Macromolecules **1983,** *16,* 1588-1592

Crystal Structure of Form II of Poly(vinylidene fluoride)

Yasuhiro Takahashi,* Yoshiaki Matsubara, and Hiroyuki Tadokoro

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received January 17, 1983*

ABSTRACT: The crystal structure of form II of poly(vinylidene fluoride) was analyzed in detail by using new intensity data measured by a drum scanner, where the sample was prepared by annealing at 175 °C after stretching at 150 °C. The molecular conformation is essentially $TGT\bar{G}$ and the space group is $P2_1/c$-C_{2h}^5. In the unit cell, four molecules with different orientations, AC, $A\bar{C}$, $\bar{A}C$, and $\bar{A}\bar{C}$, were found to occupy a crystal site with the different existence probabilities $w_{AC} = 0.54$, $w_{A\bar{C}} = 0.29$, $w_{\bar{A}C} = 0.10$, and $w_{\bar{A}\bar{C}} = 0.07$. Here, A and $\bar{A}$ denote molecular orientations of opposite polarity along the *a* axis, and C and $\bar{C}$ correspond to the up and down molecules along the *c* axis, respectively. On the other hand, the previously reported intensity data did not give significant values for $w_{\bar{A}C}$ and $w_{\bar{A}\bar{C}}$. This suggests that the existence probabilities depend on the conditions of sample preparation.

The structure analysis of form II of poly(vinylidene fluoride) has been carried out by two groups, Lando et al.[3,4] and us.[2]. The structure analyses gave essentially the same molecular conformation $(TGT\bar{G})_n$ and the same rectangular unit cell with parameters $a = 4.96$ Å, $b = 9.64$ Å, and c (fiber period) = 4.62 Å but different molecular packings. Doll and Lando[3] proposed two possible structures, "parallel" and "antiparallel". In the parallel structure, two molecular chains in the unit cell point in the same direction and the space group is $P2_1$-C_2^2, and in the antiparallel structure, the molecules are antiparallel to each other in the unit cell with space group $P1$-C_1^1. We independently analyzed the crystal structure of form II,[2] in which two molecules pack antiparallel in the unit cell with space group $P2_1/c$-C_{2h}^5. Recently, Bachmann and Lando[4] reexamined the crystal structure by using our intensity data reported in the previous paper[2] and reported that form II is the statistical structure with the orthorhombic space group $P2cm$-C_{2v}^4, where up and down molecules statistically locate at the same crystal site with equal probabilities. However, this structure is in conflict with the tilting phenomena.[5] The X-ray diffraction pattern of the tilt sample, on which hkl and $\bar{h}kl$ reflections are observed to have different intensities, obviously suggests that the crystal structure should belong to the monoclinic or triclinic system and not to the orthorhombic system. Therefore, the crystal structure needs to be reexamined in greater detail.

In the previous papers,[6-9] we reported that conformational disorders, i.e., kink bands, exist in the crystallites of form I and streak II and that the conformational disorder plays an important role in crystal transformations of poly(vinylidene fluoride). Recently, Lovinger reported that the reflections 011 and 031 of form II change their intensities depending upon the annealing temperature.[10] This suggests that some kind of packing disorder occurs in the crystallite of form II.

The purpose of the present study is to settle the controversy by analyzing the crystal structure in detail and to clarify what kind of disorder is contained in the crystallite of form II.

Experimental Section

Sample. The poly(vinylidene fluoride) sample used for this study was KF-1100 (Kureha Chemical Industry Co., Ltd.). A uniaxially oriented sample of form II was prepared by stretching at 150 °C and annealing at 175 °C for 24 h. A cubic sample with size 0.2 × 0.2 × 0.2 mm^3 was cut and used for the X-ray measurements. A tilt sample was prepared by annealing a fiber specimen at about 170 °C with the ends free, where the fiber specimen was prepared by stretching and crystallizing the melt at room temperature.

