place the upper bound on the length of a threefold helix. The average number of prolyl residues separating those occupying the minor region of low conformational energy is about 17, which is significantly larger than the 7-8 residues found in the longest threefold helices in the representative chain depicted in Figure 4. Therefore the origin of the upper limit must lie in the major region of low conformational energy.

The shape attributed to the major region of low conformational energy depends on the choice of the contour line used to define that shape. The shape is nearly rectangular if the contour used is that at 5 or 10 kcal/mol. For present purposes the boundary of this region is better described by the 1 kcal/mol contour line. Most prolyl residues will adopt conformations within this contour, and the local configuration required for propagation of a precisely threefold helix is to be found here. The upper limit to the number of turns in a recognizable threefold helix is provided by the slight flexibility about ψ when ϕ is held constant at 110° and the minor region of low conformational energy is ignored. The representative chain depicted in Figure 10 shows this upper limit to be about three turns. A significant fraction of the prolyl residues adopt ϕ near 130° when the constraint on ϕ is relaxed. There is then an additional disordering influence on the chain and consequent reduction in the maximum length of recognizable threefold helix from three turns to two. Since a change in ϕ requires an alteration in geometry of the pyrrolidine ring system, the flexibility of this ring plays a role in establishing the upper limit for the length of recognizable threefold helices for poly(L-proline) in solution. The pyrrolidine ring of poly(γ-hydroxy-L-proline) is less flexible than that in poly(L-proline).[17-20] Consequently, the maximum length of recognizable threefold helices should be somewhat larger in poly(γ-hydroxy-L-proline) than that found here for poly(L-proline).

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Notes

Orthorhombic vs. Monoclinic Structures for the α and γ Phases of Poly(vinylidene fluoride): An Analysis

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Recently, we investigated the crystal structures of the α, γ, and δ crystal forms of poly(vinylidene fluoride).[1-4] This effort was precipitated by the realization that the crystal structure of the γ phase originally proposed by Hasegawa et al.[5] was inconsistent with the X-ray fiber (and powder) diffraction pattern of that material.[1] Our structure analysis of the γ phase[2] appeared simultaneously with a short communication from Takashashi and Tadokoro[6] describing the results of a new investigation into the structure of the γ phase. The results of the two investigations are summarized in Table I. While the two structures are basically very similar, a few significant differences do exist. The most significant discrepancy is that the structure proposed by us is orthorhombic, while that proposed by Takahashi and Tadokoro belongs to the monoclinic crystal system. The higher symmetry of our proposed structure is due to the statistical parallel–antiparallel chain packing we believe to be present; if this packing were replaced by exclusively parallel chains, as is the case in the structure of Takahashi and Tadokoro, the symmetry of the resulting structure would be monoclinic even though the cell remained orthogonal.

After determining the structure of the γ phase, we investigated that of the δ phase and found that statistical parallel–antiparallel chain packing appeared to be present in that material as well.[3] These results suggested that this sort of statistical packing might also be present in the α phase of PVF_2, and so we reinvestigated that structure.

Two investigations into the structure of the α phase had already been performed: one by Doll and Lando[7] and, shortly thereafter, one by Hasegawa et al.[5] In our reinvestigation we employed the observed intensity data set of Hasegawa et al.[5] because it was the more complete of the two available. Our investigation confirmed the following points: the chain conformation proposed by Hasegawa et al. was preferable to the slightly different conformation originally proposed by Doll and Lando. The orientation of the chains about their axis is such that the component of the net chain dipole moment normal to the chain axis is directed in exactly the [100] direction, in agreement with the results of Hasegawa et al. and con-

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Table I
Summary of the Two Proposed Crystal Structures of the γ Phase of PVF$_2$

investigators	crystal system	unit cell parameters				chain conformation	chain packing	space group
		a, Å	b, Å	c, Å	β, deg			
Weinhold et al.[1,2]	orthorhombic	4.97	9.66	9.18	90.0	$\sim t_3gt_3\bar{g}$	statistical parallel-antiparallel	*C2cm*
Takahashi and Tadokoro[6]	monoclinic	4.96	9.58	9.23	92.9	$\sim t_3gt_3\bar{g}$	parallel	*Cc*

tradicting the proposal by Doll and Lando of slightly rotated chains. Finally, statistical parallel–antiparallel chain packing almost certainly was present in the sample examined. Statistical disorder often raises the apparent symmetry of a structure above that of its nondisordered counterpart; in this case, the effect of the statistical packing was to increase the symmetry from monoclinic to orthorhombic, leaving the size and shape of the unit cell unaltered.

However, the results of two very recent studies support the contention that the structures of the α and γ phases are monoclinic rather than orthorhombic. Lovinger[8] has prepared single crystals of the γ phase by epitaxially crystallizing PVF$_2$ from the melt onto a NaCl substrate at 165 °C. Electron diffraction unequivocally showed that the unit cell angle β is 93° for this material, in perfect agreement with the monoclinic γ phase unit cell proposed by Takahashi and Tadokoro.

