

Crystal structure of poly(butylene-2,6-naphthalate)

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The two crystal structures of poly(butylene-2,6-naphthalate) (PBN) have been determined by X-ray diffraction. The space group is $P\bar{1}$ for both forms. The unit cell parameters of the B form are $a = 4.55 \text{ \AA}$, $b = 6.43 \text{ \AA}$, c (fibre axis) = 15.31 \AA , $\alpha = 110.1^\circ$, $\beta = 121.1^\circ$ and $\gamma = 100.6^\circ$. The major difference in crystal structure between the A and B forms lies in the conformation of four methylene group sequences: $\overline{S}\overline{G}\overline{T}\overline{G}\overline{S}$ for the A form and $\overline{T}\overline{S}\overline{T}\overline{S}\overline{T}$ for the B form. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(butylene-2,6-naphthalate); crystal structure; conformation)

INTRODUCTION

The crystal structures of poly(ethylene terephthalate) (PET)^{1,2}, poly(ethylene-2,6-naphthalate) (PEN)³ and poly(butylene terephthalate) (PBT)^{4,5} were reported. A structural study on poly(butylene-2,6-naphthalate) (PBN) (Figure 1) was reported only by Watanabe⁶.

Two crystal modifications A and B of PBN have been reported. According to Watanabe⁶, the form A assigned to the structure formed by uniaxial drawing of the undrawn PBN specimen has the triclinic form having a unit cell with $a = 4.87 \text{ \AA}$, $b = 6.22 \text{ \AA}$, $c = 14.36 \text{ \AA}$ (fibre axis), $\alpha = 100.78^\circ$, $\beta = 126.90^\circ$ and $\gamma = 97.93^\circ$. One repeating unit is contained in the unit cell. However, neither the unit cell parameters of the B form nor the conformations and crystal structures of the two forms were determined.

This article reports the crystal structures of the A and B forms and the double orientation and tilting of the chains as studied by X-ray diffraction.

EXPERIMENTAL

Specimens

Unoriented crystalline PBN film with a thickness of $100 \mu\text{m}$ was used as the original specimen. Two kinds of uniaxially drawn films were prepared: (1) film drawn to ~ 3 times at room temperature and annealed under tension at 200°C in a silicone bath; (2) film drawn to ~ 9 times at 180°C . The former contains the A and B forms, but the latter only the B form.

A doubly oriented specimen was prepared by drawing the original film at 170°C to ~ 3 times, keeping the film width constant.

X-ray diffractometry

X-ray diffractograms were taken by using nickel-filtered $\text{Cu K}\alpha$ radiation (from a Rigaku Denki Rotaflex X-ray

generator or Geigerflex X-ray generator). The X-ray fibre patterns are shown in Figure 2a for the sample containing A and B forms and Figure 2b for the sample containing only B form. From Figure 2, 23 independent reflections were observed for both A and B forms. To estimate intensity, the multiple-film method was applied to the X-ray fibre patterns, and the diffraction spots were measured by visual comparison with a standard intensity scale. The usual corrections were made for spot intensities.

An X-ray photograph of doubly oriented film taken by plate camera is shown in Figure 3, where the incident X-ray beam was parallel to the drawing direction. On this photograph, the reflections of two modifications were recorded.

Density

Density measurement was carried out at 25°C in a solution of heptane and carbon tetrachloride in a density-gradient column.

ANALYSIS AND RESULTS

Unit cells and space groups

The 23 independent reflections shown in Figure 2b can be indexed satisfactorily on the basis of a triclinic cell with $a = 4.55 \text{ \AA}$, $b = 6.43 \text{ \AA}$, c (fibre axis) = 15.31 \AA , $\alpha = 110.1^\circ$, $\beta = 121.1^\circ$ and $\gamma = 100.6^\circ$, which can be assigned to the B form whose structure had not been determined. It is found that only the B form can be obtained at high temperature (180°C) and high draw ratio (~ 9 times) and is stable at room temperature after cooling. The tilt displacements of the reflections from normal layer lines, where the positions are corrected to reciprocal coordinates, are shown schematically in Figure 4b. The residual reflections of the fibre diagrams of the mixture of A and B forms shown in Figure 2a, from which those corresponding to type B have been eliminated, can be indexed with the same unit lattice as