X-ray Measurements. X-ray measurements were made with Cu Kα radiation monochromatized by a graphite monochromator. Fiber photographs were taken in vacuo or in a He gas atmosphere by cylindrical cameras with 5- and 10-cm radii. The fiber diagram of form II, which was taken by a vacuum camera with a 10-cm radius, is shown in Figure 1. The integrated intensities of the strong five reflections were measured by a position-sensitive proportional counter. A drum scanner (Optronics), which is installed in the Crystallographic Research Center of this university, was applied to measurements of the integrated intensities of the other reflections. After the photographs were taken by the multiple-film method, the optical density of a 100-μm square was measured over the whole film and was digitally recorded on a magnetic tape. The digital data were summed along each reflection arc after the density was converted to the intensity in reference to a standard intensity scale. The intensities thus obtained were plotted along layer lines and were graphically integrated. The intensity data were corrected by the Lorentz-polarization factor and the oblique effect. Finally, the integrated intensities of 53 independent reflections were measured. These intensity data are considered to be far better than the data used previously,[2] which were visually estimated.

Structural Analysis

Tilting Phenomena and Space Group. The X-ray diffraction pattern of a tilt sample of form II is shown in Figure 2 along with a schematic representation. The interpretation of this X-ray diffraction pattern was described in a previous paper[5] along with that of form III. All the reflections on the diffraction pattern could be indexed by the unit cell of form II. Indexing shows that the *c* axis of the crystallite tilts about 20° around the *b* axis from the fiber direction of the sample, and the crystallites are equally distributed over all angles around the fiber direction. Several pairs of hkl and $\bar{h}kl$ reflections, which can be observed independently on the diffraction pattern, have different intensities. Furthermore, there are no observed reflections contrary to the systematic absences of the space group $P2_1/c$-C_{2h}^5, and the calculated structure factors based on the reported structure[2] agree well with the observed structure factors.[5] Therefore, it is concluded that the space group is $P2_1/c$-C_{2h}^5.

Model Free from Disorder. Constrained least-squares refinement[11,12] was first carried out starting from the reported structure,[2] in which two molecules having up- and down-pointing directions locate on definite sites of the unit cell. During the refinement, the following parameters were fixed: bond lengths C-C = 1.54 Å, C-F = 1.34 Å, and C-H = 1.09 Å, bond angle C-C-H = 110°, and the isotropic temperature parameter for the hydrogen atoms $B_H = 5.0$ Å^2. Furthermore, two interatomic distances C(1)···C(2) and C(1)···H(1) between neighboring monomeric units were fixed by using Lagrange's undertermined multipliers. The

0024-9297/83/2216-1588$01.50/0

Table I
Structure Models for Form II of Poly(vinylidene fluoride) and Existence Probabilities of Molecules with Different Orientation[a]

model	existence probability, % AC	$\mathrm{A\overline{C}}$	$\mathrm{\overline{A}C}$	$\mathrm{\overline{A}\overline{C}}$	no. of variable parameters[b]	R factor, %
1	100				15 − 2	28.5
2	64	36 (3)[c]			16 − 2	17.6
3-1	54	29 (4)	10 (5)	7 (5)	18 − 2	11.7
3-2	61	33 (3)	3 (4)	3 (3)	18 − 2	16.2
3-3	56	27 (3)	9 (2)	8 (3)	19 − 2	11.1
3-4	54	29 (5)	11 (4)	6 (4)	20 − 2	11.0
4	77			23 (2)	17 − 2	18.9
5	77		23 (4)		17 − 2	21.9
6	75		5 (5)	20 (4)	18 − 2	18.0
7	54	30 (2)	16 (2)		18 − 2	11.8
8	61	24 (2)		15 (2)	18 − 2	11.7
2[d]	76	24 (8)			16 − 2	13.2

[a] Molecular orientation is shown in Figure 3. [b] The number of the constraining conditions is denoted by "−2". [c] Parentheses show standard deviations. [d] Result for the intensity data in the previous paper.[3]

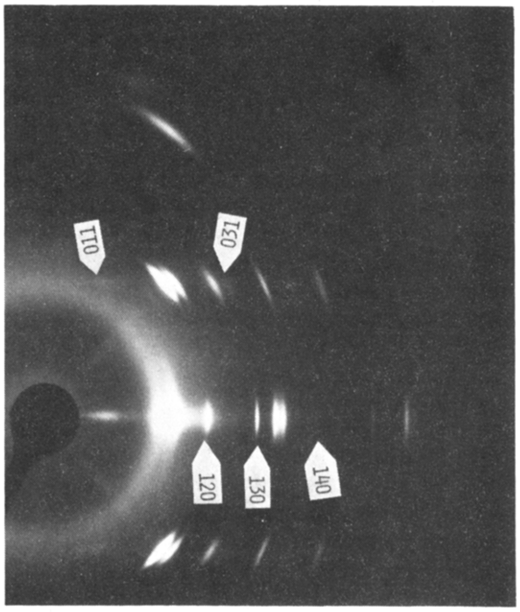


Figure 1. Fiber diagram of form II of poly(vinylidene fluoride). The sample was prepared by annealing at 170 °C for 24 h after stretching at 150 °C.

