A Reexamination of the Crystal Structure of Phase II of Poly(vinylidene fluoride)

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ABSTRACT: The crystal structure of phase II (α phase) of poly(vinylidene fluoride) was studied by reexamining the work of earlier investigators. The reflections of phase II can be indexed to an orthorhombic unit cell with lattice parameters $a = 0.496$ nm, $b = 0.964$ nm, and c (chain axis) $= 0.462$ nm. There are two chains in this unit cell. The two chains pack with the chain dipole moments antiparallel. Three different ways of packing the chains, with respect to chain sense, were studied: both chains up, one up and one down, and a statistical up–down packing. It was found that to within a 96% confidence level, the chains pack with a statistical up–down packing.

Introduction

A great deal of work has been done in the past on elucidating the crystal structure of poly(vinylidene fluoride). The early X-ray diffraction[1] studies showed that at least two crystalline phases exist. Later X-ray diffraction studies[2-5] and IR studies[6,7] confirmed the existence of two crystal forms, designated as phase I and II or β and α phases, respectively. Phase I was found to have a planar zigzag chain conformation because that was the only conformation which would satisfy the observed 0.256-nm repeat distance. The chain conformation of phase II was postulated to be either a 2_1 helix or trans–gauche–trans–minus gauche (TGTG′). Normal-coordinate calculations[8,9] along with conformational analysis and factor group analysis[10] indicated that the chain conformation was approximately TGTG′, rather than a 2_1 helix. The crystal structure of phase II has subsequently been attempted by using a TGTG′ chain conformation by two groups: Doll and Lando[11] and Hasegawa et al.[12] The structures reported by Doll and Lando[11] and Hasegawa et al.[12] differ slightly with respect to both the chain conformation and packing of the chains. This difference in the two reported structures is postulated[13] to be due to the different amounts of head-to-head followed by tail-to-tail units in the polymer samples used by the two groups.

It has been found that for phase III[14] (γ phase) and phase IV[15] (polar α phase) of PVF$_2$, a statistical up–down model of the chain packing applies to both crystal structures. Phase III can be produced directly from phase II by annealing at high temperature and pressure[16] or by various atmospheric-pressure thermal treatments[17-19] of phase II. Phase IV is produced directly from phase II by applying large electric fields to phase II.[15,20-22] Thus, since phase III and phase IV are found to have statistically packed up–down chains and since both can be produced directly from phase II material, the possibility exists that the chains in the phase II unit cell are statistically packed. The X-ray data and proposed structures of Doll and Lando[11] and Hasegawa et al.[12] have been reexamined in order to test the hypothesis that the chains in the phase II unit cell are statistically packed.

Calculations

The computer program used for this reinvestigation of the crystal structure of phase II was LALS (linked-atom least squares) Mark Six of Smith and Arnott.[23] The LALS program only utilizes reflections with d spacings greater than 0.125 nm; hence all results reported in this paper are for data for which $d > 0.125$ nm. As with most least-squares refinement programs, LALS refines parameters by minimizing the "weighted" residual (R_w)

$$R_w = \left[\frac{\sum_i w_i(|F_o|_i - |F_c|_i)^2}{\sum_i w_i |F_o|_i^2} \right]^{1/2}$$

as opposed to the "normal" residual (R_N) which is usually reported

$$R_N = \frac{\sum_i w_i^{1/2} ||F_o|_i - |F_c|_i|}{\sum_i w_i^{1/2} |F_o|_i}$$

All results of calculations reported in this work will be for a minimization of R_w, with the weighting factor $w_i = 1.0$.

Reflections which are not systematically absent and are too weak to be observed on the diffraction photograph are labeled as unobserved data. Structure factors for all of the unobserved data of Doll and Lando[11] and Hasegawa et al.[12] were calculated but were not used directly in any refinement process. These unobserved structure factors were calculated so that they may be compared with an estimation of the threshold structure factors for these reflections. The threshold intensity was estimated to be $^1/_2 I_0$ of the weakest reflection observed, while taking the Lorentz–polarization correction into account.

Because of the round-off error in the reported values of atomic positions of Doll and Lando,[11] the internal rotation angles around the C–C bonds were changed slightly to 58° so that the model chain would have the observed repeat distance of 0.462 nm. All of the other chain parameters, bond lengths, bond angles, and internal rotation angles involving H–C and F–C bonds were preserved when the chains of Doll and Lando[11] and Hasegawa et al.[12] were duplicated for use in this investigation.

One significant difference between the previous[11,12] investigations and the present work involves the Debye–Waller (temperature) factor. In this work we used a single isotropic Debye–Waller factor for every atom in the chain, whereas Hasegawa et al.[12] used individual isotropic Debye–Waller factors for each atom in the monomer unit of the phase II chain. The use of a single isotropic Debye–Waller factor proved to be sufficient. This is demonstrated by comparing the residuals for the proposed model of phase II calculated by Hasegawa et al.[12] ($R_w = 0.206$, $R_N = 0.170$) and the residuals for the proposed model[12] using

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a single isotropic Debye–Waller factor (B = 0.052 nm^2) (R_w = 0.204, R_N = 0.185). Doll and Lando[11] used a single isotropic Debye–Waller factor, which was determined from a Wilson plot,[24] for data taken at 20 °C (B = 0.036 nm^2) and for data taken at −145 °C (B = 0.022 nm^2). The Debye–Waller factors used in this work have been determined by considering B as a refinable parameter. When considering the chains packed in the monoclinic unit cell of Doll and Lando[11] (20 °C data), B is refined to 0.051 nm^2 with the residuals being R_w = 0.226 and R_N = 0.198 as opposed to the residuals of Doll and Lando[11] with B = 0.036 nm^2: R_w = 0.277 and R_N = 0.233. When considering the chains packed in the triclinic unit cell of Doll and Lando[11] (20 °C data), B is refined to 0.045 nm^2 with the residuals being R_w = 0.201 and R_N = 0.182 as opposed to the residuals of Doll and Lando[11] with B = 0.036 nm^2: R_w = 0.257 and R_N = 0.218.

