X-ray Analysis of Poly(vinyl fluoride)

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ABSTRACT: Three different X-ray analysis techniques were used to investigate the chain defect content present in the crystalline regions of poly(vinyl fluoride). The techniques used were a fiber pattern analysis, a powder pattern analysis, and a meridional intensity analysis. The fiber pattern analysis proved unable to determine either the tacticity or regic defect content in PVF. However, it was found that the refinement favored a statistical packing of the chains in the crystalline regions. This packing arrangement was supported by the powder pattern analysis and molecular modeling calculations. The meridional intensity analysis proved to be sensitive to the regic defect content of the sample. The results of this analysis correlated well with previous DSC work.

Introduction

The initial crystal structure work pertaining to poly(vinyl fluoride) (PVF) was reported by Golike[1] in 1960. It was determined in his work that the unit cell was hexagonal with dimensions of $a = b = 4.93$ Å and $c = 2.53$ Å, resulting in a crystalline density of 1.44 g/cm^3. This compared well with the measured value of 1.38 g/cm^3. Although the experimental d-spacings correlated very well with the proposed unit cell, a hexagonal or trigonal system implies a minimum of 6-fold or 3-fold symmetry, respectively, along the z-axis. This would require that the chains crystallize in a helical conformation; the reported c-dimension of 2.53 Å, however, does not support this requirement. Instead, the c-spacing implies that the chains are in an extended conformation which would not generate the required symmetry for a hexagonal system.

In 1961 Natta et al.[2] reported their work on the crystal structure of PVF. They classified the structure as an orthorhombic system with two chains in the unit cell, with the second chain centered in the C-face. The unit cell dimensions were determined to be $a = 8.57$ Å, $b = 4.95$ Å, and $c = 2.52$ Å. It was realized that the c-spacing implied an extended conformation of the chains and thus assigned the space group $Cm2m$. This space group requires a mirror plane perpendicular to both the a- and c-axes with a 2-fold rotation axis parallel to the b-direction. See Figure 1 for a diagram of the unit cell. In their analysis, a statistical weighting of the fluorine was assumed such that an average of half of a fluorine was present in each position on the first carbon of the repeat unit. This is permitted due to the isomorphous relationship of fluorine and hydrogen and arises from the uncertainty of the position of the fluorine atom which is a consequence of the random nature in which the monomer attaches to the polymer chain. The resulting repeat unit could be generated by either a syndiotactic or atactic chain. Natta makes reference to a very weak off-meridional intensity at half of a layer spacing, indicative of a syndiotactic bias in the chain. However, with the data reported in the paper it is not possible to investigate this possibility.

The random nature of the monomer addition in radically polymerized poly(vinyl fluoride) is known to produce both tacticity and regic defects in the polymer.

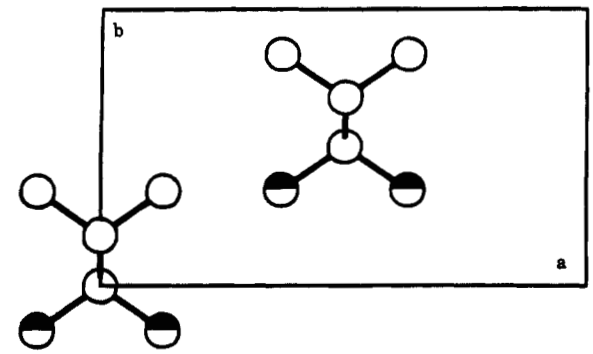

Figure 1. $a-b$ projection of the unit cell for PVF determined by Natta.[45] The shaded atoms indicate the statistical placement of fluorine in the chain.

The defects, though, do not prevent the polymer from crystallizing; crystallinities as high as 60%[3] have been found for PVF. This, in combination with the observation that the head-to-head/tail-to-tail (HH/TT) content of the sample affects the melting temperature of PVF,[4] suggests that the tacticity and regic defects do indeed crystallize in PVF. In addition, molecular modeling work involving the crystallization behavior of PVF (reported in the preceding paper) has provided no compelling reason why any of the defect structures should be completely excluded from the crystalline regions.

Therefore, based on the premise that defect structures do crystallize in PVF, the purpose of this work was to determine if X-ray analysis would provide a useful technique for measuring the defect content in the crystalline regions of PVF. Toward that end, three different techniques were investigated. The first method was a structure refinement based on fiber data. The second method made use of a relationship between the HH/TT content and the meridional intensity. The third method was a Rietveld analysis of powder data.

Experimental Section

The samples used for the first two methods were provided by Du Pont and received in a powder form. In order to collect X-ray data for the fiber analysis and meridional intensities, the powder was first processed into a fiber. The processing method used was a gel extrusion technique. The reason the material was not melt drawn, as is typically done, is that the material experienced severe degradation before the flow region was reached.

After drying, stretching, and annealing, the fibers produced samples with good orientation and high crystallinity. A typical

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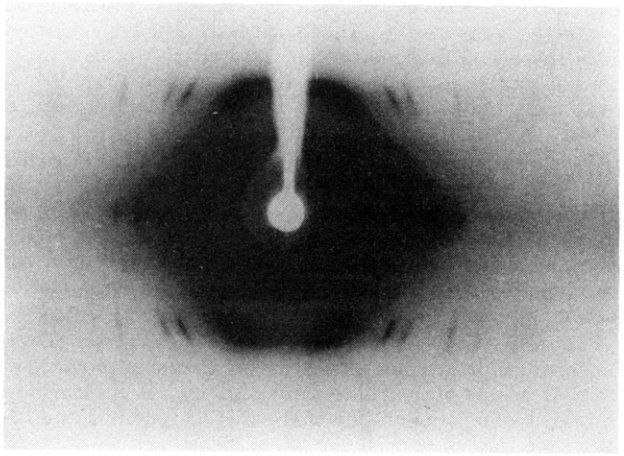

Figure 2. X-ray photograph of PVF taken on a cylindrical camera.

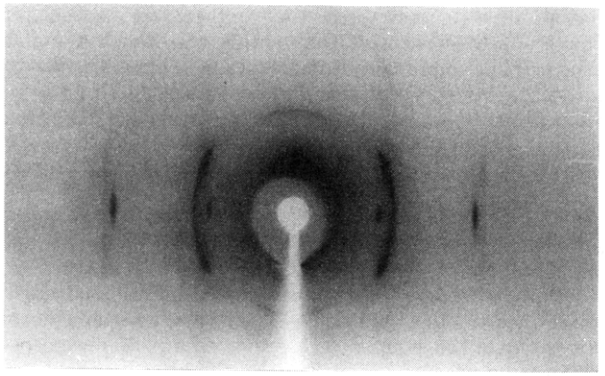

Figure 3. X-ray oscillation photograph of PVF taken on a cylindrical camera. Angle of oscillation is ±45°.

