The statistical factor doubles the reactivity of ethylene sulfide.

References and Notes

(1) Penczek, S.; Slazak, R.; Duda, A. *Nature (London)* **1978**, *273*, 738.
(2) Polish Patent 78934, 20.09.76; *Chem. Abstr.* **1976**, *85*, 537.
(3) Duda, A.; Penczek, S. *Makromol. Chem.* **1980**, *181*, 995.
(4) Morton, M.; Kammereck, R. F.; Fetters, L. J. *Br. Polym. J.* **1970**, *3* (3), 120.
(5) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.
(6) Grant, D.; van Wazer, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 3012.
(7) Dumas, P.; Spassky, N.; Sigwalt, P. *J. Polym. Sci.* **1976**, *14*, 1015.
(8) Corno, C.; Roggero, A.; Salvatore, T.; Mazzei, A. *Eur. Polym. J.* **1977**, *13*, 77.
(9) Aliev, A. D.; Solomatina, I. P.; Zhumabaev, Zh.; Alieva, S.; Krentzel, B. A. Auth. Cert. USSR N51 6711, 1976. *Referat. Khim.* **1978**, *11*, C399π.
(10) Aliev, A. D.; Zhumabaev, Zh.; Krentzel, B. A. *Nature (London)* **1979**, *280*, 846.
(11) Penczek, S.; Slazak, R.; Duda, A. *Nature (London)* **1979**, *280*, 846.

Annealing of Poly(vinylidene fluoride) and Formation of a Fifth Phase

Andrew J. Lovinger

Bell Laboratories, Murray Hill, New Jersey 07974. *Received July 2, 1981*

ABSTRACT: Annealing behavior in films of poly(vinylidene fluoride) containing $\mathrm{TGT\bar{G}}$ chains in either an antipolar packing (α phase) or a polar arrangement (δ phase) has been studied. As regards the α phase, single crystals, or films isothermally drawn at high temperatures, do not undergo solid-state transformations to the γ form during annealing; defect-ridden structures or adjacent γ crystals are generally required to produce an $\alpha \rightarrow \gamma$ transformation. However, annealing of drawn α films causes changes in the diffraction pattern that imply conversion to a nonstatistically packed arrangement of α chains. The polar analogue of the α phase (δ phase) easily transforms at high temperatures to yield a mixture of polymorphs: dominant among these is the polar γ phase, while smaller amounts of its antipolar analogue (ϵ phase) and of the α phase are also formed. The previously suggested existence of this ϵ phase is demonstrated on the basis of X-ray diffraction data.

Introduction

Four crystalline polymorphs of poly(vinylidene fluoride) ($\mathrm{PVF_2}$) have been described in the literature. The α phase is the one commonly obtained by crystallization from the melt;[1,2] its molecular chains adopt a distorted $\mathrm{TGT\bar{G}}$ conformation and pack in a unit cell with a = 4.96 Å, b = 9.64 Å, c = 4.62 Å, and all angles = 90°.[3,4] Although each $\mathrm{TGT\bar{G}}$ chain possesses a net dipole moment, the α-unit cell is not polar because alternate chains pack with their dipole components normal to c in an antiparallel fashion.[3,4] However, poling under a high electric field causes reversal of these dipole components in every second chain,[5,6] leading to a polar analogue of α-$\mathrm{PVF_2}$ known as the δ phase.[7] This reversal may be accomplished by physical rotation of alternate chains through 180°[5,6] or through propagation of a 180° twist along the molecular chain;[8] however, a seemingly simpler mechanism requiring no physical rotation of chains, but only small intramolecular rotations that alter the $\mathrm{TGT\bar{G}}$ conformation to $\mathrm{T\bar{G}TG}$, has recently been proposed.[9] The common ferroelectric[10] phase of $\mathrm{PVF_2}$ is the β phase, in which the molecules assume an all-trans conformation[11] (or a statistically distorted version thereof[3]) and pack in an orthorhombic unit cell with a = 8.58 Å, b = 4.91 Å, and c = 2.56 Å.[3] The fourth known polymorph of $\mathrm{PVF_2}$ is the γ phase, which was shown by Weinhold and co-workers[12,13] to have essentially the same ab cell base as the α form but double the c-axis repeat. This conclusion has been confirmed by subsequent studies,[2,14–16] although the structure appears to be monoclinic,[15,16] rather than the originally suggested orthorhombic.[12,13]

In a recent paper[16] dealing with the structure of the γ phase, the possibility for existence of a fifth polymorph of $\mathrm{PVF_2}$ (ϵ phase) was noted; the present study offers experimental evidence and a discussion of the conditions for manifestation of such a fifth form.

