Unit Cell of the γ Phase of Poly(vinylidene fluoride)

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ABSTRACT: There has been recent controversy regarding the unit-cell structure of the γ phase of poly(vinylidene fluoride) as determined by X-ray diffraction analysis from uniaxially oriented samples. To resolve this uncertainty, the structure was investigated by use of electron diffraction on single crystals of γ-PVF_2. Various reciprocal-lattice planes were examined through tilting of single crystals about different crystallographic axes; preferred orientations of such single crystals had been obtained by crystallization on mica and NaCl. It was found that γ-type chains ($T_3GT_3\bar{G}$) pack in a monoclinic unit cell with a = 4.96 Å, b = 9.67 Å, c = 9.20 Å, and β = 93°. Existence of an antipolar analogue of the γ phase (ε-PVF_2) is discussed and possibilities for its occurrence are examined.

Introduction

The γ phase of poly(vinylidene fluoride) has attracted much interest recently, particularly in regard to its unit-cell structure. For many years, this polymorph could not be obtained in oriented form because it transforms very readily to the β phase under mechanical deformation. Nevertheless, Hasegawa and co-workers,[1] based on X-ray diffraction patterns from unoriented samples, suggested a monoclinic unit cell (very similar to that of the β form) with dimensions a = 8.66 Å, b = 4.93 Å, c = 2.58 Å, and β = 97°; the chain conformation was considered to be essentially all-trans.[1] However, in 1979, Weinhold, Litt, and Lando[2] succeeded in orienting an especially high-molecular-weight sample of γ-PVF_2 crystallized from solution; from this, they deduced an orthorhombic unit cell of dimensions a = 4.97 Å, b = 9.66 Å, and c = 9.18 Å. This cell has essentially the same ab base as the α phase of PVF_2 but approximately double the c-axis length. At about that time, Lovinger and Keith[3] obtained melt-grown single crystals of γ-PVF_2, whose electron-diffraction patterns were consistent with the unit cell proposed by Weinhold et al.[2] In the meantime, Weinhold, Litt, and Lando[4] have conducted a very detailed crystal-structure analysis of the γ-phase, confirming their unit-cell dimensions and showing that the chain conformation is essentially $T_3GT_3\bar{G}$. However, Takahashi and Tadokoro[5] have now reported an alternative crystal structure for γ-PVF_2, differing slightly from that of Weinhold et al.:[4] their cell is monoclinic, with a = 4.96 Å, b = 9.58 Å, c = 9.23 Å, and β = 92.9°, and their molecular conformation is also $T_3GT_3\bar{G}$.

Both of these unit-cell structures[4,5] have been proposed on the basis of X-ray diffraction patterns from uniaxially drawn specimens. A much more fruitful technique in this regard is electron diffraction because, on the one hand, it probes structure at the level of single crystals and, on the other, it allows individual reciprocal-lattice nets to be imaged and examined separately. This paper describes an attempt to resolve the unit-cell structure of γ-phase poly(vinylidene fluoride) by use of electron microscopy and electron diffraction.

Experimental Section

Extremely thin films of PVF_2 (Kynar 821 from Pennwalt Corp.) were prepared by depositing a drop of a 0.1% solution of the polymer in *N,N*-dimethylformamide on a substrate and evaporating the solvent at 180 °C. Two different substrates were used, muscovite mica and NaCl; both were freshly cleaved, exposing (001) faces upon which the molten films were crystallized at 165 °C. The polymeric films were shadowed with Pt/C, coated with carbon, floated off in water, and transferred to copper grids for electron-microscopic examination at 120 keV in a JEOL 100-CX transmission electron microscope.

Results and Discussion

Films crystallized on mica yielded platelets of the γ phase in a flat orientation (i.e., with their broad faces parallel to the substrate), as described previously.[3,6] Molecular chains in these crystals are inclined at 28.5° to the lamellar normal, with the b axis of the unit cell parallel to the substrate;[3] as a result, the reflecting reciprocal-lattice net is hkh (see Figure 1). The interplanar spacings of the reflections in Figure 1 were accurately determined by evaporating a calibrating compound (TlCl) directly on these crystals. For each reflection of γ-PVF_2, the nearest TlCl rings were used to calibrate the camera constant, thus minimizing any errors arising from lens aberrations or from the slight curvature of the Ewald sphere; also, measurements for both the PVF_2 and TlCl reflections were made at the same azimuthal angle in order to eliminate possible distortions from the magnetic lenses. In the case of Figure 1, the 020, 040, and 060 reflections were used to evaluate the length of b; from a total of 20 measurements, b was found equal to 9.67 ± 0.02 Å (within 95% (2σ) confidence limits). Thus, the b axis of the γ cell is appreciably larger than proposed by Takahashi and Tadokoro[5] and essentially the same as that suggested by Weinhold et al.[4] It should be mentioned that the values given in this paper are not expected to reflect unit-cell distortions from electron irradiation because beam currents were kept extremely low, so that crystallinity persisted for quite some time after the diffraction patterns had been photographed. To verify this, electron-diffraction patterns from single crystals of the α phase were measured in the same manner, yielding the accepted values[1] of a and b.

