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Neutron Structure Analysis of Poly(pyridobisimidazole) (PIPD)

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ABSTRACT: Neutron structure analysis of poly(pyridobisimidazole) (PIPD) was carried out at 10, 100, 200, and 295 K. The crystal structure projected through the fiber axis was clarified. Two molecular chains pass through a rectangular unit cell with parameters $a' = 12.85$ Å and $b = 3.462$ Å (at 295 K), the plane group, pgg. PIPD assumes the statistical structure between two molecules with different orientation of pyridine ring. Two hydroxyl groups −OH extend outside from the chain axis. The temperature dependence of the cell parameters, a' and b, is very small, which is comparable to those of the rigid-rod polymers, poly(*p*-phenylenebenzobisoxazole) and poly(*p*-phenylenebenzobisthiazole), and is far smaller than the flexible polymers, polyethylene and poly(vinyl alcohol).

Introduction

Neutron diffraction method has several advantages in comparison with the X-ray diffraction method.[1−5] The scattering length of the atom by neutron is independent of the Bragg angle 2θ, while the atomic scattering factor for X-rays decreases as the Bragg angle increases. This is especially suitable for fibrous materials, of which the X-ray diffraction intensity rapidly decreases as the Bragg angle increases, due to disorientation of the crystallites and disorder. Furthermore, the scattering length of the atom for neutrons is independent of the atomic number. Especially, the hydrogen atom possesses a scattering length larger than X-ray diffraction (H, −3.74 and D, 6.67 for neutron; 1.0 for X-ray) in comparison with carbon atom (6.65 for neutron; 6.0 for X-ray). The position of the hydrogen atoms can be determined more easily than using X-ray diffraction. Usually, hydrogen atoms locate on the outer shell of the molecule, and therefore, the molecular orientation around the fiber axis can be determined more precisely than using X-ray diffraction. Moreover, the scattering lengths of carbon and nitrogen atoms by neutron are 6.646 and 9.36, respectively, while the scattering factors of carbon and nitrogen atoms for X-rays are 6 and 7, respectively. Accordingly, in the case of neutron diffraction, the carbon and nitrogen atoms can be distinguished more clearly than X-ray diffraction. Finally, absorption of neutrons by most elements is very small. Accordingly, the equipments for the low- and high-temperature measurements can be easily designed; i.e., neutron diffraction measurements at low and high temperature can be easily made.

Poly(pyridobisimidazole) (PIPD) was developed at Akzo Nobel (The Netherlands) and at present has the strongest tensile strength.[6−8] The chemical structure is shown in Figure 1 along with those of poly(*p*-phenylenebenzobisthiazole) (PBZT) and poly(*p*-phenylenebenzobisoxazole) (PBO). PIPD is a conjugated polymer[9] and the alternating polymer of pyridobisimidazole and dihydroxyphenyl rings. X-ray crystal structure analysis of PIPD was reported by Klop and Lammers.[7] In the present study, the neutron structure analysis of PIPD was carried out and the temperature dependence of the crystal structure was clarified in the range from 10 to 295 K, in which the conformation of OH group, i.e., the hydrogen-bonding network, is clarified to be different from that reported by Klop and Lammers.