Also, Takahashi et al.[9] have recently prepared uniaxially oriented specimens of α- and γ-PVF$_2$ in which the crystallite orientation was such that the chain axes were uniformly tilted from the fiber axis. The specimens were prepared by first orienting PVF$_2$ from the melt. Annealing this material at high temperatures (150–175 °C) with unconstrained ends resulted in the "tilted" α-phase samples. On the other hand, annealing the oriented material at 175 °C (for, presumably, a long period of time[6]) with fixed ends to prevent shrinkage gave rise to "tilted" γ-phase specimens. The tilting causes certain reflections in the X-ray diffraction patterns of these samples to split; that is, *hkl* and $\bar{h}kl$ reflections do not overlap as they do in an ordinary fiber diffraction pattern. For both the α- and γ-phase samples, *hkl* and $\bar{h}kl$ reflections had different intensities. This is clear proof that the observed structures did not have orthorhombic symmetry.

The purpose of this note is to reconcile the differences in the structures of the α and γ phases proposed by us and by Takahashi et al.

Some recent work done by Lovinger[10] strongly suggests that two modifications of the α phase exist. The diffraction pattern of melt-pressed films unaxially oriented at 145 °C is consistent with the statistically packed orthorhombic structure proposed by us. However, after such a film was annealed for many days at 175 °C, its diffraction pattern indicated that a transformation had occurred to a structure differing only in that regular antiparallel chain packing had replaced statistical chain packing; hence, the symmetry of the structure resulting from annealing would be monoclinic, as proposed by Takahashi et al.

The only readily detectable differences in the diffraction patterns of the two modifications of the α phase are the intensities of the 011 and 031 reflections. Lovinger's work[10] shows that, before annealing, these reflections are not visible; this is in agreement with the very low intensities calculated for these reflection in the case of the statistically packed orthorhombic modification (and, to a lesser extent, in the case of a nonstatistical structure of *parallel* chains[4]). Upon annealing, both reflections increase in intensity and become visible, with the 031 distinctly the stronger of the two; this is in agreement with the intensities calculated for the antiparallel chain monoclinic modification of the α phase.[4,5]

It is interesting to note that in our reinvestigation of the structure of the α phase[4] we employed the observed intensity data of Takahashi et al. In this data set the 031 reflection was barely visible as a very weak reflection, while 011 was not observed.[5] The very weak intensity observed for these two reflections was virtually the sole reason for preferring the statistically packed orthorhombic structure over the antiparallel monoclinic structure.[4] For the same reason, even the nonstatistical parallel chain structure is preferable to the antiparallel chain monoclinic structure.[4] Thus it is evident that the specimen investigated by Takahashi et al.[5] in 1972 consisted predominantly of the statistically packed orthorhombic modification of the α phase, with the balance consisting of the monoclinic modification. This is not surprising in light of Lovinger's findings,[10] since the specimen apparently was not annealed for a long time.[11]

On the other hand, the "tilted" α-phase specimens of Takahashi et al.[9] were annealed at high temperatures (for an unstated length of time). In the published reproduction of the X-ray diffraction pattern of such a specimen the 031 reflection is clearly visible and is included in the schematic representation of the diffraction pattern[9] (the 031 reflection falls just outside of the 121 reflection). The 011 reflection is not visible in the reproduction of the diffraction pattern; this is not surprising, since in the monoclinic modification of the α phase, the calculated intensity of the 011 reflection is only about 0.11–0.15 that of the 031 reflection[4,5] and such very weak reflections often do not appear in reproductions. Thus we agree with Takahashi et al. in concluding that the "tilted" specimen contains large amounts of monoclinic α-PVF$_2$. however, the evidence is consistent with the suggestion that the specimen transformed from the orthorhombic α phase to the monoclinic α phase during annealing.

We believe that two modifications of the γ phase of PVF$_2$ also may exist. These are, of course, the orthorhombic structure proposed by us[1,2] and the monoclinic structure proposed by Takahashi and Tadokoro[6,9] (see Table I). The evidence supporting this suggestion is not so clear-cut as in the case of the α phase. First, the obvious similarities in the chain conformation, packing, and unit cell of the α and γ phases suggest that a given thermal history may induce a similar response in both materials. The available evidence is consistent with the suggestion that crystallization of the γ phase at a high temperature (165 °C, epitaxial crystallization from the melt;[8] 175 °C, crystallization via a solid-state transformation from the oriented α phase[6,9]) results in the monoclinic modification with regular chain packing, while crystallization at lower temperatures (~100 °C, crystallization from dimethylacetamide solution followed by orientation at 178 °C[1,2]) yields the statistically disordered orthorhombic modification of the γ phase. Also, prolonged exposure to these high temperatures may induce an orthorhombic-to-monoclinic transition as in the α phase.