Hasegawa et al.[12] chose to pack the two chains in the unit cell such that the glide planes of the two chains were parallel, with the two chain dipole moments (in an ab projection) being antiparallel. The unit cell dimensions used were a = 0.496 nm, b = 0.964 nm, and c (chain axis) = 0.462 nm. Doll and Lando[11] packed the two chains in the unit cell such that the two chains are rotated about their axes in opposite directions from the chain positioning of Hasegawa et al.[12] described above by approximately 7°. The unit cell dimensions used were a = 0.502 nm, b = 0.963 nm, and c (chain axis) = 0.462 nm. These two types of chain packing will be distinguished by giving the chain rotation angle ϕ, defined by Doll and Lando.[11] The unrotated chains of Hasegawa et al.[12] will be designated by ϕ = 0°. The rotated chains of Doll and Lando[11] will be designated by ϕ = 7°.

The TGTG′ chain conformation of phase II possesses a chain dipole moment with components both perpendicular and parallel to the chain axis. The parallel component of the dipole moment gives the phase II chain a sense. In this work we have extended the calculations of Doll and Lando[11] and Hasegawa et al.[12] by considering three models of chain packing with respect to chain sense, for both unrotated (ϕ = 0°) and rotated (ϕ = 7°) chains. The up–up (or down–down) model has two chains in the unit cell packed parallel to one another. The up–down (or down–up) model has two chains in the unit cell packed antiparallel to one another. The third model considered was the statistical up–down model. This unit cell is modeled such that it contains four chains: two up chains and two down chains, each assigned an occupancy of 0.5. An up–down pair of chains is placed at each of the two positions in the unit cell such that the glide planes of each individual chain superimpose. This means that the two chains at each of the two positions in the unit cell are indistinguishable in an ab projection. The statistical up–down model allows the two chains in any given unit cell of the crystallite to be either up–up (or down–down) or up–down (or down–up), all with equal probability.

Discussion

As pointed out in the Introduction, Doll and Lando[11] and Hasegawa et al.[12] have both performed crystal structure determinations of phase II by utilizing the approximate chain conformation TGTG′, after rejecting a 2_1 helix as the chain conformation. In this section we will describe the calculations of Doll and Lando[11] and Hasegawa et al.[12] and will compare the two proposed structures.

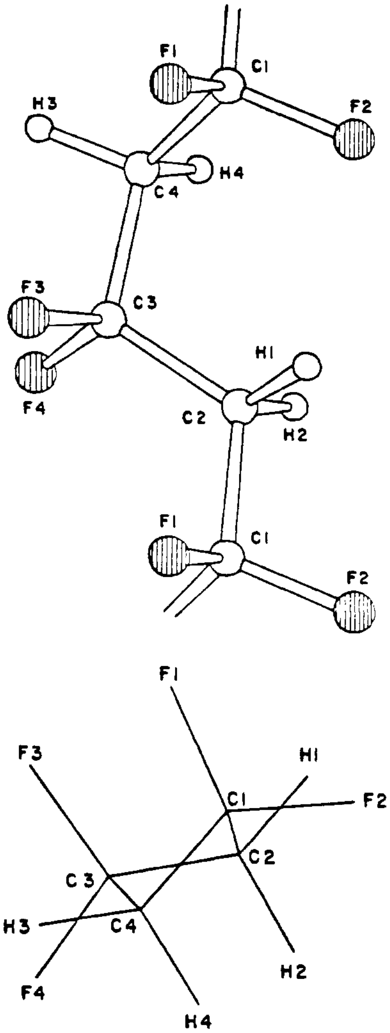

Figure 1. Single chain of PVF$_2$ phase II with the approximate chain conformation TGTG′, showing the labeling of the atoms.