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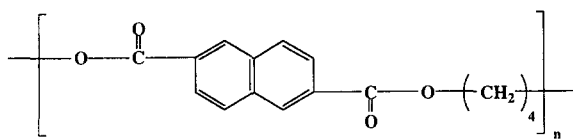
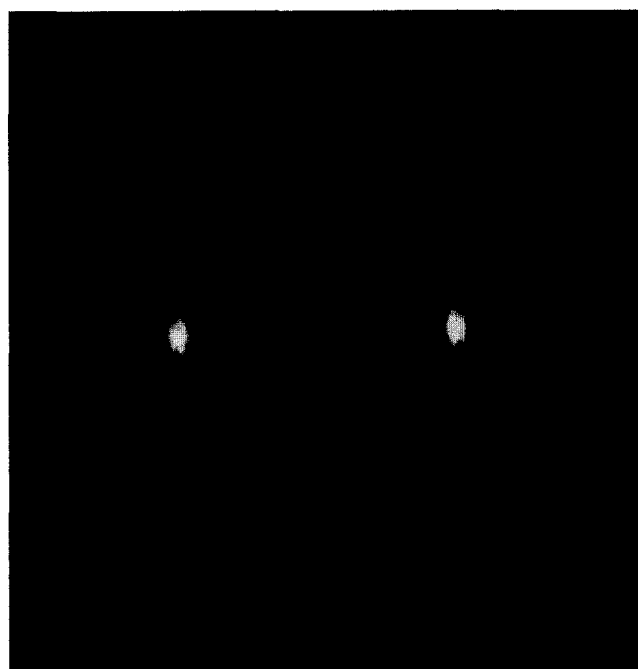
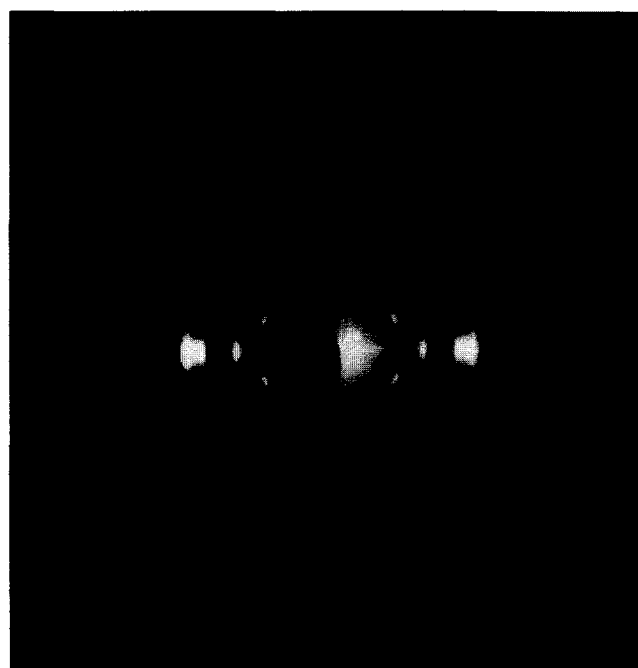


Figure 1 Molecular structure of PBN



(a)



(b)

Figure 2 X-ray fibre patterns of the modifications of PBN: (a) mixture of A and B forms; (b) B form

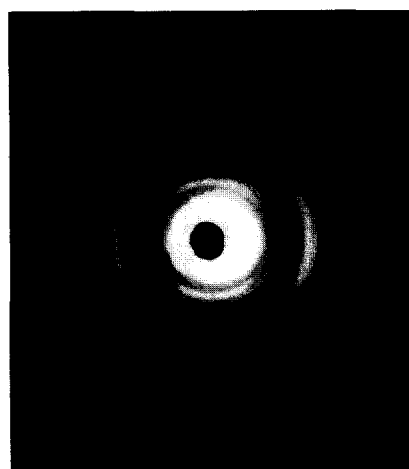


Figure 3 Plate photograph of the equatorial reflections of A and B forms of PBN

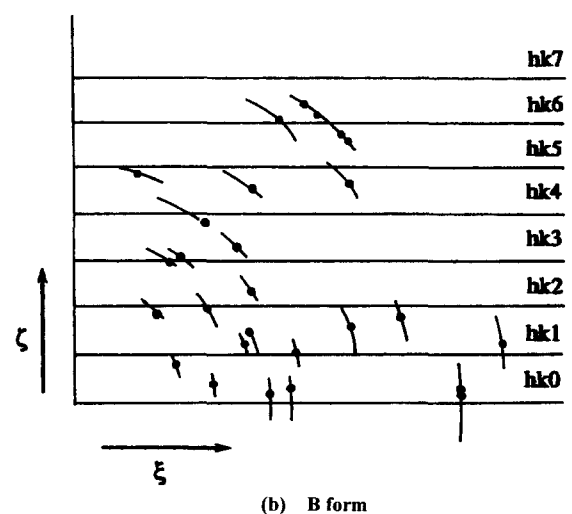
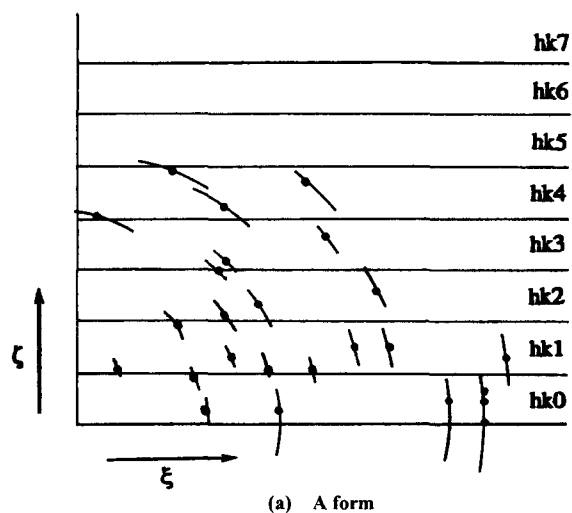