X-ray photograph is shown in Figure 2. This photograph was taken on a cylindrical camera with the fiber axis coincident with the camera cylinder axis. The photographs were digitized on an Optronics Photoscan P1000 photodensitometer. The processing of the digitized data was performed using programs provided by Dr. K. H. Gardner of Du Pont; a detailed explanation of the programs is contained in the thesis of Grasso.[5]

A total of 14 reflections was observed. Intensities for 10 of the reflections were measured; the remaining four were very weak and estimated at half the weakest measured intensity. Two reflections were unobserved, resulting in a total of 16 reflections used for the refinement.

X-ray photographs for the meridional analysis were taken on a cylindrical camera with the fibers mounted perpendicular to the X-ray beam and normal to the axis of the film cassette. The fibers were oscillated ±45° with respect to the X-ray beam such that the axis of rotation was collinear with the film cassette axis. A typical X-ray photograph is shown in Figure 3. The 001 and 002 reflections are clearly evident on the equator. An absorption factor correction was applied to the 001 and 002 intensities.

The data used for the Rietveld analysis were collected on a Philips APD 3520 diffractometer from a sample provided by R. E. Cais from Bell Labs. This instrument produced Cu Kα radiation (40 kV, 30 mA) which was nickel-filtered with a monochromator placed between the sample and the detector. The sample was in a powder form, and scans were made using a glass sample holder. The sample was run in an as received condition. A glass holder was used due to spurious reflections arising from a standard metal holder. Data were collected at room temperature from 12° to 80° 2θ. The step size for data collection was 0.05°, and the collection interval at each step was 30 s. After collection, the data were corrected to adjust for the slit geometry used in the diffractometer.

Method of Analysis. Fiber Data Refinement. The consequence of a chain defect incorporating into the crystal structure of PVF would result in a randomness in the position of the fluorine. To account for this randomness, the approach of this analysis was to simulate the uncertainty of the fluorine position by allowing the weighting of the fluorine to vary over all four positions of the repeat unit. This was performed in such a way that the sum of the fluorine weightings always equaled 1 and for any of the four positions the sum of the fluorine and hydrogen at that position always equaled 1. These rules ensured that the overall chemical composition was always preserved.

After a refinement, the resultant weightings of the fluorine were related to the structure of the material. Fluorine content that was placed on the second carbon indicated HH content, whereas the ratio of the fluorine content on one side of the carbon backbone relative to the other should be related to the tacticity of the sample.

This analysis used as a starting position the unit cell resulting from Natta's work; the refinements were performed using the LALS[6] program. This program refines the structure of a molecule by minimizing the difference between the observed and calculated structure factors within the limitations imposed by stereochemical and user-supplied constraints and, if applied, nonbonded contact distances. In the present analysis standard bond lengths, bond angles, and torsion angles were used. The bond lengths were as follows: C–C, 1.54 Å; C–F, 1.36 Å; C–H, 1.07 Å. All bond angles were set to 109.47° except for the C–C–C angles which were 109.8°. The value of 109.8° is required for a chain in an all-trans conformation with C–C bond lengths of 1.54 Å and a c-dimension of 2.52 Å. The backbone torsion angles were 180°, while the hydrogen and fluorine torsion angles were either +60° or −60° depending on their placement. The bond angles and torsion angles were not allowed to vary. This is due to the constraints imposed by the symmetry of the system and the unit cell dimensions and due to the limited number of reflections that were observed. Additionally, the modeling work reported in the preceding paper indicates that significant deviation from the standard bond angles and torsion angles does not occur.

Two refinement schemes were used. The first was a rigid-body refinement where the generalized coordinates were fixed. In order to preserve symmetry, the coordinates describing the placement of the molecules within the unit cell were also fixed. The parameters allowed to vary were the scale and attenuation factors along with the occupation factors for the fluorine and hydrogens.

A second analysis was performed in a manner similar to that of the first with the addition of an allowance for statistical packing of the chains. Statistical packing was investigated due to this possibility being raised during modeling work (see preceding paper). This was performed in such a way that the symmetry of the system was preserved. Two superimposed chains were placed at each molecule position in the unit cell (the origin and the position defined by the C-centering), and each chain was assigned an occupancy factor of $^1/_2$. The axial rotation of one chain was allowed to vary with the rotation of the superimposed chain defined by a mirror plane in the b–c plane. This ensured the preservation of the symmetry of the system. In addition, a constraint was imposed to require one chain at the origin and one placed in the C-face to maintain an equal rotation angle. Thus this method added only one additional variable to the refinement. For a diagram of the system, see Figure 4.

Meridional Intensity Analysis. An examination of the chain structure and unit cell indicates that a dependence should exist between the HH/TT content and the meridional reflections. This arises because the polymerization direction of vinyl fluoride with respect to the propagating chain is asymmetric. The preference is for the propagating radical to be located on a carbon bearing a fluorine. Hence, the average repeat of the chain will have a fluorine content on one carbon of the repeat unit due only to HT units, whereas the fluorine content occurring on the second carbon of the repeat will be due only to HH units. This assumes the formation of a HH unit is immediately followed by a TT unit. (This assumption is fairly accurate and will be considered later.) When these

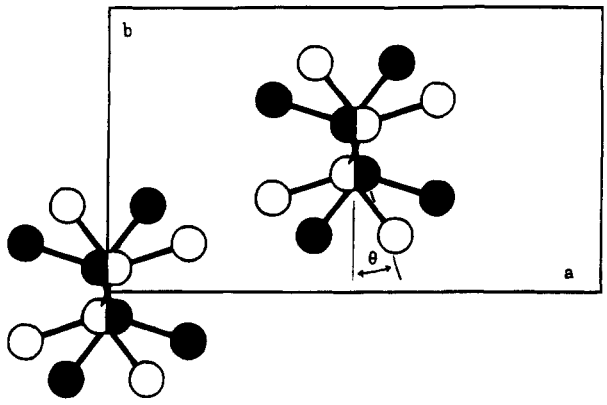

Figure 4. $a-b$ projection of the unit cell for PVF allowing for statistical packing of the chains. There are two chains in each position, all with an occupancy of $^1/_2$. The system is described by the axial rotation angle θ.