Tilting of these flat γ crystals about b by 28.5° in one direction and by 61.5° in the other yielded the $hk0$ and $0kl$ sections of the reciprocal lattice, respectively; the first of these is shown in Figure 2, while the second is to be published elsewhere.[8] a^*b^* views such as Figure 2 allow precise measurement of the a axis. From five such measurements, a was found to be 4.96 ± 0.01 Å, in agreement with previous values.[4,5] An equal number of measurements on the b^*c^* net gave a value of c = 9.20 ± 0.02 Å, which is intermediate between the two earlier values.[4,5] Unit-cell dimensions were also determined for three specimens of a Kureha KF-1100 resin crystallized at 168 °C on mica; these are known[1] to have a somewhat lower percentage of inverted monomeric units. No consistent differences in axial lengths were found between the unit cells of the two resins.

With respect to unit-cell angles, γ is clearly 90° from Figure 2, and so is α from the $0kl$ diffraction pattern. The angle β could in theory be determined by measuring precisely the angle involved in tilting from an a^*b^* to a b^*c^* view, or vice versa. However, because each reflection is in reality a reciprocal-lattice spike,[3] such angular measurement cannot be made with the required confidence. For this reason, PVF_2 was crystallized epitaxially on KBr with the hope that edge-on lamellae of γ-PVF_2 would grow

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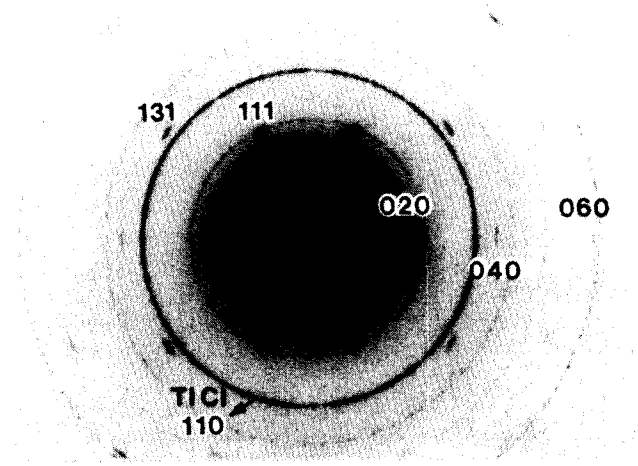

Figure 1. Electron-diffraction pattern from untilted lamellae of γ-PVF_2 crystallized on mica. The reflecting net is *hkh*.

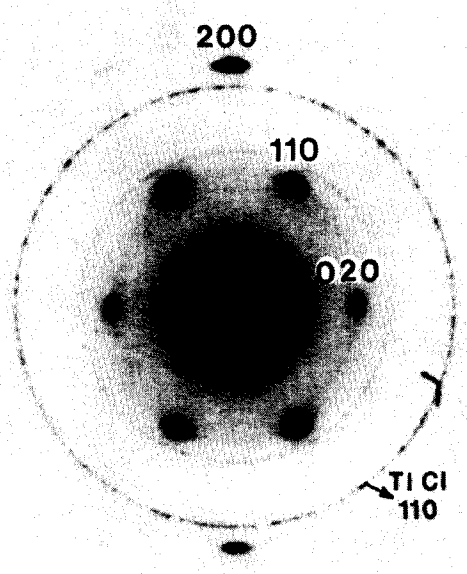

Figure 2. Electron-diffraction pattern from lamellae of γ-PVF_2 crystallized on mica and tilted 28.5° about *b*. The reflecting net is *hk*0.

in the desired a^*c^* orientation. However, as is described elsewhere[9], this approach yielded the β phase instead. Edge-on lamellae of the γ phase were ultimately grown epitaxially on NaCl, yielding a cross-hatched morphology of crystals aligned in two perpendicular directions as seen in Figure 3. Electron-diffraction patterns from such crystals (Figure 4), however, do not correspond to the *h*0*l* section of the reciprocal lattice. There are two orthogonal patterns of 004 and 142 reflections oriented in such a manner with respect to the specimen that the molecular chains are either normal or parallel to the long axes of the crystals in Figure 3; the former is obviously much more likely and is assumed here.