Figure 4 Reciprocal lattice diagrams of (a) A and (b) B forms of PBN, showing tilt displacements. Arcs show the observed positions of reflections, and dots the calculated positions

Watanabe's A-form crystal. The tilt displacements of these reflections of the A form are shown in Figure 4a.

The phenomenon in which the diffraction spots on each layer line are displaced is known as tilting. The method applied to PET by Daubeny *et al.*¹ and to PBT by Yokouchi

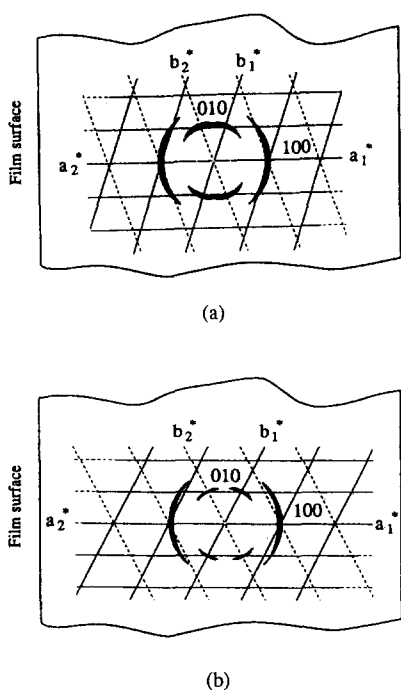


Figure 5 Equatorial reciprocal lattice nets for the doubly oriented sample of the (a) A and (b) B forms of PBN. Both nets form into twins by the line parallel to film surface line

Table 1 Crystallographic data for poly(butylene-2,6-naphthalate)

	A form ^b	B form ^a
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ ^a	$P\bar{1}$
Cell parameters		
a (Å)	4.87	4.55
b (Å)	6.22	6.43
c (Å) ^b	14.36	15.31
α (°)	100.78	110.1
β (°)	126.90	121.1
γ (°)	97.93	100.6
Number of repeating units per unit cell	1	1
Density (g cm ⁻³)		
Observed	1.33 ^c	1.34 ^d
Calculated	1.36 ^a	1.39
Observed reflection	23 ^a	23

^a This work

^b Fibre axis

^c Sample containing A and B forms

^d Sample containing only B form

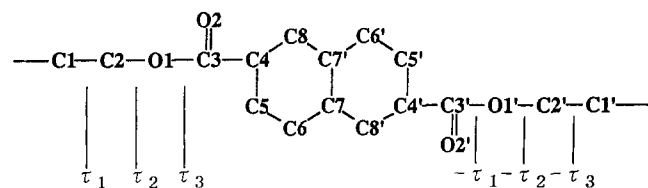


Figure 6 Numbering of atoms and internal rotation angles differing from *trans*

*et al.*⁴ was used here. The magnitude of the tilt displacements was calculated according to this method and used also to confirm the reflection indices. The tilting angle, the angle between the fibre axis and the tilted c -axis, was found to be 5° in both the $1\bar{1}0$ plane for the A form and the $3\bar{2}0$ plane for the B form. The calculated positions in the reciprocal coordinates are dotted in *Figure 4a* for type A and *Figure 4b*

Table 2 Bond lengths and bond angles

Bond	Length (Å)	Bonds	Angle (°)
C1–C1'	1.54 ¹	C2–C1–C1'	109 ¹
C2–C1	1.54 ¹	O3–C2–C1	110 ¹
O3–C2	1.43 ¹	C4–O3–C2	111 ¹
C4–O3	1.36 ¹	C5–C4–O3	114 ¹
C5–C4	1.49 ¹	C6–C5–C4	120
C6–C5	1.41 ⁸	C7–C6–C5	120
C7–C6	1.40 ⁸	C8–C7–C6	120
C8–C7	1.41 ⁸	C8'–C8–C7	120
C8'–C8	1.40 ⁸	C9–C5–C4	120
C9–C5	1.39 ⁸	C10–C4–O3	123 ⁸
O10–C4	1.23 ¹		

Table 3 Anisotropic temperature factors and coefficients^a

Factor	A form	B form
B_{11}	0.1578 (8.6)	0.2685 (13.0)
B_{22}	0.0547 (7.3)	0.1069 (12.4)
B_{33}	0.0231 (10.8)	0.0427 (21.4)
B_{12}	0.0260 (7.0)	0.0903 (18.3)
B_{23}	0.0018 (1.3)	0.0214 (9.9)
B_{31}	0.0297 (7.4)	0.0700 (17.3)

^a Values in parentheses are the coefficients (Å²) of the general temperature factor

for type B, showing reasonable agreement with the observed diagram of each form.

