Macromolecules **1993,** *26,* 1471–1473

Structural Disorder of Poly(vinylidene fluoride) Form I: Glides

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Received September 1, 1992
Revised Manuscript Received November 9, 1992

In previous papers,[1,2] it was clarified that, on the fiber diagram of poly(vinylidene fluoride) form I, the diffuse streak scattering observed on the line binding the (110) and (001) reflections is attributed to the kink bands of GTḠ contained in the planar zigzag conformation and that, from the temperature dependence, the kink motion occurs at a high temperature. On the other hand, from the superlattice spots observed on the fiber diagram of poled form II, a new crystalline form was found, in which the kink bands of GTḠ are regularly arranged in the planar zigzag crystal.[3] In the present study, diffuse streak scatterings are newly found on the X-ray diffraction patterns of the doubly-oriented form I,[4] which are attributed to glide planes contained in the crystallite of form I.

X-ray measurements were made by Cu Kα radiation monochromatized by a pyrolyzed graphite crystal. Weissenberg cameras with radii of 3.5 and 4.5 cm were used to take the X-ray photographs of doubly-oriented form I samples. The Weissenberg photographs of the equator and of the first layer line taken by the equi-inclination method are shown in parts a and b of Figure 1, respectively.

On the Weissenberg photograph of the equator, the diffuse streak scatterings are observed on the lines binding 110 and 200 reflections, 110 and 110 reflections, and 020 and 220 reflections. On the photograph of the first layer line, the diffuse streak scattering from the 111 reflection to the 201 reflection can be observed. These diffuse streak scatterings are plotted on the reciprocal lattices of form I in parts a and b of Figure 2. The two diffuse streak scatterings on lines binding 110 and 110 reflections and 020 and 220 reflections suggest that there exists a disorder in which the structural units (sheet structures) parallel to the *bc*-plane slip parallel to each other in the *b*-direction; i.e., there exists a glide parallel to the {100} (slip plane) in the direction ⟨010⟩. Two-dimensional periodicity is kept on the planes parallel to the *bc*-plane (on the sheet structure), while the periodicity in the *a*-direction is broken due to the slip plane. Therefore, the reflections are subject to the condition of the Laue function on the planes parallel to the plane (0*kl*), while, in the direction perpendicular to (0*kl*), they are not subject to the conditions and become diffuse streak scatterings. This glide is schematically shown in Figure 3. On the other hand, the diffuse streak scatterings on the lines binding the 110 and 200 reflections and the 111 and 201 reflections suggest that there exists a disorder in which the structural units (sheet structures) parallel to the {110} planes slip parallel to each other in the direction ⟨110⟩. On the planes perpendicular to the diffuse streak scatterings, the structure is two-dimen-