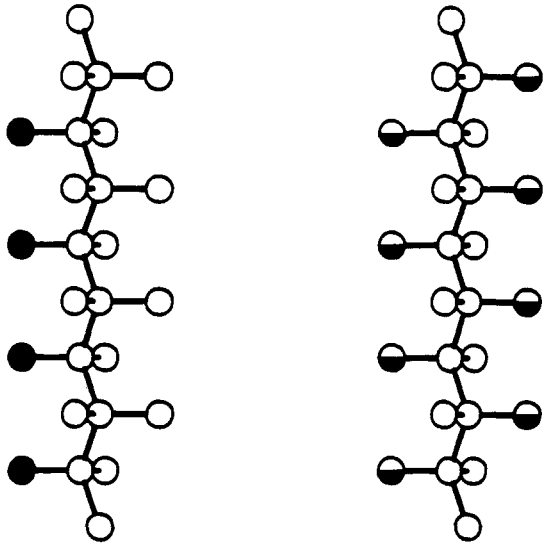

Figure 5. Comparison of two ideal chain structures.

chains crystallize, since PVF has a C-centered unit cell, the z-coordinates of the atoms on one chain correspond to those on the other chain. Thus all HT fluorines should reside on a plane defined by a constant z-coordinate, while all the fluorines from HH units will reside on a plane defined by a constant $(z + {}^1/_2)$-coordinate. (The validity of this assumption will likewise be considered later in the paper.) Therefore, the presence of HH/TT defects should have a direct correlation with the meridional intensities.

The correlation between the structure and the meridional intensities can be illustrated by examining two ideal chains; see Figure 5. The first chain is a perfect HT structure where the black atoms represent the fluorine atoms. Considering first the 001 reflection and neglecting the hydrogens, the atoms that contribute to the intensity are the fluorine atoms. The carbon atoms will not contribute since, although there are atoms at multiples of the lattice spacing, there is a set of carbon atoms offset half of a lattice spacing from the first set. The consequence of this is that all of the carbon atoms will destructively interfere. On the other hand, the diffraction for the 002 reflection corresponds to a lattice spacing of half of the c-dimension. Thus the intensity for this reflection will be composed of diffraction from both the fluorine and carbon atoms.

The second chain is structurally the opposite of the first chain and represents the average chain for a completely random HH/TT chain. On average there is half of a fluorine located on every carbon; this is indicated by the black half-circle. For this structure, the 001 reflection should be absent. This is the result of both the carbons and the fluorines destructively interfering. The fluorines destructively interfere since there is a fluorine content at multiples of the lattice spacing and an equal content that is shifted by half of a c-spacing. The 002 reflection will again be composed of diffraction from the carbons and the fluorines.

Thus a ratio of the 001 to the 002 intensity should provide a measure of the HH/TT content. It is expected that as the HH/TT content is increased the intensity ratio will decrease. This behavior should extend beyond the 001 and 002 reflections and in general should have an odd–even effect. The odd meridional reflections should be sensitive to the HH/TT content, whereas the even reflections will not.

Rietveld Analysis. The Rietveld analysis in this work was done using a program developed by Immirzi[7] and provided by Dr. S. Bruckner of the Politecnico di Milano. It is a complete and flexible implementation of the Rietveld method and has been used to study a wide variety of structures.

For this work a rigid-body refinement was performed. The coordinates of the atoms were fixed, and the scale and attenuation factors were varied. The unit cell dimensions were also allowed to vary since the Rietveld method is quite sensitive to these values. One feature of a Rietveld analysis is the presence of numerous nonstructural variables. For this analysis, several of these parameters were allowed to vary. The peak width parameters, v and w, were varied due to the fact that there were no isolated peaks with which the parameters could be directly calculated. A zero correction term, which ideally is zero, was refined to allow for the possibility that the 2θ scale of the diffractometer was not in perfect calibration. The refined value should always be close to zero, and, if not, this either indicates a problem with the structure or with the diffractometer. A preferred orientation parameter was refined to allow for the possibility of a nonhomogeneous orientation of the sample. The preferred direction was specified as coincident with the vector defining the 001 reflection. This direction was selected since the lamellar morphology of polymers favors the probability that a set of diffracting planes will be normal to the 001 direction. Last, a set of parameters defining the background intensity and amorphous peaks were refined to allow the removal of their intensity from the observed data. The background was divided into five segments with allowance made for one amorphous peak.

Results and Discussion

Refinement of Natta's Data. A LALS refinement was first applied to the structure factors reported in Natta's paper. The purpose was to determine the degree to which the original refinement could be improved. Three refinements were performed; the first simply reproduced Natta's original structure and was a rigid-body analysis, with the fluorine weightings fixed at half of a fluorine in each position of the first carbon. The scale and attenuation factors were allowed to vary. The refinement resulted in a weighted residual of 0.181 with a value of 10.5 for the temperature factor.

A second rigid-body refinement was performed to determine if Natta's refinement could be improved. The fluorine weightings were allowed to vary over all four positions of the repeat unit, allowing for refinement of the defect structures in the polymer chain. However, when this is done, except for special cases, the symmetry of the system is reduced and the system no longer possesses symmetry sufficient for the $Cm2m$ space group; the crystal structure loses the 2-fold rotation about the chain axis and the mirror plane perpendicular to the a-axis. The only symmetry element left is the mirror plane perpendicular to the c-axis; the crystal reduces to the space group Pm. This is a monoclinic cell with the dimensions $a = b = 4.93$ Å, $c = 2.52$ Å, and $\delta = 120.0°$ (a metrically hexagonal cell). A list of the reindexed d-spacings is contained in Table 1.

Table 1. Indexing for a Monoclinic Unit Cell of PVF[a]

#	h	k	l	d(obs)	d(calc)	diff	% diff
1	4	0	0	1.070	1.069	0.001	0.077
2	4	−4	0	1.070	1.69	0.001	0.077
3	0	4	0	1.070	1.069	0.001	0.077
4	3	1	1	1.070	1.073	−0.003	0.282
5	4	−3	1	1.070	1.073	−0.003	0.282
6	4	−1	1	1.070	1.073	−0.003	0.282
7	3	−4	1	1.070	1.073	−0.003	0.282
8	1	3	1	1.070	1.073	−0.003	0.282
9	1	−4	1	1.070	1.073	−0.003	0.282
10	4	−2	1	1.110	1.108	0.002	0.138
11	2	2	1	1.110	1.108	0.002	0.138
12	2	04	1	1.110	1.108	0.002	0.138
13	4	−1	0	1.200	1.186	0.014	1.154
14	3	1	0	1.200	1.186	0.014	1.154
15	4	−3	0	1.200	1.186	0.014	1.154
16	3	04	0	1.200	1.186	0.014	1.155
17	1	3	0	1.200	1.186	0.014	1.154
18	1	−4	0	1.200	1.186	0.014	1.155
19	4	−2	0	1.200	1.235	−0.035	2.882
20	2	2	0	1.200	1.235	−0.035	2.882
21	2	−4	0	1.200	1.235	−0.035	2.882
22	3	0	1	1.240	1.241	−0.001	0.041
23	3	−3	1	1.240	1.240	0.000	0.040
24	0	3	1	1.240	1.240	0.000	0.040
25	3	−1	1	1.360	1.360	0.000	0.015
26	3	−2	1	1.360	1.360	0.000	0.015
27	2	1	1	1.360	1.360	0.000	0.015
28	1	2	1	1.360	1.360	0.000	0.015
29	2	−3	1	1.360	1.360	0.000	0.015
30	1	−3	1	1.360	1.360	0.000	0.015
31	3	0	0	1.430	1.426	0.004	0.310
32	3	−3	0	1.430	1.426	0.004	0.310
33	0	3	0	1.430	1.426	0.004	0.310
34	3	−1	0	1.620	1.616	0.004	0.219
35	3	−2	0	1.620	1.616	0.004	0.219
36	2	1	0	1.620	1.616	0.004	0.219
37	1	2	0	1.620	1.616	0.004	0.219
38	2	−3	0	1.620	1.616	0.004	0.220
39	1	−3	0	1.620	1.616	0.004	0.220
40	2	0	1	1.640	1.630	0.010	0.622
41	2	02	1	1.640	1.630	0.010	0.622
42	0	2	1	1.640	1.630	0.010	0.622
43	2	−1	1	1.760	1.763	−0.003	0.161
44	1	1	1	1.760	1.763	−0.003	0.161
45	1	−2	1	1.760	1.763	−0.003	0.161
46	2	0	0	2.140	2.138	0.002	0.077
47	2	−2	0	2.140	2.138	0.002	0.077
48	0	2	0	2.140	2.138	0.002	0.077
49	1	0	1	2.170	2.170	0.000	0.020
50	1	−1	1	2.170	2.170	0.000	0.020
51	0	1	1	2.170	2.170	0.000	0.020
52	2	−1	0	2.480	2.469	0.011	0.437
53	1	1	0	2.480	2.469	0.011	0.437
54	1	−2	0	2.480	2.469	0.011	0.437
55	0	0	1	2.520	2.518	0.002	0.096
56	1	0	0	4.280	4.277	0.003	0.077
57	1	−1	0	4.280	4.277	0.003	0.077
58	0	1	0	4.280	4.277	0.003	0.077