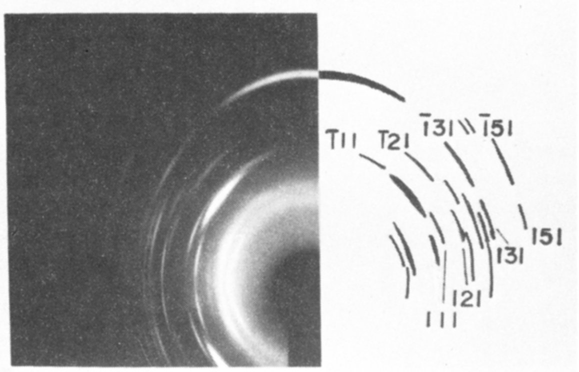


Figure 2. X-ray diffraction pattern of a tilt sample of form II and its schematic representation.

variable parameters were two Eulerian angles, θ and ϕ, the Cartesian coordinates of the F(1) atom chosen as the origin, X_0, Y_0, and Z_0, two bond angles, F(1)–C(1)–C(2) and F(1)–C(1)–F(2), two internal rotation angles, Y_m–F(1)–C(1)–C(2) and F(1)–C(1)–C(2)–H(1), the difference between the internal rotation angles Y_m–F(1)–C(1)–C(2) and Y_m–F(1)–C(1)–F(2), four isotropic temperature parameters, $B_{C(1)}$, $B_{C(2)}$, and $B_{F(1)}$, and $B_{F(2)}$, and the scale factor. The number of parameters to be refined was 15 − 2. The refinement converged to the discrepancy factor $R = 28.5\%$ for 53 observed reflections (model 1 in Table I). This insufficient R value suggests that the reported structure[2] is not necessarily correct for the sample used in the present study.

Model Containing Disorder between Up and Down. On the fiber diagram (Figure 1), the reflections 011 and 031 are streaky and the half-widths are broader than those of the other reflections on the first layer line. Although the previous analysis[2] gave, on the whole, fairly good agreement between the observed and calculated structure factors ($R = 17\%$), the reflections 011 and 031 gave rather poor agreement, and the observed values are less than the calculated ones. Furthermore, the reflection intensities of 011 and 031 change, depending upon the conditions of sample preparation. Lovinger pointed out these features and the behavior of the 011 and 031 reflections.[10]

These facts are consistent with the disorder that the up (or down) molecule occupied the crystal site of the down (or up) molecule with a certain probability. The reflections 011 and 031, i.e., $0kl$ reflections with k = odd, would become weaker with increasing disorder, and, in an extreme state, the systematic absences $0kl$, k = odd, for the b-glide symmetry perpendicular to the a axis would appear in addition to the symmetries of the space group $P2_1/c$, where the up and down molecules statistically occupy the same crystal site with equal probabilities. The statistical structure presumed in the extreme state would have space group symmetry $Pbcm$-D_{2h}^{11}.

Constrained least-squares refinement for the above-mentioned model converged to $R = 17.6\%$ (model 2 in Table I). In the refinement, two molecules with orientations AC and $\mathrm{A\overline{C}}$ (Figure 3) at the same crystal site were assumed to have the same conformation, and the existence probability of the down molecule at the site of an up molecule, $w_{\mathrm{A\overline{C}}}$, was taken into account in the parameters used in the refinement of model 1. Here, the existence probability of the up molecule, w_{AC}, at the up molecular crystal site is given by $1 - w_{\mathrm{A\overline{C}}}$. In this model, the atomic coordinates and the temperature parameters are related by space group $Pbcm$, but the existence probabilities are not. Therefore, the real space group is $P2_1/c$. The number of variable parameters to be refined was 16 − 2. The value $R = 17.6\%$ seems to be insufficient, judging from the accuracy of the intensity data measured in the present work, although the value, generally speaking, suggests that the structure is essentially correct. Further refinement was tried by releasing the mirror symmetry and twofold rota-

