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Short-Range Order in Form II of Poly(vinylidene fluoride): Antiphase Domain Structures

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ABSTRACT: The crystal structure of form II of poly(vinylidene fluoride) was reported to include the disorder that four molecules with different orientation occupy a crystal site with different existence probabilities. In the present study, it is established that there exists a short-range order, antiphase domain structures, in the crystallite of form II. The antiphase domain structures on the c projection and for the up and down molecules explain the half-widths of two series of the reflections: 120, 130, 140, and 011, 021, 031, respectively. In the antiphase domain structure on the c projection, the size of a domain is much longer in the a direction than in the b direction, while, in the antiphase domain structure for the up and down molecules, the size of a domain in the a direction is considered to be comparable to that in the b direction. From the antiphase domain structures, it is concluded that the locally stable structure of form II is the antipolar and antiparallel structure.

In previous papers,[1-4] it was established that a conformational disorder, a kink band, exists in form I and streak II of poly(vinylidene fluoride), and it was reported that the conformational disorder plays an important role in the crystal phase transformation. On the other hand, it is also very interesting to clarify what kind of disorder with respect to the molecular packing exists in the crystalline region. In the preceding paper,[5] the crystal structure of form II was analyzed in detail. The analysis showed that four molecules with different orientation statistically coexist at a crystal site with different existence probabilities (Figure 1). Among two series of reflections $1k0$: 120, 130, 140, and $0k1$: 011, 021, 031, the superlattice spots with $h + k = 2n + 1$ were much broader than the reflections with $h + k = 2n$. This suggests that there exists a short-range order in the crystalline region. The purpose of the present study is to clarify what kind of short-range order exists in the crystalline region and what structure is locally stable in form II.

Experimental Section

The poly(vinylidene fluoride) sample used for this study is KF-1100 (Kureha Chemical Industry Co., Ltd.). A uniaxially oriented sample was prepared by stretching at 150 °C, followed by annealing at 175 °C for 24 h. X-ray measurements were made with Cu Kα radiation monochromatized by a graphite monochromator. Fiber photographs were taken in a He gas atomosphere with a cylindrical camera with a 5-cm radius. Intensity was digitally measured by a drum scanner (Optronics) installed in the Crystallographic Research Center of this University. The digital data were summed along each reflection arc after the density was converted to the intensity. The profiles of the reflections 120, 130, 011, 021, and 031 are plotted along the layer lines in Figure 2, where the reflections 021 and 031 are separated from the reflections 111 and 121 by assuming a Gaussian distribution, respectively.

Antiphase Domain Structure on the c Projection

From the crystal structure (Figure 1), the reflections with $h + k$ = odd for hkl correspond to the so-called "superlattice spots".[6] On the equator, the half-widths of the reflections 120, 130, and 140 are found to be broad, very sharp, and broad, respectively (Figure 2).[5] This relation in half-width cannot be interpreted by the anisotropy in the crystallite size and disorder of the second kind.[7] It should be rather considered that there exists a short-range order in packing of the molecules with different orientation A and $\bar{\mathrm{A}}$ (Figure 3) on the c projection. In comparison with reflections of other crystalline polymers, the reflections 120 and 140 are not so broad. This suggests that the short-range order on the c projection is very regular. Accordingly, a domain structure is reasonably considered for the short-range order. Furthermore, the intermolecular distance calculated for the crystal structure[5] requires that the molecules aligned along the a axis have the same orientation A or $\bar{\mathrm{A}}$. Accordingly, the size of a domain is considered to be very long in the a direction and could be assumed to be infinite in the a direction, while the size in

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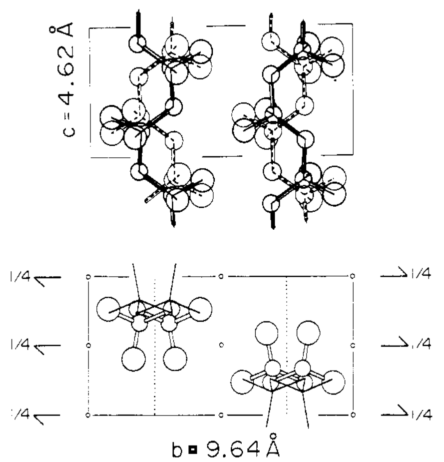

Figure 1. Crystal structure of form II of poly(vinylidene fluoride). In the sample prepared by annealing at 175 °C for 24 h, the existence probabilities of four molecules with different orientation AC, $A\bar{C}$, $\bar{A}C$, and $\bar{A}\bar{C}$ are 54, 29, 10, and 7%, respectively.