[a] $a = 4.938$ Å; $b = 4.938$ Å; $c = 2.518$ Å; $\alpha = 90.000°$; $\beta = 90.000°$; $\gamma = 120.000°$.

Using the new unit cell and reindexed data, the second refinement was performed. The resultant structure is shown in Figure 6. The refinement produced a structure that contained approximately 20% HH units, which is in the range of up to 25% that has been reported to occur in PVF.[3] Also the refinement indicated a strong isotactic bias in the chain. However, the refinement only reduced the residual to 0.166 with a temperature factor of 10.5. Considering the fact that the refinement varied three additional parameters (the occupancies of the fluorines), the improvement in the residual was not valid when a Hamilton test for significance[8] was applied.

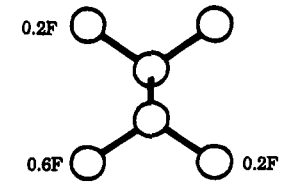

Figure 6. Structure refined for Natta's data, allowing all four fluorine weightings to vary.

One observation that was made during this work was, except in special cases, the tacticity of the sample was concealed due to the statistical nature of the polymerization. This occurs since the X-ray is only "looking" at the average position of the fluorine; it is not looking at the relation of a fluorine on one repeat unit with those on adjacent units as do spectroscopic means of determining structure. Thus in an X-ray analysis an atactic and syndiotactic chain would look the same with the fluorine weightings symmetric about the carbon backbone, while a perfect isotactic chain would result in all the fluorines on the same side. However, if the chain has only an isotactic bias and is not a pure isotactic chain, it will appear in an X-ray analysis as an atactic/syndiotactic system. This occurs because, for an isotactic sequence containing a HH/TT unit, there is only a 50% chain that the carbons will be of the same chirality on either side of the defect. The same argument can be made when a syndiotactic defect is present in an otherwise isotactic chain. Consequently, it can be argued that an X-ray analysis is only going to see the atactic unit cell regardless of the actual chain structure. In consideration of this observation, all subsequent structure analyses assumed the chain possessed random tacticity and was performed using an orthorhombic unit cell.

A final refinement was made, allowing for the possibility of statistical packing of chains of random tacticity. This structure was considered in light of modeling work (see the previous paper) that indicated it might be a possibility. The structure refined to a HH content of 10% and a temperature factor of 10.3; the resultant axial rotation of the chain was 1.8°. The residual, however, decreased to only 0.178. Again it must be concluded that this is not a statistically significant improvement of the structure. Thus for the X-ray data in Natta's paper, the best fit is Natta's original structure.

Refinement of Fiber Data. The refinements performed using Natta's data were repeated with data collected for a commercially polymerized sample. The structure factors are listed in Table 2. Using these structure factors, several refinements were performed. First, assuming no HH content and refining only the scale and attenuation factors, the structure produced a residual of 0.200 and a temperature factor of 17.3. The residual was not as good as that achieved for Natta's data, and the large temperature factor is troublesome. The sensitivity of the refinement to the temperature factor was checked by fixing it at a more reasonable value and redoing the refinement. This resulted in a much higher residual, indicating the refinement was strongly dependent on the temperature factor and not simply in a shallow minima.

Table 2. Structure Factors Determined for the Commercial Sample A1

spot	refl	*hkl*	*F*(ours)	*F*(Natta's)
1	1	200		
	2	110	14.70	16.22
2	3	201		
	4	111	9.14	11.00
3	5	020		
	6	310	3.18	9.14
4	7	400		
	8	220	1.96	4.26
5	9	130		
	10	510		
	11	420	2.95	7.78
6	12	600		
	13	330	1.23	3.10
7	14	021		
	15	311	2.37	3.04
8	16	401		
	17	221	1.65	3.00
9	18	131		
	19	511		
	20	421	1.43	2.58
10	21	601		
	22	331	1.00	2.22
11	23	621		
	24	041	0.50	1.64
12	25	531		
	26	711		
	27	241	0.50	1.64
13	28	800		
	29	440	0.50	1.34
14	30	530		
	31	710		
	32	240	0.50	1.24
15	33	040		
	34	620	0.10	0.10
16	35	441		
	36	801	0.10	0.10

A second refinement was performed, allowing for the possibility of HH/TT units. The structure producing the lowest residual was one with an equal weighting of fluorine, i.e., 50%, on each carbon. This produced a residual of 0.150 and a temperature factor of 16.8. Applying Hamilton statistics indicates the result is in the 95–98% confidence level. A confidence level of 95% or higher is considered significant, and thus the result should statistically be valid. However, the physical result is unrealistic. For this weighting of fluorines to occur, either a completely random chain structure or a random packing of the chains relative to the fluorine *z*-coordinates is required. In either case, the 001 reflection would be absent. However, the 001 reflection was observed for this sample; therefore, the results of this refinement can be rejected.

The surprising result for this sample was the stubbornly high temperature factor. It is possible that this indicates the presence of additional disorder in the system in addition to that associated with the placement of the fluorine. This could be due, among other things, to a slight conformational distortion of the chain backbone or to statistical packing of the chains. It was this possibility combined with the previous modeling work that prompted the consideration of statistical packing of the chains.