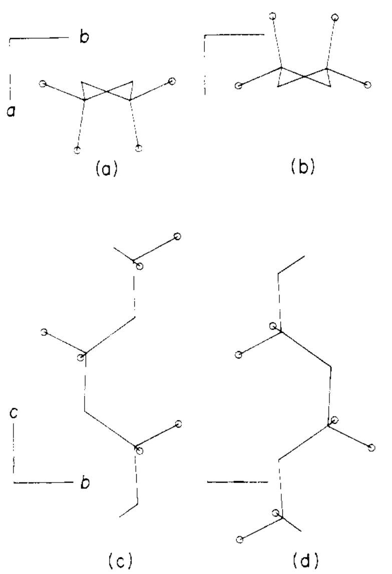


Figure 3. Molecular orientation in form II. (a), (b), (c), and (d) are denoted by the symbols A, Ā, C, and C̄, respectively, whose combinations AC, AC̄, ĀC, and ĀC̄ denote the orientation of the molecule.

tion axis relating the atomic coordinates of two molecules at the same crystal site, but the R factor did not improve.

On the other hand, the same structure model was refined by using the reported intensity data[2] and improved to R = 13.2% (Table I).

Model Containing Disorder among Four Different Orientations. On the equator (Figure 1), the reflections 120 and 140 are observed to be broader than the reflection 130. This suggests that, on the c projection, the structure also contains some disorder with a short-range order, because this relation in half-widths among a series of reflections $1k0$ cannot be interpreted by the anisotropy in the crystallite size and disorder of the second kind.[13] The disorder between two opposite orientations along the a axis (orientations A and Ā in Figure 3) was considered to be the most probable for this disorder.

Four models, models 3-1, 3-2, 3-3, and 3-4, containing disorder among four molecules with different orientations, AC, AC̄, ĀC, and ĀC̄ (Figure 3), were built and refined. In the refinements, the existence probabilities $w_{A\bar{C}}$, $w_{\bar{A}C}$, and $w_{\bar{A}\bar{C}}$ were independently refined as variable parameters and w_{AC} was given by $1 - w_{A\bar{C}} - w_{\bar{A}C} - w_{\bar{A}\bar{C}}$. Accordingly, the real space groups of all the models are the same, $P2_1/c$, although each model has the apparent space group holding only for the atomic and temperature parameters. In model 3-1, the coordinates of two molecules with orientations ĀC and ĀC̄ were generated by introducing the apparent mirror symmetry prependicular to the a axis in addition to the apparent space group symmetry $Pbcm$ for model 2. The apparent space group of model 3-1 is $Cmcm$-D_{2h}^{17}. In model 3-2, the apparent space group is $Cccm$-D_{2h}^{20} and the coordinates of the molecules with orientations ĀC and ĀC̄ were related to the molecules with orientations AC and AC̄ by the apparent c-glide symmetry perpendicular to the a axis. In model 3-3, the z coordinate of the molecules with orientations ĀC and ĀC̄ was refined independently against that of the molecules with orientations AC and AC̄ under the apparent space group symmetry $Pbcm$. In model 3-4, the z coordinates of two molecules with orientations ĀC and ĀC̄ were independently refined by releasing the apparent mirror symmetry relating these two molecules.

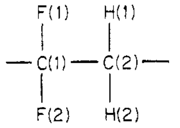
Models 3-1, 3-2, 3-3, and 3-4 converged to R = 11.7%, 16.2%, 11.1%, and 11.0%, respectively. In these models, the packing of the molecules with orientations AC and AC̄ is the almost same, although the molecules with orientations ĀC and ĀC̄ are different in packing among the models. The R value of model 3-1 is a little larger than those of models 3-3 and 3-4, but the difference of R factor, 0.6% or 0.7%, is not physically significant, and, moreover, the apparent symmetry of model 3-1, $Cmcm$, is higher than those of models 3-3 ($Pbcm$) and 3-4 ($P2_1/c$). Therefore, model 3-1 with higher apparent symmetry is considered to be more probable. On the other hand, the antiphase domain structure in form II (Figure 6), the details of which will be given in the following paper,[14] strongly support model 3-1. The molecules with orientation Ā in the antiphase domain prefer to have the same molecular packing as the molecules with orientation A in the regular structure from an energetic viewpoint. Models 3-1 and 3-2 satisfy this requirement because, in these models, the molecules with orientation Ā assume relatively the same molecular packing as the molecules with orientation A. Consequently, model 3-1 is the case because model 3-2 is excluded from the poor agreement between the observed and calculated structure factors (R = 16.2%).

