Macromolecules **2003,** *36,* 8652−8655

Crystal Structure of Poly(pyridobisimidazole), PIPD

Yasuhiro Takahashi

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received May 27, 2003; Revised Manuscript Received September 2, 2003

ABSTRACT: Poly(pyridobisimidazole), PIPD, is known to be the strongest fiber. X-ray crystal structure analysis was carried out by using the imaging plate, on the basis of the neutron structure analysis (*Macromolecules* **2002**, *35*, 3942). Two molecular chains, which are slightly deviated from the planar structure, pass through a monoclinic unit cell with parameters $a = 13.33$ Å, $b = 3.462$ Å, c (fiber axis) = 12.16 Å, $\beta = 105.4°$, and the space group, $P2_1/a\text{-}C_{2h}$.[5] Two molecules with different oriented pyridine groups statistically occupied a crystal site. The intramolecular hydrogen bond is formed between NH and O and the intermolecular hydrogen bonds are formed between OH groups extending outside from the molecule.

Introduction

Poly(pyridobisimidazole) (PIPD) was developed at Akzo Nobel and at present has the strongest tensile strength.[1−3] The chemical structure is shown in Figure 1 along with those of poly(*p*-phenylenebenzobisoxazole) (PBO) and poly(*p*-phenylenebenzobisthiazole) (PBZT). PIPD is a fully conjugated polymer[4] and the alternating copolymer of pyridobisimidazole and dihydroxyphenyl rings. In the pervious paper,[5] the neutron structure analysis of PIPD was carried out on the *c*-projection, which shows that two molecules with different orientation of pyridine rings statistically occupy a crystal site and OH groups extend to the outside of the molecule, differing from the reported structure.[2] In the present study, X-ray crystal structure analysis was made by using an imaging plate.[6]

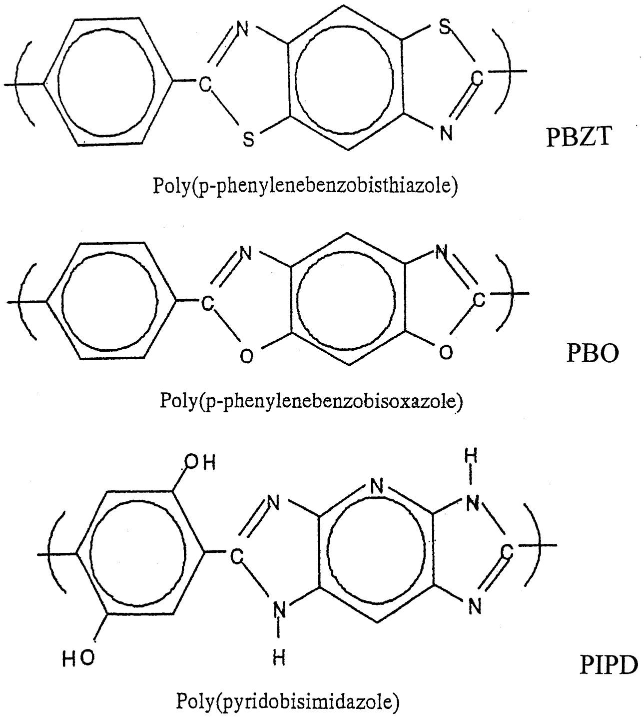

Figure 1. Chemical structure of poly(pyridobisimidazole) PIPD.

Experimental Section

PIPD fiber was kindly supplied by Dr. Sikkema of Akzo Nobel. The fibers were rolled up on a metal folder in a shape of cylinder with 0.5 mm diameter and served for taking fiber and Weissenberg diagrams.