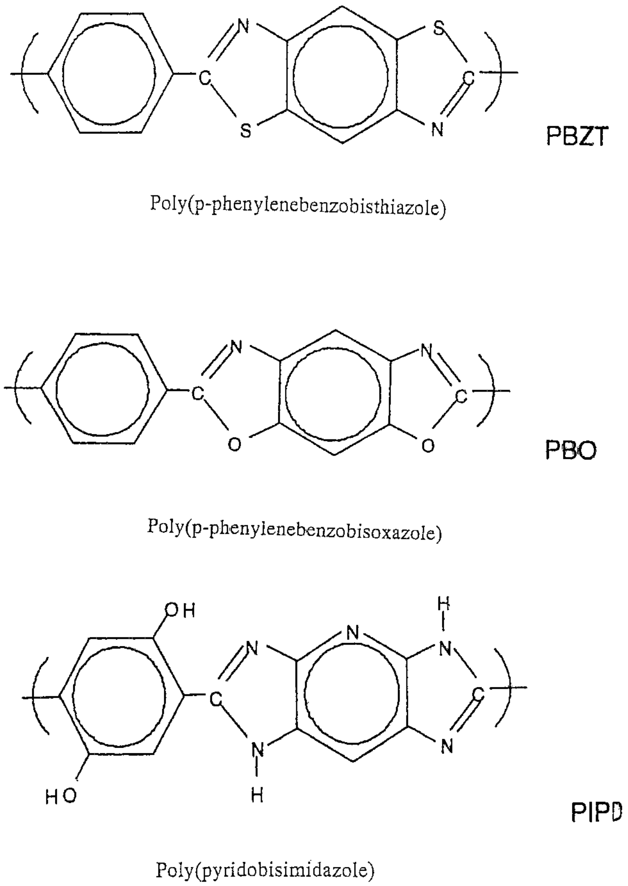

Figure 1. Chemical structure of poly(pyridobisimidazole) (PIPD).

Experimental Section

The fiber specimen of PIPD was kindly supplied by Dr. Sikkema of Akzo Nobel.

Neutron diffraction measurements were carried out by a powder diffractometer (HERMES)[10] equipped with an atomic reactor JRR-3M installed by Japan atomic Energy Research Institute (JAERI) using $\lambda = 1.8196$ Å. The specimen for neutron diffraction measurements was prepared by arranging

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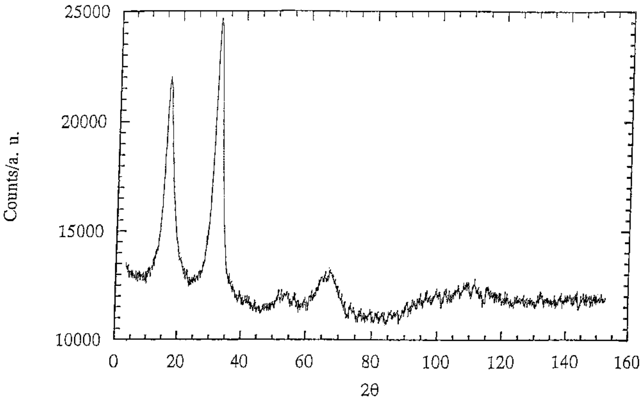

Figure 2. Intensity distribution on the equator of PIPD at 10 K.

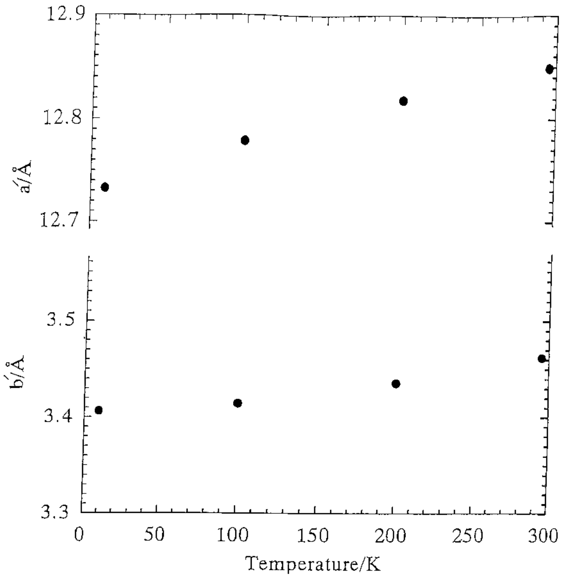

Figure 3. Temperature dependence of cell parameters.

Table 1. Temperature Dependence of Cell Parameters

	10 K	100 K	200 K	295 K
a′	12.73	12.78	12.81	12.85
b	3.407	3.415	3.436	3.462

the fibers in a cylindrical bundle about 13 mm in diameter, covered by Vanadium foil, and set into the aluminum sample tube with 6.5 cm diameter. Intensity distributions in the range $5° \leq 2\theta \leq 150°$ on the equator were measured at 10, 100, 200, and 295 K. Twelve independent reflections were observed. The number of the observed reflections on the equator in the X-ray work reported by Klop and Lammers is only four.[7] This clearly shows an advantage of the neutron diffraction method. The intensity distribution on the equator measured at 10 K is shown in Figure 2.