The parameters obtained by the constrained least-squares method and the fractional coordinates for model 3-1 are given in Tables II and III, respectively. Table IV gives a comparison between the observed and calculated structure factors. The crystal structure of model 3-1 is shown in Figure 4.

Table II
Final Parameters Obtained for Form II of Poly(vinylidene fluoride) (Model 3-1) by the Constrained Least-Squares Method[a,d]

parameter	value	std dev
weights of molecules		
$w_{A\bar{C}}$	0.29	0.04
$w_{\bar{A}C}$	0.10	0.05
$w_{\bar{A}\bar{C}}$	0.07	0.05
Eulerian angles, deg		
θ	191.2	2.8
ϕ	−9.8	1.6
Cartesian coordinates of the origin atom in the molecular coordinate system, Å		
X_0	2.936	0.02
Y_0	1.638	0.02
Z_0	0.717	0.04
bond angles, deg		
F(1)-C(1)-C(2)	97.0	2.9
F(1)-C(1)-F(2)	106.3	3.0
internal rotation angles, deg		
Y_m-F(1)-C(1)-C(2)[b]	96.4	2.4
F(1)-C(1)-C(2)-H(1)	167.9	2.3
Y_m-F(1)-C(1)-F(2)[c]	107.7	4.1
temperature parameters, Å²		
$B_{C(1)}$	4.3	0.9
$B_{C(2)}$	3.3	0.8
$B_{F(1)}$	6.0	0.6
$B_{F(2)}$	11.0	1.0

[a] The following parameters were fixed during the refinement: $x_M = 0.5$, $y_M = 0.0$, $z_M = 0.0$, $\chi = 0.0°$, $w_{AC} = 1 - w_{A\bar{C}} - w_{\bar{A}C} - w_{\bar{A}\bar{C}}$, bond lengths C-C = 1.54 Å, C-F = 1.34 Å, and C-H = 1.09 Å, bond angle C-C-H = 110.0°, and temperature parameters of the hydrogen atoms B_H = 5.0 Å². [b] Y_m is the y axis of the Cartesian coordinate system fixed on the origin atom F(1) of the molecule. [c] This value denotes the difference between the internal rotation angles Y_m-F(1)-C(1)-C(2) and Y_m-F(1)-C(1)-F(2). [d] Atoms numbered as



$$-\overset{\mathrm{F(1)}}{\underset{\mathrm{F(2)}}{\mathrm{C(1)}}}-\overset{\mathrm{H(1)}}{\underset{\mathrm{H(2)}}{\mathrm{C(2)}}}-$$

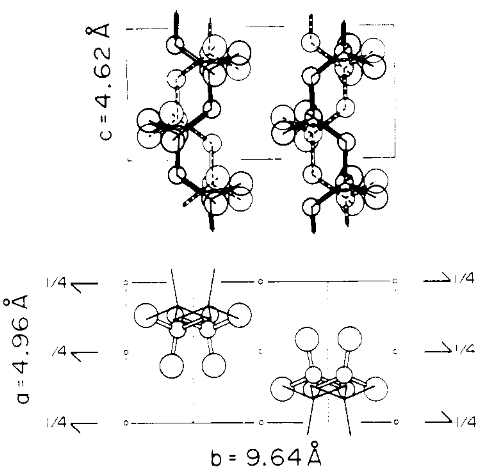


Figure 4. Crystal structure of form II (model 3-1). The existence probabilities of four molecules with orientations AC, $\mathrm{A\bar{C}}$, $\mathrm{\bar{A}C}$, and $\mathrm{\bar{A}\bar{C}}$ are 54, 29, 10, and 7%, respectively.