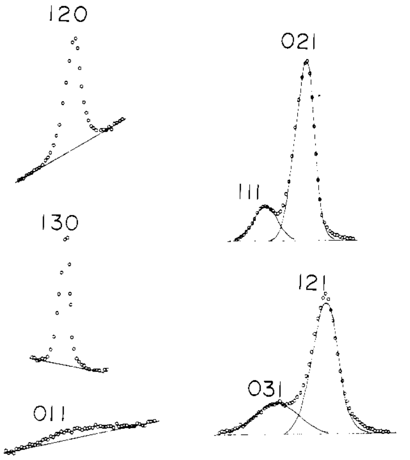

Figure 2. Profiles of the reflections 120, 130, 011, 021, and 031.

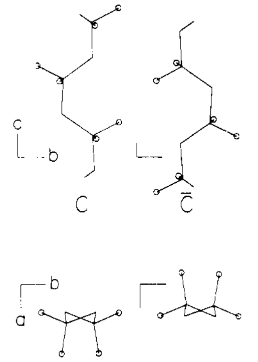

Figure 3. Molecular orientation at a crystal site. (a), (b), (c), and (d) are denoted by the symbols A, $\bar{A}$, C, and $\bar{C}$, respectively. Combinations of the symbols, AC, $A\bar{C}$, $\bar{A}C$, or $\bar{A}\bar{C}$, define the orientation of the molecule.

the b direction is relatively small, and therefore, in reciprocal space, the reflections are considered to be broad or streaky in the direction parallel to the b^* axis. The manner that the reflection sphere crosses the reflection spots 120, 130, and 140 is consistent with the observed half-widths (Figure 4).

By taking the above-mentioned facts into account, two domain models, the antiphase domain and polar domain models (Figure 5), could be considered. These models are composed of four kinds of unit structures, A, B, C, and D (Figure 5), whose width is the unit cell parameter b = 9.64 Å and whose length along the a axis is infinite. The antiphase domain model is constructed by two kinds of domains that are of the sequence of the unit structures A and B, respectively. Two kinds of domains have the same antipolar structure, but the origins of the lattices are shifted by $a/2$ and $b/2$ to each other. The polar domain model is constructed by three kinds of domains that are of the sequences of A, of C, and of D, respectively. A domain of the unit structure A assumes the antipolar structure, while two kinds of domains of C and D assume the same polar structure as polar II[8-11] but differ in the orientation. Here, it should be noted that a model cannot be built only by domains of C and D having the polar structure because it cannot explain the existence probabilities of the molecules with different orientation.

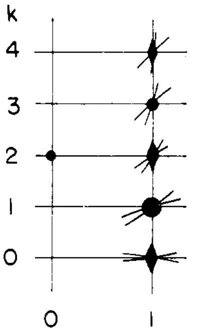

Figure 4. Shapes of a series of the reflections 1k0 in reciprocal space. Arcs show the reflection sphere crossing the reflections.

The intensity equation for the stacking faults derived by Kakinoki and Komura[12,13] was applied to the intensity distribution calculation. The scattering intensity by a stack of $2N + 1$ layer structures of n kinds is given by

$$I = N\mathbf{V}\mathbf{F}\tilde{\mathbf{V}}^* + \sum_{m=1}^{N-1}(N-m)\mathbf{V}\mathbf{F}\mathbf{Q}^m\tilde{\mathbf{V}}^* + \text{conj} \qquad (1)$$

$$\mathbf{V} = [V_1, V_2, \ldots, V_n]$$

$$\mathbf{F} = \begin{bmatrix} F_1, & 0 & \ldots, & 0 \\ 0, & F_2, & \ldots, & 0 \\ \vdots & \vdots & & \vdots \\ 0, & 0, & \ldots, & F_n \end{bmatrix}$$

$$\mathbf{Q} = \Phi\mathbf{P} = \begin{bmatrix} e^{-i\phi_1}, & 0, & \ldots, & 0 \\ 0, & e^{-i\phi_2}, & \ldots, & 0 \\ \vdots & \vdots & & \vdots \\ 0, & 0, & \ldots, & e^{-i\phi_n} \end{bmatrix}$$