Doll and Lando[11] utilized a chain which has internal rotation angles of 180° for trans and 58° for gauche for their crystal structure analysis. All of the CCC bond angles are assumed equal and must be 115.9% in order for the chain to fit the repeat distance of 0.462 nm for the internal rotation angles used. This chain conformation has one H–F bad contact (contacts are defined as nonbonded interatomic distances which are less than the sum of the van der Waals radii of the atoms) of 0.217 nm, which is approximately 0.038 nm less than the sum of the van der Waals radii of the hydrogen (~0.12 nm) and fluorine (~0.135 nm) atoms. There is also an F–F contact of 0.256 nm, which is approximately 0.014 nm less than the sum of the van der Waals radii of the two fluorine atoms. Figure 1 shows an isolated chain of PVF$_2$ with the chain conformation being approximately TGTG′. The atoms are labeled in Figure 1 for future reference. All of the bond distances, bond angles, internal rotation angles, and contacts for the chain conformation utilized by Doll and Lando[11] are listed in Table I. The two chains in the unit cell have been packed with ϕ = 7°. Two models of chain packing, with respect to chain sense, were investigated. One was the chains packed in an up–down (antiparallel) sense. This results in a monoclinic unit cell with β = 90°, with the space group being $P2_1$. The second packing model was with the chains packed in an up–up (parallel) sense. This results in a triclinic unit cell with all angles being 90° and the space group being $P1$. Figure 2 illustrates these two models of Doll and Lando.[11] The relative chain shifts are those refined by utilizing the LALS[23] program. Doll and Lando[11] concluded that the chains in phase II may pack either with the monoclinic symmetry (up–down chains) or with the triclinic symmetry (up–up chains) because of the

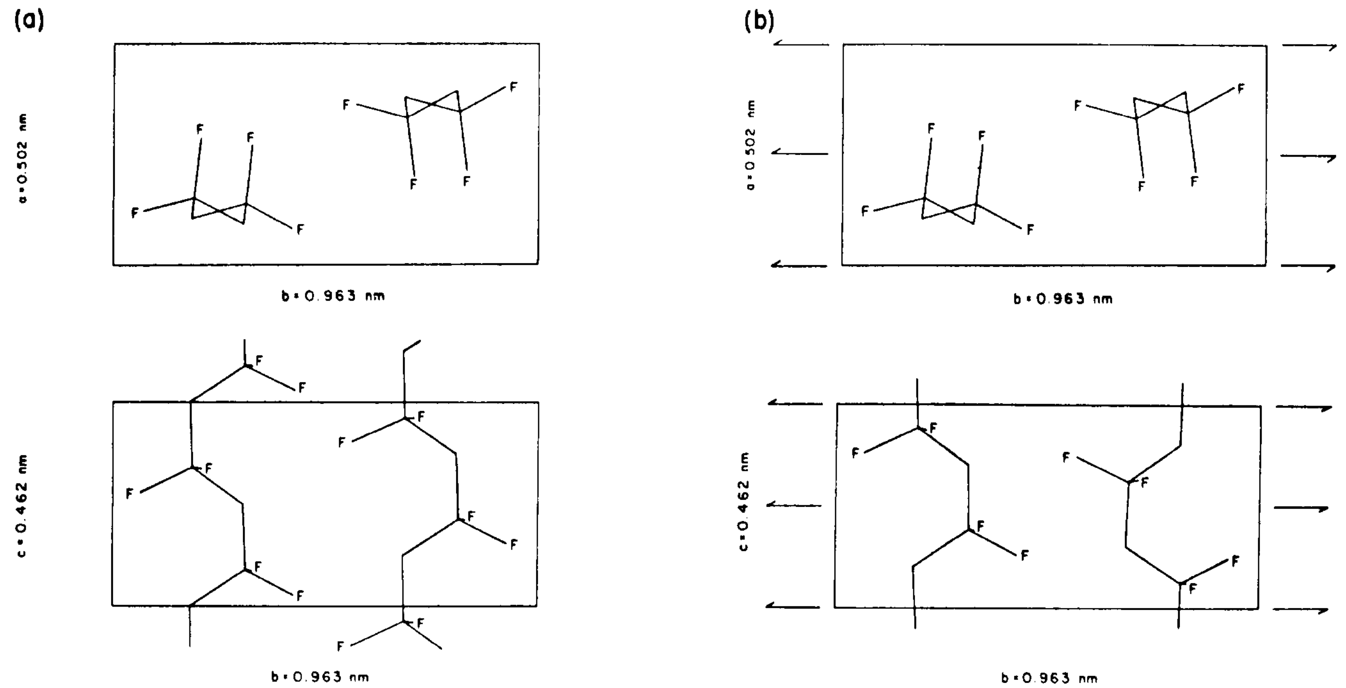

Figure 2. Chain packing of phase II with $G = 58°$, $\phi = 7°$ for (a) up-up packing ($P1$ space group) and (b) up-down packing ($P2_1$ space group).

Table I
Molecular Dimensions of Phase II of PVF$_2$ for a Chain with the Gauche Angle $G = 58°$

	Bond Lengths (nm)		
C-C	0.154	C-H	0.107
C-F	0.134		
	Contacts (nm)		
F3-H1	0.250	H1-F2	0.253
F2'-H1	0.217	F3-F1	0.256
	Bond Angles (Deg)		
C4-C3-C2[a]	115.9	H2-C2-C3	108.0
C3-C2-C1	115.9	H1-C2-C3	108.1
F3-C3-C4	107.9	F1-C1-F2	109.4
F4-C3-C4	108.0	H1-C2-H2	108.9
	Internal Rotation Angles (Deg)		
C4-C1-C2-C3	57.6	F2-C1-C2-C3	-177.2
C1-C2-C3-C4	108.0	F4-C3-C4-C1	177.2
C2-C3-C4-C1	-57.6	H2-C2-C3-C4	-58.9
C3-C4-C1-C2	180.0	H4-C4-C1-C2	58.9
F1-C1-C2-C3	-59.0	H1-C2-C3-C4	58.8
F3-C3-C4-C1	59.0	H3-C4-C1-C2	-58.8

[a] Atoms are labeled in Figure 1.

