Crystal Structure of Natural Rubber

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ABSTRACT: The crystal structure of natural rubber has been studied by many researchers including Bunn and Nyburg. However, the accepted crystal structure has not been reported. In the present study, the X-ray crystal structure analysis was carried out by using an imaging plate at −50 °C. Four molecular chains with ST$\bar{S}$cis$\bar{S}$TScis conformation pass through a unit cell with $a = 12.41$ Å, $b = 8.81$ Å, $c = 8.23$ Å, $\beta = 94.6°$, and $P2_1/a$-C_{2h}^5. In the crystal lattices, two molecular chains related by the mirror symmetry statistically occupy a crystal site with the ratio 0.67:0.33.

Introduction

In 1925, the crystallization of natural rubber was found.[1,2] In 1928, Mark, Meyer, and Susich first proposed the crystal structure of natural rubber.[3] Four molecular chains pass through a unit cell with almost the same size as those reported by Bunn[4] and Nyburg.[5] After that, the crystal structure of natural rubber has been studied.[6,7] In 1942, Bunn[4] reported the crystal structure of natural rubber, in which four molecular chains with essential ST$\bar{S}$cis$\bar{S}$TScis conformation pass through a monoclinic unit cell with parameters $a = 12.46$ Å, $b = 8.89$ Å, $c = 8.10$ Å, $\beta = 92°$, and the space group, $P2_1/a$. However, the comparison between the observed and calculated intensities is qualitative. In 1954, Nyburg[5] reported the quantitative structure analysis of natural rubber, in which four molecular chains with ST$\bar{S}$cis$\bar{S}$TScis conformation pass through a rectangular unit cell with parameters, $a = 12.46$ Å, $b = 8.89$ Å, $c = 8.1$ Å, and the space group, $P2_1/a$, and furthermore, two molecular chains related by a mirror symmetry statistically occupy a crystal site. However, the *R*-factor is 24.1%, which is not good and is not necessarily accepted at present. In 1956, Natta and Corradini[8] supported the crystal structure reported by Nyburg except for the space group *Pbca*. In 1975, Benedetti et al.[9] proposed the conformational isomorphism between ST$\bar{S}$cis$\bar{S}$TScis and ST$\bar{S}$cis$\bar{S}$TScis conformations and reported that the *R*-factor corresponds to the Nyburg structure.

Recently, Tanaka[10] reported the natural rubber purified by excluding the proteins. This sample shows the elasticity completely without cross-links. In the present study, this sample was served for the X-ray crystal structure analysis.

Experimental Section

The sample of natural rubber excluding the proteins was supplied by Sumitomo Rubber Co. Ltd. The original sample was the sheet with 3 mm thick. The strip with 3 mm wide was cut and stretched by about 7 times in order to avoid double orientation.

X-ray measurements were made by the imaging plates. Fiber diagrams were taken at −50 °C with Rigaku RAXIS-RAPID (127.4 mm radius) by using Mo Kα radiation monochromatized by a pyrolytic graphite. Weissenberg photographs were taken at room temperature by a cylindrical camera with 4.5 cm radius by using Ni-filtered Cu Kα radiation according to Norman's method.[11] The fiber diagram and Weissenberg diagram with a schematic representation are shown in Figures 1 and 2, respectively. Integrated intensities were estimated by the following procedures,[12] in the same way as by the drum scan densitometer procedures of X-ray films.[13−15] First, the digital data for one pixel (100 μm^2) of the reflection are summed up along the arc with constant 2θ, and the summed intensities are plotted against a layer line. From the one-dimensional intensity curve thus obtained, the integrated intensity was estimated. For overlapped reflections, the one-dimensional intensity curve was fitted and separated under the assumption of pseudo-Voigt function: a linear combination of Gauss and Cauchy functions.[16]

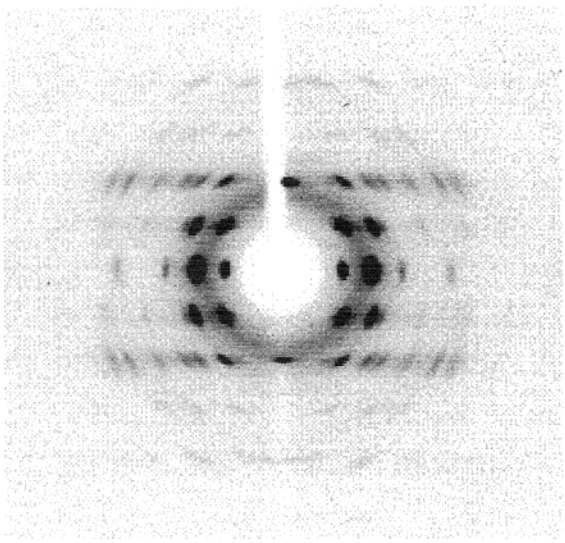

Figure 1. Fiber diagram of natural rubber taken by imaging plate.