Tilt sequences of these crystals about one of the *c*-axis directions (the vertical one in Figures 4, 5, and 8) brought a number of diffraction patterns into view, most prominent of which was the pattern seen at a tilt angle of 27° in Figure 5. Both the value of this angle and the spacings of all reflections imply that the reciprocal-lattice section imaged in Figure 5 is the 0*kl*. Interestingly, this diffraction pattern appeared irrespective of whether the crystals had

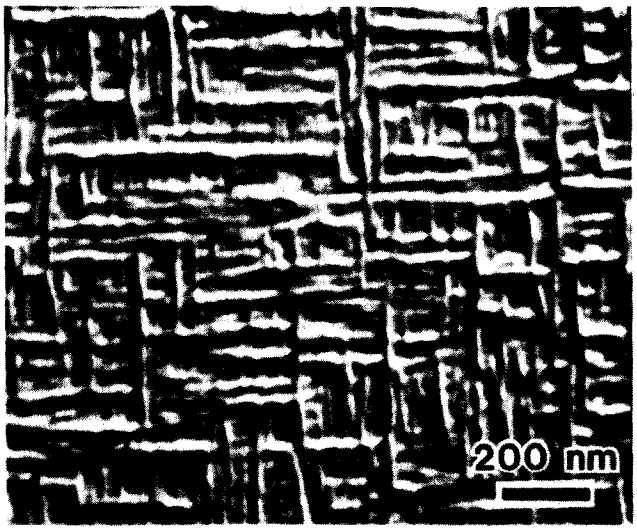

Figure 3. Electron micrograph showing the appearance of γ crystals of PVF_2 grown epitaxially on NaCl.

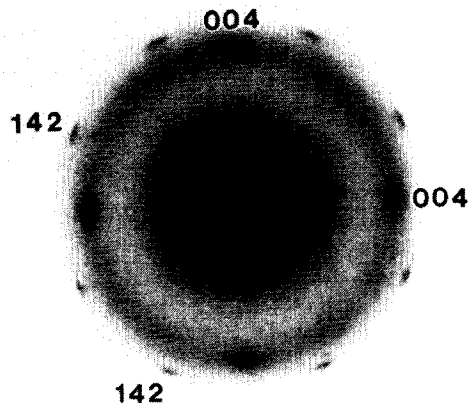

Figure 4. Electron-diffraction pattern from untilted crystals of γ-PVF_2 grown epitaxially on NaCl.

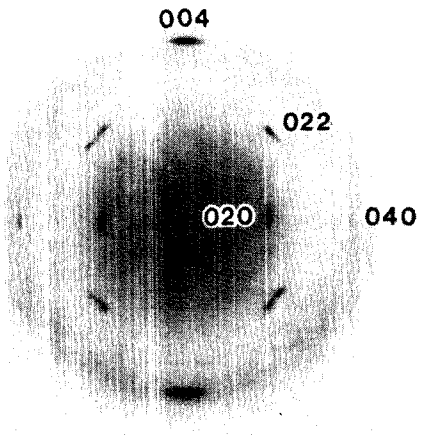

Figure 5. Electron-diffraction pattern from crystals of γ-PVF_2 grown epitaxially on NaCl and tilted 27° about one of the *c*-axis directions (vertical). The reflecting net is 0*kl*.

been tilted by 27° clockwise *or* counterclockwise. Since the untilted position does not correspond to a major symmetry plane of the unit cell, this result must be ascribed

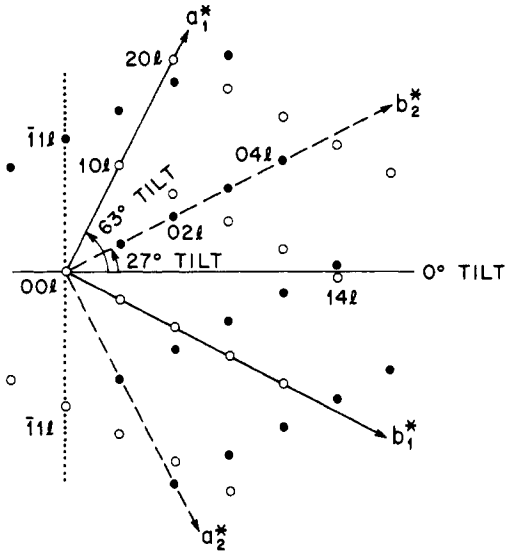

Figure 6. Reciprocal-lattice geometry for crystals of γ-PVF_2 grown epitaxially on NaCl.

to a double orientation of the lattice.