Table II
Molecular Dimensions of Phase II of PVF$_2$ for a Chain with the Gauche Angle $G = 45°$

	Bond Lengths (nm)		
C-C	0.154	C-H	0.109
C-F	0.134		
	Contacts (nm)		
F3-H1	0.244	H1-F2	0.251
F2'-H1	0.237	F1'-H1	0.236
	Bond Angles (Deg)		
C4-C3-C2[a]	118.4	H2-C2-C3	107.7
C3-C2-C1	116.5	H1-C2-C3	110.7
F3-C3-C4	109.9	F1-C1-F2	103.3
F4-C3-C4	109.5	H1-C2-H2	115.8
	Internal Rotation Angles (Deg)		
C4-C1-C2-C3	45.2	F2-C1-C2-C3	175.5
C1-C2-C3-C4	-179.1	F4-C3-C4-C1	-175.5
C2-C3-C4-C1	-45.2	H2-C2-C3-C4	-58.2
C3-C4-C1-C2	179.1	H4-C4-C1-C2	58.2
F1-C1-C2-C3	-71.7	H1-C2-C3-C4	69.3
F3-C3-C4-C1	71.7	H3-C4-C1-C2	-69.3

[a] Atoms are labeled in Figure 1.

similarity in the residuals; however, the monoclinic space group was considered more acceptable because the two chains in the unit cell are related by symmetry.

Hasegawa et al.[12] utilized a chain for their crystal structure analysis which has internal rotation angles of 179° for trans and 45° for gauche. The gauche angle is extremely small compared to the exact gauche (60%) angle. The small gauche angles require the chain to be slightly extended in order to fit the repeat distance of 0.462 nm. The CCC angles for this extended chain are 118.5° when the vertex carbon atom has fluorine pendants and 116.5° when the vertex carbon atom has hydrogen pendants. This chain conformation has several poor H-F contacts, the worst being 0.236 nm, which is approximately 0.019 nm less than the sum of the van der Waals radii of the hydrogen and fluorine atoms. There are no poor F-F contacts with this chain conformation. Table II lists all of the bond distances, bond angles, internal rotation angles, and contacts for the chain conformation utilized by Hasegawa et al.[12] The two chains in the unit cell have been packed with $\phi = 0°$. Only one model of chain packing, with respect to chain sense, was investigated by Hasegawa et al.[12] The model chosen was one in which the chains are packed in an up-down (antiparallel) sense and is illustrated in Figure 3. This chain packing results in a monoclinic unit cell with $\beta = 90°$, the space group being $P2_1/c$. The relative chain shift is that refined by the LALS[23] program.

The postulated source of the differences between the two structures reported by Doll and Lando[11] and Hasegawa et al.[12] is the difference in the amount of head-to-head followed by tail-to-tail (HHTT) units in the polymers used by the two groups.[13] The samples used by Doll and Lando[11] were commercial grade Kynar (Pennwalt Chemicals Co.) which are found by NMR to contain 5-6% HHTT defects.[25,26] The samples used by Hasegawa et al.[16] were supplied by Kureha Chemical Industry Co., Ltd., and were

Table III
Comparison of Chain Potential Energy (in kcal/mol) for the Structures of Doll and Lando[11] and Hasegawa et al.[12]

	without HHTT[a] defects				with 5% HHTT defects			
	intramolecular	strain	intermolecular	total	intramolecular	strain	intermolecular	total
Doll and Lando								
monoclinic	−21.6	0	−57.7	−79.3	−19.5	0	−56.5	−76.0
triclinic	−21.6	0	−63.9	−85.5	−19.5	0	−56.9	−76.4
Hasegawa et al.								
monoclinic	−27.0	1.8	−52.0	−77.2	−25.2	1.8	−49.8	−73.2

[a] HHTT = head-to-head followed by tail-to-tail defect units.

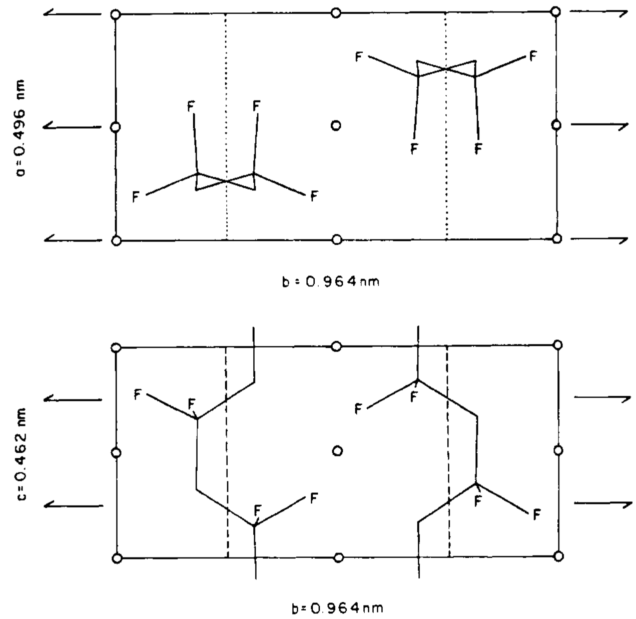

Figure 3. Chain packing of phase II with $G = 45°$, $\phi = 0°$ for up-down packing ($P2_1/c$ space group).