The X-ray photograph in *Figure 2* is considered as the superposition of the equatorial reciprocal lattices for the doubly oriented sample of types A and B shown in *Figure 5*. These reciprocal nets are available to confirm the equatorial reciprocal lattice constants for both types. Lattice parameters of the A and B forms are listed in *Table 1*. The density of the A and B forms, calculated by assuming one monomer unit per unit cell, is reasonable in comparison with the observed value as listed in *Table 1*.

The space group for these crystal forms is either $P1$ or $P\bar{1}$. Assuming that the PBN repeating unit has centres of symmetry at the midpoints of the four-methylene-group sequence and naphthalene unit, the space group of these forms should be $P\bar{1}$ by correlation with those of the crystal lattice.

Molecular models

The numbering of atoms and internal rotation angles are shown in *Figure 6*. The bond lengths and bond angles used in this work were standard values as listed in *Table 2*. The 2,6-naphthalene dicarboxylic acid residue was assumed to be planar because the conjugated system of this part should be planar. The conformations of the four methylene group sequences for the A and B forms were estimated from the conformation of this part for the α and β forms respectively of PBT reported by Yokouchi *et al.*⁴ [α form: $\overline{GGTGG}(-88^\circ, -68^\circ, 180^\circ, 68^\circ, 88^\circ)$ and β form: $\overline{TST\bar{S}T}(-179^\circ, 113^\circ, 180^\circ, -113^\circ, 179^\circ)$], because a similarity in crystal structure of PBN to that of PBT is expected. Thus the conformations of the four-methylene-group sequences were determined to be approximately $\overline{SGTGS}(-125^\circ, -60^\circ, 180^\circ, 60^\circ, 125^\circ)$ for the A form and $\overline{TST\bar{S}T}(180^\circ, 110^\circ, 180^\circ, -110^\circ, 180^\circ)$ for the B form. The fibre period calculated from these molecular models is identical with the length of the c -axis.

Crystal structures

The primary crystal structure models for the A and B forms were determined by rotating the molecular models

Table 4 Fractional atomic coordinates

Atom	x	y	z
A form			
C1	-0.106	-0.127	-0.020
C2	0.113	-0.218	0.088
O1	0.154	-0.090	0.191
C4	0.020	-0.232	0.226
C5	0.033	-0.110	0.329
C6	0.175	0.133	0.381
C7	0.187	0.249	0.477
C8	0.057	0.122	0.522
C9	-0.095	-0.234	0.373
O2	-0.101	-0.444	-0.177
B form			
C1	0.175	0.011	0.055
C2	0.031	-0.178	0.081
O1	0.059	-0.054	0.185
C3	-0.016	-0.212	0.219
C4	-0.002	-0.097	0.324
C5	0.083	0.156	0.379
C6	0.096	0.265	0.479
C7	0.024	0.122	0.523
C8	-0.074	-0.238	0.369
O2	-0.089	-0.431	0.167

around the *c*-axis. The atomic coordinates calculated from these crystal structure models were used to estimate the structure factors. In the calculation of the structure factors, the isotropic temperature factors *B* were assumed to be 5.7 Å² and 5.5 Å² for the A and B forms respectively. At this stage, the discrepancy factor $R = \frac{\sum ||F_{obs}| - |F_{calc}||}{\sum |F_{obs}|}$ for all the observed reflections was 21.8% for the A form and 27.0% for the B form.