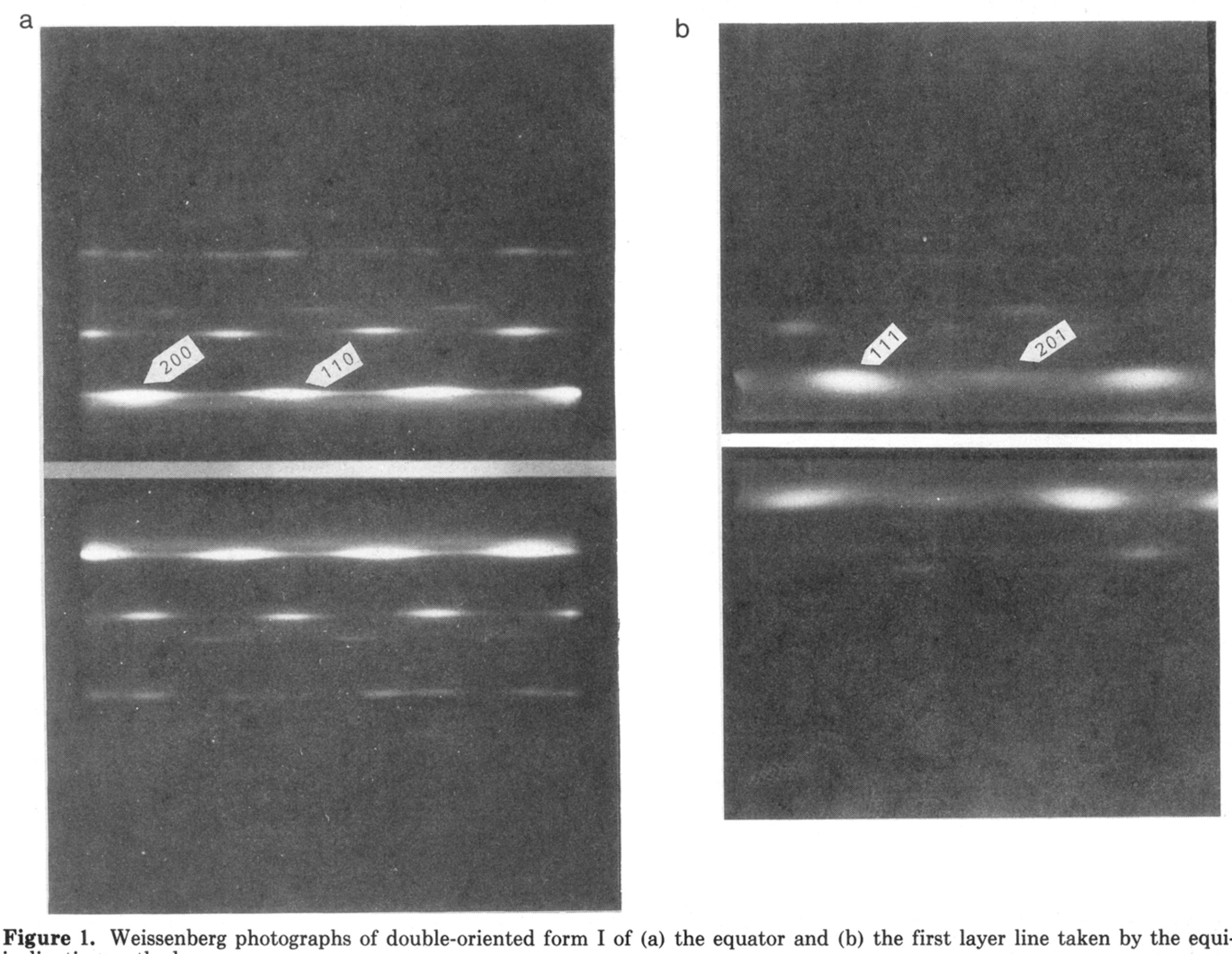

Figure 1. Weissenberg photographs of double-oriented form I of (a) the equator and (b) the first layer line taken by the equi-inclination method.

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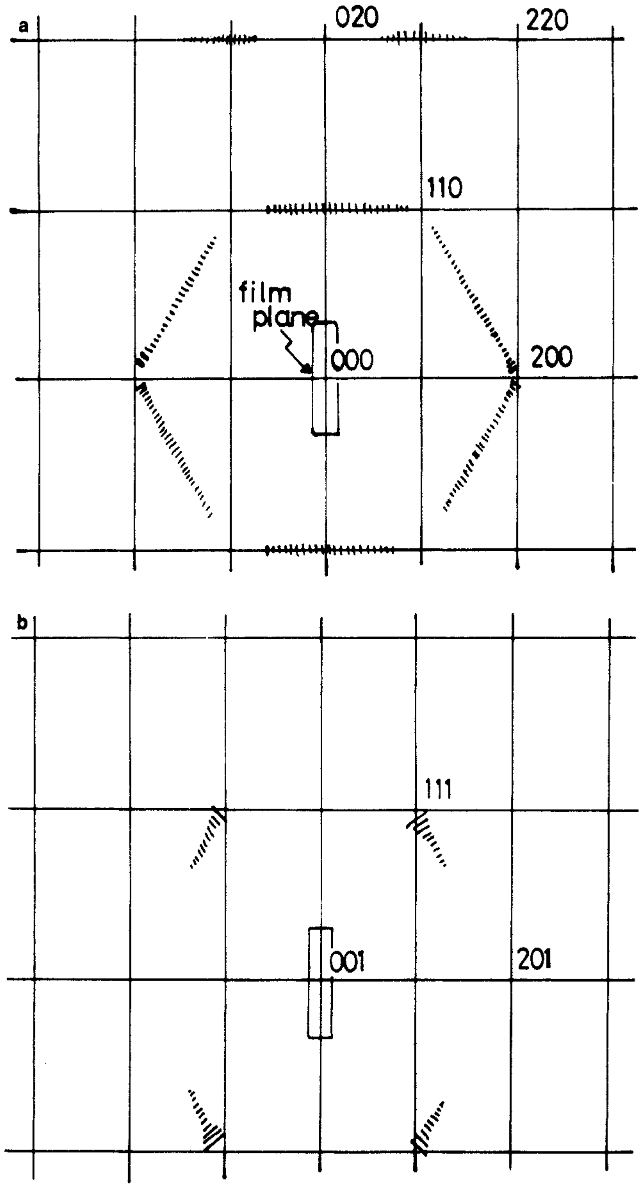

Figure 2. Diffuse streak scatterings and the reciprocal lattices of form I: (a) the equator and (b) the first layer line.