$$\mathbf{P} = \begin{bmatrix} P_{11}, & P_{12}, & \ldots, & P_{1n} \\ P_{21}, & P_{22}, & \ldots, & P_{2n} \\ \vdots & \vdots & & \vdots \\ P_{n1}, & P_{n2}, & \ldots, & P_{nn} \end{bmatrix}$$

where $\tilde{\mathbf{V}}$ is the transpose of the vector $\mathbf{V}$, $\mathbf{V}^*$ is the complex conjugate of $\mathbf{V}$, conj is the complex conjugate of the preceding term, V_j is the structure factor of the layer j, F_j is the existence probability of the layer j, ϕ_j is the phase shift due to the thickness of the layer j, and P_{ij} is the probability of finding the layer j after the layer i. The following relations exist among the parameters F_j and P_{ij}:

$$\sum_j^n F_j = 1 \qquad (2)$$

$$\sum_j^n P_{ij} = 1 \qquad (3)$$

$$\sum_i^n F_i P_{ij} = F_j \qquad (4)$$

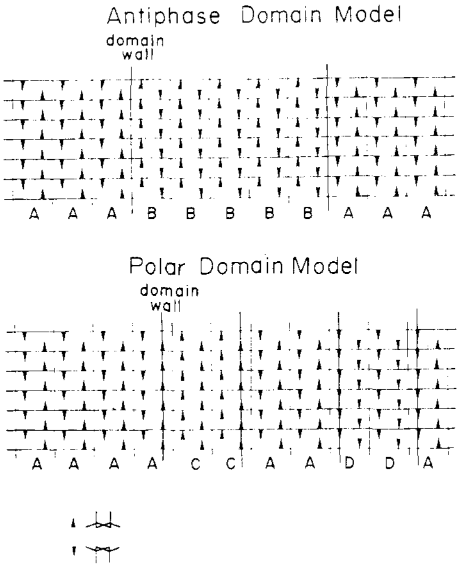

Figure 5. Antiphase domain model and polar domain model on the *c* projection. A, B, C, and D denote the unit structures constructing the models.

By diagonalizing the **Q** matrix, one can obtain the following equation:

$$I = N\mathbf{V}\mathbf{F}\tilde{\mathbf{V}}^* + \sum_{m=1}^{N-1}(N-m)\mathbf{V}\mathbf{F}\mathbf{O}^{-1}\mathbf{Q}_0^m\mathbf{O}\tilde{\mathbf{V}}^* + \text{conj}$$

$$= N\mathbf{A}\tilde{\mathbf{B}} + \sum_{m=1}^{N-1}(N-m)\mathbf{A}\mathbf{Q}_0^m\tilde{\mathbf{B}} + \text{conj} \qquad (5)$$

$$\mathbf{O}\mathbf{Q}\mathbf{O}^{-1} = \mathbf{Q}_0$$

$$\mathbf{Q} = \mathbf{O}^{-1}\mathbf{Q}_0\mathbf{O}$$

$$\mathbf{Q}_0 = \begin{bmatrix} \lambda_1, & 0, & \ldots, & 0 \\ 0, & \lambda_2, & \ldots, & 0 \\ \vdots & \vdots & & \vdots \\ 0, & 0, & \ldots, & \lambda_n \end{bmatrix}$$

$$\mathbf{A} = \mathbf{V}\mathbf{F}\mathbf{O}^{-1} = [a_1, \quad a_2, \quad \ldots, \quad a_n]$$

$$\mathbf{B} = \mathbf{V}^*\mathbf{O} = [b_1, \quad b_2, \quad \ldots, \quad b_n]$$

The intensity I can be separated into two terms, I_1 for $|\lambda_j| = 1$ and I_2 for $|\lambda_j| \neq 1$.

$$I = I_1 + I_2 \qquad (6)$$

$$I_1 = N \sum_{\substack{j \\ |\lambda_j|=1}} a_j b_j + \sum_{m=1}^{N-1}(N-m) \sum_{\substack{j \\ |\lambda_j|=1}} a_j b_j \exp(-im\alpha_j) + \text{conj} = \sum_{\substack{j \\ |\lambda_j|=1}} a_j b_j \sum_{m=-(N-1)}^{N-1} (N-|m|) \exp(-im\alpha_j) \qquad (7)$$

where

$$\lambda_j = |\lambda_j| \exp(-i\alpha_j) = \exp(-i\alpha_j)$$

The summation with respect to m in eq 7 is the Laue function, which is approximated by the delta function. The term I_2 is given by

$$I_2 = N \sum_{\substack{j \\ |\lambda_j|\neq 1}} a_j b_j + \sum_{\substack{j \\ |\lambda_j|\neq 1}} a_j b_j \left[\frac{(N-1)\lambda_j}{1-\lambda_j} - \frac{\lambda_j(\lambda_j - \lambda_j^N)}{(1-\lambda_j)^2} \right] + \text{conj}$$