X-ray measurements were carried out by Cu Kα radiation monochromatized by a pyrolyzed graphite. X-ray diffraction patterns were recorded by imaging plates and read digitally by R-AXIS DSS (Rigaku Denki Co. Ltd). Fiber diagrams were taken by the cylindrical camera with 5 cm radius in He gas atmosphere and Weissenberg photographs were taken by the cylindrical camera with 4.5 cm radius according to Norman's method.[7] Figure 2 shows the fiber diagram. Integrated intensities were estimated by the following procedures,[6] in the same way as by the drum scan densitometer.[8] First, the digital data of the reflection are summed up along the arc with constant 2θ and the summed intensities are plotted against a layer line. Then, the integrated intensities are estimated. Here, the X-ray diffraction pattern of PIPD shows the high crystallinity of the sample but the profiles of the reflection spots are broad and not necessarily symmetric. Therefore, the one-dimensional reflection intensity curves thus obtained are fitted and separated by the asymmetric Pearson VII function (Winfit).[9] Thus, the integrated intensities of 17 independent reflections could be estimated.

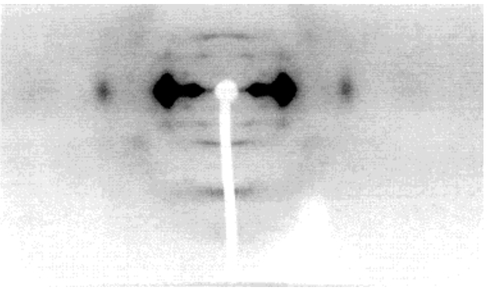

Figure 2. Fiber diffraction pattern of PIPD taken by an imaging plate.

Results and Discussion

All the observed reflections can be indexed by a monoclinic unit cell with parameters $a = 13.33$ Å, $b = 3.462$ Å, c (fiber axis) = 12.16 Å, and $\beta = 105.4°$. From the fact that the plane group for the *c*-projected structure is pgg,[5] two space groups $P2_1/a$ and $P2_1/n$ are possible. From the systematic absences, the space group

10.1021/ma030289f CCC: $25.00

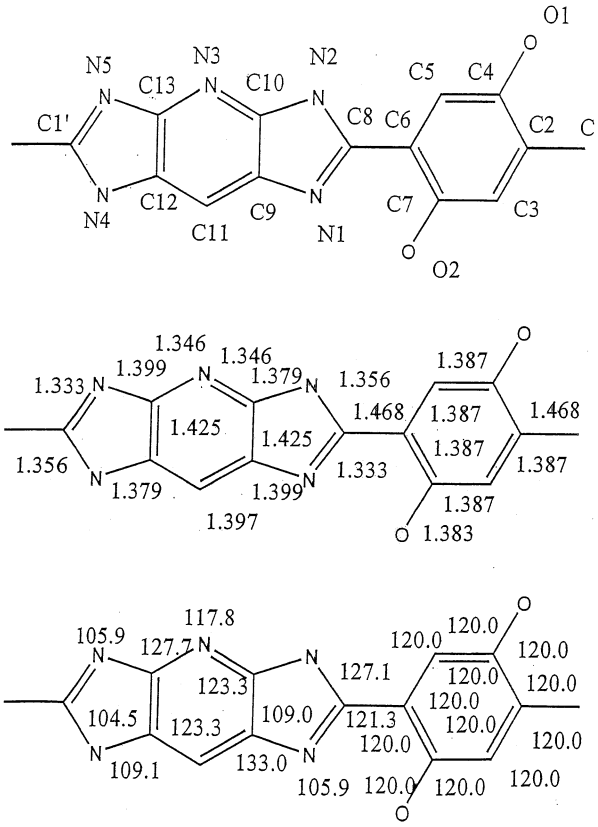

Figure 3. Bond lengths and bond angles of PIPD.

Table 1. Atomic Parameters Finally Obtained by the Constrained Least-Squares Refinement

	values	standard deviations
	Coordinates of the Origin Atom C1	
x	0.044	0.010
y	−0.044	0.041
z	−0.023	0.011
	Eulerian Angle (deg)	
	−11.2	5.7
	Internal Rotation Angle C5−C6−C8−N1 (deg)	
τ	7.0	5.9
	Overall Temperature Parameter (Å^2)	
B	0.81	2.13