Table III
Fractional Coordinates of Form II of Poly(vinylidene fluoride) (Model 3-1)

molecule	atom	*x*	*y*	*z*
AC, $w_{\mathrm{AC}} = 0.54$	C(1)	0.331	0.193	0.211
	C(2)	0.230	0.184	−0.103
	F(1)	0.592	0.170	0.155
	F(2)	0.237	0.078	0.339
	H(1)	0.010	0.181	−0.107
	H(2)	0.309	0.091	−0.207
$\mathrm{A\bar{C}}$, $w_{\mathrm{A\bar{C}}} = 0.29$	C(1)	0.331	0.193	0.289
	C(2)	0.230	0.184	0.603
	F(1)	0.592	0.170	0.345
	F(2)	0.237	0.078	0.162
	H(1)	0.010	0.181	0.607
	H(2)	0.309	0.091	0.707
$\mathrm{\bar{A}C}$, $w_{\mathrm{\bar{A}C}} = 0.10$	C(1)	0.169	0.193	0.211
	C(2)	0.270	0.184	−0.103
	F(1)	−0.092	0.170	0.155
	F(2)	0.263	0.078	0.339
	H(1)	0.490	0.181	−0.107
	H(2)	0.191	0.091	−0.207
$\mathrm{\bar{A}\bar{C}}$, $w_{\mathrm{\bar{A}\bar{C}}} = 0.07$	C(1)	0.169	0.193	0.289
	C(2)	0.270	0.184	0.603
	F(1)	−0.092	0.170	0.345
	F(2)	0.263	0.078	0.162
	H(1)	0.490	0.181	0.607
	H(2)	0.191	0.091	0.707

Refinement was also carried out for models 3-1, 3-3, and 3-4 by using the reported intensity data,[2] but *R* factors did not improve significantly and the existence probabilities of the molecules with orientations $\mathrm{\bar{A}C}$ and $\mathrm{\bar{A}\bar{C}}$, $w_{\mathrm{\bar{A}C}}$ and $w_{\mathrm{\bar{A}\bar{C}}}$, converged to the physically insignificant minus values. This suggests that the existence probabilities of the molecules with orientation $\mathrm{\bar{A}}$ cannot be significantly estimated in the range of the accuracy of the reported intensity data because of the small probabilities.

Other Models. Models 4–8, in which two or three molecules with different orientations occupy a crystal site, were also refined. Models 4–6, which do not contain the moledule with orientation $\mathrm{A\bar{C}}$, gave rather poor agreement between the observed and calculated structure factor, *R* = 18.0–21.9% (Table I). Models 7 and 8, which are of the molecules with orientations AC, $\mathrm{A\bar{C}}$, and $\mathrm{\bar{A}C}$ and of the molecules with orientations AC, $\mathrm{A\bar{C}}$, and $\mathrm{\bar{A}\bar{C}}$, respectively, gave *R* = 11.8% and *R* = 11.7%, respectively. However, these models are less probable because they do not obviously satisfy the apparent *b*-glide symmetry presumed from the feature of the 011 and 021 reflections.

Table IV
Observed and Calculated Structure Factors for Form II of Poly(vinylidene fluoride) (Model 3-1)[a]

hkl	$I_{\mathrm{o}}^{1/2}$	$I_{\mathrm{c}}^{1/2}$
100	29.5	26.9
020	43.5	41.0
110	65.9	66.0
120	20.8	21.0
130	21.4	22.8
200	36.0	38.1
040 210	28.7	26.3
220	4.4	3.0
140	7.9	7.1
230	4.6	4.2
150	17.4	13.7
240	4.6	2.4
310 300	39.6	40.6
060		19.4
320	6.8	6.5
160 250	12.1	15.1
330		5.2
340		0.6
260	5.3	3.3
170	7.3	7.0
410 350 400	9.8	12.4
420 270 080	19.7	19.5
180		4.5
430		1.9
360		2.4
440		0.3
280	13.6	9.5
370	15.3	11.9
190 450	13.7	12.1
011	3.5	1.6
021	48.5	49.9
111	17.8	21.3
121	19.6	23.7
031	12.0	11.0
131	21.0	18.1
041 211	13.1	11.4
141 221	26.7	23.4
051 231	8.9	8.2