A refinement was performed for this sample, allowing for the possibility of statistical packing; see Figure 4 for a diagram of the unit cell. Only the scale, attenuation, and axial rotational angle were varied. The HT structure refined to a residual of 0.101 with a temperature factor of 13.9. The resulting rotation angle was 17.6°. A residual of 0.10 for a polymer refinement indicates a very good fit and certainly provides a statistically significant solution (greater than 99.5% with the addition of only one variable). See Table 3 for a comparison of the observed and calculated structure factors. Additionally, the decrease in the temperature factor is encouraging. However, it is still higher than normally observed; this may indicate disorder in the system higher than what is currently taken into account.

Table 3. Comparison of Observed and Calculated Structure Factors for the Statistical Packing Refinement of a Commercial Sample of PVF

spot	refl	*hkl*	*F*(calc)	*F*(obs)	diff
1	1	200			
	2	110	26.55	26.40	−0.15
2	3	201			
	4	111	14.77	16.42	1.65
3	5	020			
	6	310	7.15	5.71	−1.44
4	7	400			
	8	220	4.29	3.52	−0.77
5	9	130			
	10	510			
	11	420	4.43	5.30	0.87
6	12	600			
	13	330	1.71	2.21	0.50
7	14	021			
	15	311	5.94	4.26	−1.68
8	16	401			
	17	221	2.77	2.96	0.19
9	18	131			
	19	511			
	20	421	2.63	2.57	−0.06
10	21	601			
	22	331	1.61	1.80	0.19
11	23	621			
	24	041	1.28	0.90	−0.38
12	25	531			
	26	711			
	27	241	1.19	0.90	−0.29
13	28	800			
	29	440	0.19	0.90	0.71
14	30	530			
	31	710			
	32	240	1.11	0.90	−0.21
15	33	040			
	34	620	1.19	0.18	−1.01
16	35	441			
	36	801	0.32	0.18	−0.14

It should be mentioned that this refinement was performed with nonbonded contacts applied. All possible contacts were included except those due to intrachain interactions and those occurring from superimposed chains. At a rotation angle of 17.6°, one might expect some nonbonded distances to be unexceptable, and this was found to be the case for one F–H interaction. It is possible that a small conformational disorder would alleviate the observed contact.

A final refinement was performed, allowing for variation in the weighting of the fluorines. The favored structure again contained 50% of the fluorine on each carbon. The residual was 0.084, and the temperature factor was 14.6. The rotation angle refined to 13.5°. In this refinement it was observed that as the HH content increased the temperature factor increased and the rotation angle decreased. The decrease of the rotation angle was due directly to the contacts produced by the HH fluorines. Although this is certainly a very good fit, as before, the additional data available, namely, the observation of a 001 reflection, prohibit this structure.

The conclusions from the results coupled with the results using Natta's data indicate that the refinement of fiber data, at least with the present reflection sets, is insensitive to the presence of HH defects. The X-ray

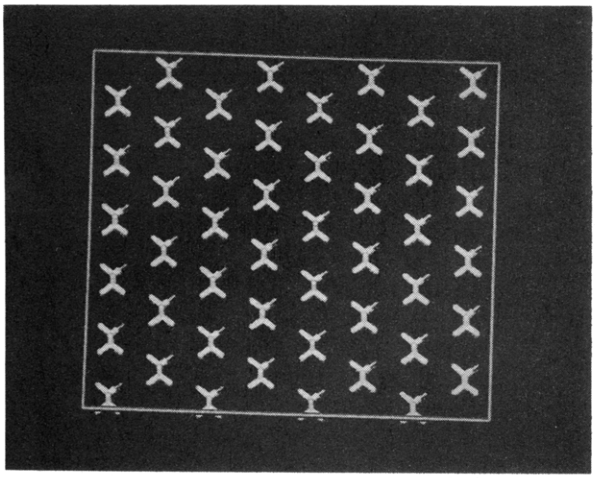

Figure 7. Packing arrangement after minimizing the energy of a pure syndiotactic system.

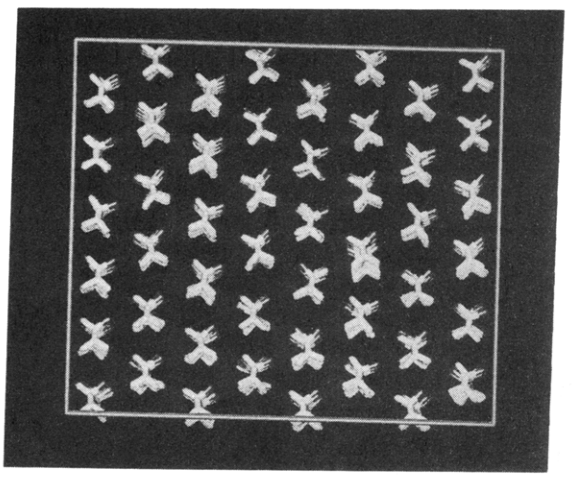

Figure 8. Packing arrangement after minimizing the energy of a syndiotactic system with 8% isotactic defects.

data, though, do appear to indicate radically polymerized PVF possesses some disorder in the packing of the chains. It is logical to question whether this is correct in light of the refinement using Natta's data. It is important to realize, however, that there is a strong possibility that the polymer used by Natta contained a significant syndiotactic bias and was not made by a radical polymerization method. This is a possibility due to the observation of weak off-meridional intensity at a layer spacing of 5 Å which could only arise from a syndiotactic repeat. As reported in the previous paper, modeling work has indicated that energy minimization of an array of syndiotactic chains will converge to a structure that has much less chain distortion than for systems composed of nonsyndiotactic chains. This can be seen by examining Figures 7 and 8. Figure 7 is a minimized array of syndiotactic chains, and Figure 8 is a minimized array of syndiotactic chains containing 8% tacticity defects. Regardless of the type of chain defect present, all produced results similar to those shown in Figure 8 and reinforce the conclusions drawn from the X-ray work that radically polymerized PVF possesses some disorder in the packing of the chains.

Meridional Discussion. In order to determine the behavior of the meridional intensities, LALS was used to calculate the 001 and 002 structure factors for unit cells containing various HH contents. The calculations were made on the crystal structure from Natta's paper, although the exact structure is unimportant, using a

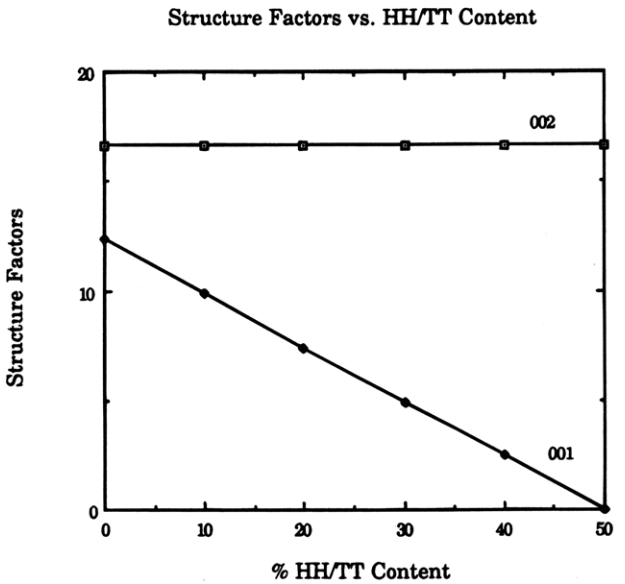

Figure 9. Theoretical dependence of the 001 and 002 structure factors on the HH/TT content of PVF.