found by NMR to contain less than 5% HHTT defects. Potential energy calculations were carried out by Farmer et al.[13] to determine the effect of HHTT units on the chain packing and chain conformation of phase II. The potential energy calculations on an isolated chain with chain conformation TATB (A = −B) as a function of the angle A and percent concentration of HHTT defects show a minimum in potential energy for $A = 30°$ for 0% HHTT through 5% HHTT defects. A plateau in the potential energy vs. A develops for $A = 60°$ at 5% HHTT defect content, but this plateau is higher in energy than for $A = 30°$. An estimation of the strain energy to extend the CCC angles, which is necessary for the smaller internal rotation angle, must also be considered in these calculations. These isolated-chain calculations[13] indicate that the chain conformation used by Hasegawa et al.[12] ($A = 45°$) may be lower in energy than the chain used by Doll and Lando[11] ($A = 58°$) for all concentrations of HHTT defects from 0 to 5%. This might be expected if one considers only the contacts involved in the two chain conformations. The H–F and F–F contacts in the $A = 58°$ chain conformation are relieved by slightly increasing the CCC angles and changing A to 45°. The potential energy calculations[13] taking the intermolecular interactions into account along with the intramolecular (isolated chain) interactions are summarized in Table III. The numbers presented for the Doll and Lando[11] model are for chains packed with $\phi = 7°$ and with the chain conformation for which the gauche angle is taken to be 60°. The numbers presented for the Hasegawa et al.[12] model are for chains packed with $\phi = 0°$ and with the chain conformation for which the gauche angle is taken to be 45°.

Table IV
Effect of Chain Conformation and Packing on the Zero Layer Line Residual

	F_o of Doll and Lando[11]			F_o of Hasegawa et al.[12]		
	$G =$ 58° $\phi = 0°$	$G =$ 58° $\phi = 7°$	$G =$ 45° $\phi = 0°$	$G =$ 58° $\phi = 0°$	$G =$ 58° $\phi = 7°$	$G =$ 45° $\phi = 0°$
R_w	0.235	0.176	0.182	0.212	0.174	0.140
R_N	0.229	0.166	0.148	0.211	0.162	0.128

The total energy for the conformation and packing used by Hasegawa et al.[12] must lie somewhere between −77.2 kcal/mol (for 0% HHTT) and −73.2 kcal/mol (for 5% HHTT). The lowest HHTT content which could be expected for PVF_2, either by using a modified Ziegler–Natta catalyst[25] or by radiation polymerization,[26] is approximately 3%. Hence the lowest total energy for the Hasegawa et al.[12] model which might be expected (from linear interpolation) is −74.8 kcal/mol. The small difference in energy between the two proposed models does not allow one to make an unambiguous statement about whether the differences between the two polymers used (i.e., HHTT content) would be reflected in a difference in chain conformation or packing. The potential energy calculations[13] do show that if the chain conformation used by Doll and Lando[11] is assumed, the chains show a propensity to rotate around their axes with increasing HHTT content (from 0% → 5%). However, if the chain conformation used by Hasegawa et al.[12] is assumed, the potential energy minimum remains at zero rotation ($\phi = 0°$) with increasing HHTT content. So the chain packing, in particular chain rotation, is a strong function of chain conformation.

Doll and Lando[11] came to the conclusion that the chains were rotated by 6–8° by examining only zero layer line ($hk0$) data using the TGTG′ ($G = 58°$) chain. This rotation does in fact improve R_w from 0.235 for unrotated chains to 0.176 for a $\phi = 7°$ rotation. The same improvement in the residual can be obtained, however, by simply using the chain conformation of Hasegawa et al.[12] and packing the chains unrotated ($\phi = 0°$). When the observed structure factors of Doll and Lando[11] and calculated structure factors with the chain conformation and packing ($\phi = 0°$) of Hasegawa et al.[12] are used, the residual for the zero-layer data only is $R_w = 0.182$. The same effect on the residual for the zero-layer data can be seen to occur when considering the observed structure factors of Hasegawa et al.[12] These results are summarized in Table IV. It is obvious that the ambiguity involving the chain conformation and packing cannot be resolved by relying on the potential energy calculations or on the zero-layer X-ray data alone.

All of the X-ray data, observed and unobserved data for all layer lines, must be examined in order to determine if the HHTT content in the samples used by the two groups does indeed account for the differences in chain conformation and packing. The observed data of Doll and

Table V
Effect of Chain Conformation and Packing on the Overall Residual[a]

	up-down		up-up		stat up-down	
	G = 58° ϕ = 7°	G = 45° ϕ = 0°	G = 58° ϕ = 7°	G = 45° ϕ = 0°	G = 58° ϕ = 7°	G = 45° ϕ = 0°
R_w	0.226	0.231	0.201	0.230	0.230	0.222
R_N	0.198	0.192	0.182	0.184	0.198	0.181
B, nm^2	0.051	0.052	0.045	0.052	0.046	0.045

[a] The observed structure factors of Doll and Lando were used.[11]

Lando[11] were previously[13] thought to be inconsistent with the chain conformation and packing used by Hasegawa et al.[12] This was cited as evidence that the difference between the two polymers used by the two groups[11,12] was indeed significant and resulted in the two different models for phase II. In this investigation we have reexamined this premise by calculating residuals using the observed structure factors of Doll and Lando[11] and calculated structure factors using the extended-chain conformation of Hasegawa et al.[12] with ϕ = 0°. These residuals are to be compared with residuals calculated from the observed structure factors using the G = 58° chain of Doll and Lando[11] with ϕ = 7°. Three different models, up–up, up–down, and statistical up–down, were examined and are described above.