Experimental Section

The $\mathrm{PVF_2}$ samples used were KF-1100 resin, a Kureha Chemical Industry Co., Ltd., polymer having 3.8% of inverted monomeric units ("head-to-head, tail-to-tail") as determined by $^{19}\mathrm{F}$ NMR.[17] Films of this polymer, ~100 μm thick, prepared by compression molding, were uniaxially drawn at 145 °C in an Instron apparatus at a rate of ~10%/min to extension ratios of 4:1–5:1. These films were coated with Al electrodes in a vacuum evaporator and then poled for 30 min at 80 °C under an electric field of 1.2 MV/cm. These specimens were annealed under vacuum with their ends restrained in a metallic holder. To prevent melting of the original samples at the high temperatures employed, the annealing temperature was gradually raised to its final value in accordance with the following heating program: 160 °C/2 h → 165 °C/2 h → 170 °C/2 h → 175 °C/1 day → 180 °C/5–25 days. After completion of heat treatment, the specimens were examined at room temperature by X-ray diffraction and IR spectroscopy.

Results and Discussion

The changes occurring in these samples as a result of the experimental procedure are reflected in their X-ray diffraction patterns depicted in Figure 1. The drawn films are initially of the α phase, whose antipolar packing is evidenced by the presence of reflections with odd $h + k$ indices (e.g., 100, 120, 121), as seen in Figure 1a. Heat treatment of the α phase has been found[15,18] to result in a gradual change in conformation from $\mathrm{TGT\bar{G}}$ to $\mathrm{T_3GT_3\bar{G}}$. However, in the case of our drawn α specimens, no such changes were ever observed, as may be seen in Figure 1b: here, even after excessive annealing (25 days at 175 °C), neither new layer lines characteristic of the γ phase[12,13,15] nor diffuse streaks consistent with intermediate defect structures[15,19–21] are apparent (such changes in conventionally drawn α-$\mathrm{PVF_2}$ have also been found missing in the