These primary crystal structures were then refined by the constrained least-squares method⁷ (the software for performing the constrained least squares was compiled in FORTRAN77 by ourselves). The internal rotation angles (τ_1 , τ_2 and τ_3 in Figure 6) and the isotropic temperature factors *B* were chosen as the main parameters which should be detraind in refining. Other internal rotation angles, the bond lengths and the bond angles were fixed. On refining, unobserved reflections were taken into account with a weighting factor of 0.5 and the intensity as half the weakest observed intensity. After refining, the internal rotation angles (τ_1 , τ_2 and τ_3) are 59°, 123° and -177° for the A form and -107°, 188° and

Table 5 Observed and calculated structure factors: A form

<i>hkl</i>	$ F_{obs} $	$ F_{calc} $	<i>hkl</i>	$ F_{obs} $	$ F_{calc} $	<i>hkl</i>	$ F_{obs} $	$ F_{calc} $
010	32.9	31.4	$\bar{2}15$	8.0	15.0	$\bar{1}02$	-	1.4
100	65.9	63.1	reflection unobserved			$\bar{1}\bar{1}2$	-	2.0
$\bar{1}\bar{1}0$		29.4	$\bar{2}\bar{1}0$	-	6.0	013	-	4.0
$\bar{1}\bar{3}0$	14.6	14.5	120	-	3.5	$\bar{1}13$	-	10.2
200	18.2	5.9	110	-	3.6	$0\bar{2}3$	-	19.9
$\bar{2}20$		2.8	$\bar{1}\bar{2}0$	-	9.5	$\bar{1}23$	-	18.6
030		17.1	020	-	12.4	$\bar{1}03$	-	0.4
001	14.1	9.0	201	-	2.2	$\bar{1}\bar{1}3$	-	7.5
$0\bar{1}1$	44.7	41.4	$2\bar{2}1$	-	5.7	$\bar{2}13$	-	8.0
011	32.1	21.4	121	-	10.2	$\bar{2}03$	-	5.5
$\bar{1}11$	21.4	18.6	101	-	10.2	$\bar{2}\bar{1}3$	-	1.4
$\bar{1}\bar{1}1$	53.4	54.9	$\bar{1}\bar{2}1$	-	7.0	014	-	0.2
021	16.9	14.8	$\bar{1}\bar{3}1$	-	4.0	004	-	0.7
111	10.9	9.3	031	-	4.1	$0\bar{1}4$	-	6.2
$2\bar{1}1$	23.9	21.6	$0\bar{2}1$	-	1.7	$0\bar{2}4$	-	0.5
$\bar{2}31$		3.3	031	-	4.1	$\bar{1}\bar{1}4$	-	2.1
$0\bar{1}2$	6.5	2.7	$\bar{1}31$	-	6.4	$\bar{2}14$	-	4.5
$\bar{1}12$	32.2	32.4	$\bar{1}21$	-	0.7	$\bar{2}04$	-	7.8
012	21.1	16.0	$\bar{1}01$	-	9.2	005	-	9.4
$0\bar{1}3$	13.7	15.1	$\bar{1}\bar{1}1$	-	4.2	$0\bar{1}5$	-	4.2
003	13.7	13.4	$\bar{1}21$	-	2.4	$0\bar{2}5$	-	3.8
$\bar{1}23$	10.3	15.7	$\bar{1}\bar{3}1$	-	6.2	$\bar{1}15$	-	6.8
$\bar{1}04$	1.2	2.5	$\bar{2}21$	-	7.1	$\bar{1}05$	-	14.0
$\bar{2}\bar{1}4$	8.3	2.2	$\bar{2}11$	-	8.4	$\bar{1}25$	-	0.7
$\bar{1}24$		0.5	$\bar{2}01$	-	4.8	$\bar{2}15$	-	5.8
$\bar{1}14$	5.9	2.1	$\bar{2}\bar{1}1$	-	7.2	$\bar{2}05$	-	5.0
$\bar{1}\bar{1}5$	4.6	7.5	002	-	0.09			