More substantial evidence suggesting that two modifications of the γ phase may exist is given in Table II, which

Table II
Interplanar *d* Spacings Calculated from the Monoclinic γ-Phase Unit Cell Proposed by Takahashi and Tadokoro

reflection	d,[a] Å	reflection	d,[a] Å
152	1.676	$\bar{2}42$	1.595
$\bar{1}52$	1.656	442	1.081
242	1.632	$\bar{4}42$	1.059

[a] Calculated from the unit cell a = 4.96 Å, b = 9.58 Å, c = 0.23 Å, and β = 92.9° (ref 6).

lists three pairs of interplanar spacings calculated from the γ-phase unit cell proposed by Takahashi and Tadokoro.[6] For this set, the difference between d_{hkl} and dh_{kl} is within the range of about 0.02–0.04 Å. At the fairly large scattering angles where these reflections occur, two adjacent reflections with d spacings differing by such an amount should be marginally distinguishable. Even if the two reflections were not quite resolvable, the resulting composite reflection would be unusually broad when compared to the width of reflections in which the h or l index was zero (in which case $d_{hkl} = d_{\bar{h}kl}$). We have reexamined our diffraction photographs of the γ phase and have found that none of the reflections listed in Table II (nor any other susceptible reflections) are split or unusually broad. This supports our proposed orthogonal γ-phase unit cell.

One additional piece of evidence exists to support the suggestion that more than one version of the γ phase exists. Lovinger[10,12] has found that annealing the δ phase of PVF_2 can result in transformation to the α, γ, and ϵ phases; the γ phase is by far the major transformation product. The 012 and 032 reflections of the γ phase are visible in the diffraction pattern of such annealed films. In a manner similar to the case of the α phase, the presence of these reflections strongly suggests that the chain packing is nonstatistical. However, the 012 and 032 reflections are systematically absent in structures having C-centered symmetry. The structures for the γ phase proposed both by us[2] and by Takahashi and Tadokoro[6] are C centered. Since the Takahashi samples are obtained under similar annealing conditions to the Lovinger samples, if the 012 and 032 γ-phase reflections are present, the Takahashi structure must be wrong. They appear to be present in their photographs.[9] In the unlikely event that they are due to the presence of α material, three variations of the γ form must be proposed.

To summarize: the recent work of Lovinger[10] strongly suggests the existence of two modifications of the α phase of PVF_2. The monoclinic version results from annealing the orthorhombic modification at high temperatures. Both modifications are crystallographically well defined and are stable for long periods under most conditions; neither version can be claimed as the only "true" α phase of PVF_2. In addition, we feel that a similar situation exists in the case of the γ phase of PVF_2.

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Unperturbed Rotational Isomeric State and Wormlike Polymethylene Stars of High Branch Point Functionality

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Rotational isomeric state theory provides a connection between local covalent structure and the mean unperturbed dimensions of chain molecules.[1] Calculations can rigorously be extended to branched molecules, but complexity of the calculation rapidly increases as branch points increase in number or in functionality, f.[2-4] Polymethylene stars with functionalities of 3 and 4 have been studied using rotational isomeric state calculations which retain a detailed treatment of the geometry and short-range interactions at the branch point.[5-8] Branch point geometries used were those observed in isobutane and neopentane.

Simpler expressions, based on a wormlike chain treatment of the chain statistics,[9] also quite accurately describe unperturbed dimensions of finite polymethylene stars with f = 3 or 4.[9,10] However, the wormlike chain model is not so successful in describing properties of starlike branched molecules obtained from certain other polymers.[10] Here we extend the rotational isomeric state calculations to polymethylene stars with f as large as 20. Detailed geometry at the branch point has been ignored because it becomes somewhat arbitrary for polymethylene stars when f rises above 4. The final approach of g to its asymptotic limit is found to depend on branch point functionality in the manner described by the wormlike chain treatment of stars developed by Mansfield and Stockmayer.[9] Here g is the ratio of unperturbed mean square radii of gyration for branched and linear polymethylenes containing the same number of bonds.[11]

Calculations

The rotational isomeric state model adopted for the unperturbed polymethylene chain is that described by Flory and co-workers.[12] The value of g for an f-functional rotational isomeric state star containing n bonds, or $n_b = n/f$ bonds per branch, was estimated as

$$g = [(f-1)(2n_b+1)^2C_c - (f-2)(n_b+1)^2C_b]/[(n+1)^2C_l] \tag{1}$$

Here C_i denotes the characteristic ratio, $\langle s^2\rangle_i/n_il^2$, where $\langle s^2\rangle_i$ is the mean square radius of gyration and l is the bond length. For C_l we have the linear chain in which n_i is n. By C_c we mean the characteristic ratio for a main chain of $2n/f$ bonds within the branched molecule. Its mean square radius of gyration is calculated using the matrix expression appropriate for a linear chain containing the same number of bonds. The characteristic ratio of one of the branches containing n/f bonds is denoted by C_b. The pertinent mean square radius of gyration is that for a subchain of n/f bonds, located at one end of a main chain