The results of these calculations are shown in Table V. A significance test[28] was used to determine if the differences in the residuals for the various models indicate that the observed data of Doll and Lando[11] are inconsistent with the chain conformation of Hasegawa et al.[12] The overall conclusion which is drawn from this significance test is that the observed data of Doll and Lando[11] are not inconsistent with the extended chain (G = 45°) and ϕ = 0° packing of the chains.

If we examine the data of Doll and Lando,[11] we find another motivation for rotating the chains about their axes, other than the good fit of the zero layer line data. The (201) reflection is listed as observed and has the lowest intensity on the first layer line. If this reflection exists, it would be in violation of a $P2_1/c$ space group (antiparallel chain dipole moments, ϕ = 0°). We have, however, remeasured the d spacings of the observed reflections from the original low-temperature photograph of Doll and Lando[11] and find that this reflection has a d spacing of d_{obsd} = 0.212 nm. This is to be compared to the calculated d spacings (using the −145 °C lattice parameters a = 0.492 nm, b = 0.938 nm, and c (chain axis) = 0.462 nm) for the (201) reflection d_{calcd} = 0.217 nm and the (041, 211) reflection d_{calcd} = 0.210 nm. It would appear that the reflection reported by Doll and Lando[11] as the (201) reflection probably should be indexed instead as the (041, 211) reflection. This removes one motivation for rotating the chains about their axes. This also indicates that the systematic absences of Doll and Lando[11] should be (0k0) for k odd, as well as the (h0l) for l odd.

Another effect of rotating the chains around their axes involves the calculated structure factors of the unobserved reflections on the first layer line of Doll and Lando.[11] We have estimated a threshold value for the intensity of a reflection and find that four of the twelve unobserved reflections have calculated structure factors that are 2–6 times the estimated threshold value of the structure factors. If, however, the extended chain (G = 45°) and ϕ = 0° packing are used for calculating the structure factors for the unobserved data, all of the unobserved calculated structure factors are less than 2 times the estimated threshold value of the structure factors.

Neither the potential energy calculations of Farmer et al.[13] nor residuals simply calculated on the basis of observed data only can resolve the ambiguity involving the chain conformation and packing. However, if one considers the unobserved data of Doll and Lando[11] with rotated chains (ϕ = 7°) and the fact that the systematic absences of Doll and Lando[11] probably should be (0k0) for k odd and (h0l) for l odd instead of just (0k0) for k odd, the rotated-chain model of Doll and Lando[11] must be abandoned in favor of the ϕ = 0° packing of Hasegawa et al.[12] All discussion of phase II crystal structure work now will center on the data of Hasegawa et al.[12] and the extended-chain conformation will be packed in the unit cell with ϕ = 0°.

Results

In this work we have extended the calculations done by Hasegawa et al.[12] on phase II $\mathrm{PVF_2}$ by calculating structure factors for up–up and statistical up–down models as well as structure factors for the up–down model investigated by Hasegawa et al.[12] Other than the Debye–Waller factor and overall scale factor, the only parameter which was refined in this work for each particular model was the relative shift of the chains along the chain axis. One interesting feature is that the relative chain shifts of the up–up model and the up–down model are preserved in the statistical up–down model. That is, the up–up chains in the statistical model are coupled with the same relative shift as for the up–up model, and the up–down chains in the statistical model are coupled with the same relative shift as for the up–down model.

The observed data of Hasegawa et al.[12] along with the calculated structure factors for all three models are given in Table VI. The unobserved data in Table VI indicate that the systematic absences are (h0l) for l odd and (0k0) for k odd. The residuals and Debye–Waller factors for all of the models are summarized in Table VII. Although Doll and Lando[11] reported similar results for up–up and up–down chain packing, Hasegawa et al.[12] considered only up–down packing. It should be noted that in Table VII up–up packing, using the data and chain conformation of Hasegawa et al.,[12] yields a lower residual than the up–down packing reported by Hasegawa et al.[12]

The unit cell of the up–up model would appear to have symmetry elements c glide $\perp$ b and 2_1 screw $\parallel$ b, as indicated by the calculated systematic absences (h0l) for l odd and (0k0) for k odd, respectively. However, the up–up unit cell cannot have a 2_1 screw $\parallel$ b, and so the apparent (0k0) for k odd systematic absences must be a fortuitous result. The unit cell for this up–up model is monoclinic with β = 90° (b unique) with the glide plane of the polymer chain coinciding with the c glide of the unit cell. The space group which has the appropriate symmetry element c glide $\perp$ b, and hence the systematic absences (h0l) for l odd, is Pc (C_s^2).[27] The two chains in the unit cell are not related to each other by symmetry in any way. The unit cell and chain packing of the up–up model is shown in Figure 4.