Table 6 Observed and calculated structure factors: B form

<i>hkl</i>	$ F_{\text{obs}} $	$ F_{\text{calc}} $	<i>hkl</i>	$ F_{\text{obs}} $	$ F_{\text{calc}} $	<i>hkl</i>	$ F_{\text{obs}} $	$ F_{\text{calc}} $
010	36.9	40.0				$\bar{1}\bar{1}2$	–	0.7
$\bar{1}\bar{1}0$	38.7	42.2	200	–	13.3	013	–	3.1
100	71.2	73.1	120	–	0.3	$0\bar{2}3$	–	3.5
$2\bar{1}0$	18.1	14.5	110	–	7.3	$\bar{1}23$	–	1.5
			reflection unobserved					
$\bar{2}\bar{2}0$		6.4	$\bar{1}\bar{2}0$	–	6.7	$\bar{1}\bar{1}3$	–	7.4
$0\bar{1}\bar{1}$	41.6	34.1	$\bar{1}\bar{3}0$	–	9.2	$\bar{1}\bar{1}3$	–	12.2
$\bar{1}\bar{1}1$	27.6	23.5	030	–	4.8	$\bar{1}\bar{2}3$	–	7.0
011	28.4	24.5	020	–	1.4	$\bar{2}\bar{1}3$	–	0.6
$\bar{1}\bar{1}\bar{1}$	41.9	43.5	$2\bar{2}\bar{1}$	–	8.6	$\bar{2}03$	–	2.8
$\bar{1}\bar{2}\bar{1}$	24.4	17.5	111	–	6.3	004	–	4.5
021	22.0	17.9	101	–	5.2	$0\bar{1}4$	–	2.3
$2\bar{1}\bar{1}$	23.5	17.4	$\bar{1}\bar{2}\bar{1}$	–	3.1	$0\bar{2}4$	–	3.9
$0\bar{1}\bar{2}$	10.3	7.1	$\bar{1}\bar{3}\bar{1}$	–	1.2	$\bar{1}\bar{1}4$	–	1.4
$\bar{1}02$	11.0	1.8	031	–	6.0	$\bar{1}04$	–	0.2
$\bar{1}\bar{1}2$	26.2	28.9	001	–	7.7	$\bar{1}\bar{2}4$	–	0.5
$0\bar{1}\bar{3}$	8.4	10.8	$0\bar{2}\bar{1}$	–	10.9	$\bar{2}\bar{1}4$	–	6.5
$\bar{1}03$	18.6	8.9	$0\bar{3}\bar{1}$	–	1.5	$\bar{2}04$	–	1.3
003	14.4	15.9	$\bar{1}\bar{3}\bar{1}$	–	13.1	005	–	3.0
$\bar{1}\bar{1}4$	14.1	2.6	$\bar{1}01$	–	6.1	$0\bar{1}5$	–	1.2
$\bar{1}\bar{1}5$	1.3	1.4	$\bar{1}\bar{1}\bar{1}$	–	4.1	$0\bar{2}5$	–	2.3
$\bar{1}\bar{2}5$	12.4	0.4	$\bar{1}\bar{2}\bar{1}$	–	5.6	$0\bar{3}5$	–	2.6
$\bar{2}\bar{1}5$	6.8	5.2	$\bar{2}\bar{3}\bar{1}$	–	8.3	$\bar{1}\bar{1}5$	–	2.4
$\bar{2}06$	12.7	9.0	$\bar{2}\bar{2}\bar{1}$	–	2.1	$\bar{1}05$	–	12.5
$0\bar{1}\bar{6}$	20.6	2.8	$\bar{2}\bar{1}\bar{1}$	–	6.6	$\bar{2}\bar{1}5$	–	2.2
$\bar{2}\bar{1}6$		13.9	$\bar{2}01$	–	3.2	$\bar{2}05$	–	9.5
$\bar{1}\bar{2}6$		11.9	$\bar{2}\bar{1}\bar{1}$	–	1.4	$0\bar{2}6$	–	5.0
$\bar{1}06$		11.5	002	–	0.06	$\bar{1}\bar{1}6$	–	1.1
			$0\bar{2}2$	–	7.6	$\bar{2}\bar{1}6$	–	1.7

–178° for the B form, respectively, and the isotropic temperature factors are 5.9 Å² for the A form and 14.7 Å² for the B form. At this stage, the *R* factors for all the observed reflections decreased to 17.4% for the A form and 21.8% for the B form.

The *R* factors were much improved by introducing the anisotropic temperature factor as

$$\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2klB_{23} + 2lhB_{31})]$$

with the coefficients obtained by the least-squares method. Each coefficient is given in Table 3. The resulting *R* factors for all the observed reflections are 15.4% for the A form and 19.4% for the B form.

Table 4 lists the final atomic coordinates. The calculated and observed values of the structure factor for the final crystal structures are listed in Table 5 and Table 6. The final crystal structures are shown in Figures 7 and 8, respectively.

Table 7 and Table 8 list the interatomic distances between the adjacent molecules. When these distances are compared with the sums of van der Waals radii⁸ for each atom pair, the interatomic distances between the adjacent molecules are found to be reasonable.

DISCUSSION

Molecular and crystal structures

As listed in Table 1, the cell dimensions of the A and B forms are very similar to each other except for the fibre identity period. The molecular packings of the two crystal forms are almost similar as shown in Figure 7 and Figure 8 respectively. The main difference between the two modifications can be seen in the fibre period, due to the molecular conformations of the four-methylene-group sequences as in the case of PBT⁴. In PBN, the conformation of the four-methylene-group sequence is $\overline{S}GTGS$ for the A form and \overline{TSTST} for the B form. Consequently, the main chain of the B form is more extended than that of the A form.

The crystal structures of the A and B forms of PBN are similar to those of the α and β forms of PBT⁴, respectively. Thus the crystal structures of the A and B forms of PBN are considered to be equivalent to the structures obtained by replacing the benzene ring in the crystal structure of the α and β forms of PBT⁴ by the naphthalene double ring.