Results and Discussion

All the observed reflections could be indexed by a rectangular unit cell with parameters $a' = 12.85$ Å and $b' = 3.462$ Å (at 295 K). In Figure 3 and Table 1, the temperature dependence of the cell parameters a' and b' is shown. The temperature dependence is very small in comparison with the flexible polymers, polyethylene[3] and poly(vinyl alcohol),[2] and is similar to the rigid polymers, poly(*p*-phenylenebenzobisoxazole)[4] and poly(*p*-phenylenebenzobisthiazole).[5] The plane group could not be specified, because the systematic absences could not be observed clearly. First, trial and error procedures were carried out on the basis of the plane groups, pmg, pm, and pg, because two molecular chains are considered to pass through a unit cell. In the case of the plane group pmg, the molecule assumes the planar structure and locates on the mirror symmetry of the plane group. In the cases of the plane groups, pm and pg, two molecules in the unit cell locate on two general equivalent positions, and trial and error procedures were carried out, starting from the molecular structure reported by Klop and Lammers,[7] by changing the molecular position. However, good agreements between observed and calculated intensities could not be obtained. Subsequently, the statistical structure between two molecules with different orientations of pyridine in pyridobisimidazole ring was taken into consideration. Here, it should be noted that the scattering length of nitrogen atom by neutron (9.36) are far larger than that of carbon atom (6.646). Two plane groups, pmg and pgg, which possess four general equivalent positions, were taken into account. Only the plane group pgg gave good agreement between the observed and calculated intensities.

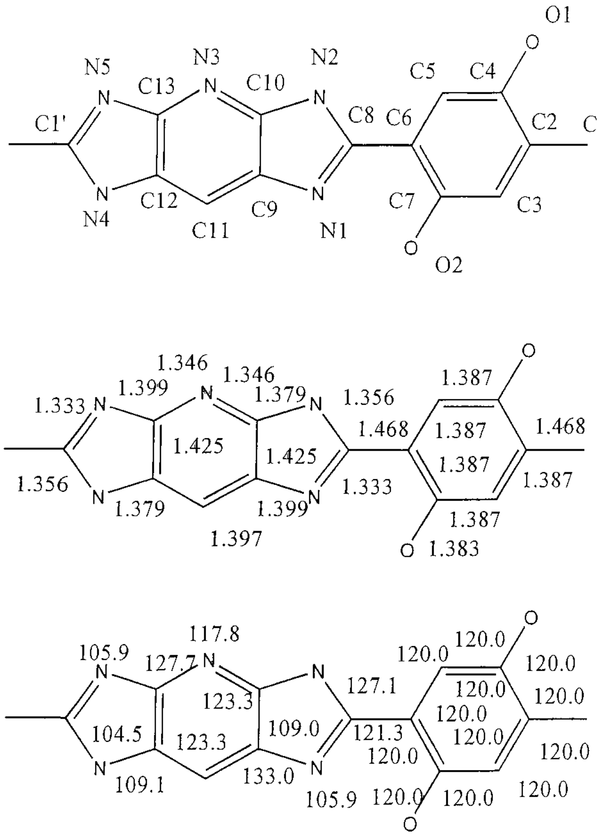

Figure 4. Numbering of atoms and bond lengths and angles fixed on the constrained least-squares refinements.

The structure refinements were carried out by the constrained least-squares method,[11] where the bond lengths and bond angles were fixed on the values given in Figure 4. These values were determined on the basis of the low molecular weight model compounds.[12–16] Variable parameters are an Eulerian angle ϕ, the fractional coordinates of the origin atom, x and y, the angle between dihydroxyphenyl and piridobisimidazole rings, τ, the internal rotation angle of hydroxyl groups, ψ and ω, and the overall isotropic temperature parameter, B. The refinements for the intensity data at 10, 100, 200, and 295 K converged to the R factors 15.6, 13.0, 16.5, and 10.5%, respectively. The final parameters obtained