When $N \rightarrow \infty$

$$I_2/N = \sum_{\substack{j \\ |\lambda_j|\neq 1}} a_j b_j + \sum_{\substack{j \\ |\lambda_j|\neq 1}} a_j b_j \frac{\lambda_j}{1-\lambda_j} + \text{conj} \qquad (8)$$

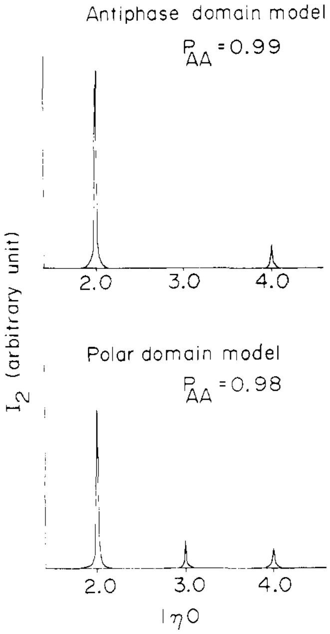

Figure 6. Intensity distributions I_2/N along 1η0 for the antiphase domain model and the polar domain model.

The antiphase domain model is composed of unit structures A and B. Accordingly, the orders of the matrices **F**, **P**, and **Q** are 2. From the crystal structure analysis,[5] $F_A = 0.84$ and $F_B = 0.16$ were adopted for the diagonal elements of the **F** matrix, which correspond to the values calculated by using the following relations:

$$F_A = w_{AC} + w_{A\bar{C}}$$

$$F_B = w_{\bar{A}C} + w_{\bar{A}\bar{C}}$$

where w_{AC}, $w_{A\bar{C}}$, $w_{\bar{A}C}$, and $w_{\bar{A}\bar{C}}$ are the existence probabilities of the molecules with orientation AC, A$\bar{C}$, $\bar{A}$C, and $\bar{A}\bar{C}$, respectively (Figure 3). The number of variable parameters reduce to one by using relations 2–4. In the polar domain model, which consists of unit structures A, C, and D, unit structure C is considered to have the same surroundings as unit structure D, since external forces do not act. Therefore, the following relations were reasonably assumed:

$$F_C = F_D$$

$$P_{CC} = P_{DD}$$

$$P_{AC} = P_{AD}$$

$$P_{CA} = P_{DA}$$

Furthermore, the relation $P_{CD} = P_{DC} = 0$ was assumed, because the polar structure is a stable structure. From the crystal structure analysis,[5] $F_A = 0.68$, $F_C = 0.16$, and $F_D = 0.16$ were adopted, which correspond to the values calculated by using the relation

$$F_C = F_D = w_{\bar{A}C} + w_{\bar{A}\bar{C}}$$

In both models, the diagonalization of the **Q** matrices gave a solution with $|\lambda| = 1$. Therefore, the intensity distribution I_2/N was calculated by using eq 8.

The calculated intensity distributions for the antiphase domain model with $P_{AA} = 0.99$ and the polar domain model with $P_{AA} = 0.98$ are shown along the line 1η0 in Figure 6. The intensity distribution gives sharp peaks at the point with η = integer where the Laue term I_1 should appear. The profile of the sharp peak depends on the value P_{AA}. The P_{AA} dependence of the peak profile around 120 for the antiphase domain model is shown in Figure 7. The

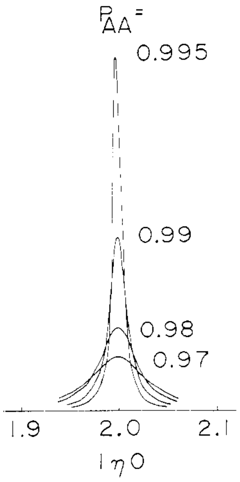

Figure 7. Peak profile at 120 for the antiphase domain model.

actual intensity distribution, which should be compared with the fiber diffraction pattern, should be composed of the calculated intensity distribution I_2/N and the Laue term I_1 for $|\lambda| = 1$. Accordingly, the sharp peak on the calculated intensity distribution is considered to be the origin, which makes the Laue spot broad. On the intensity distribution for the antiphase domain model, the peaks appear at 120 and 140 but not at 130. This suggests that the reflections 120 and 140 are broadened by the peaks, while the 130 reflection remains very sharp because it is only of the Laue spot. This is consistent with the observed relation in half-width: 120, broad; 130, sharp; and 140, broad (Figure 2). On the other hand, on the intensity distribution for the polar domain model, the peaks that would broaden the reflection appear at 120, 130, and 140. This is inconsistent with the observed half-widths.