hkl	$I_{\mathrm{o}}^{1/2}$	$I_{\mathrm{c}}^{1/2}$
151	12.6	12.2
241	18.4	18.7
311	10.8	13.8
061	7.9	6.2
321		6.5
161 251	3.4	6.3
331	6.7	7.1
071 341	9.8	10.4
261	6.2	0.9
171	10.3	9.5
351		1.6
411		3.3
081 271 421		8.4
181 431 361	10.3	9.5
441	7.9	11.7
191 451	6.6	6.8
022 102	15.8	15.7
112	10.9	11.4
122	6.5	7.9
032		3.7
132[b]		5.1
202	4.9	4.1
042 212	6.5	7.8
222 142	2.1	4.9
232 052		3.5
152	7.4	6.0
242		1.3
302 312 062	7.7	7.1
322		4.8
162 252	2.3	4.8
332		2.8
072 342 262 172	3.3	4.1

[a] On the first and second layer lines, indices *hkl* denote the overlapped reflections of *hkl* and $\bar{h}kl$. [b] The intensity cannot be estimated because the reflection due to form I overlaps.

Discussion

In the present study, it was clarified that in form II, four molecules with different orientations, AC, $\mathrm{A\bar{C}}$, $\mathrm{\bar{A}C}$, and $\mathrm{\bar{A}\bar{C}}$, were found to occupy a crystal site with the existence probabilities $w_{\mathrm{AC}} = 0.56$, $w_{\mathrm{A\bar{C}}} = 0.27$, $w_{\mathrm{\bar{A}C}} = 0.10$, and $w_{\mathrm{\bar{A}\bar{C}}} = 0.07$. On the other hand, the reported intensity data[2] did not give the physically significant existence probabilities for the molecules with orientations $\mathrm{\bar{A}C}$ and $\mathrm{\bar{A}\bar{C}}$ because of the small probability and the insufficient accuracy of the reported data. This suggests that different existence probabilities may be alloted to the samples in the present and previous studies, which were prepared by annealing at 175 and 150 °C, respectively.

The space group is $P2_1/c\text{-}C_{2h}^5$, although the only apparent space group that holds, for the atomic and temperature parameters is $Cmcm\text{-}D_{2h}^{17}$. Even if the statistical structure in which up and down molecules occupy a crystal

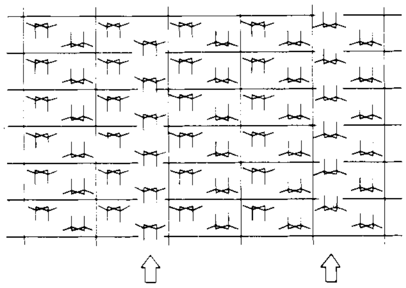


Figure 5. Schematic representation of disorder of form II on the c projection. Only the molecules with the same orientation align along the a axis and the disorder occurs along the b axis.

Table V
Bond Angles and Internal Rotation Angles (Deg) of Form II of Poly(vinylidene fluoride) (Model 3-1)[a]

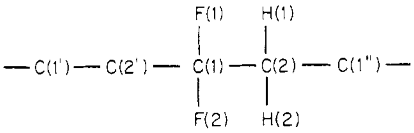
Bond Angles

C(2)-C(1)-C(2′)	117.5	C(2′)-C(1)-F(1)	123.4
C(1)-C(2)-C(1″)	112.1	C(1′)-C(1)-F(2)	106.1
C(2)-C(1)-F(1)	97.0	F(1)-C(1)-F(2)	106.3
C(2)-C(1)-F(2)	104.8		

Internal Rotation Angles

C(1′)-C(2′)-C(1)-C(2)	176.2
C(2′)-C(1)-C(2)-C(1″)	65.3

[a] Atoms numbered as



$$-\mathrm{C(1')}-\mathrm{C(2')}-\underset{\mathrm{F(2)}}{\overset{\mathrm{F(1)}}{\mathrm{C(1)}}}-\underset{\mathrm{H(2)}}{\overset{\mathrm{H(1)}}{\mathrm{C(2)}}}-\mathrm{C(1'')}-$$

site with equal probabilities exists, the space group would be $Pbcm$-D_{2h}^{11}, which is different from the space group $P2cm$ proposed by Bachmann and Lando.[4]

The bond angles and internal rotation angles of model 3-1 are listed in Table V. The bond angle C(2)–C(1)–F(1) = 97.0° is smaller than the generally accepted value, while the bond angle C(2′)–C(1)–F(1) = 123.4° is larger. This may be attributed to the assumption adopted in the analysis that the molecules with different orientations assume the same molecular conformation. This assumption is not necessarily the case, since molecules with different orientations have different surroundings in the crystal lattice.