0024-9297/82/2215-0040$01.25/0

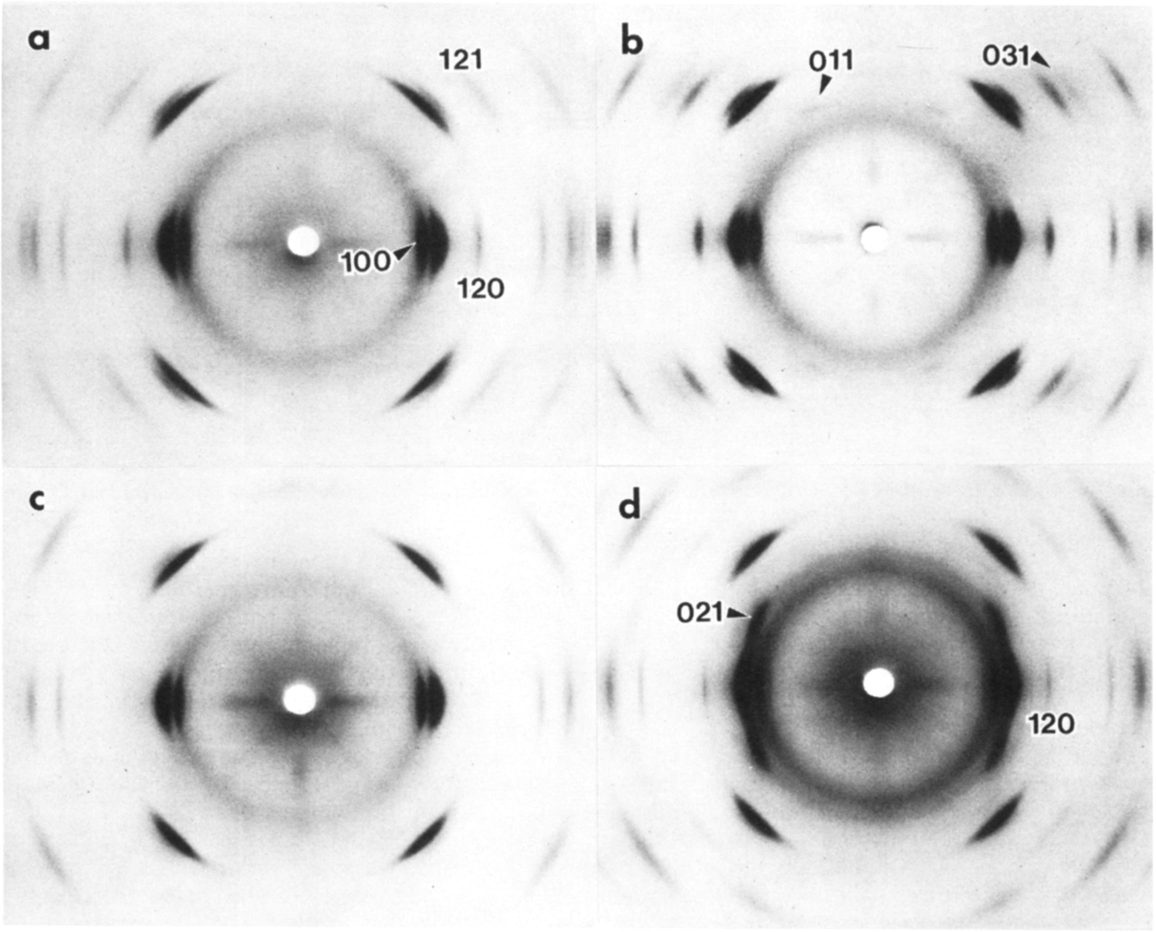

Figure 1. Wide-angle X-ray diffraction patterns of uniaxially drawn PVF_2 recorded at room temperature (fiber axis vertical): (a) after drawing at 145 °C, ~5 mm/min, 5:1 extension ratio; (b) same as (a), after annealing at 175 °C for 25 days; (c) same as (a), after poling at 1.2 MV/cm, 80 °C; (d) same as (c), after annealing at 175 °C for 20 days.

recent studies of Servet and co-workers[22] and Takahashi et al.[21]). The only immediately obvious difference between diffraction patterns a and b of Figure 1 lies in the sharpening of all existing reflections consistently with perfection of the α structure at the high annealing temperatures.

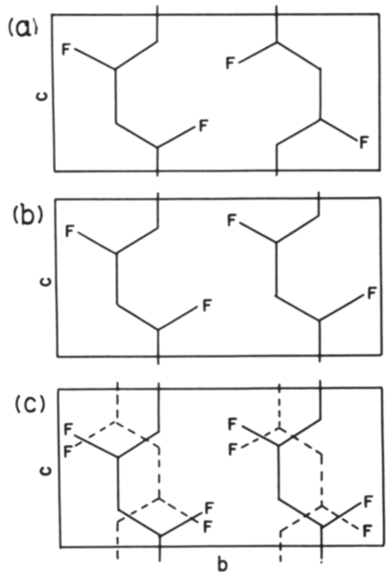

Figure 2. Schematic models of (a) up–down arrangement, (b) up–up arrangement, and (c) statistical arrangement of chains in α-PVF_2, seen in projection along a.

However, an important effect of annealing in α-PVF_2 may be noted by careful inspection and comparison of patterns a and b in Figure 1: The latter is seen to contain two extra sets of reflections identified as 011 and 031 of the α phase that are absent in the unannealed specimen (Figure 1a). The 011 reflection was also absent in the X-ray data of Hasegawa et al.,[3] while the 031 reflection was weakly present.[3] Appearance of these reflections following heat treatment provides a major clue with respect to the arrangement of α chains along c. Three types of arrangement were recently examined by Bachmann and Lando:[4] these are defined in Figure 2 on the basis of the inclination of their CF_2 dipoles to the chain axis as (a) up–down (equivalent to down–up), (b) up–up (equivalent to down–down), or (c) a statistical arrangement of up and down chains, each having a 50% probability of existence. A very detailed structure-factor analysis by Bachmann and Lando[4] led to their adoption of the statistically arranged unit cell as the most appropriate to the X-ray data, while an earlier study by Hasegawa et al.[3] reported an up–down packing. Among most of the 60 reflections observed,[3] the differences in calculated[4] structure factors for the three packing models are very small; the only substantial difference is seen for reflections of the $0kl$ type with $k = 2n + 1$, to which the 011 and 031 reflections belong. Specifically, for 011 the calculated[4] structure factors are 10.6 (up–down), 9.3 (up–up), and 2.0 (statistical mixture), while for 031 they are 31.3 (up–down), 6.7 (up–up), and 6.0 (statistical mixture). In this light, the appearance of 011 and 031 in Figure 1b indicates that annealing disfavors the statistical packing and tends instead to induce a regular directional arrangement of chains. Whether this regular arrangement is up–up or up–down cannot be unequivocally