Table 2. Final Parameters Obtained by the Constrained Least-Squares Refinements

	10 K	100 K	200 K	295 K
ϕ (deg)	−2.3 (24.4)[a]	−5.6 (12.7)	0.0 (25.9)	−16.3 (11.3)
X	0.031 (0.007)	0.029 (0.006)	0.022 (0.009)	0.020 (0.006)
Y	0.064 (0.019)	0.062 (0.011)	0.067 (0.015)	0.064 (0.008)
τ (deg)	−5.6 (28.0)	−2.8 (16.8)	−8.6 (24.6)	−11.8 (14.2)
ψ (deg)	−130.4 (128.9)	−141.8 (100.9)	−122.0 (195.51)	−179.1 (84.7)
ω (deg)	172.4 (91.4)	119.7 (153.3)	170.2 (108.2)	155.9 (95.4)
B (Å^2)	2.19 (1.67)	1.15 (1.61)	0.59 (2.48)	1.48 (1.86)
R (%)	15.6	13.0	16.5	10.5

Table 3. Finally Obtained Fractional Coordinates

	10 K		100 K		200 K		295 K	
atom	x	y	x	y	x	y	x	y
C1	0.031	0.064	0.029	0.062	0.022	0.067	0.020	0.064
C2	0.031	0.064	0.029	0.062	0.022	0.067	0.020	0.064
C3	−0.063	0.078	0.097	0.097	−0.071	0.067	−0.070	0.162
C4	0.126	0.050	0.028	0.028	0.116	0.067	0.110	−0.033
C5	0.126	0.050	0.028	0.028	0.116	0.067	0.110	−0.033
C6	0.031	0.064	0.029	0.062	0.022	0.067	0.020	0.064
C7	−0.063	0.078	−0.065	0.097	−0.071	0.067	−0.070	0.162
C8	0.031	0.064	0.029	0.062	0.022	0.067	0.020	0.064
C9	0.091	0.034	0.088	0.030	0.081	0.034	0.080	0.047
C10	−0.020	0.091	−0.022	0.090	−0.028	0.096	−0.031	0.079
C11	0.148	0.004	0.145	−0.002	0.138	0.002	0.137	0.030
C12	0.096	0.031	0.093	0.027	0.086	0.031	0.084	0.045
C13	−0.015	0.088	−0.017	0.088	−0.024	0.093	−0.026	0.077
O1	0.220	0.036	0.216	−0.006	0.209	0.067	0.199	−0.131
O2	−0.157	0.092	−0.158	0.131	−0.165	0.067	−0.159	0.259
N1	0.120	0.019	0.117	0.014	0.110	0.018	0.109	0.038
N2	−0.053	0.108	−0.055	0.109	−0.061	0.115	−0.064	0.089
N3	−0.071	0.117	−0.073	0.119	−0.080	0.125	−0.082	0.094
N4	0.121	0.018	0.118	0.013	0.111	0.017	0.110	0.038
N5	−0.052	0.107	−0.054	0.108	−0.060	0.114	−0.063	0.089
H(C3)	−0.136	0.089	−0.137	0.123	−0.144	0.067	−0.139	0.237
H(C5)	0.198	0.040	0.195	0.002	0.188	0.067	0.179	−0.109
H(C11)	0.231	−0.038	0.228	−0.048	0.220	−0.045	0.220	0.006
H(N2)	−0.132	0.149	−0.134	0.152	−0.140	0.159	−0.143	0.112
H(N4)	0.198	−0.022	0.195	−0.030	0.188	−0.026	0.187	0.015
H(O1)	0.265	−0.180	0.267	−0.207	0.255	−0.181	0.260	−0.202
H(O2)	−0.216	0.138	−0.195	0.402	−0.228	0.117	−0.208	0.436