Antiphase Domain Structure for the Up and Down Molecules

On the first layer line, the series of reflections 011, 021, and 031 is observed to be broad, sharp, and broad, respectively (Figure 2). The $0kl$ reflections reflect the structure on the a projection, i.e., the disorder between the up and down molecules (Figure 1). In fact, from the fact that the 011 and 031 reflections are broad and weak, the disorder between the up and down molecules was taken into the structure analysis.[5] Furthermore, it was reported that the intensities of 011 and 031 depend on the temperature,[14] on the annealing temperature,[15,16] and on the elongation temperature.[15]

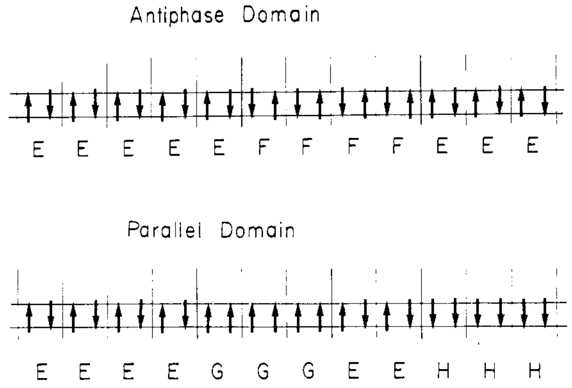

Figure 8. Antiphase domain model and parallel domain model on the bc plane. The direction of the arrow denotes the up or down molecule. E, F, G, and H denote the unit structures constructing the models.

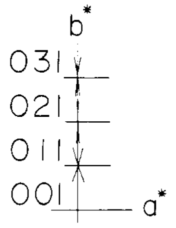

Figure 9. Manner in which the reflection sphere crosses a series of reflections $0k1$.

The relation in half-width among the series of reflections 011, 021, and 031 is also considered to be attributable to the domain structure. The intermolecular distance calculation did not give any limitations for the pakcing of the up and down molecules, differing from the antiphase domain structure on the c projection. Accordingly, the size of a domain in the a direction is predicted to be comparable to the size in the b direction. This may be supported by the fact that the half-widths of the 011, 021, and 031 reflections are much broader than the reflections on the equator and the fact that the temperature dependences of the reflection intensities of 120 and 031 are different from each other.[14] In the present study, the intensity distribution calculation was made for the layer structure that has the thickness a = 4.96 Å and an infinite size in the b and c direction (Figure 8). The calculation for the layer structure gives only the intensity distribution along the line $0\eta 1$. However, from the manner that the reflection sphere crosses the reflections 011, 021, and 031 (Figure 9), the intensity distribution along $0\eta 1$ is considered to be able to be compared with the observed intensity distribution on the fiber diagram. Two kinds of domain models, the antiphase domain model and parallel domain model, can be considered for the layer structure (Figure 8). These models are constructed by stacking of four kinds of unit structures, E, F, G, and H (Figure 8). In the antiphase domain model, two kinds of domains, which are of the unit structure E and of F, respectively, have the same antiparallel structure but the origins of the lattices are shifted by $b/2$ to each other. The parallel domain model is constructed by three kinds of domains that are of E, of G, and of H, respectively. Two kinds of domains that are of G and of H, respectively, have the same parallel structure but differ in polarity. In the antiphase domain model, F_E = 0.64 and F_F = 0.36 were adopted for the diagonal elements of the **F** matrix, using the following relations:

$$F_E = w_{AC} + w_{\bar{A}C}$$

$$F_F = w_{A\bar{C}} + w_{\bar{A}\bar{C}}$$

In the parallel domain model, the following relations among the parameters were assumed in the same way as in the polar domain model on the c projection:

$$F_G = F_H$$

$$P_{GG} = P_{HH}$$

$$P_{EG} = P_{EH}$$

$$P_{GE} = P_{HE}$$

$$P_{GH} = P_{HG} = 0$$

For the diagonal elements of the **F** matrix, F_E = 0.28, F_G = 0.36, and F_H = 0.36 were adopted, using the following relation:

$$F_G = F_H = w_{A\bar{C}} + w_{\bar{A}\bar{C}}$$

Diagonalization of the **P** matrices for both models gave a solution with $|\lambda| = 1$. Therefore, the intensity distribution calculation was made by using eq 8. The calculated intensity distributions for the antiphase domain with P_{EE}