Double orientation and tilting

From the X-ray photograph shown in Figure 3, the equatorial reciprocal lattices for the oriented sample of A

and B form were obtained as shown in Figure 5a and b. The latter indicates that the film surface coincides approximately with the *bc* plane of each crystal and the crystal forms into twins mirrored by the *bc* plane of both forms. The *bc* plane of these forms of PBN is essentially parallel to the plane containing the naphthalene ring, indicating that the naphthalene rings are arranged nearly parallel to the film surface in the specimen obtained by drawing at

constant width and not changed by heat treatment. The double orientation of PBN is similar to that of PBT⁴ in which a doubly oriented specimen was obtained by rolling the uniaxially oriented α form but not obtained for the α form of another modification.

The displacements of the diffraction spots on each layer line of the two forms shown in Figure 2 and Figure 5 were

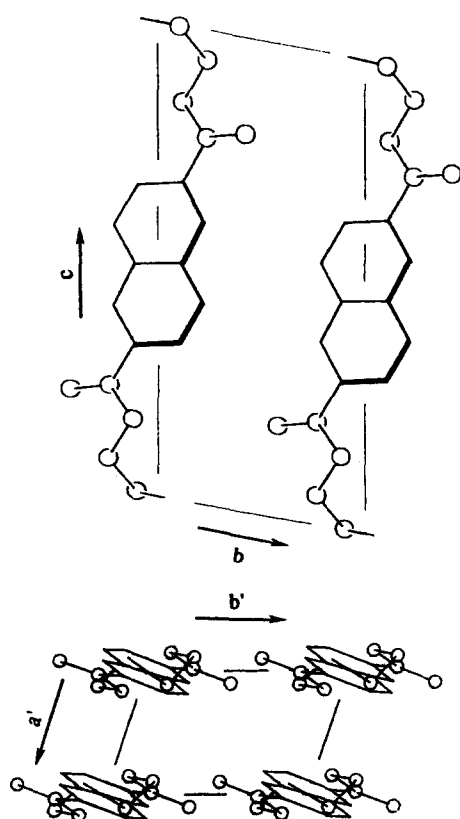


Figure 7 Arrangement of molecules in crystal of A form of PBN: above, projection along the *a*-axis; below, projection along *c*-axis

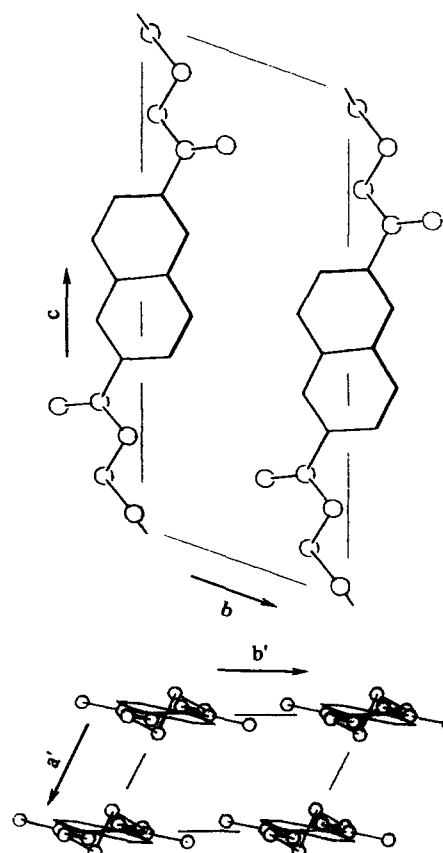


Figure 8 Arrangement of molecules in crystal of B form of PBN: above, projection along *a*-axis; below, projection along *c*-axis

Table 7 Interatomic distances^a: A form

Atom pair	Distance (Å)	Atom pair	Distance (Å)	Atom pair	Distance (Å)
C2(0)–C3(1)	3.62	C4(0)–C8(1)	4.11	C6(0)–O2'(1)	3.96
C2(0)–C4(1)	3.49	C4(0)–C4'(1)	3.96	C7(0)–O1'(1)	3.64
C2(0)–C5(1)	4.07	C4(0)–C5'(1)	3.66	C7(0)–C3'(1)	3.52
C2(0)–C8(1)	3.60	C4(0)–C6'(1)	3.47	C7(0)–C4'(1)	3.61
C2(0)–C9(1)	3.81	C4(0)–C7'(1)	3.61	C7(0)–C5'(1)	3.83
O1(0)–C3(1)	4.18	C4(0)–C8'(1)	4.07	C7(0)–O2'(1)	4.01
O1(0)–C4(1)	3.51	C5(0)–C6(1)	4.14	C8(0)–C4'(1)	4.07
O1(0)–C5(1)	3.81	C5(0)–C7(1)	3.50	C8(0)–C5'(1)	3.51
O1(0)–C6(1)	3.96	C5(0)–C4'(1)	3.66	C8(0)–C6'(1)	3.60
O1(0)–C7(1)	3.83	C5(1)–C5'(1)	3.88	O2(0)–C8(1)	3.73
O1(0)–C8(1)	3.36	C5(0)–C6'(1)	3.96	O2(0)–C6'(1)	3.96
O1(0)–C7'(1)	3.64	C5(0)–C7'(1)	3.83	O2(0)–C7'(1)	4.01
C3(0)–C4(1)	4.11	C5(0)–C8'(1)	3.51	C5(0)–C6'(2)	3.84
C3(0)–C7(1)	4.01	C6(0)–C7(1)	4.10	C6(0)–C5'(2)	3.84
C3(0)–C8(1)	3.48	C6(0)–C3'(1)	3.69	C6(0)–C6'(2)	3.70
C3(0)–C6'(1)	3.67	C6(0)–C4'(1)	3.47	C5(0)–O2(3)	4.05
C3(0)–C7'(1)	3.53	C6(0)–C5'(1)	3.96	C6(0)–C8'(3)	3.87
C4(0)–C7(1)	3.81	C6(0)–C8'(1)	3.60	C6(0)–C6'(3)	3.97