Results and Discussion

Unit Cell and Space Group. All the observed reflections were indexed by a monoclinic cell with parameters $a = 12.41$ Å, $b = 8.81$ Å, c(fiber axis) $= 8.23$ Å, and $\beta = 93.1°$. This unit cell is very similar to that reported by Bunn.[4] The space group was determined as $P2_1/a$-C_{2h}^5 from the systematic absence: $h0l$; $h \neq 2n$. The orthogonal unit cell reported by Nyburg[5] and Natta and Corradini[8] could not explain the reflection with $\xi = 0.301$ on the second layer line.

Crystal Structure Analysis and Refinements. Structure refinements were carried out by using the

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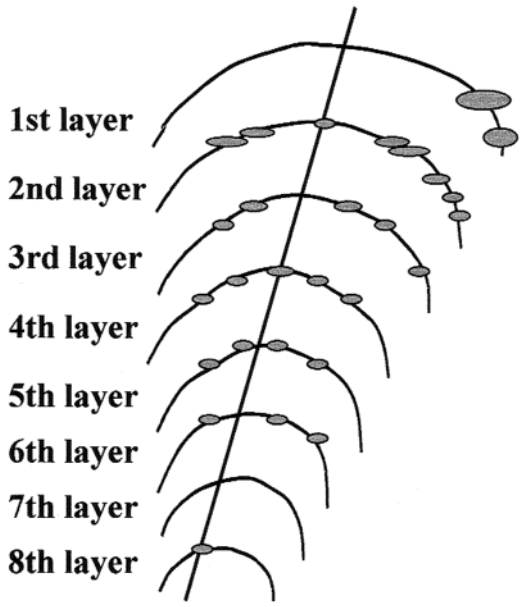


Figure 2. Weissenberg diagram of natural rubber and its schematic representation.

constrained least-squares method.[15,17] Here, the accepted bond lengths shown in Figure 6 were used, and the configuration of the double bond was fixed on cis: τ(C=C) = 0.0°. The bond angles C−C−H and C=C−H are fixed on 109.5° and 120.0°, respectively, and the isotropic temperature parameters of the hydrogen atoms are fixed on 10.0 Å^2. First, the structure reported by Bunn with STScisSTScis conformation which has the 2-fold screw symmetry was refined after trial and error. The molecular model with STScisSTScis conformation is shown in Figure 3 along with STScisSTScis conformation. The parameters to be refined are the Eulerian angles, θ, φ, and χ, the coordinates of the origin atom, x_0, y_0, and z_0, bond angles, C1−C2−C3, C1−C2−C4, and C2−C4−C5, internal rotation angle, y_m−C1−C2−C4 (y_m: the y axis of the coordinate system fixed on the molecule), and the isotropic temperature parameters of the atoms, B(C1), B(C2), B(C3), B(C4), and B(C5). Here,