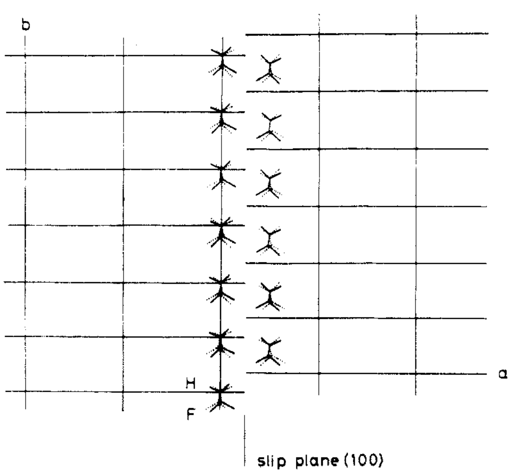

Figure 3. Schematic representation of the glide parallel to the {100} in the direction ⟨010⟩.

sionally ordered and is subject to the condition of the Laue function, while in the direction along the diffuse streaks, the structure is disordered because the Laue function is not kept. This glide is parallel to the slip planes {110} in the direction ⟨110⟩, which is schematically shown in Figure

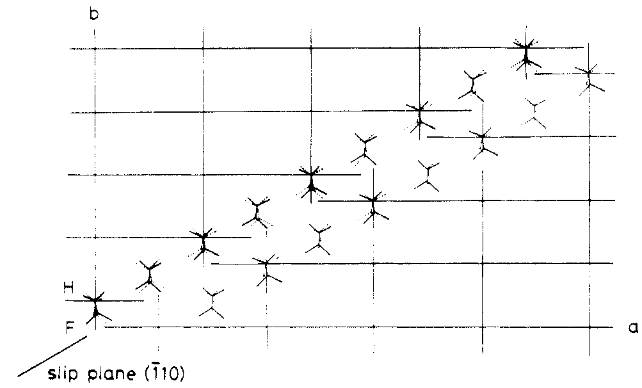

Figure 4. Schematic representation of the glide parallel to the {110} in the direction ⟨110⟩.

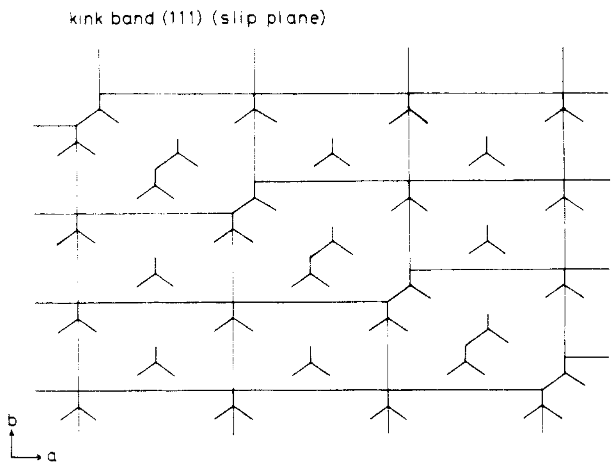

Figure 5. Schematic representation of kink bands, which can be called a glide parallel to the {111}.

4. These glides may be created by the shear stress caused in the crystallite during the deformation process of the sample. In poly(vinylidene fluoride) form II,[5-7] antiphase domain structures are formed in the crystallite and, therefore, the crystal structure assumes a statistical structure in which four molecules with different orientation occupy a crystal site with different probabilities. In form I, the sheet structures parallel to the {100} and {110} planes slip with respect to each other in the direction ⟨010⟩ and ⟨110⟩, respectively, and form the glides resulting in packing disorder. These glides can be compared with the kink bands (Figure 5),[1] which can be considered a glide parallel to the {111}. On the fiber diagram of poly(vinylidene fluoride) form I, the rather sharp halo observed just inside the overlapped reflection of 110 and 200 may be composed of these diffuse streak scatterings of structural disorder, the glides and the kink bands, and of the halo due to the amorphous region.

The same types of diffuse streak scatterings were observed on the electron diffraction pattern of *st*-polypropylene,[8-10] where they are interpreted by the stacking of two ultimate structures different in the molecular packing.

Acknowledgment. The author expresses his sincere thanks to Mr. T. Mizuno, Kureha Chemical Industries Co., Ltd., for kindly supplying the doubly oriented sample of poly(vinylidene fluoride) form I.

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