was determined to be $P2_1/a$-C_{2h}.[5] On the basis of the *c*-projected structure determined by the neutron structure analysis,[5] the structure analysis was proceeded by the trial and error method. Main variable parameters are the molecular height, which determines the relative heights of two molecules statistically occupied a crystal site, and the directions of dihydroxyphenyl and pyridobisimidazole rings perpendicular to the molecular axis, which determine the intramolecular hydrogen bonding scheme. Finally, only one model gave the good agreement between the observed and calculated structure factors. The structure refinement was carried out by the constrained least-squares method,[10] where the conformation of the OH group was fixed on the result of the neutron structure analysis[5] and the bond lengths and bond angles were fixed on the values shown in Figure 3 which were adopted in the reference to the low-molecular-weight model compounds.[11−15] The parameters to be refined are the fractional coordinates of the origin atom C1, *x*, *y*, and *z*, the Eulerian angle φ, the internal rotation angle τ, which determines the angle between the phenyl and benzobisimidazole rings, and the overall temperature parameter *B*. Finally, the discrepancy factor ($R = \Sigma|\sqrt{I_o} - \sqrt{I_c}|/\Sigma\sqrt{I_o}$) converged to 17.0%. The parameters finally obtained by the

Table 2. Final Obtained Fractional Coordinates

atom	*x*	*y*	*z*
C1	0.044	−0.044	−0.023
C2	0.044	−0.044	0.097
C3	−0.047	0.023	0.128
C4	0.136	−0.112	0.181
O1	0.228	−0.179	0.151
C5	0.136	−0.112	0.295
C6	0.044	−0.044	0.325
C7	−0.047	0.023	0.242
O2	−0.139	0.091	0.272
C8	0.044	−0.044	0.446
N1	0.132	−0.069	0.529
N2	−0.040	−0.021	0.489
C9	0.104	−0.061	0.631
C11	0.161	−0.077	0.746
C10	−0.006	−0.030	0.607
N3	−0.058	−0.016	0.688
C13	−0.002	−0.031	0.797
C12	0.109	−0.062	0.831
N4	0.134	−0.069	0.949
N5	−0.039	−0.021	0.895
H(C3)	−0.118	0.075	0.063
H(C5)	0.206	−0.164	0.360
H(N2)	−0.119	0.001	0.440
H(C11)	0.243	−0.100	0.768
H(N4)	0.211	−0.091	1.004
H(O1)	0.293	−0.130	0.222
H(O2)	−0.199	0.173	0.198

Table 3. Comparison between Observed and Calculated Structure Factors

index	$\sqrt{I_o}$	$\sqrt{I_c}$	index	$\sqrt{I_o}$	$\sqrt{I_c}$
200	131.4	156.4	−112	59.4	21.6
110	435.2	419.5	012		
400			−212		
210			112		
310	–	35.1	−402		
410	–	19.7	203	19.3	19.8
600	14.9	17.9	−403		
510			−113	–	8.3
610	161.5	180.5	013	–	4.8
020			113	–	16.7
120			−213	–	4.8
220	143.7	149.8	−313	–	11.9
710			403	84.9	47.0
320			313		
420	–	3.3	−603		
800	–	25.4	213		
520	–	36.2	−413		
810	76.7	75.6	−513	–	14.2
1000			413	–	18.9
910			−613	–	7.5
720			603	18.7	57.4
1010	110.1	92.2	513		
820			023		
130			−123		
−201	21.5	38.4	−223		
201			−803		
−111	–	21.3	−713		
111	–	12.2	214	72.3	75.0
−211	–	26.8	−414		
401	12.4	21.1	−604		
−311			404		
211			015	67.1	55.4
−202	27.0	20.6	−315		
202	–	26.8	−215		
			205		
			016	25.2	28.7
			−316		
			206		
			−216		