Table 4. Meridional Structure Factor Ratios and Melting Tempertures for Several Samples of PVF

sample	polym temp (°C)	melting temp (°C)	001/002
	Set #1		
A1	80.0	199.1	1.662
A2	86.0		1.575
A3	91.0	195.5	1.206
A4	103.0	191.7	1.059
	Set #2		
B1	100.0	193.6	1.122
B2	100.0	192.8	0.955
B3	100.0	196.0	1.032

temperature factor of 1.0. The results are plotted in Figure 9, and it is seen that the 002 structure factor is invariant with respect to the HH content, whereas the 001 structure factor linearly decreases to zero as the HH content is increased. Thus, for any sample, the ratio of the 001 to the 002 structure factor should provide a sensitive measure of the HH content. Since this method simply looks at scattering from planes of fluorines, it is completely independent of either the tacticity of the sample or the packing of the chains in the $a-b$ plane.

Structure factors were measured for several samples and are listed in Table 4 along with the corresponding melting points. (The melting point of PVF, in work by Cais and Kometani,[4] has been correlated to the HH/TT content.) There is good correlation between the melting temperatures and the structure factor ratios. The ratios reported here, however, do not provide an absolute measure of the HH/TT content due to the fact that the temperature factor is not known for the reflections. It should provide an accurate indication of the relative defect content.

A comparison of the structure factors with the corresponding polymerization temperatures shows a good correlation; see Figure 10. This of course in turn implies a correlation of the polymerization temperature with the HH/TT content of the sample. The trend observed agrees with that determined from previous DSC work:[9] as the polymerization temperature is increased, the HH/TT content increases.

The use of the meridional intensities for the measurement of HH/TT defects appears to be a sensitive method for characterization. However, the analysis is based on

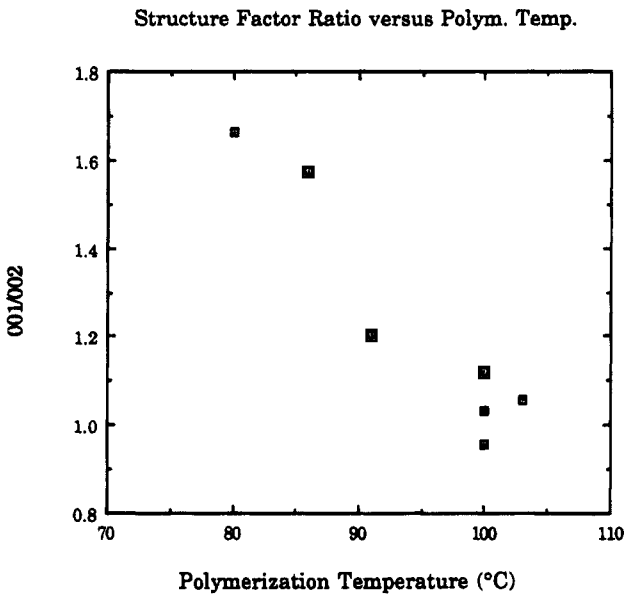

Figure 10. Dependence of the HH/TT content on the polymerization temperature of PVF.

an assumption and it is important to verify whether it is reasonable or not. The assumption is that the fluorines will crystallize into planes with a d-spacing equal to the c-axis length. The only instance where this will not be true is when a HH chain segment crystallizes, and this will result in a fluorine being displaced from the regular fluorine plane by a distance of half the c-length. The question arises as to whether this is a valid assumption. If it is not, then the analysis of the data is flawed.

There are two possible events, excluding a HH unit, that could produce a displaced fluorine. The first would result from a packing irregularity and is produced by incorporation into the crystalline region of a chain that is rotated 180° about the chain axis and shifted half of a unit cell spacing in the c-direction. This would allow the chain to pack in generally the same manner with the notable exception that the fluorines on the chain would be located at $z = {}^1/_2$ instead of $z = 0$; see Figure 11. The result would be that all of the fluorines on this chain would diffract in a manner equivalent to fluorines from HH units, thus producing an overestimation of the HH content.

The central question to the problem of a shifted chain is whether a chain can pack in this manner. The crystal structure of PVF implies that a shifted chain is not energetically favored in the crystalline region. This was reinforced by performing energy calculations for several systems. The calculations were performed for a syndiotactic system and two isotactic systems each composed of 48 packed chains, with each chain 12 monomer units long. One chain in the middle of the system was selected to be the aberrant chain and was rotated 180° about the chain axis and shifted half of a c-spacing along the z-direction. Statistical packing of the chains was not considered. The energy of the system was then calculated.

There is only one unique way (without varying the handedness of the chain) to pack the syndiotactic system, and there are two possible arrangements for the isotactic case. For the syndiotactic system, the total energy was −3680 kcal/mol, resulting in an energy penalty of +37 kcal/mol relative to a regular syndiotactic system. (See the previous paper for calculations on reference systems.) The first isotactic system was produced by a rotation and shift of a chain and resulted in an energy of −2748 kcal/mol which corresponds to an energy penalty of +76 kcal/mol. The second isotactic system, which involved an inversion of the rotated, shifted chain, produced an energy of −2797 kcal/mol, resulting in an energy penalty of +27 kcal/mol. In all three cases the systems were less favorable than the corresponding regular systems. This is a result of the 12° rotation of the chain placing the fluorines of one chain directly facing the fluorines on the adjacent chains.