The unit cell of the up–down model has symmetry elements c glide $\perp$ b and 2_1 screw $\parallel$ b, as indicated by the systematic absences (h0l) for l odd and (0k0) for k odd, respectively. The unit cell is monoclinic with β = 90° (b unique) with the glide plane of the polymer chain coinciding with the c glide of the unit cell. The space group which has the appropriate symmetry elements, c glide $\perp$ b and 2_1 screw $\parallel$ b, and hence the systematic absences (h0l) for l odd and (0k0) for k odd, respectively, is $P2_1/c$ (C_{2h}^5),[27] as was shown earlier by Hasegawa et al.[12] The two chains in the unit cell are related to each other by the 2_1 screw

Table VI
Comparison of Calculated and Observed Structure Factors of Phase II of PVF$_2$ for the Three Models of Chain Packing Investigated, Up-Down, Up-Up, and Statistical Up-Down[a]

		F_c[c]		
hkl	F_o[b]	up-down	up-up	stat up-down
010		0.0	0.0	0.0
100	40.5	39.0	39.0	39.3
020	44.4	36.1	36.1	36.4
110	69.2	66.4	66.4	67.1
120	32.7	39.0	39.0	39.7
030		0.0	0.0	0.0
110	33.3	36.2	36.2	37.2
200	37.7	37.6	37.6	38.7
040 210	32.8	30.7	30.7	31.7
220 140	6.3	15.9	15.9	16.5
230	13.1	6.5	6.5	6.8
050		0.0	0.0	0.0
150	26.1	19.1	19.0	20.2
240	5.1	2.3	2.3	2.5
300 310	37.9	44.5	44.5	47.8
060		13.6	13.6	14.7
320	13.0	12.7	12.7	13.8
160 250	19.5	21.1	21.1	22.9
330		7.5	7.5	8.2
070		0.0	0.1	0.0
340 260	6.1	10.9	10.9	12.1
170	15.8	7.7	7.7	8.5
350		3.6	3.6	4.1
001		0.0	0.0	0.0
011		10.6	9.3	2.0
101		0.0	0.0	0.0
021	51.4	49.3	53.5	49.3
111	28.6	32.2	30.1	30.5
121	28.9	32.1	34.8	31.9
031	12.5	31.3	6.7	6.0
131	36.1	34.5	35.1	31.8
201		0.0	0.0	0.0
211 041	24.0	21.2	35.2	21.5
221 141	35.3	44.8	43.3	42.8
231 051	14.5	21.5	12.8	11.8
151	24.8	24.1	25.3	24.1
241	34.9	35.5	35.9	37.1
301		0.0	0.0	0.0
311	23.7	24.2	23.7	25.4
061	19.7	13.4	14.2	14.3
321 161	9.7	11.4	11.1	8.8
251		6.5	4.5	1.5
331	14.5	8.8	14.9	8.8
071 341	21.1	18.4	13.3	14.6
261 171	20.9	14.2	14.0	15.7
012		11.6	16.4	4.4
102 022	18.5	23.7	32.2	15.8
112	23.1	32.5	25.6	20.1
122	20.1	15.9	21.5	15.5
032		12.5	7.0	4.9
132	27.8	24.0	23.9	23.5
202 042 212	26.3	26.0	25.9	22.8
222 142	18.7	14.4	13.0	13.3
232	7.4	6.5	7.3	4.0
052		9.9	3.7	4.0
152	24.9	15.8	13.5	14.3
242		2.3	3.4	1.7
302 312	21.7	21.3	21.4	20.9
062		2.4	9.6	2.5
322 162 252	11.5	13.0	15.0	12.0

[a] The observed structure factors of Hasegawa et al. were used.[12] [b] F_o are put on the same scale as F_c by setting $\Sigma kF_o = \Sigma F_c$, where k is the scale factor. [c] F_c of reflections which overlap are $(\Sigma mF_c^2)^{1/2}$, where m is the multiplicity.

Table VII
Summary of the Residuals and Debye-Waller Factors for the Three Models of Chain Packing Investigated, Up-Down, Up-Up, and Statistical Up-Down[a]

	up-down	up-up	stat up-down
R_W	0.204	0.195	0.178
R_N	0.185	0.170	0.169
B, nm^2	0.052	0.052	0.045

[a] The observed structure factors of Hasegawa et al.[12] were used.

Table VIII
Atomic Coordinates of the Statistical Up-Down Packing Model of Phase II of PVF$_2$, Where a = 0.496, b = 0.964, and c = 0.462 nm

up chain at (0,0)				up chain at ($^1/_2$,$^1/_2$)			
atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
H1	−0.217	−0.084	0.217	H1	0.732	0.416	0.157
H2	0.127	−0.154	0.263	H2	0.388	0.346	0.203
C2	0.0	−0.067	0.199	C2	0.515	0.433	0.139
F3	0.338	0.072	0.340	F3	0.177	0.572	0.280
F4	−0.020	0.180	0.247	F4	0.535	0.680	0.187
C3	0.071	0.064	0.374	C3	0.444	0.564	0.314

axis. The unit cell of the up–down model is shown in Figure 3.