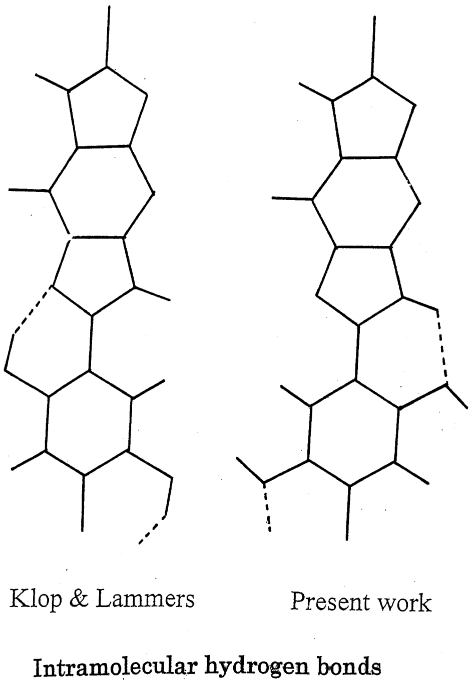

Figure 4. Molecular structure of poly(pyridobisimidazole) PIPD.

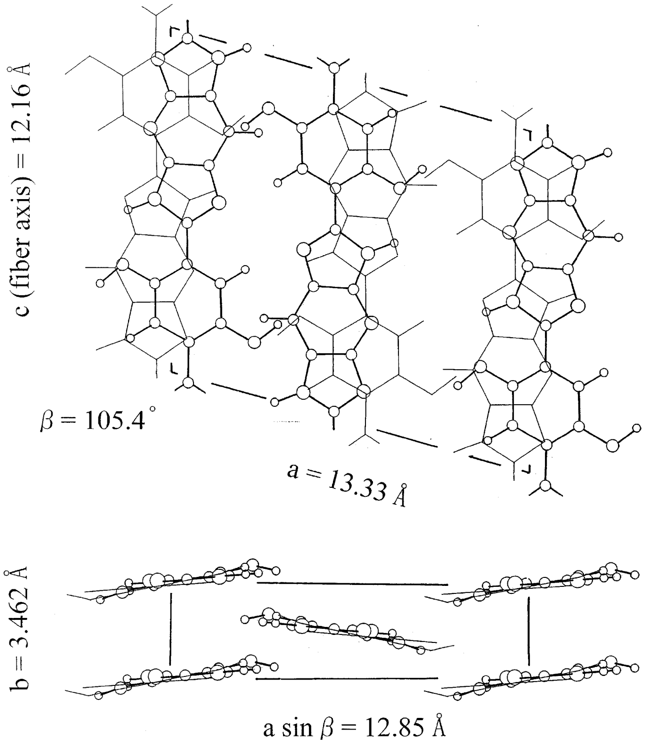

Figure 5. Crystal structure of PIPD.

constrained least-squares method are given in Table 1, and the fractional coordinates are given in Table 2. Table 3 gives the comparison between the observed and calculated structure factors. Figure 4 shows the molecular structure of poly(pyridobisimidazole) (PIPD) in comparison with the one reported by Klop and Lammers.[2] Figure 5 shows the crystal structure of PIPD.

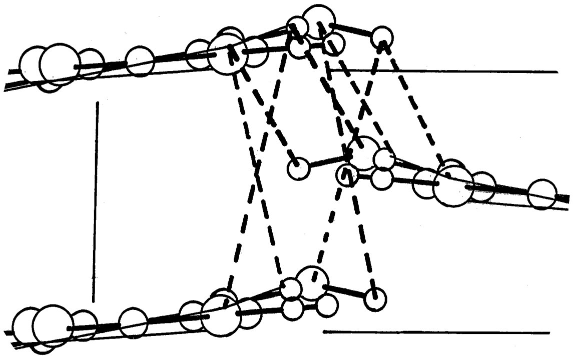

Figure 6. Intermolecular hydrogen bonds of PIPD. The molecules located on the center and corner of the unit cell are related by the *a*-glide symmetry parallel to the *ac* plane and the 2-fold screw symmetry parallel to the *b* axis.