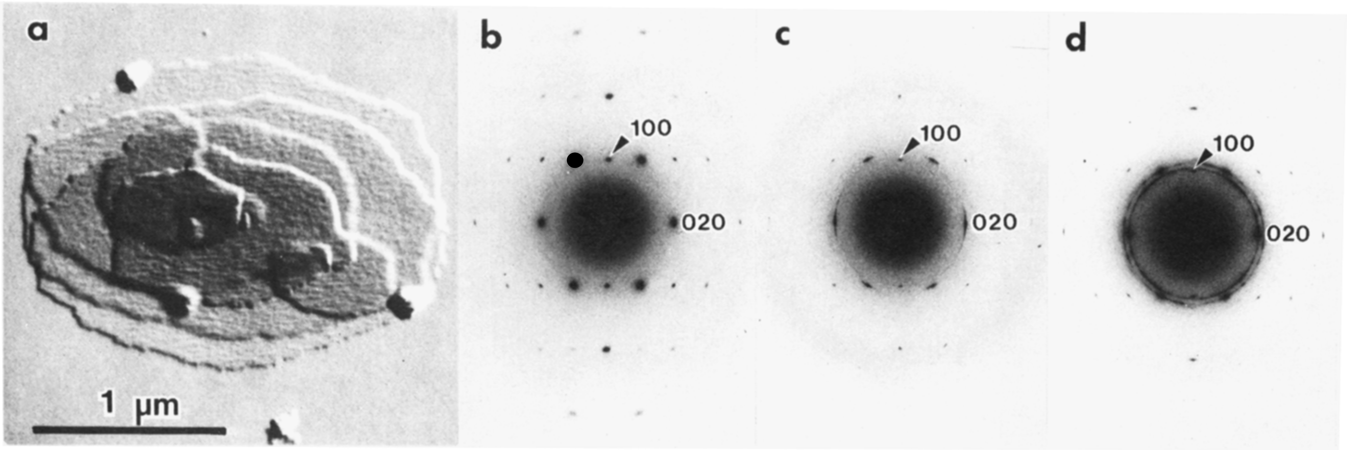

Figure 3. (a) Electron-microscopic appearance of a single crystal of α-PVF$_2$ crystallized from dilute solution in 90/10 chlorobenzene/dimethylformamide. (b) Electron-diffraction pattern from this crystal. (c) Electron-diffraction pattern from a similar crystal after annealing at 168 °C for 3 days. (d) Electron-diffraction pattern from a similar crystal after further annealing at 180 °C for 3 days.

concluded from these two reflections alone, but requires instead refinement of the complete structure using all reflections; however, the strength of the 011 and 031 reflections in Figure 1b appears to be more compatible with the up–down packing (Figure 2b).

To investigate further whether different types of α specimen may undergo transformation to the γ phase, oriented samples were prepared under conditions similar to those employed by Takahashi and Tadokoro:[15] Films of PVF$_2$ (KF-1100) were melted on a very thin Teflon substrate and then rapidly drawn manually at room temperature while they crystallized. Upon subsequent annealing under the conditions described above, many (but not most) of these films, particularly the highly extended ones, exhibited the behavior described by Takahashi and Tadokoro:[15,19–21] Streaks in the diffraction pattern along c^*, appearing in the initial stages of annealing, ultimately shifted to form layer lines of new reflections characteristic of the γ phase.[12,13,15,21] Moreover, the samples undergoing these transformations generally showed weak precursors of streaks even prior to annealing, thus implying existence of an *originally* disordered α structure.