The unit cell for the statistical up–down model would appear to have the same symmetry elements as for the up–up model. Assuming that Friedel's law holds, the calculations indicate that the unit cell is orthorhombic. None of the primitive orthorhombic space groups which have both of the symmetry elements c glide ⊥ b and 2_1 screw || b will satisfy the statistical up–down unit cell. There are primitive orthorhombic space groups which contain just the 2_1 screw || b symmetry element or the c glide ⊥ b symmetry element. Of these only the space group $P2cm$ (C_{2v}^4)[27] will satisfy the statistical up–down unit cell. This space group's translational symmetry element, c glide ⊥ b, will generate only the ($h0l$) for l odd systematic absences, and so the apparent ($0k0$) for k odd absences must be a fortuitous result, as in the up–up model. The up and down chains which are modeled as being in the same position in the unit cell in an ab projection are related by the symmetry elements of the $P2cm$ space group. The unit cell of the statistical up–down model is shown in Figure 5. The atomic positions for the statistical up–down

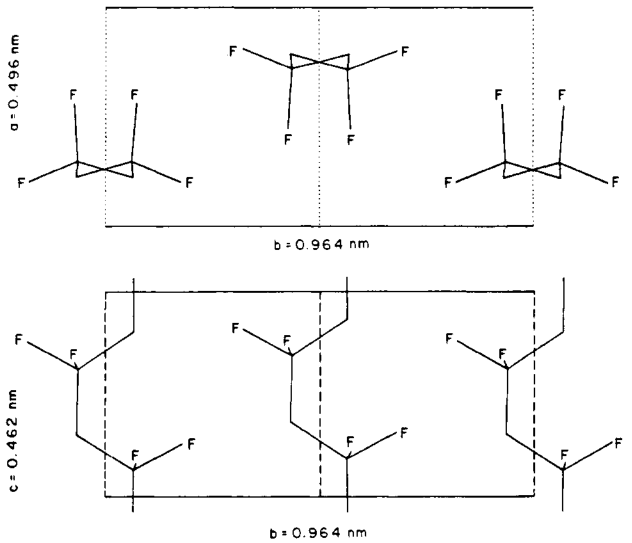

Figure 4. Chain packing of phase II with $G = 45°$, $\phi = 0°$ for up–up packing (*Pc* space group).

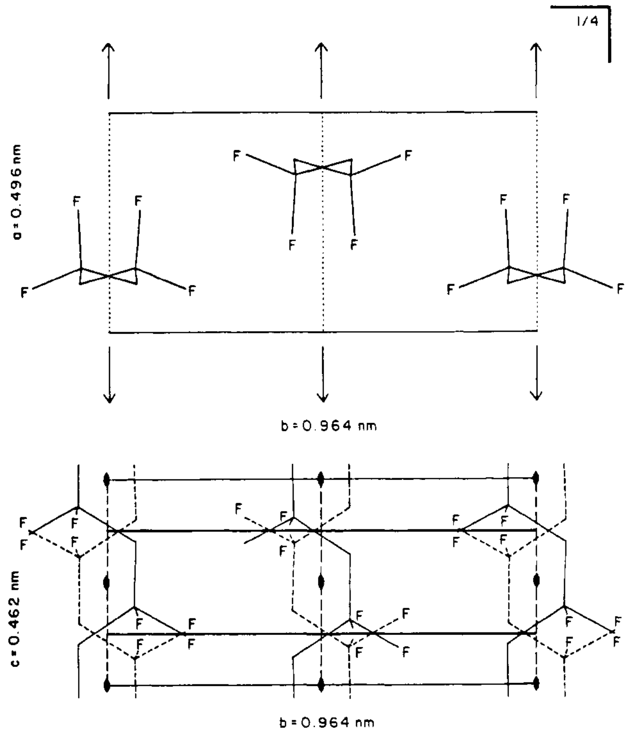

Figure 5. Chain packing of phase II with $G = 45°$, $\phi = 0°$ for statistical up–down packing (*P*2*cm* space group).

model are listed in Table VIII.

The statistical up–down model, while having the lowest residual of the three models, also has more degrees of freedom involved in the refinement than does a two-chain model. A significance test[28] was used to determine if the differences in R_w between the statistical up–down model and the up–up or up–down models was just a result of the additional degrees of freedom. It was found that to within a 99% confidence level the R_w of the statistical up–down model indicates that the chains are statistically packed rather than being simply an up–down model, and to within a 96% confidence level the chains are statistically packed rather than being an up–up model.

The fact that the unit cell is statistically packed and is orthorhombic is not too surprising. As mentioned above, a statistical up–down model of chain packing applies to both phase III[14] (γ phase) and phase IV[15] (polar α phase) of PVF_2. These two phases can be produced directly from phase II material. Hence the chains in the original phase II material should be statistically packed, unless the statistical "disorder" in phases III and IV is brought about by the various external forces which are necessary to cause the phase II → phase III or IV transformations. Neither Doll and Lando[11] nor Hasegawa et al.[12] were able to resolve the (*hkl*) and ($\bar{h}kl$) reflections, indicating that the unit cell of phase II was at least metrically orthorhombic. The electron diffraction studies[29] on single-crystal phase II yield Laue spots which are typical of a crystal with orthorhombic symmetry. The fact that the unit cell is orthorhombic is satisfying because it accounts for the observed symmetry that had been obtained for phase II.

Conclusion

In this work we have resolved the ambiguity that had existed between the crystal structures reported previously[11,12] for phase II poly(vinylidene fluoride). We find that a statistical up–down model applies to the crystal structure of phase II. The chains pack in a primitive orthorhombic unit cell with space group P2*cm* (C_{2v}^4).

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