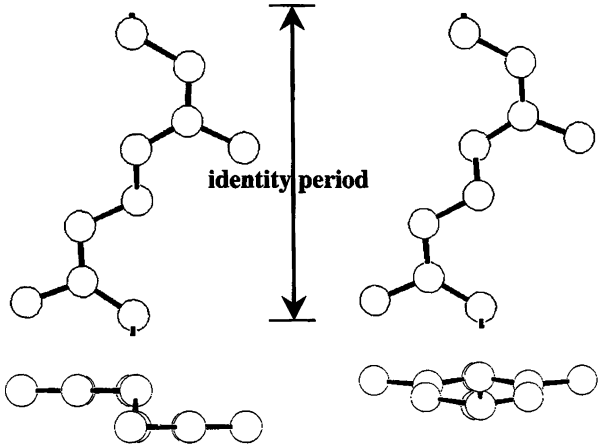
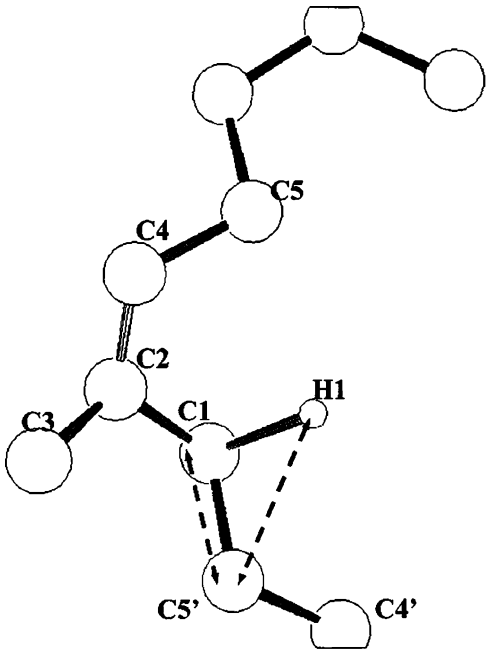


Figure 3. Molecular models of natural rubber.



Constrained distance (Å)	
C5' ⇔ C1	:1.540
C5' ⇔ H1	:2.161

Figure 4. Distance constraints by Lagrange's undetermined multipliers.

the molecular chain was assumed to possess the 2-fold screw symmetry, although, crystallographically, an asymmetric unit is composed of two monomeric units, and no symmetry relates two monomeric units. Two distances between two monomeric units are fixed on by Lagrange's undetermined multipliers as shown in Figure 4. Finally, the R-factor reduced to 20.8%, which is insufficient to accept the structure. Subsequently, the crystal structure with STScisSTScis conformation was examined. The refined parameters and constrained

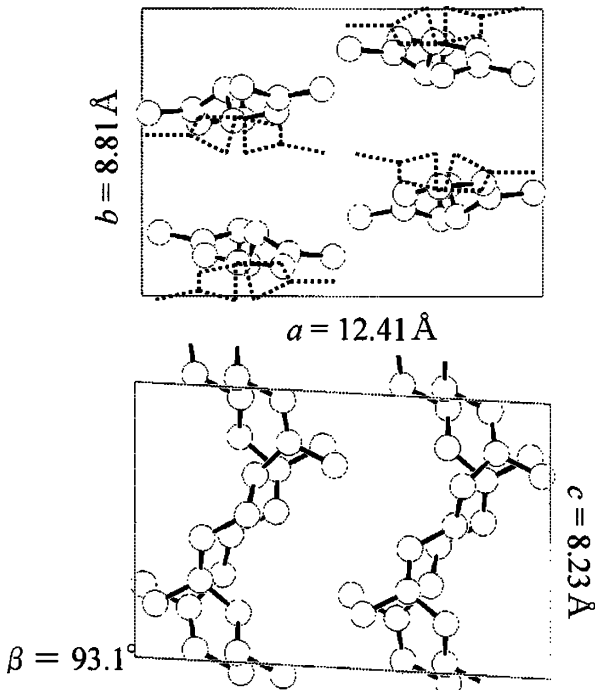


Figure 5. Crystal structure of natural rubber.

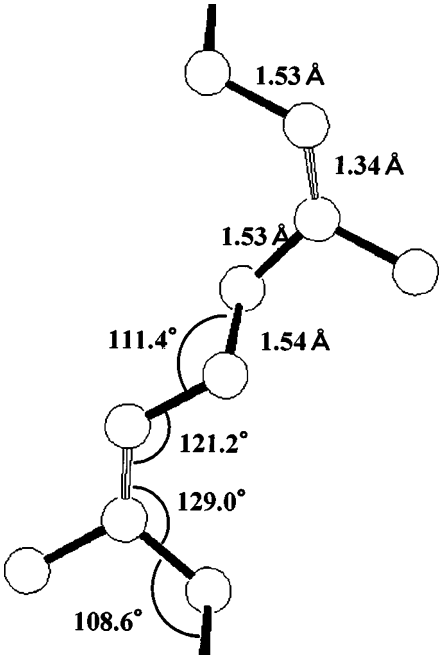


Figure 6. Bond lengths and bond angles of natural rubber. The bond lengths are fixed during the refinement.