From the above, it is seen that the $\alpha \rightarrow \gamma$ transformation in oriented films, far from being a general phenomenon, occurs only under very special circumstances. Clearly, slow, controlled drawing of a spherulitic α material at high temperatures strongly disfavors subsequent transformation to the γ polymorph. What appears to favor transformation in oriented α-PVF$_2$ is existence of a more defect-ridden structure such as found in samples melt crystallized by high and rapid extension at low temperatures and exhibiting precursors of streaks even without annealing. These results on drawn films are also supported by evidence from solution-grown single crystals or melt-grown spherulites of the α phase. In the first case, α single crystals were grown by slowly cooling a 90/10 chlorobenzene/dimethylformamide solution to room temperature.[23] After these crystals were annealed in the dry state first at 168 °C for 3 days and then at 180 °C for 3 more days, their electron-diffraction patterns were examined in the electron microscope. As may be seen in Figure 3, no phase change is seen in the electron-diffraction pattern after annealing at 168 °C: the 100 reflection, characteristic of the antipolar packing in α-PVF$_2$, survives the heat treatment, showing that no measurable transformation to the polar γ phase has been induced. Following further heat treatment at 180 °C, although some melting and recrystallization have occurred, reflections with $h + k$ = odd are still visible. With respect to solid-state transformations during annealing of spherulites of α-PVF$_2$, it has previously[18] been found that such processes are generally initiated at those regions of α spherulites that are in contact with γ spherulites; lamellae of α-PVF$_2$ isolated from their γ counterparts undergo transformation only rarely.[18]

We can now move on to the effects of annealing on the polar counterpart of α-PVF$_2$, the δ phase. As has also been found in earlier studies,[5–7,21,22,24] its X-ray diffraction pattern prior to annealing is seen in Figure 1c to be devoid of the 100, 120, and 121 reflections of Figures 1a and 1b. Annealing of these δ samples yields diffraction patterns such as that seen in Figure 1d; appearance of new layer lines signifying a conformational change from $TGT\bar{G}$ to $T_3GT_3\bar{G}$ has also been noted by Servet and co-workers[22,24] and Takahashi et al.[21] As in annealed α-PVF$_2$ (Figure 1b), here, too, reflections implying a nonstatistical arrangement of chains with respect to c are again observed, although less prominently than in Figure 1b. However, the aspect of major importance in this transformation is whether or not the conformational change resulting from annealing is also accompanied by a change in packing normal to c. This issue was first mentioned in a previous publication,[16] in which the two possible types of packing of $T_3GT_3\bar{G}$ chains (polar, corresponding to the γ phase, or antipolar, corresponding to a hypothetical ϵ phase) were discussed. Possibilities for existence of such a fifth phase were raised[16] on the basis of the observation by Servet and Rault[24] that annealing of δ-PVF$_2$ causes reappearance of the 100 and 120 reflections; although this implication of their observation was not presented in their original paper,[24] Servet and colleagues have, in the meantime, discussed it in a subsequent publication,[22] in which they concluded that these reflections reappear as a result of partial conversion back to the α form. Takahashi et al.[21] state that annealing of δ-PVF$_2$ yields the γ phase and make no mention of reappearance of other reflections.

An attempt to clarify this matter by examining the X-ray and infrared evidence from δ-PVF$_2$ subjected to annealing is presented below. In the first place, it was confirmed that the 100 and 120 reflections reappear in all specimens (see Figure 1d), although their intensities vary somewhat relative to those of the remaining reflections. There are two possible reasons for reappearance of these reflections: either (1) a transformation of δ-PVF$_2$ partly to the polar γ phase and partly back to the antipolar α phase, or (2) a transformation of the δ phase to an antipolar analogue of γ-PVF$_2$ (ϵ phase).

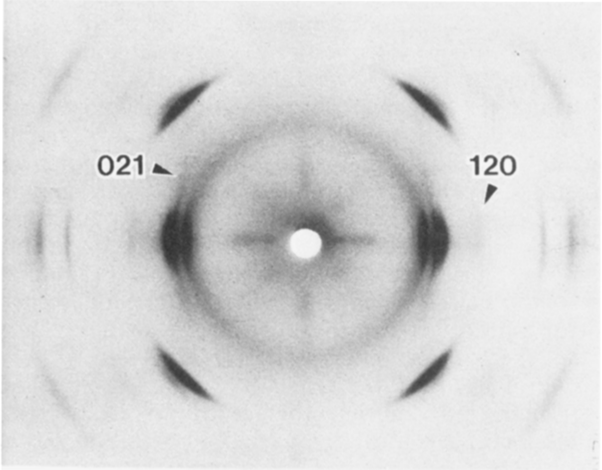

Figure 4. X-ray diffraction patterns from uniaxially drawn δ-PVF_2 after annealing at 155 °C for 2 days.