^a Distance between atoms of molecules at (*x,y,z*) and (1) (*x* + 1, *y,z*), (2) (*x* + 1, *y* + 1, *z*), (3) (*x,y* + 1, *z*)

Table 8 Interatomic distances^a: B form

Atom pair	Distance (Å)	Atom pair	Distance (Å)	Atom pair	Distance (Å)
C1(0)–C1'(1)	4.10	C3(0)–C7(1)	3.92	C8(0)–C8'(1)	4.09
C1(0)–C2(1)	4.16	C4(0)–C6(1)	3.96	O2(0)–C4(1)	3.89
C1(0)–O1(1)	3.63	C4(0)–C7(1)	3.61	O2(0)–C8(1)	3.60
C1(0)–C3(1)	4.10	C4(0)–C7'(1)	3.88	O2(0)–C7'(1)	4.02
C1(0)–C5(1)	4.09	C4(0)–C8'(1)	4.01	C1(0)–O2(2)	3.53
C2(0)–O1(1)	3.89	C5(0)–C6(1)	3.86	C5(0)–C5'(2)	3.96
C2(0)–C3(1)	3.80	C5(0)–C7(1)	3.76	C5(0)–C6'(2)	3.67
C2(0)–C4(1)	3.78	C5(0)–C8'(1)	3.90	C6(0)–C5'(2)	3.67
C2(0)–C5(1)	3.91	C6(0)–C8'(1)	3.89	C6(0)–C6'(2)	3.89
O1(0)–C4(1)	3.78	C7(0)–C3'(1)	3.92	C1(0)–O2(3)	4.09
O1(0)–C5(1)	3.60	C7(0)–C4'(1)	3.89	C5(0)–C8(3)	4.13
O1(0)–C6(1)	3.86	C7(0)–C8'(1)	3.97	C5(0)–C6'(3)	4.08
O1(0)–C8(1)	4.17	C7(0)–O2'(1)	4.02	C6(0)–C8(3)	4.11
C3(0)–C4(1)	3.83	C8(0)–C7(1)	3.96	C6(0)–C5'(3)	4.08
C3(0)–C5(1)	3.95	C8(0)–C4'(1)	4.01	C6(0)–C6'(3)	3.24
C3(0)–C6(1)	3.99	C8(0)–C5'(1)	3.90	C6(0)–C7'(3)	4.09
C3(0)–C7(1)	3.91	C8(0)–C6'(1)	3.89	C7(0)–C6'(3)	4.09
C3(0)–C8(1)	3.74	C8(0)–C7'(1)	3.98		

^a Distance between atoms of molecules at (x,y,z) and (1) (x+1,y,z), (2) (x+1,y+1,z), (3) (x,y+1,z)

investigated as 'tilting' resembling those in PET⁹ and PBT⁴. The tilting angles of $\sim 5^\circ$ for the two forms of PBN are rather larger than those of PET and PBT and appear to vary with annealing temperature and annealing and drawing conditions. At present, the reason for tilting is considered to be related to aromatic rings such as phenylene and naphthalene in the main chain of the polymer but has not been clarified so far.

Irregularity in the crystal structure

The coefficients of anisotropic temperature factors for both A and B forms, listed in *Table 3*, indicate qualitatively that the regularity in the direction along fibre axis is less than in the lateral direction. This indicates that, as in the drawing of PEN at a high temperature¹⁰, the film comes to have an oriented structure accompanied by lattice distortion due to the axial shift of polymer chains relative to one another along the chain axis, caused by rapid lateral

stacking of naphthalene planes regularly, with some irregularity in the planes.

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