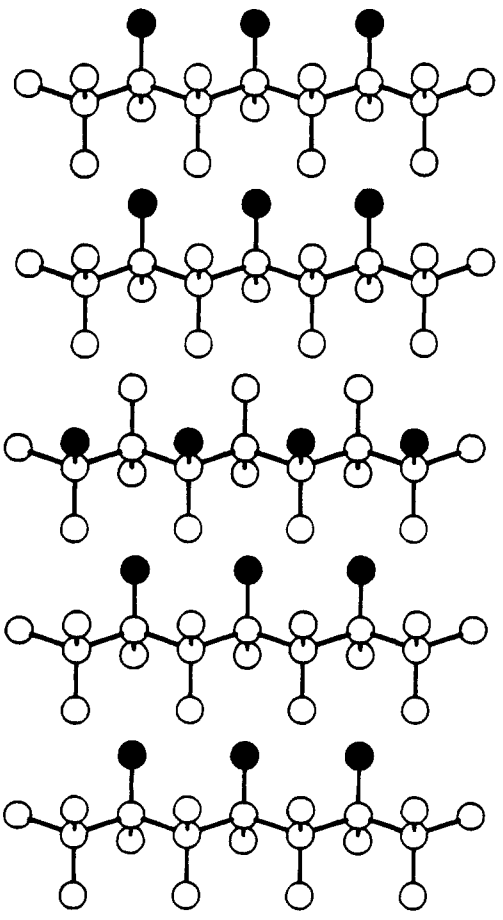

Figure 11. Diagram of a shifted chain in a crystalline region.

The packing energy for the regular syndiotactic system is −2092 kcal/mol which corresponds to −44 kcal/mol per chain. Shifting one chain in the system increases the energy by +37 kcal/mol, which indicates the energy savings associated with the chain crystallizing has been reduced to only −7 kcal/mol. Thus it is very unlikely the chain would crystallize in this manner.

Similar behavior is observed for the two isotactic cases. The packing energy for the regular isotactic system is −2344 kcal/mol, corresponding to a per chain packing energy of −49 kcal/mol. Thus the rotated, shifted chain actually produces a repulsive force of +27 kcal/mol, relative to a normally oriented chain, eliminating the possibility that the chain would pack in this fashion. The inverted chain generates an energy savings of −22 kcal/mol by crystallizing in this manner compared to an energy of −49 kcal/mol if it crystallizes in a regular fashion. Even though this is the most favored of the three cases, there is still a large energy penalty. Also, these calculations are only for a chain length of 12 monomer units, and thus as the chain length in the crystal increases, the energy penalty

associated with packing shifted chains increases. Thus the energy calculations support the crystal structure results that a shifted chain occurring in the crystal structure of PVF is not energetically favored.

The second possibility deals with the polymer chain structure. In this work it was assumed that the formation of a HH linkage is immediately followed by a TT unit. However, if this is not true, then the possibility arises that monomer units can add after the HH unit in a TH or "backward" fashion. If this chain crystallizes, then all the units that added in a backward fashion will place the fluorines at the wrong z-coordinate and they will reduce the 001 intensity. This would again cause an overestimation of the HH content.

The problem of monomer arrangement after a HH unit can be addressed by examining the polymerization probabilities. The radical polymerization of vinyl fluoride favors propagation in a HT fashion. This is due to the fluorine bearing carbons being the preferred propagating species. However, the monomer will occasionally add in a reverse direction, in which case a HH unit is formed. In the polymerization of PVF this is expected to occur 10–20% of the time. For this discussion an average value of 15% is used. The formation of a HH linkage results in a propagating radical of $-CH_2$. This is less stable than the $-CHF$ radical, and consequently the addition of the next unit favors a TT linkage in order to return to a $-CHF$ radical. To a first approximation, this probability (of a TT linkage) should be the same as a HT addition and thus would be 85%. This implies, however, that 15% of the time the HH unit will not be immediately followed by a TT unit but instead will be followed by a backward unit. Using these probabilities, the content of backward units can be calculated. The probability of one backward unit occurring in the chain is 0.15×0.15 or 2.25%; the probability of two sequential HH units is $0.15 \times 0.15 \times 0.15$ or 0.34%. Neglecting additional terms, this gives a total of approximately 2.6% TH units compared with 15% for HH units.

Thus it can be concluded that backward or reversed monomer units will occur in the chain. If they are incorporated into the crystalline regions, the HH content would be overestimated by a corresponding amount. Of course, as the probability of HH addition increases, the problem of backward units becomes more important. Aronson et al.[10] have pointed out the uncertainty backward units create; however, the apparent value for the HH content measured by X-ray can be corrected if the polymerization probabilities are known. In any event, whether the polymerization probabilities are known or not, the occurrence of backward units is dependent on the probability of HH units; the relative HH contents determined by X-ray will be correct. Therefore, the presence of backward units is of little concern for a relative comparison of HH content between samples.

Rietveld Discussion. The Rietveld method is based on a refinement of powder diffraction data. It provides an alternative method to a fiber analysis and therefore was investigated to see if it would support the previous X-ray work suggesting statistical packing in radically polymerized PVF. Additionally, although the fiber analysis proved inconclusive for determining the HH content, the 001 peak, which in the meridional analysis was shown to be sensitive to the HH content, is contained in powder diffraction data and therefore may provide an additional X-ray method for determining the HH content. This possibility, however, has not yet been investigated.

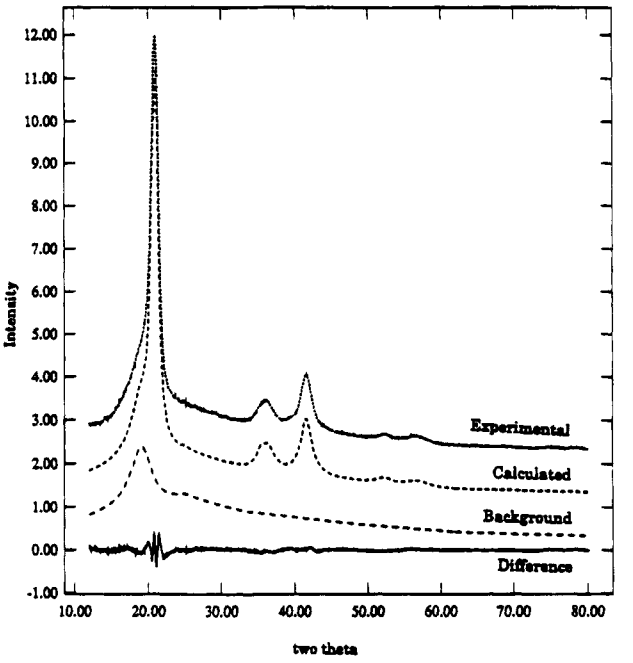

Figure 12. Comparison of calculated and experimental diffraction profiles for a conventional packing refinement.

Table 5. Comparison of the Two Refinements Using the Rietveld Method

	case 1	case 2
θ (rotation angle, deg)	0.0	8.0
R_2	0.079	0.114
R_3	0.070	0.107
peak width param		
u	0.0	0.0
v	13.35	12.89
w	−1.82	−1.32
sf (scale factor)	55.11	4.32
z (zero corr.)	0.054	−0.283
g (pref. orient.)	0.362	0.0379
b (temp fact.)	11.33	8.43
a (Å)	8.62	8.57 (fixed)
b (Å)	4.82	5.00
c (Å)	2.53	2.54

In order to eliminate several variables in this analysis, a perfect HT, perfectly random tacticity, linear PVF sample was used. The sample, which has been fully characterized by NMR,[4] was supplied by R. E. Cais from Bell Labs. This sample simplified the analysis since the HH content and tacticity were not variables.