Short intermolecular distances were found between molecules with orientations A and Ā neighboring along the a axis. The intermolecular distances F(1)···F(1) and C(1)···F(1) between molecules with orientations AC and ĀC are 1.568 and 2.844 Å, respectively, and the distances F(1)···F(1) and C(1)···F(1) between molecules with orientations AC̄ and ĀC are 1.796 and 2.937 Å, respectively. These values are much less than the sums of the van der Waals radii. No short intermolecular distances were found between molecules neighboring in the other directions. This suggests that, on the c projection, both of the molecules with orientations A and Ā do not align in the a direction; i.e., only the molecule with the same orientation, either A or Ā, aligns regularly along the a axis and disorder occurs only along the b axis (Figure 5). This manner of packing disorder is very similar to that in *cis*-1,4-polyisoprene proposed by Natta and Carradini,[15] where the molecule aligns regularly in the b direction and disorder occurs only along the a axis. On the other hand, from the viewpoint of unequal existence probabilities, disorder in form II of poly(vinylidene fluoride) is similar to the statistical structure of polypropylene.[16,17] Furthermore, the disorder on the c projection was clarified to be the antiphase domain structure (Figure 6), which will be published soon.

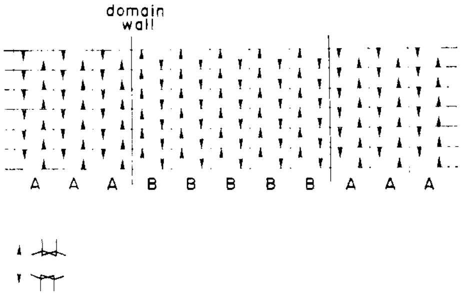


Figure 6. Antiphase domain structure on the c projection. The domain wall is the dislocation line, at which the origin of the unit cell is shifted by $1/2a$ and $1/2b$.

Acknowledgment. We thank Drs. M. Kusunoki and N. Yasuoka, Crystallographic Research Center, Institute for Protein Research, Osaka University, for their advice on the use of the drum scanner.

Registry No. Poly(vinylidene fluoride), 24937-79-9.

References and Notes

(1) Presented in part at the IUPAC International Symposium on Macromolecules, Amherst, MA., 1982.
(2) Hasegawa, R.; Takahashi, Y.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1972**, *3*, 600.
(3) Doll, W.; Lando, J. B. *J. Macromol. Sci., Phys.* **1970**, *B4*, 309
(4) Bachmann, M. A.; Lando, J. B. *Macromolecules* **1981**, *14*, 40.
(5) Takahashi, Y.; Kohyama, M.; Matsubara, Y.; Iwane, H.; Tadokoro, H. *Macromolecules* **1981**, 14, 1841.
(6) Takahashi, Y.; Kohyama, M.; Tadokoro, H. *Macromolecules* **1976**, *9*, 870.
(7) Takahashi, Y.; Tadokoro, H. *Macromolecules* **1980**, *13*, 1316.
(8) Takahashi, Y.; Tadokoro, H.; Odajima, A. *Macromolecules* **1980**, *13*, 1318.
(9) Takahashi, Y.; Matsubara, Y.; Tadokoro, H. *Macromolecules* **1982**, *15*, 334.
(10) Lovinger, A. J. *Macromolecules* **1982**, *15*, 40.
(11) Arnott, S.; Wonacott, A. J. *Polymer* **1966**, *7*, 157.
(12) Takahashi, Y.; Sato, T.; Tadokoro, H.; Tanaka, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 233.
(13) Hosemann, R.; Bagchi, S. N. "Direct Analysis of Diffraction by Matter"; North-Holland Publishing Co.: Amsterdam, 1962.
(14) Takahashi, Y.; Tadokoro, H, in press.
(15) Natta, G.; Corradini, P. *Angew. Chem.* **1956**, *68*, 615.
(16) Mencik, Z. *J. Macromol. Sci., Phys.* **1972**, *B6*, 101.
(17) Hikosaka, H.; Seto, T. *Polym. J.* **1973**, *5*, 111.