conditions are the same as those for the ST$\bar{S}$cisST$\bar{S}$cis model. Here, the molecular chain assumed to possess the glide symmetry along the fiber axis. After the constrained least-squares refinement, the *R*-factor reduced to 17.0%. However, some unobserved reflections gave strong calculated intensity. While $\sqrt{I_0}$ of the weakest observed reflection $\bar{3}13$ assumes the value 12.25, $\sqrt{I_c}$ of unobserved reflection 130 assumes 82.40. Therefore, the statistical structure was introduced to the ST$\bar{S}$cis$\bar{S}$TScis model. The statistical structure was first introduced by Nyburg,[5] where the two molecules related by the mirror symmetry at $y = {}^1/_8$ statistically occupy a crystal site with 1:1 ratio. In the present study, the mirror symmetry at $y = {}^1/_8$, which is not included in the symmetries of the space group $P2_1/a$, was also introduced into ST$\bar{S}$cis$\bar{S}$TScis model. Here, the statistical occupancy was introduced into the refined parameters mentioned above. The statistical occupancy was first introduced in the case of poly(vinylidene fluoride) form II,[18] which is well described the crystal structures of silk[15] and amylose triacetate I.[19] Finally, the *R*-factor reduced to 14.4%. Here, the value $\sqrt{I_c}$ of unobserved reflection 130 reduced to 40.25. The parameters finally obtained by the constrained least-squares method are given in Table 1. The atomic parameters in fractional coordinates are given in Table 2. Table 3 gives the comparison between the observed and calculated structure factors. Figure 5 shows the crystal structure of natural rubber. In Figure 6, the bond lengths and bond

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

	values	std dev
fractional coordinates of the origin atom C1		
x_0	0.248	0.006
y_0	0.229	0.009
z_0	0.180	0.007
Eulerian angles (deg)		
θ	59.8	2.4
φ	322.7	3.5
χ	−137.7	2.6
bond angles (deg)		
C1−C2−C3	109.0	5.6
C1−C2−C4	129.6	8.7
C2−C4−C5	121.2	7.0
internal rotation angle (deg)		
y_m−C1−C2−C4	113.8	3.8
temperature parameters (Å^2)		
B(C1)	6.36	0.07
B(C2)	7.70	0.09
B(C3)	0.11	0.06
B(C4)	8.11	0.10
B(C5)	3.47	0.04
statistical occupancy (%)		
W	33.2	8.7

Table 2. Fractional Atomic Coordinates[a]

atom	*x*	*y*	*z*
C1	0.248	0.229	0.180
C2	0.156	0.193	0.291
C3	0.048	0.222	0.199
C4	0.161	0.142	0.446
C5	0.270	0.113	0.537
C6	0.289	0.221	0.683
C7	0.370	0.151	0.809
C8	0.480	0.138	0.734
C9	0.356	0.104	0.961
C10	0.246	0.117	1.035
H1	0.029	0.336	0.152
H2	0.041	0.151	0.091
H3	−0.018	0.197	0.277
H4	0.080	0.129	0.487
H5	0.275	−0.006	0.574
H6	0.335	0.138	0.459
H7	0.325	0.220	0.249
H8	0.237	0.344	0.133
H9	0.521	0.240	0.693
H10	0.473	0.066	0.626
H11	0.538	0.088	0.823
H12	0.432	0.060	1.015
H13	0.218	0.005	1.069
H14	0.188	0.167	0.946
H15	0.213	0.242	0.740
H16	0.321	0.328	0.639

[a] The molecules which statistically occupy a crystal site are related by the mirror symmetry at $y = {}^1/_8$.