Table 4. Distances and Angles for Possible Hydrogen Bonds

molecules	OH distances (Å)	OHO angles (deg)
corner to center	2.016	132.1
	2.093	125.1
	1.856	110.5
	1.977	77.4
corner to corner	3.784	64.5
	3.493	81.6
	3.341	102.4
	3.886	73.2

The molecule assumes the planar structure when the internal rotation angle τ is zero. Accordingly, the value $\tau = 7.0°$ shows that the molecular structure slightly deviates from the planar structure. The value of standard deviation 5.7° supports the deviation from the planar structure. The calculated values for τ is reported to be 7−10°,[16] which corresponds well to the present structure analysis. The molecules of poly(*p*-phenylenebenzobisoxazole) (PBO) and poly(*p*-phenylenebenzobisthiazole) (PBZT) assume the angles 25.7 and 27.7°, respectively, and also deviate from the planar structure. The deviation from the planar structure of PIPD is less than those of PBO and PBZT, which may be attributed to the intramolecular hydrogen bond. The molecular structure of PIPD is shown in Figure 5 in comparison with the structure reported by Klop and Lammers.[2] In the molecular structure reported by Klop and Lammers,[2] the intramolecular hydrogen bond is formed between OH and N, while, in the molecular structure clarified in the present study, the intramolecular hydrogen bond is formed between NH and O.

Two molecules statistically occupied a crystal site are related by the center of symmetry, and therefore, the pyridobisimidazole rings have different orientations with respect to the nitrogen atom of pyridine ring. In other words, the disorder is the substitutional disorder between two molecules with different orientations of pyridine rings. The center of symmetry of the space group is not located on the pseudo inversion center of the molecule, which is considered to be on the center of phenyl and benzobisimidazole rings. The statistical structure is different from the one reported by Klop and Lammers,[2] in which the N and CH of the pyridine are randomly distributed over two positions. The present analysis suggests that the directions of pyridine rings arrange regularly in the molecule or the regular parts form the crystal. The OH groups of the hydroxyphenyl ring of the molecules with the same orientation on the center and corner are almost on the same height in the unit cell (Figure 5). Accordingly, intermolecular hydrogen bonds are formed between OH groups of the molecules with the same orientation on the center and corner (Figure 6). Along the *b* axis, the hydrogen bonds can be formed between two molecules with the same orientation (Figure 6). The distances and angles for possible hydrogen bonds are given in Table 4. On the fiber diagram, the reflections are wholly broad in comparison with the usual crystalline polymers. This may suggest that the crystal region of PIPD is composed of the small domains which are formed by the molecules with the same orientation.

Acknowledgment. I thank Dr. D. J. Sikkema of Akzo Nobel (at present, Magellan Systems International) for supplying the fiber sample of PIPD.

References and Notes

(1) Sikkema, D. J. *Polymer* **1998**, *39*, 5981.
(2) Klop, E. A.; Lammers, M. *Polymer* **1998**, *39*, 5987.
(3) Lammers, M.; Klop, E. A.; Northolt, M. G.; Sikkema, D. J. *Polymer* **1998**, *39*, 5999.
(4) Takahashi, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1791.
(5) Takahashi, Y. *Macromolecules* **2002**, *35*, 3942.
(6) Takahashi, Y.; Sul, H. Manuscript in preparation.
(7) Norman, N. *Acta Crystallogr.* **1954**, *7*, 462.
(8) Takahashi, Y.; Matsubara, Y.; Tadokoro, H. *Macromolecules* **1982**, *15*, 334.
(9) Krumm, S. Unpublished work.
(10) Takahashi, Y.; Sato, T.; Tadokoro, H.; Tanaka, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 233.
(11) Tomlin, D. W.; Fratini, A. V.; Hunsaker, M.; Adams, W. W. *Polymer* **2000**, *41*, 9003.
(12) Herbstein, F. H.; Schmidt, G. M. J. *Acta Crystallogr.* **1955**, *8*, 399.
(13) Phillips, D. C.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1960**, *13*, 365.
(14) Philips, D. C. *Acta Crystallogr.* **1956**, *9*, 237.
(15) Wheatly, P. J. *Acta Crystallogr.* **1960**, *13*, 80.
(16) Hageman, J. C. L.; van der Horst, J. W.; de Groot, R. A. *Polymer* **1999**, *40*, 1313.

MA030289F