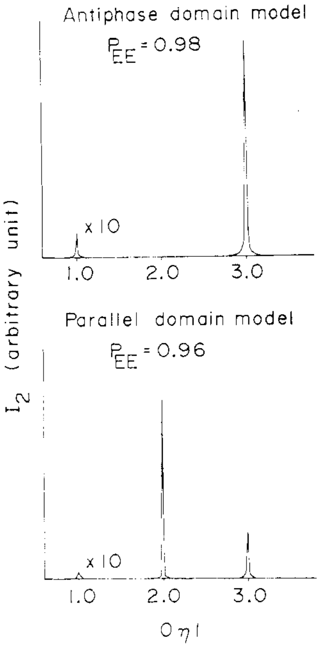

Figure 10. Intensity distributions I_2/N along 0η1 for the antiphase domain model and the parallel domain model for the up and down molecules.

= 0.98 and for the parallel domain model with P_{EE} = 0.96 are shown in Figure 10. The antiphase domain model gives sharp peaks at 011 and 031 but it does not gave a peak at 021. On the other hand, the parallel domain model gives peaks at 011, 021, and 031. Since the peak apparently makes the reflection broad, the calculated intensity distribution for the antiphase domain model is consistent with the observed relation among the half-widths: 011, broad; 021, sharp; and 031, broad (Figure 2).

Discussion

In the previous paper,[5] by crystal structure analysis, form II of poly(vinylidene fluoride) was reported to have a disordered structure with the long-range order that four molecules with different orientation occupy a crystal site with different existence probabilities. In the present study, from the half-widths of the series of three reflections, it was clarified that the disordered structure has a short-range order: the antiphase domain structures on the *c* projection and for the up and down molecules. From the antiphase domain structures, it is concluded that the locally stable structure in form II is the antipolar and antiparallel structure, which essentially coincides with the crystal structure reported in 1972.[17] In the antiphase domain structure on the *c* projection, the size of a domain in the *a* direction is considered to be much longer than that in the *b* direction, judging from the intermolecular distance calculation.[5] On the other hand, in the antiphase domain structure for the up and down molecules, the domain size in the *a* direction is considered to be comparable to that in the *b* direction, judging from the fact that the intermolecular distance calculation did not give any limitations to the packing of the up and down molecules.[5] This may be supported by the fact that the series of reflections 0*k*1 are broader than the reflections 1*k*0. In Figure 11, the antiphase domain structure for the up and down molecules is schematically shown. From the temperature dependence of the long-range order parameters,[14] $S_A = 2w_A - 1$ and $S_C = 2w_C - 1$, two antiphase domain structures are considered to behave almost independently and to be little correlated with each other.

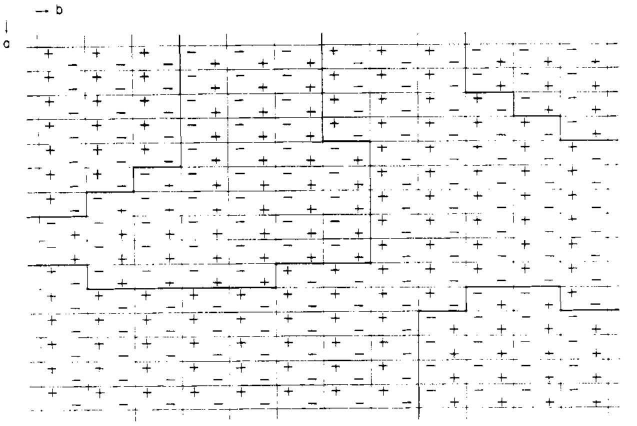

Figure 11. Schematic representation for the antiphase domain structure for the up and down molecules on the *c* projection. "+" and "–" denote the up and down molecules, respectively.

The antiphase domain structures are predicted to influence the physical properties of the crystalline region of form II. For example, there exists much difference between the observed and calculated linear compressibilities.[18,19] This might be attributed to the antiphase domain structures.

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

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