Table 3. Comparison between Observed and Calculated Structure Factors

index			$I_o^{1/2}$	$I_c^{1/2}$	index			$I_o^{1/2}$	$I_c^{1/2}$	index			$I_o^{1/2}$	$I_c^{1/2}$
2	0	0	126.21	128.91	−5	2	1		21.64	2	1	3		1.49
2	1	0		14.73	0	4	1		6.66	−1	2	3		
1	2	0	284.7	290.91	−1	4	1		15.22	0	2	3	39.06	37.25
3	1	0		1.69	1	4	1		8.13	1	2	3		
2	2	0		13.83	−4	3	1			−3	1	3	12.25	13.52
4	0	0	68.25	81.3	4	3	1	38.51	29.26	−2	2	3		13.36
3	2	0			5	2	1			2	2	3		1.34
4	1	0		29.06	2	4	1			3	1	3		15.84
1	3	0		40.25	−2	4	1			−4	0	3		38.78
2	3	0		40.58	−6	0	1	45.65	42.1	−3	2	3	48.01	42.83
4	2	0		10.47	6	0	1			−4	1	3		
3	3	0		21.28	−6	1	1	43.47	51.33	0	3	3		25.22
5	1	0		20.05	6	1	1		19.86	4	0	3		21.81
0	4	0	60.27	59.65	−3	4	1		2.77	3	2	3		42.53
1	4	0	33.43	23.24	3	4	1		3.59	−1	3	3		3.61
5	2	0			−5	3	1		0.71	1	3	3		8.33
4	3	0	21.47	26.54	5	3	1		18.54	4	1	3		6.8
2	4	0		17.15	−6	2	1		2.65	−2	3	3		12.76
6	0	0		1.55	6	2	1		12.47	2	3	3		20.95
6	1	0		0.96	−4	4	1		13.14	−4	2	3		3.12
3	4	0		5.43	4	4	1		2.07	4	2	3		1.62
4	4	0		0.75	1	5	1			−3	3	3		4.57
2	5	0		23.86	−1	5	1	39.66	37.11	3	3	3		17
3	5	0		13.43	−7	1	1			−5	1	3		0.98
5	4	0		0.96	7	1	1		25.69	−5	2	3		10.15
5	3	0		9.24	−2	5	1		10.65	−4	3	3		12.33
6	3	0		12	2	5	1		35.29	0	4	3		13.55
6	2	0		1.72	−7	2	1			−1	4	3		5.03
7	1	0		9.28	5	4	1	32.94	33.72	1	4	3		7.53
7	2	0		2.24	−5	4	1			5	1	3		8.98
8	0	0			−3	5	1		12.79	5	2	3		
4	5	0	60.27	48.08	3	5	1		23.22	4	3	3		
7	3	0			7	2	1		2.89	2	4	3	36.02	43.2
8	1	0			−8	0	1			−2	4	3		
6	4	0		25.19	−4	5	1	19.45	33.72	−6	1	3		
0	6	0		5.96	4	5	1			−6	0	3		
1	6	0		16.62	−8	1	1			0	1	4	41.42	29.23
8	2	0		5.77	−8	3	1		6.96	−1	1	4		
2	6	0		6.45	0	1	2			−2	0	4		3.38
5	5	0		4.33	−1	1	2	44.14	39.27	1	1	4		17.38
3	6	0		13.37	1	1	2			−2	1	4		15.6
7	4	0		8.3	−2	0	2	92.13	95.43	2	0	4		10.94
8	3	0		17.26	2	0	2			0	2	4		
9	1	0		37.94	−2	1	2		16.4	−1	2	4	61.85	46.68
9	2	0			0	2	2			2	1	4		
4	6	0	66.38	63.53	2	1	2	76.2	62.9	−3	1	4		29.85
6	5	0			−1	2	2			1	2	4		34.4
5	6	0		0.55	1	2	2	66.72	56.14	−2	2	4		0.62
8	4	0		47.45	−3	1	2			2	2	4		5.35
1	7	0		28.26	3	1	2	61.34	52.05	3	1	4		10.22
9	3	0			−2	2	2			−4	0	4		0.47
2	7	0	46.02	44.51	2	2	2		10.52	−3	2	4		14.8
10	0	0			−4	0	2	13.32	17.44	−4	1	4		4.42
7	5	0			−3	2	2	28.72	54.09	4	0	4		
−1	1	1	32.27	40.12	4	0	2			3	2	4		
1	1	1			3	2	2			0	3	4	43.6	45.4
−2	0	1	159.14	131.23	0	3	2	63.86	117.8	1	3	4		
2	0	1			−4	1	2			−1	3	4		
−2	1	1	53.63	56.12	4	1	2			0	1	5		9.06
2	1	1			−1	3	2		9.69	−1	1	5		9.34
0	2	1		2.45	1	3	2		36.51	1	1	5		
1	2	1	136.59	139.04	−2	3	2		1.45	−2	0	5	34.38	26.35
−1	2	1			2	3	2		9.75	2	1	5		
−3	1	1	42.64	45.41	−4	2	2		4.47	0	2	5		
3	1	1			3	3	2			−1	2	5	52.19	37.58
−2	2	1		20.17	−3	3	2			−3	1	5		
2	2	1		14.49	−5	1	2	84.18	75.87	1	2	5		
−4	0	1		8.19	4	2	2			−2	1	5		14.78
4	0	1		9.41	5	1	2		42.05	−4	3	6		18.04
−4	1	1		10.18	1	4	2			2	3	6		
4	1	1		8.56	−1	4	2			−5	1	6	75.41	59.94
−3	2	1		18.88	−4	3	2			−3	3	6		
3	2	1		0.18	−5	2	2	95.42	96.91	4	1	6		
0	3	1		47.21	−2	4	2			3	3	6		20.04
−1	3	1		22.37	2	4	2			5	1	6		
1	3	1		13.36	−6	1	2			0	4	6		
−2	3	1	45.24	55.91	4	3	2		37.59	−1	4	6	48.16	45.38
2	3	1			5	2	2		18.81	−6	1	6		
−4	2	1		6.7	0	1	3	40.07	19.59	−6	0	6		
4	2	1		3.99	−1	1	3			1	4	6		2.21
−3	3	1		10.87	−2	0	3	24.23	21.99	−2	4	6		16.96
3	3	1		35.53	1	1	3							
−5	1	1		26.96	2	0	3		8.31					
5	1	1		16.54	−2	1	3		21.07					

