Acknowledgment. We thank Dr. T. Wirthlin of the Varian Zug for technical assistance in recording the spectra.

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(5) The notation >P signifies PP or IP. Analogously the notation $(>)_2$P means IIP or PIP or IPP or PPP.

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Received March 18, 1980

Formation Mechanism of Kink Bands in Modification II of Poly(vinylidene fluoride). Evidence for Flip-Flop Motion between TGTḠ and TḠTG Conformations[1]

In a previous paper,[2] it was reported that the X-ray diffuse streak scatterings found on the fiber diagram of modification II (Figure 1), which was prepared by heat treatment with the ends fixed, are attributed to kink bands *contained in the crystallite. In the kink bands, the molecule* assumes a planar zigzag conformation, and, therefore, a molecular chain consists of both regular TGTḠ and planar zigzag segments in the crystallite. The intensity distribution calculation was carried out for the X-ray diffuse streak scatterings. This suggested that the kink bands are one monomeric unit thick and are mainly formed by the flip-flop motion between TGTḠ and TḠTG conformations during the heat treatment of a fiber specimen of modification II. We briefly describe here results of the intensity distribution calculation.

When the kink bands are formed in a crystallite of modification II, the molecular conformation changes that occur depend upon whether *the number of monomeric* units constituting the kink in a molecular chain is odd or even:

odd $\cdots\mathrm{TGT\bar{G}TGT\bar{G}TGT\bar{G}\underline{T}GT\bar{G}}\cdots \rightarrow$
$\cdots\mathrm{TGT\bar{G}\underline{TT}TGT\bar{G}TGT\bar{G}TG}\cdots$

even $\cdots\mathrm{TGT\bar{G}TGT\bar{G}TGT\bar{G}\underline{T}GT\bar{G}}\cdots \rightarrow$
$\cdots\mathrm{TGT\bar{G}\underline{TTTT}TGT\bar{G}TGT\bar{G}}\cdots$

(underline denotes the kink)

When the kink is composed of an odd number of monomeric units, the conformation after the kink must change from TGTḠ to TḠTG. If it does not, the chain direction of the regular TGTḠ segment makes an angle with the fiber direction. This contradicts the X-ray diffuse streak scatterings which require the chain direction of the regular segment to be parallel to the fiber direction.[2] When the kink has an even number of monomeric units, the regular segments retain their TGTḠ conformation during the formation of the kink bands. Accordingly, the kink is formed only by the conformational change from G or Ḡ to T which forms the kink itself. By taking the abovementioned facts into account, we built five kink-band models (models I–V) and calculated the intensity distributions along the X-ray diffuse streak scatterings by using the intensity equation for stacking faults.[3-5] Here, for the case of a kink with an odd number of monomeric units, only the kink with one monomeric unit was considered because it is unlikely that kinks with an odd number of monomeric units equal to or more than three are exclusively formed without the formation of kinks with an even number of monomeric units. For example, a kink with three monomeric units can be formed by a conformational change from G or Ḡ to T in three subsequent monomeric units and from TGTḠ to TḠTG in the regular segment. Energetically, the kink with two monomeric units, which is formed only by the conformational change from G or Ḡ to T in two subsequent monomeric units, is considered *to be formed more easily than a kink with three monomeric* units.

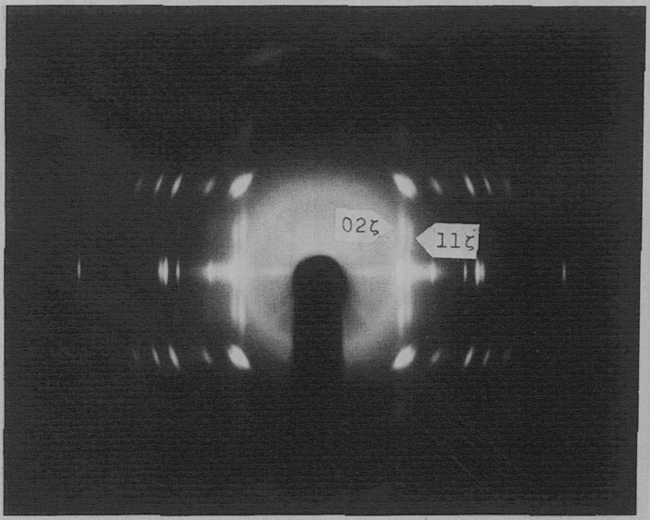

Figure 1. Fiber diagram of modification II giving the X-ray diffuse streak scatterings.