The situation can now be analyzed with the aid of Figure 6, which is a projection of the prevailing geometry along the c direction used as the tilt axis. The two reciprocal lattices $a_1^*b_1^*$ and $a_2^*b_2^*$ incorporating this c axis are denoted by open and closed circles, respectively, and are placed with their b axes 27° away from the untilted position. In addition to these two lattices, two others, stemming from crystals grown orthogonally to the above, are also present but are not shown in Figure 6, since they are not being tilted about their c axis and thus contribute little to the composite diffraction patterns. The fact that only $00l$ and $14l$ reflections were seen in the untilted position is clearly substantiated by Figure 6. Further, it is seen in this figure that the $(\bar{1}10)$ planes of *both* lattices are parallel to the untilted position (the same holds true for the two lattices in the second population of crystals that have grown orthogonally to the above). This immediately reveals the origin of the double orientation, as well as the crystallographic arrangement of the γ unit cell on the NaCl substrate: the crystals grew edge-on with their most densely packed {110} planes in contact with the (001) surface of NaCl. Two equivalent orientations, depending upon the inclination of molecular chains to the substrate, are possible (see Figure 7), leading to growth of two lattices for each population of orthogonally grown crystals. These two lattices are mirror images of each other with respect to reflection in the (001) plane of the substrate; in a sense, the two lattices are mutually in a quasi-twinned relationship, having $(\bar{1}10)$ as the composition plane.

The geometry depicted in Figure 6 clearly suggests that the desired a^*c^* view, needed for determination of the angle β, will be imaged by tilting of the crystals to 63° from their original position in either direction. This was indeed the case, and the resulting $h0l$ diffraction pattern is now depicted in Figure 8. The angle β was consistently found equal to 93°, in exact agreement with the prediction of Takahashi and Tadokoro;[5] the spacings of all reflections of Figures 4, 5, and 8 agree well with the unit-cell dimensions given above, thus confirming that this monoclinic angle is not an artifact introduced by epitaxy on NaCl.

Presence of the 100 reflection in Figure 8 and of the 142 reflection in Figure 4 should be noted. The 100 reflection is not expected from a polar unit cell, while the 142 reflection should be absent in the case of a polar unit cell containing chains directed statistically up and down as

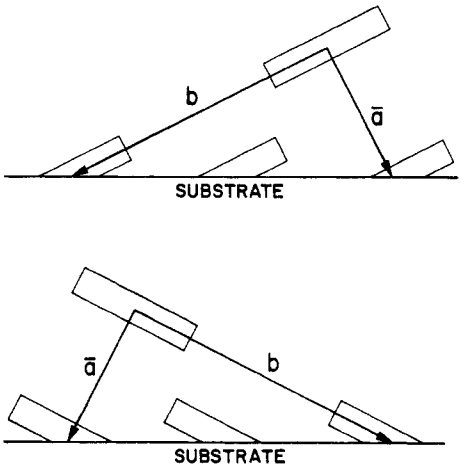

Figure 7. Two equivalent possibilities for molecular deposition of γ-type chains on the NaCl substrate; the rectangles show schematically the positions of chains in the γ unit cell.

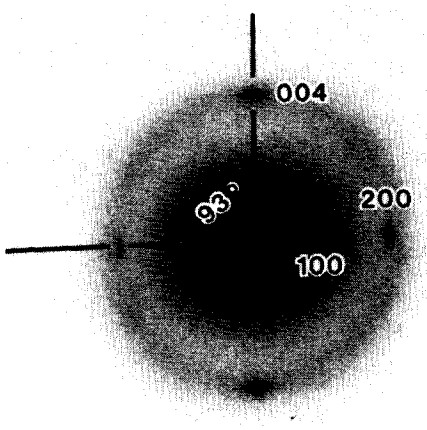

Figure 8. Electron-diffraction pattern from crystals of γ-PVF_2 grown epitaxially on NaCl and tilted 63° about the vertical c-axis direction. The reflecting net is $h0l$.