If the 120 reflection recurs solely from a reversion to the α phase, then it must be accompanied by a contribution to the intensities of the other even-layer-line reflections in Figure 1d that is slightly less than the intensities of corresponding reflections in Figure 1a (since 120 in Figure 1d is slightly less intense than in Figure 1a). Now, the 021 reflection in Figure 1d is attributable solely to the γ phase; since drawn α and γ specimens contain the same even-layer-line reflections (i.e., identical in location and differing only slightly in intensity), this 021 reflection must also be accompanied by a substantial contribution to the intensities of its counterparts in even-layer lines. In essence, the diffraction pattern of Figure 1d should then consist of a superposition of patterns from the oriented α and γ forms, whose relative contributions can be scaled from the intensities of the 120 and 021 reflections, respectively. In this manner, the intensities of many reflections in Figure 1d would be expected to be significantly higher than they actually are.

A second check of the relative amounts of α and γ phases expected by heat treatment of δ-PVF_2 is based on a study of X-ray diffraction patterns as a function of annealing temperature. It is known that the $TGT\bar{G} \rightarrow T_3GT_3\bar{G}$ conformational change occurs at high temperatures,[18-22] whereas the δ phase (in unrestrained samples) commences reversion to the α phase at much lower temperatures (~120 °C). We investigated the relative occurrence of these phenomena in *restrained* films of δ-PVF_2 by monitoring the first appearance of the 120 and 021 reflections in our annealing experiments. Contrary to the behavior characterizing free specimens, the 120 reflection was not observed at low temperatures in their restrained counterparts; as seen in Figure 4, both the 120 and the 021 reflections appeared simultaneously at ~155 °C. This tends to point toward common, rather than disparate, origins for both of these reflections.

If the 120 and 021 reflections do not arise from separate $\delta \rightarrow \gamma$ and $\delta \rightarrow \alpha$ transformations, then their common origin must lie in a polymorph that combines the intramolecular conformation of the γ form ($T_3GT_3\bar{G}$) with the intermolecular packing of the α form (antipolar). Conclusive evidence that such an ϵ phase exists can be obtained by careful examination of the first layer line of annealed δ specimens, as in Figure 1d. A higher magnification of the relevant region of the diffraction pattern is seen in Figure 5 to contain a very weak, yet undoubtedly present, reflection at the precise intersection of the *hk*1 layer line and the 12*l* row line; since this reflection is not at the tail end of other, stronger reflections and since neither the α nor the γ phase ought to diffract at this reciprocal-space location, the reflection is unequivocally identified as 121 of ϵ-PVF_2. However, it should at once be pointed out that its intensity is weaker than what would be expected if all other reflections in Figures 1d and 5 were attributable to this ϵ phase. Moreover, the 121 reflection varied in intensity among our specimens (even within the same specimen), becoming in some cases practically invisible. All these observations imply that, while the ϵ phase is indeed real, it is by no means the exclusive product of the high-temperature annealing of δ-PVF_2 but constitutes most probably only a minority population.

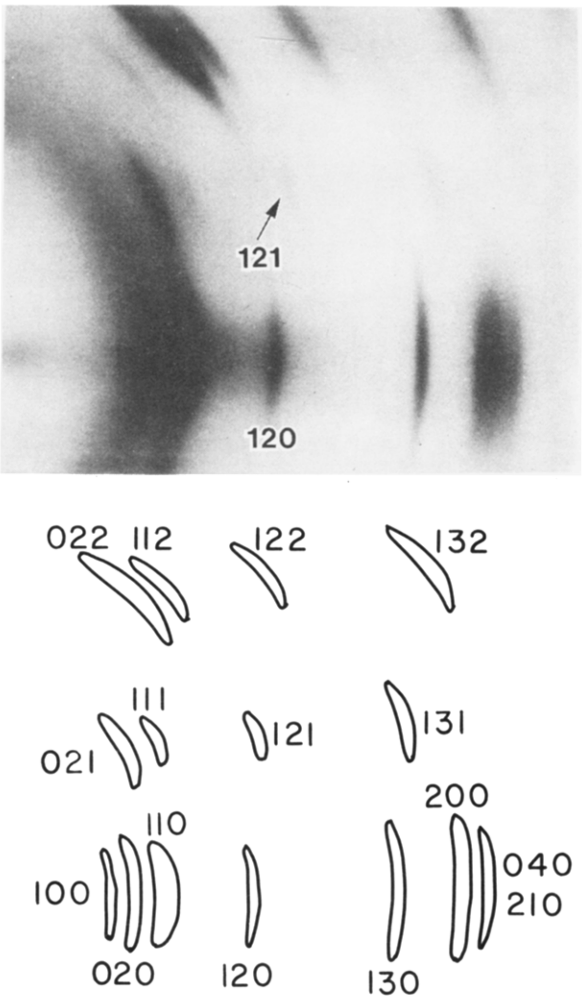

Figure 5. Enlargement of a portion of the diffraction pattern of Figure 1d and identification of the observed reflections.

