

Figure 4. Structure of the kink band in modification II. Broken lines show the regular structure of modification II.

bands can be reconstructed by stacking four kinds of unit-layer structures, A, B, C, and D, which have a thickness half of the fiber period of modification II and infinite size in the ab plane (Figure 2). Model I was constructed by stacking these four kinds of unit-layer structures, so that the kink bands of both odd and even numbers of monomeric units coexist in a crystallite. In model II, the kink bands are composed of an even number of monomeric units. This model was constructed by stacking four kinds of layer structures, A, B, CC, and DD; CC and DD were made by putting unit-layer structures C and D on themselves. In model III, the kink bands are composed only of one monomeric unit; this model was constructed by layer structures A, B, CB, and DA, where CB and DA were made by putting unit-layer structure B on C and A on D, respectively. In model IV, which was constructed by two kinds of layer structures, AB and DD, the regular TGTG segments shift only to one direction by the kink bands of an even number of monomeric units. Model V was constructed by layer structures A, B, CBD, and DAC, where CBD and DAC were made by combining three unit-layer structures in this order; in the kink bands, the molecule assumes a T_3GT_2 or $T_3\bar{G}T_2$ conformation.

By assuming that $w_A = w_B = 0.4$ (w_A and w_B are the existence probabilities of the unit-layer structures A and B), the number of parameters could be reduced to one parameter P_{ij} for all models, where P_{ij} is the probability of finding layer j after layer i . The intensity distribution calculations were made by changing the value of P_{ij} . The best fit to the observed intensity distribution in each model is chosen and shown in Figure 3 along with the value of P_{ij} . In Figure 3, the observed intensity distributions are somewhat smeared by the incomplete orientation of the crystallites in the fiber specimen. The intensity distributions calculated for models III and V agree well with the observed ones with respect to the position of the intensity maximum, which is almost independent of the value of P_{ij} . In model IV, there are no intensity maxima on the calculated intensity distributions along 02ζ and 11ζ and in models I and II, the position of the calculated intensity maximum on 11ζ is different from the observed position. Furthermore, from the broadness of the intensity maximum, model III seems to give rather good agreement between the observed and calculated intensity distributions. Anyway, it must be considered that the conformational change between TGTG and TGTG, i.e., the "flip-flop motion", takes place in the molecular chain of modification II, since the kink bands in models III and V are composed of one monomeric unit, a pair of T conformations. Accordingly, during the heat treatment, the kink bands are formed by the flip-flop motion between TGTG and TGTG and the motion from G or \bar{G} to T which forms the kink bands themselves. Here, the flip-flop motion between TGTG and TGTG seems to play a major role rather than the motion from G or \bar{G} to T, since model III gives good agreement between the observed and calculated intensity

distributions and model V does not. Therefore, the kink bands are considered to be formed as a joint between two successive regular segments where the flip-flop motion between TGTG and TGTG took place and did not take place (Figure 4). Furthermore, from the formation of the band structure, it might be considered that the flip-flop motion between TGTG and TGTG takes place cooperatively in several molecules. The results of the calculation will be published in detail elsewhere.

References and Notes

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Crystal Structure of Form III of Poly(vinylidene fluoride)

We previously found that form III of poly(vinylidene fluoride) results from high-pressure heat treatment and also from casting from dimethyl sulfoxide or dimethylacetamide.¹ On the basis of X-ray diagrams of unoriented form III, we reported what we thought was a reasonable crystal structure.² Recently, Weinhold et al.³ prepared a special high-molecular-weight sample of poly(vinylidene fluoride) by using radiation polymerization. By casting from dimethylacetamide and stretching just below the melting point (178 °C) they obtained an oriented fiber specimen which they considered to be form III. They indexed the fiber diagram by an orthorhombic unit cell with lattice constants $a = 4.97$, $b = 9.66$, and $c = 9.18$ Å. The values of a and b are equal to those of form II, and the c value is close to twice the c value of form II (4.62 Å). They⁴ proposed a preferred $T_3GT_3\bar{G}$ molecular conformation, based on energy calculations of Tripathy et al.⁵ But they did not rule out other possible conformations such as $(TG)_2(T\bar{G})_2$ etc.⁴ Lovinger and Keith⁶ reported that the form obtained by crystallization at high temperature coincides with form III reported by Weinhold et al.³

Quite independently, we have approached the structure analysis of form III again. We have found the appearance of streaks along the ξ -constant lines on heat treatment of form II (KF-1100, Kureha Chemical Industry Co. Ltd.). We interpreted this phenomenon by a kink band structure.^{7,8} By heat treatment of this sample at 175 °C for 10 days, we obtained a sample that gave the highly oriented crystalline X-ray diagram shown in Figure 1 (top). In the process of heat treatment at 175 °C, intensities of Bragg reflections change, and the diffuse streaks coalesce to new spots. In Figure 1 (top), the reflections from the odd-layer lines are broader than those from the even-layer lines; this broadness reveals the existence of conformational disorder.

