of the α form. This may explain the experimental fact that the α form is stable under ordinary condition, but the stability should be compared, in the exact sense, with the free energy taking into consideration the entropy term.

Double Orientation and Tilting. From the x-ray photograph in Figure 3, the equatorial reciprocal lattice for the doubly oriented sample of the α form was obtained as shown in Figure 11. The planes corresponding to the reciprocal points on the bold line are parallel to the rolled plane (twinned plane). It was found that the rolled plane coincides approximately with $\bar{2}10$ plane and the plane containing the benzene ring in the crystal (Figure 7) is essentially parallel to the $\bar{2}10$ plane. In the case of PET, the rolled plane also corresponds to the plane parallel to the benzene ring.[16,17] For the β form, no doubly oriented specimen has yet been obtained.

Figure 4 illustrates the reciprocal lattices. For the α form, it is found that the reciprocal lattice point 110 is roughly on the tilt line and, say, $\bar{1}11$ and $1\bar{1}1$ move up and down, respectively. In other words, the tilting occurs so that the 110 plane remains parallel to the stretched direction and the lattice point (0, 1, 1) tends to approach the stretched direction by about 1°. On the other hand, for the β form, the tilt occurs in the 130 plane by about 1° to the same direction as the α form. The tilting line and angle found in the present study may vary with annealing temperature, annealing duration, and drawing speed. At present, the reason for the phenomenon of the tilting of PBT is not clear.

Transition between the α and β Forms. The pure β form can be obtained by stretching about 12% of the pure α form, and the β form is transformed spontaneously into the pure α form when the tension is removed. The transition is reversible (Figure 1). At a middle strain, both modifications coexist as shown in Figure 2b. Although the ratio of the reflection intensities of the α and β forms varies according to the extent of strain, the pattern of the reflections is all due to the α and β forms and no intermediate crystalline phase is observed. In other words, some regions of the α form change discontinuously to those of the β form when more than some extent of strain is worked, and the α form remains under the smaller strain. On the other hand, the effect of heat treatment is considered to affect the increase of crystallinity and contribute nothing to the transition between the α and β forms.

Note Added in Proof. The authors were informed by the referee that the reversible stress-induced solid-phase transition in PBT was reported independently by Boye and Overton: C. A. Boye, Jr., and J. R. Overton, *Bull. Am. Phys. Soc., Ser. 2*, **19**, 352 (1974).

Miniprint Material Available: Full-sized photocopies of Table IV (4 pages). Ordering information is given on any current masthead page.

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Determination of the Structure of Cellulose II

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Abstract: The structure of regenerated cellulose is shown by x-ray diffraction to be comprised of an array of antiparallel chain molecules. The determination was based on the intensity data from rayon fibers and utilized rigid-body least-squares refinement techniques. The unit cell is monoclinic with space group $P2_1$ and dimensions $a = 8.01$ Å, $b = 9.04$ Å, $c = 10.36$ Å (fiber axis), and $\gamma = 117.1°$. Models containing chains with the same sense (parallel) or alternating sense (antiparallel) were refined against the intensity data. The only acceptable model contains antiparallel chains. The $-CH_2OH$ groups of the corner chain are oriented near to the gt position while those of the center chain are near to the tg position. Both chains possess an O3–H···O5′ intramolecular hydrogen bond, and the center chain also has an O2′–H···O6 intramolecular bond. Intermolecular hydrogen bonding occurs along the 020 planes (O6–H···O2 bonds for the corner chains and O6–H···O3 bonds for the center chains) and also along the 110 planes with a hydrogen bond between the O2–H of the corner chain and the O2′ of the center chain. This center–corner chain hydrogen bonding is a major difference between the native and regenerated structures and may account for the stability of the latter form.

Cellulose is composed of 1 → 4 linked β-D-glucose residues, and is known to exist in at least four polymorphic crystalline forms, of which the structures and properties of cellulose I (native cellulose) and cellulose II (regenerated cellulose and Mercerized cellulose) have been most extensively studied. Cellulose II has a monoclinic unit cell with reported dimensions $a = 7.93$ Å, $b = 9.18$ Å, $c = 10.34$ Å, and $\gamma = 117.3°$ (average values over a variety of cellulose II preparations).[1] The unit cell contains sections of two cellulose chains (four glucose residues) and the space group is generally thought to be $P2_1$. The cellulose chains are thought to possess twofold screw symmetry, and lie with their axes through the origin $(0, 0, z)$ and the center $(\frac{1}{2}, \frac{1}{2}, z)$ of the unit cell. Thus, the space group requirements are satisfied whether the molecules have the same sense (parallel) or opposite sense (antiparallel).

Jones[2,3] compared the observed[4] and calculated x-ray intensities for models of the cellulose II structure consistent with the above requirements. The most favorable structure in terms of the infrared spectrum had the chains in an antiparallel arrangement with a relative shift between the glycosidic oxygens of the origin and center chain of approximately $0.29c$. He was unable to determine the exact positions of the $-CH_2OH$ groups, but those of the center chain were thought to have an orientation different from those of the origin chain. More recently, Watanabe and Hayashi[5] proposed a "bent-twisted" model for the cellulose molecule. The proposed cellulose II structure with this modification of the twofold screw molecule had antiparallel chains with a relative shift of $0.185c$. However, satisfactory match between the observed and calculated intensities was not achieved. In a potential energy packing analysis of the cellulose II structure, Sarko and Muggli[6] were unable to choose between a number of parallel and antiparallel chain models although they considered one antiparallel model to be most favorable because of extensive hydrogen bonding possibilities, where the $-CH_2OH$ side chains may have different rotational conformations.

Thus the major details of the structure, including the polarity of the two chains in the unit cell and the hydrogen bonding network, remain undetermined. Rigid-body least-squares refinement techniques have recently been used by Gardner and Blackwell[7,8] to determine the structure of native cellulose (*Valonia*). The results of their refinement showed a significant preference for parallel rather than antiparallel chains. In the two-chain monoclinic unit cell, the chain at $(\frac{1}{2}, \frac{1}{2}, z)$ is staggered by $0.266c$ with respect to the chain at the origin and the orientation of the $-CH_2OH$ side groups are close to the tg position (see below) for both chains. The chains possess two intramolecular hydrogen bonds (O3–H···O5′ and O6···H–O2′) (see Figure 2 for numbering of the atoms) and interchain hydrogen bonds occur only along the 020 planes of the unit cell, resulting in an array of staggered sheets of hydrogen bonded cellulose chains.

The approach used in this refinement of cellulose II was similar to that employed for the native structure. The x-ray intensity data were obtained for rayon fibers and the least-squares refinement method of Arnott and Wonacott[9] was used to refine possible parallel and antiparallel chain mod-