A rigid-body refinement was performed, and a comparison of the observed and calculated diffraction profiles is shown in Figure 12. A general observation of the diffraction scan is a lack of features in the profile which is due to the metrically hexagonal unit cell of PVF. All of the peaks observed are composite profiles. Visually there is very good agreement between the calculated and experimental profiles as shown in the difference spectrum. The good agreement produced a very low R_3 factor of 0.070. However, examination of the refined parameters (see case 1 of Table 5) raises doubts concerning the validity of the refinement. First, the parameters defining the peak width, $v = 13.4$ and $w = -1.8$, appear to be large particularly when compared to values reported in other Rietveld work.[11–14] The preferred orientation parameter refined to a value of 0.362, nearly an order of magnitude larger than reported for other systems. Last, the temperature factor, $b = 11.3$, was very high. Although this magnitude would be acceptable for a refinement of fiber data,

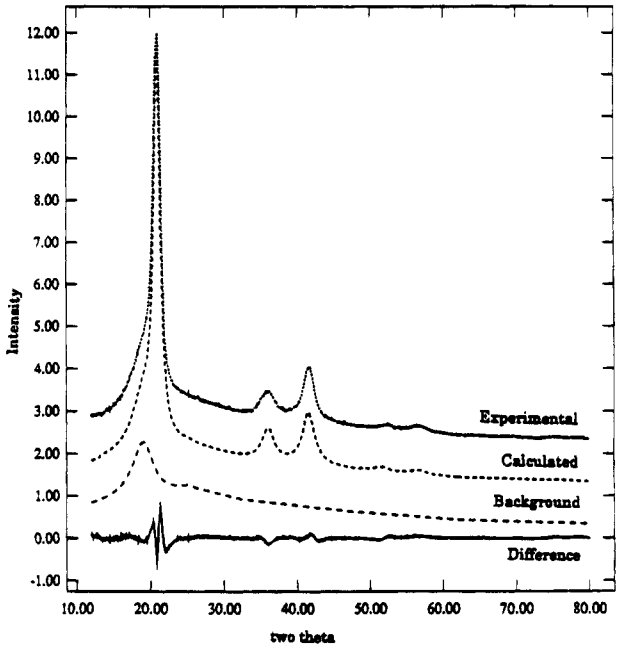

Figure 13. Comparison of calculated and experimental diffraction profiles for a statistical packing refinement with $\theta = 8.0°$.

a Rietveld analysis usually produces a temperature factor in the range 1.0–5.0 and maybe lower. Although the fit to the data is very good, the physical parameters required to produce the fit are unrealistic.

A second refinement was tried with statistical packing included. The chain rotation angle was not varied in the refinement and was instead fixed, after a period of trial and error, at an angle of 8.0°. When all of the parameters from the previous refinement were allowed to vary, unrealistic unit cell dimensions were generated. However, when the a-dimension was fixed at 8.57 Å, the refinement was much more promising. The R_3 factor was 0.107; a comparison of the observed and calculated profiles is shown in Figure 13. As before, the peak width parameters are large (see case 2 in Table 5). The preferred orientation parameter refined to an acceptable value of 0.038. The temperature factor was 8.4 and the b-dimension increased to 5.00 Å which is not unreasonable. The one new feature of this refinement was an increase of the zero-point correction to $-0.28°$ 2θ.

The allowance for disordered packing appears to provide a system that produces a physically reasonable refinement for a Rietveld analysis. In fact the allowance of disorder in the system offers an explanation for the large peak width and temperature factor; if the disorder in the system is not fully accounted for, the temperature factor will reflect this and have a higher value than otherwise expected. In addition, the presence of disorder in a system would act to disrupt long-range order in the crystalline regions. Within a crystal, one would observe a local structural order that may not translate to other parts of the same crystal. A result of this would be that diffraction from the material would have the appearance of occurring from very small crystallites which would manifest itself as a broadening of the peak widths. Thus the large peak-width parameters that were determined may themselves point to disorder in the system.

In conclusion, the Rietveld analysis appears to agree with a disordered packing for PVF. However, this can at most be a tentative conclusion as the refinement is unfinished. The refinement needs to be modified to allow the system to be described in generalized coordinates which would allow direct refinement of the axial rotation angle.

Conclusions

In the X-ray work, we have attempted to quantify the chain defects that can occur in PVF crystals. Three different methods have been used: a fiber analysis, an analysis of meridional intensities, and a Rietveld analysis. Using X-ray analysis, tacticity features of the chain are masked due to the statistical nature of the polymerization. Therefore, the analysis focused on the determination of HH/TT defects.

An analysis of fiber data proved insensitive to the HH/TT content in PVF. This was observed for data from both Natta's paper and data obtained from commercially available PVF. The commercial sample was best fit by allowance for statistical packing of the chains. An axial rotation angle of the chain was calculated to be 17.6°. Statistical packing was not observed in calculations using Natta's data. However, there is a high probability that Natta's polymer contained a syndiotactic bias. This implies that tacticity influences the packing order in PVF and is supported by molecular modeling calculations on systems of differing tacticity. The calculations revealed that only the syndiotactic system was stable in an ordered crystalline array, whereas the other systems developed distortions in both the chain conformation and packing arrangement.

The relationship of the meridional intensity and the HH content was investigated. It was shown that, as the HH content in a crystal increases, the 001 intensity decreases, while the 002 intensity is invariant. This indicates the relative HH content of a set of samples can be determined by simply measuring the ratios of the 001 to the 002 reflection. The measurements and calculations were made for several samples and compared with the polymerization temperature of the material. The data showed a correlation between the polymerization temperature and the HH content and confirm the DSC results: as the polymerization temperature is increased, the HH content of the polymer increases.

Last, the Rietveld method was used to investigate a perfect HT polymer provided by Bell Labs. An attempt to refine the structure, assuming an ordered packing arrangement, produced a very good fit to the observed diffraction profile but required that several parameters assume unrealistic values. Hence, the refinement was repeated, allowing for statistical packing of the chains. An axial rotation angle of 8° provided a structure that produced a good fit to the data and reasonable values for the parameters of the refinement. The smaller rotation angle required for the Rietveld method relative to that determined by the fiber analysis may indicate that the presence of HH/TT defects increases the disorder of the packing. However, the results presented here should be considered preliminary as a complete refinement of the rotation angle was not done.

It seems likely from both the fiber and Rietveld analysis that PVF produced by radical polymerization crystallizes in a disordered manner. The disorder has been simulated by allowing for statistical packing of the chains. However, this should probably be taken as simply an indication that disorder is present and is not necessarily descriptive of the actual order present. It

is possible and may be likely that the disorder would be better modeled by a distribution of axial rotation angles which would preserve, or very nearly so, the symmetry of the crystal.

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