The fiber diagram in Figure 1 (top) is essentially the same as that of form III reported by Weinhold et al.³ and moreover corresponds well to the X-ray diffraction pattern of the unoriented form III (Figure 1 (bottom)) except for very weak reflections from the even-layer lines which are attributed to form II. The sample of unoriented form III was prepared by casting from a dimethylacetamide solu-

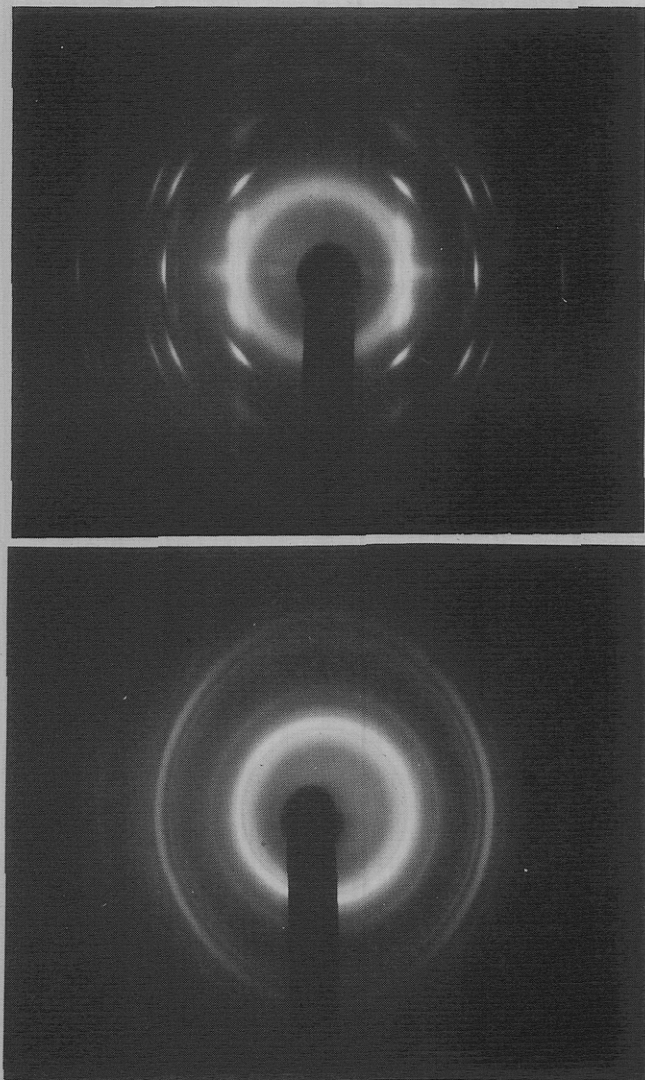


Figure 1. (Top) Fiber diagram of form III of poly(vinylidene fluoride). (Bottom) X-ray diffraction pattern of unoriented form III.

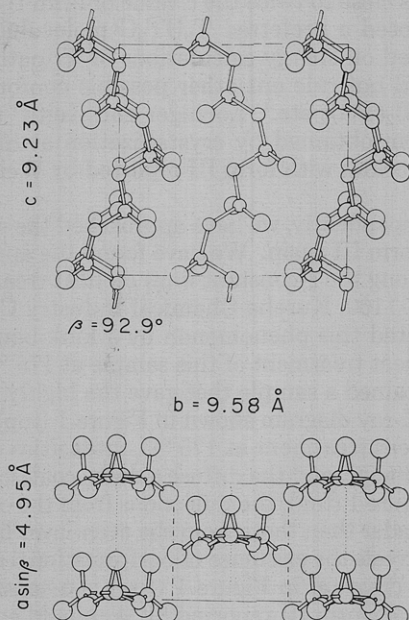


Figure 2. Crystal structure of form III of poly(vinylidene fluoride).

tion, drying in vacuo, and annealing at 175 °C for about 1 h.

All of the observed reflections were indexed by a

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monoclinic unit cell with parameters $a = 4.96 \text{ \AA}$, $b = 9.58 \text{ \AA}$, c (fiber axis) $= 9.23 \text{ \AA}$, and $\beta = 92.9^\circ$. The systematic absences $h + k \neq 2n$ for hkl and $l \neq 2n$ for $h0l$ suggested that space groups Cc and $C2/c$ be examined. We considered the $T_3GT_3\bar{G}$ and $(TG)_2(T\bar{G})_2$ conformations, which have fiber identity periods of 9.11 and 8.78 Å, respectively, as plausible molecular models.

After applying repeated trial and error and constrained least-squares methods,^{9,10} we obtained the crystal structure shown in Figure 2. The space group is $Cc-C_4$ and the molecular conformation is essentially the $T_3GT_3\bar{G}$ type. The R factor is 17% for the 47 independent reflections. The agreement between the observed and calculated intensities is better in the even-number layers than in the odd-number layers. This fact may be associated with some disorder. The structure is polar as in the case of form I. Piezoelectricity should be expected.

Form II showing streaks could be obtained by heat treatment of form II. Furthermore, formation of the fiber diagram, which coincides with form III on the even-number layers and which gives streaks along the ξ -constant lines on the odd-number layers, depends on sample preparation. This suggests that form II continuously transforms into form III via the form II that shows streaks, and the form II with the streaks is characterized as an intermediate phase between forms II and III. During the transformation, the molecular conformation continuously changes from $TGT\bar{G}$ to $T_3GT_3\bar{G}$ by flip-flop motions.⁸ Accordingly, this transition is not considered to be of the first order but of higher order.

References and Notes

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Kink Bands in Form I of Poly(vinylidene fluoride)¹

In previous papers,^{2,3} it was reported that the X-ray diffuse streak scatterings found on the fiber diagram of form II of poly(vinylidene fluoride) are attributable to kink bands which are one monomeric unit thick and are mainly formed by the flip-flop motion between the $TGT\bar{G}$ and $TGTG$ conformations. An X-ray diffuse streak scattering was also found on the fiber diagram of form I of poly(vinylidene fluoride). Here, we report that this X-ray diffuse streak scattering is also attributable to kink bands contained in the crystallite of form I.

A fiber specimen of form I was prepared by stretching at room temperature after the melt (KF-1100, Kureha