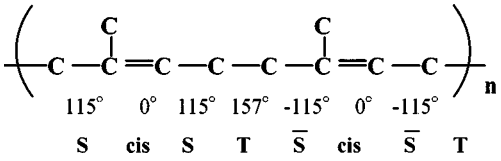


Figure 7. Internal rotation angles of natural rubber.

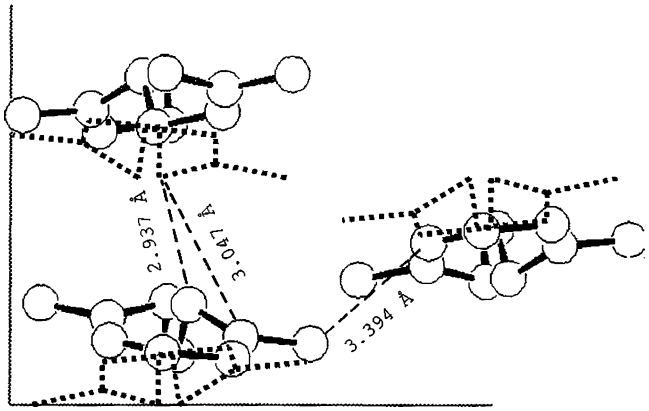


Figure 8. Short contacts in crystal of natural rubber.

angles of natural rubber are given. Here, the bond lengths are fixed during the refinement. The internal rotation angles of natural rubber are given in Figure 7.

Two bond angles around −C═ assume 121.2° and 129.0°, and two bond angles around −C− assume 111.3° and 108.6° (Figure 6). The internal rotation angles around −C−C═ and −C−C− bonds are 115° and 159°, respectively (Figure 7), which is slightly deviated from skew (120°) and trans (180°) conformations, respectively. The molecular conformation can be said to be essentially ST$\bar{S}$cis$\bar{S}$TScis.

Four molecular chains pass through the unit cell (Figure 4). Two molecules are related by the a-glide symmetry and two molecules are related by the center of symmetry. On a crystal site, two molecules which are related by the mirror symmetry at $y = {}^1/_8$ are statistically located with the ratio 0.67:0.33. These mirrors are not included in the symmetries of the space group $P2_1/a$. The short contacts 2.937 and 3.047 Å are found between two statistically relating molecules in neighboring crystal sites along the *b*-direction (Figure 8). This suggests that in the crystal the molecules regularly arrange in the *b*-direction, and the arrangement of the rows of the molecules is disordered in the *a*-direction. The half-widths of the equatorial reflections 200, 120, 400, and 040 are 1.7, 2.0, 1.6, and 1.45 in arbitrary units, respectively. The half-widths of *h*00 reflections are broader than that of 0*k*0 reflection. This supports that the molecules regularly arrange in the *b*-direction and are disordered in the *a*-direction. The broader 120 reflection suggests that the crystalline region forms some kinds of domain structure in the way similar to poly(vinylidene fluoride) form II.[20]

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