To test these conclusions further, films annealed at high temperature were examined by infrared spectroscopy. The detailed IR study of Bachmann et al.[25] shows that a region of the spectrum that can serve for clear differentiation among the various polymorphs of PVF_2 extends between 850 and 1000 cm^{-1}. Specifically, the α and δ phases absorb strongly at 976 cm^{-1}, around which no other polymorph contributes significantly; at 895 cm^{-1}, the γ phase (and, presumably, ϵ, as well) is the only form that shows a strong absorption. The relevant region of the IR spectrum before and after heat treatment of our specimens is presented in Figure 6. It is seen that annealing causes a major increase in absorption at 895 cm^{-1}, signifying adoption of the $T_3GT_3\bar{G}$ conformation. At the same time, the 976-cm^{-1} peak is substantially diminished but does not disappear. One may, therefore, infer that a small fraction of molecular chains is in the $TGT\bar{G}$ conformation (almost certainly α, since the δ phase is under a strong impetus to transform

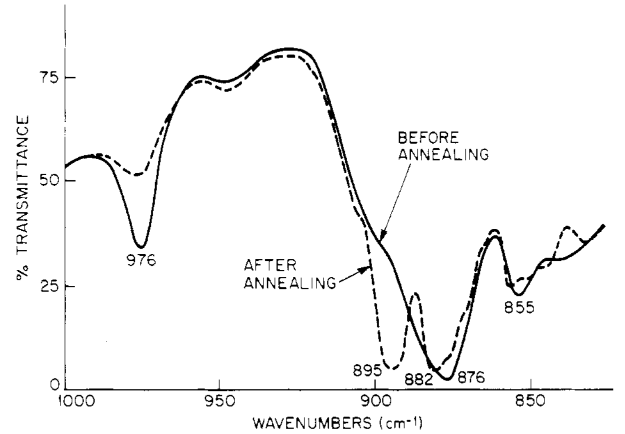

Figure 6. Portion of the infrared spectrum of uniaxially oriented δ-PVF$_2$ before and after annealing at 175 °C for 20 days.

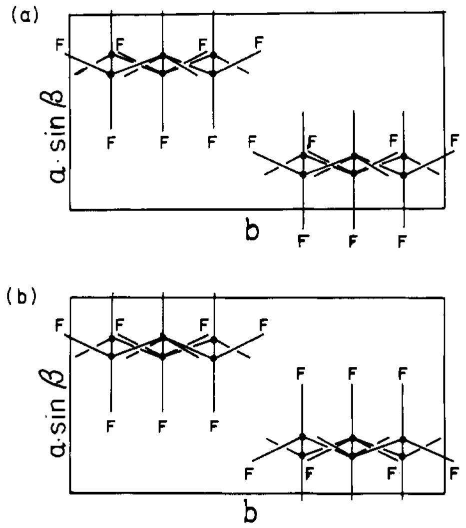

Figure 7. Projection along *c* of $T_3GT_3\bar{G}$ chains in (a) polar packing (γ phase) and (b) antipolar packing (ϵ phase).

even at lower temperatures and much shorter thermal treatments than that used to obtain Figure 6).

We may now integrate the preceding results with those of earlier publications to arrive at the following conclusions: (1) High-temperature annealing of the α phase does not generally lead to transformation, unless other factors are initially present (e.g., defects, heterogeneities, lamellae of the γ phase). Instead, there is a perfection of structure, accompanied by a regular (i.e., nonstatistical) arrangement of chains with respect to the molecular axis. (2) High-temperature annealing of the δ phase easily causes transformation to a mixture of forms, generally γ, ϵ, and α. (3) As shown by X-ray and IR evidence, only a small minority of the annealed chains reverts to the α phase; the remaining chains adopt a $T_3GT_3\bar{G}$ conformation. (4) Of the latter ones, a small fraction pack in an antipolar fashion, constituting a fifth polymorph of PVF$_2$ (see Figure 7), as evidenced by presence of the 121 reflection. (5) The weakness (and occasional imperceptibility) of this reflection and the piezoelectric data of Servet et al.[22] imply that the dominant product of the transformation is the γ phase.