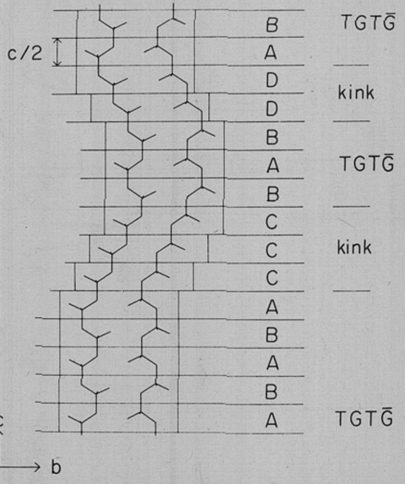

Figure 2. Construction of modification II containing the kink bands (model I) with four kinds of unit-layer structures.

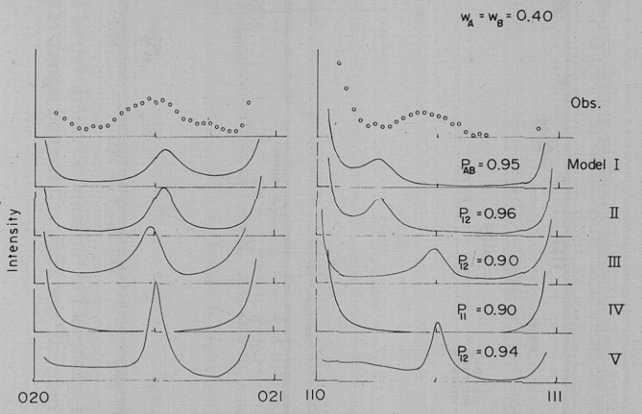

Figure 3. Observed and calculated intensity distributions along the X-ray diffuse streak scatterings on 02ζ and 11ζ.

The structure of modification II containing the kink

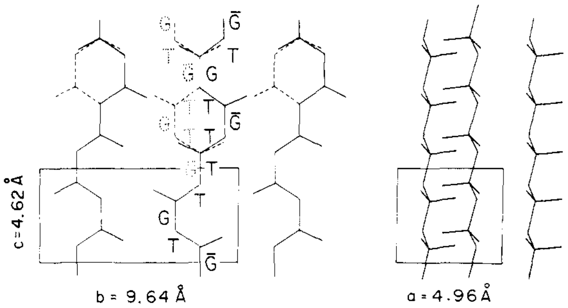

Figure 4. Structure of the kink band in modification II. Broken lines show the regular structure of modification II.

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 $\mathrm{TGT\bar{G}}$ 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 $\mathrm{T_3GT_2}$ or $\mathrm{T_3\bar{G}T_2}$ 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 $\mathrm{TGT\bar{G}}$ and $\mathrm{T\bar{G}TG}$, 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 $\mathrm{TGT\bar{G}}$ and $\mathrm{T\bar{G}TG}$ and the motion from G or $\bar{G}$ to T which forms the kink bands themselves. Here, the flip-flop motion between $\mathrm{TGT\bar{G}}$ and $\mathrm{T\bar{G}TG}$ 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 $\mathrm{TGT\bar{G}}$ and $\mathrm{T\bar{G}TG}$ 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 $\mathrm{TGT\bar{G}}$ and $\mathrm{T\bar{G}TG}$ takes place cooperatively in several molecules. The results of the calculation will be published in detail elsewhere.

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Received February 20, 1980

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). They[4] proposed a preferred $\mathrm{T_3GT_3\bar{G}}$ molecular conformation, based on energy calculations of Tripathy et al.[5] But they did not rule out other possible conformations such as $\mathrm{(TG)_2(T\bar{G})_2}$ etc.[4] Lovinger and Keith[6] 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-