described by Weinhold et al.[4] (sense of direction in these chains is defined by the inclination of CF_2 dipoles along c). In the case of γ crystals grown on mica, these reflections are always absent but are commonly observed from γ-PVF_2 epitaxially grown on NaCl. Two possibilities may account for these reflections: (1) From their shadowing lengths, the crystals grown on NaCl are estimated to be ~15–25-nm tall; therefore, when the sample is tilted by 60°, the electron beam must pass through an effective specimen thickness of ~30–50 nm. At these thicknesses, dynamical effects are prominent in electron diffraction. Such dynamical effects are, of course, well-known to yield otherwise prohibited reflections. In this context, it should be mentioned that it is these large sample thicknesses that make the diffraction patterns in Figures 4, 5, and 8 so diffuse. (2) The second possibility is that epitaxial crystallization on NaCl produces a nonpolar unit cell, or, as far as the 142 reflection is concerned, one whose molecular chains are not statistically packed. A nonpolar cell would come about if alternate $T_3GT_3\bar{G}$ chains were packed with their dipole vectors antiparallel rather than parallel. Such a situation would then yield a fifth polymorph of PVF_2 (ϵ form) related to the γ phase in the same manner as the α phase is related to the δ phase (polar α phase).[10] Because of the ready crystallization from the melt of $TGT\bar{G}$ chains in an antipolar fashion and because of the similarity in ab

cell base dimensions between α- and γ-PVF_2, it is not unreasonable to contemplate existence of an antipolar analogue of the γ phase (ϵ-PVF_2).

Irrespective of the situation prevailing in epitaxially grown crystals, existence of such a fifth polymorph of PVF_2 may be suggested with a certain degree of caution based upon our knowledge of solid-state transformations of $TGT\bar{G}$ chains at high temperatures.[5,6,11,12] Such transformations have been studied by Lovinger[6,11] in spherulites of the α phase, by Takahashi and Tadokoro[5] in drawn films of α-PVF_2, and by Servet and Rault[12] in uniaxially oriented samples of the δ form; in all three cases, the transformation has been found to yield chains of a $T_3GT_3\bar{G}$ conformation. Since the high-temperature solid-state transformation requires only *intra*molecular rearrangements,[5,6,11] it is reasonable to expect that the difference in chain packing between the α and δ phases might be reflected in the packing of $T_3GT_3\bar{G}$ chains after annealing, leading to two different polymorphs. One might then enquire whether or not the $TGT\bar{G} \rightarrow T_3GT_3\bar{G}$ transformation is also accompanied by dipole inversion in alternate chains—a process which may be achieved by rotation of every second chain by 180° or, as recently suggested,[13] by relatively small, intramolecular bond rotations. Intuitively, one would not expect annealing to cause dipole inversions in half of the chains. However, Takahashi and Tadokoro[5] found a reduction in the intensity of the 100 reflection during annealing of α-PVF_2, while Servet and Rault[12] reported an increase after heat treatment of the δ phase; both data are consistent with dipole inversions and may suggest, therefore, that high-temperature annealing causes the antipolar α phase to transform to the *polar* γ phase and the polar δ phase to transform to the *anti*polar ϵ phase. This somewhat surprising possibility is under investigation and will be discussed on the basis of current experiments in a subsequent publication.

Conclusions

It has been found that γ-type molecular chains pack in a unit cell with a slight monoclinic angle β (=93°), in agreement with the model of Takahashi and Tadokoro;[5] the *b*-axis length is, however, closer to the value reported by Weinhold, Litt, and Lando.[2,4] Epitaxial crystallization of PVF_2 on NaCl yields γ-phase crystals grown with one of their {110} planes parallel to the substrate. Possible existence of an antipolar analogue of γ-PVF_2 (ϵ phase) is suggested; the γ and ϵ forms would then be mutually related in the same manner as the δ and α phases.

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References and Notes

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Method for Estimating the Configurational Entropy of Macromolecules†

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ABSTRACT: A method is outlined by which computer simulations of the structure and dynamics of large molecules can be used to estimate the classical configurational entropy difference between molecular conformations. The method can be employed with any simulation technique, such as harmonic analysis, molecular dynamics, or Monte Carlo. The formulation permits the use of arbitrary coordinates (e.g., normal modes, internal or Cartesian coordinates) and makes possible the determination of the contributions of particular degrees of freedom to the entropy change. Illustrative applications are made to conformational transitions of butane and decaglycine. It is found that significant contributions to the entropy change arise from fluctuations of internal coordinates other than the single-bond torsion angles. This indicates that additional internal coordinates (principally the bond angles) have to be retained in statistical mechanical models of the conformational thermodynamics of large molecules.

I. Introduction

The conformations of macromolecules, such as proteins and nucleic acids, play an essential role in their biological function.[1] To understand the factors involved in the stability of a given conformation and in the change of one conformation to another, it is necessary to be able to evaluate the energetic and entropic contributions to the free energy. Since the configurational entropy is expected to be very important in many transformations (e.g., protein denaturation, helix–coil transition), considerable effort has been expended in developing methods for its evaluation.[2-7] Although there have been a number of studies of the helix–coil transition in peptides, little progress has been made

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