It is not yet known on what energetic basis conversion to the ϵ phase is possible. Clearly, of the two possible packings of $T_3GT_3\bar{G}$ chains (see Figure 7), the polar one is energetically the more favorable. Normally, the opposite packing is not expected to arise in a thermodynamic process: for example, among $TGT\bar{G}$ chains where the antipolar packing is favored, the polar arrangement is induced only under high electric field, whereas annealing causes at least a partial return to the original packing. It may be that the potential-energy difference between the two packing modes of $T_3GT_3\bar{G}$ chains is quite small; then, under annealing conditions that, on the one hand, transform the $TGT\bar{G}$ conformation to $T_3GT_3\bar{G}$, while, on the other, establish antipolar $TGT\bar{G}$ packing, kinetic considerations might permit a limited combination of these two processes, leading to antipolar packing of $T_3GT_3\bar{G}$ molecules.

Acknowledgment. The manuscript has benefited from the careful reading and comments of Dr. H. D. Keith.

References and Notes

(1) Prest, W. M., Jr.; Luca, D. J. *J. Appl. Phys.* **1975**, *46*, 4136.
(2) Lovinger, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *19*, 793.
(3) Hasegawa, R.; Takahashi, Y.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1972**, *3*, 600.
(4) Bachmann, M. A.; Lando, J. B. *Macromolecules* **1981**, *14*, 40.
(5) Davis, G. T.; McKinney, J. E.; Broadhurst, M. G.; Roth, S. C. *J. Appl. Phys.* **1978**, *49*, 4998.
(6) Naegele, D.; Yoon, D. Y.; Broadhurst, M. G. *Macromolecules* **1978**, *11*, 1297.
(7) Bachmann, M. A.; Gordon, W. L.; Weinhold, S.; Lando, J. B. *J. Appl. Phys.* **1980**, *51*, 5095.
(8) Dvey-Aharon, H.; Taylor, P. L.; Hopfinger, A. J. *J. Appl. Phys.* **1980**, *51*, 5184.
(9) Lovinger, A. J. *Macromolecules* **1981**, *14*, 225.
(10) McKinney, J. E.; Davis, G. T.; Broadhurst, M. G. *J. Appl. Phys.* **1980**, *51*, 1676.
(11) Lando, J. B.; Olf, H. G.; Peterlin, A. *J. Polym. Sci., Part A-1* **1966**, *4*, 941.
(12) Weinhold, S.; Litt, M. H.; Lando, J. B. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 585.
(13) Weinhold, S.; Litt, M. H.; Lando, J. B. *Macromolecules* **1980**, *13*, 1178.
(14) Lovinger, A. J.; Keith, H. D. *Macromolecules* **1979**, *12*, 919.
(15) Takahashi, Y.; Tadokoro, H. *Macromolecules* **1980**, *13*, 1317.
(16) Lovinger, A. J. *Macromolecules* **1981**, *14*, 322.
(17) Schilling, F. C., private communication.
(18) Lovinger, A. J. *Polymer* **1980**, *21*, 1317.
(19) Takahashi, Y.; Kohyama, M.; Tadokoro, H. *Macromolecules* **1976**, *9*, 870.
(20) Takahashi, Y.; Tadokoro, H. *Macromolecules* **1980**, *13*, 1316.
(21) Takahashi, Y.; Matsubara, Y.; Tadokoro, H. *Macromolecules*, in press; private communication.
(22) Servet, B.; Broussoux, D.; Micheron, F.; Bisaro, R.; Ries, S.; Merenda, P. *Rev. Tech. Thomson-CSF* **1980**, *12*, 761.
(23) Okuda, K.; Yoshida, T.; Sugita, M.; Asahina, M. *J. Polym. Sci., Part B* **1967**, *5*, 465.
(24) Servet, B.; Rault, J. *J. Phys. (Paris)* **1979**, *40*, 1145.
(25) Bachmann, M. A.; Gordon, W. L.; Koenig, J. L.; Lando, J. B. *J. Appl. Phys.* **1979**, *50*, 6106.