Table 4. Comparison between the Observed and Calculated Structure Factors

	10 K		100 K		200 K		295 K	
index	$I_o^{1/2}$	$I_c^{1/2}$	$I_o^{1/2}$	$I_c^{1/2}$	$I_o^{1/2}$	$I_c^{1/2}$	$I_o^{1/2}$	$I_c^{1/2}$
200	363.7	321.8	374.1	327.0	394.1	339.5	394.3	342.7
110	519.8	539.3	535.6	560.8	560.8	561.0	529.2	545.3
210 400	59.1	66.9	83.9	72.4	102.4	80.6	106.9	103.5
310	56.2	105.1	87.8	95.9	93.8	133.6	115.0	140.8
410	56.8	91.6	57.9	105.1	69.5	113.8	62.0	90.2
510 600	155.4	135.0	155.7	146.9	181.1	225.2	182.6	217.7
020 120 220 610 320	364.9	353.3	385.0	380.5	392.4	402.9	360.6	359.4
420 710 800	61.4	109.2	65.9	117.0	81.7	122.9	98.5	117.8
910 720 1000	187.8	150.1	194.0	143.4	244.5	162.7	182.9	142.6
230 1010 820 330	177.9	176.7	231.4	224.2	221.7	232.3	207.6	205.5
430	104.7	72.0	125.7	111.5	154.0	102.4	106.7	87.5
630 1200 1020	88.9	127.4	81.7	113.9	95.1	123.1	88.1	102.4

by the constrained least-squares refinements are shown in Table 2. The fractional coordinates are given in Table 3. The comparison between the observed and calculated structure factors is given in Table 4. The *c*-projected crystal structure is shown in Figure 5. The standard deviations are very large because the ratio of the number of the variable parameters to the number of the observed reflections including the scale factor is 8 to 12. Therefore, it cannot be discussed about the temperature dependence of the variable parameters. Furthermore, the values for angle τ between the dihydroxyphenyl and piridobisimidazole rings assume from −2.8 to −11.8,

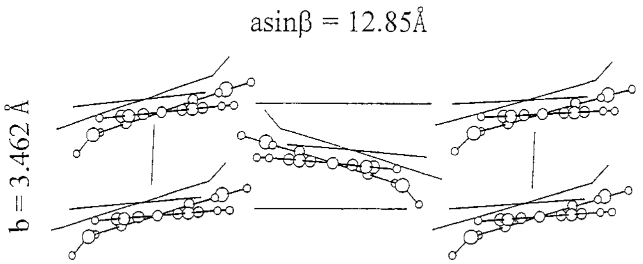

Figure 5. The *c*-projected crystal structure of PIPD.

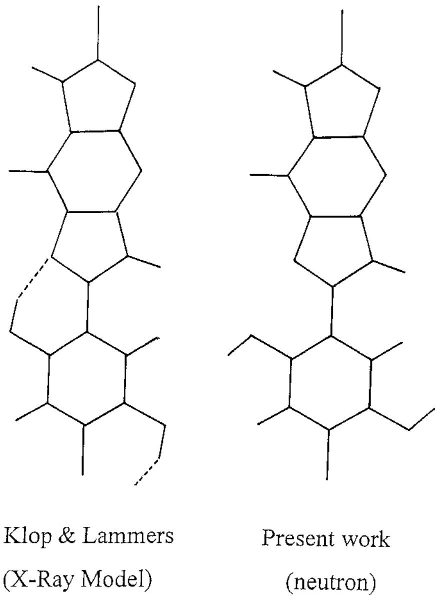

Figure 6. Molecular structures of PIPD.

which correspond well to the calculated values 7−10,[17] and on the other hand, the standard deviations assume from 14.2 to 28.0. Accordingly, it can be said that the molecule assumes the planar structure ($\tau = 0°$) within the accuracy of the standard deviation. The internal rotation angles of hydroxyl groups, ψ and ω, assume the values from −122° to −179° and from 119° to 172°, respectively, although the standard deviations assume large values from 85° to 196°. Anyway, both hydroxyl −OH groups extend from the chain axis toward outside. In the structure reported by Klop and Lammers,[7] both hydroxyl groups assume cis conformation and form the intramolecular hydrogen bonds with nitrogen atoms of the imidazole rings. Here, it should be noted that hydrogen atoms contribute to the intensity in neutron diffraction more than in X-ray diffraction. Accordingly, the hydroxyl groups are considered to be associated with intermolecular hydrogen bond and the hydrogen-bonding network different from the reported one should be considered. The molecular structure of poly(pyridbisimidazole) (PIPD) is shown in Figure 6 in comparison with the structure reported by Klop and Lammers.[7]

X-ray structure analysis in three dimensions is now in progress on the basis of the present neutron work.

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