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The Molecular Mechanism of Chain Tilt in Poly(ethylene terephthalate) Fibers

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Synopsis

The molecular mechanism of chain tilt in poly-(ethylene terephthalate) (PET) fibers was proposed. The mechanism was considered basing on the ordering process from the cold drawn state of glassy PET. It was confirmed that the direction of maximum contraction on ordering agrees with the azimuth of chain tilt which varies with annealing temperature. In the stacking structure of irregular folded chain blocks of cold drawn PET, the expansion to the chain direction and the contraction to the lateral direction yield the compressive stress and tensile stress, respectively. The stress revealed as the result of the ordering from the glassy structure to crystalline structure can be relaxed by the rotation of the resulting crystallites. Therefore, we can suggest that the chain tilt is caused by the relaxation process of the stress.

1. Introduction

It is well known that the diffraction spots in x-ray fiber pattern of PET are often moved up or down from normal layer lines. This fact shows that the crystals do not possess their c axes (those parallel to the chain molecules) exactly parallel to the fiber axes, but they are tilted in a precisely defined crystallographic direction. This chain tilting for fiber axis was firstly found by Daubeny et al.(1) in the

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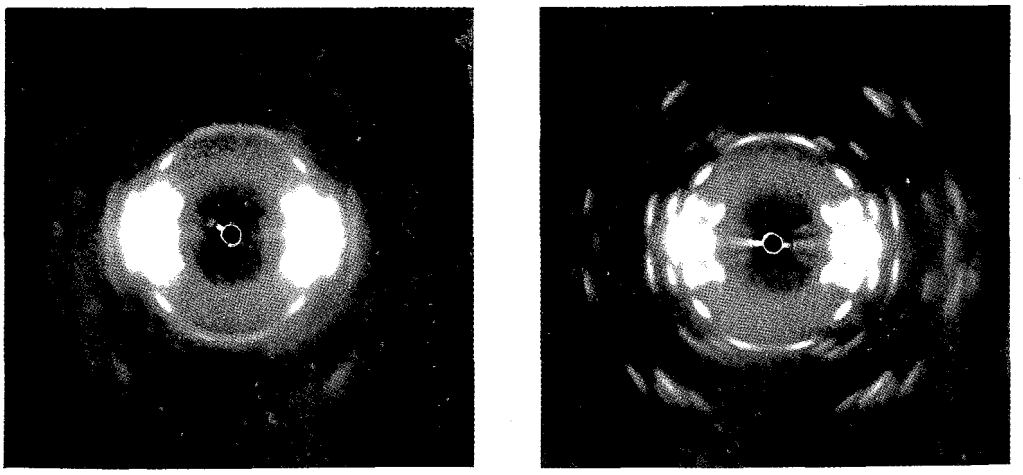
course of crystal structure determination of this polymer. They reported that the crystals are tilted by about 5° in such precisely defined direction that the $(\bar{2}30)$ plane remains vertical and the inclination of the (001) plane to the fiber axis increases. At that time, the reason for this preferred direction of tilt was not clear. Thereafter, Bonart(2) tried to explain the tilt with the inclined layer structure which had been found from the small angle x-ray diffraction patterns of fibers. He suggested that when the alternating crystalline and amorphous layers are formed, the chain axes tilt to the opposite direction owing to volume requirement of chain packing.

Recently, Asano and Seto(3) found from the further studies of the tilting behaviors in PET fibers that the tilt direction varied with annealing temperature. And they have pointed out that Bonart's explanation was not enough to interprete these experimental facts. Furthermore, they suggested that the azimuthal change of tilt can be explained by two possible mechanisms for the crystalline tilt. At low annealing temperature, the tilt is related to the transition from the monoclinic structure. At high temperature, the tilt is caused by the formation of the layer structure.

We have been studying the ordering process of cold drawn PET by annealing. In the course of our works, we felt that the cause of tilt orientation exists in the feature of chain packing in glassy PET, because the ordering process from glassy structure occurs by the solid-solid transition. In this paper, we will report the reasonable mechanism for the chain tilting in PET fibers.

2. The Feature of Chain Tilting in PET Fibers

The feature of chain tilting in PET fibers has already been studied in detail by Asano and Seto(3). Figure 1 shows the wide angle x-ray diffraction patterns of cold drawn PET annealed at 130°C and 240°C. In these patterns some diffraction spots are displaced from normal layer lines. The displacement of each spot varies clearly with annealing temperature as reported by Asano and Seto. Our reexamination of chain tilting behaviors with annealing temperature confirmed the results of them. In Figure 2, the change of tilt direction is visualized with the aid of the real lattice of PET basing on our data. Figure 3 shows plots of the direction of the tilt line vs. annealing temperature where azimuth of the tilt line is represented with the angle measured from the b* axis in basal plane. Tilt angles in our experiments are summarized in Table 1.



(a) (b)

FIGURE 1. Wide angle x-ray diffraction patterns of PET fibers. (a) annealed at 130°C and (b) annealed at 240°C.

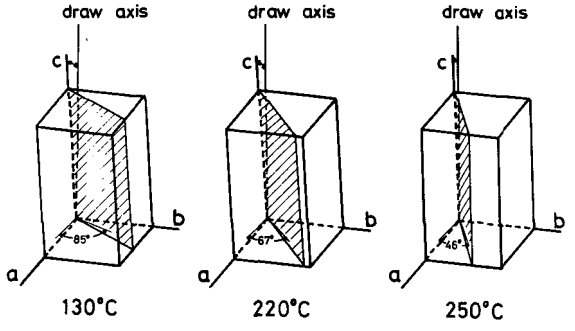


FIGURE 2. Schematic representation of chain tilting.

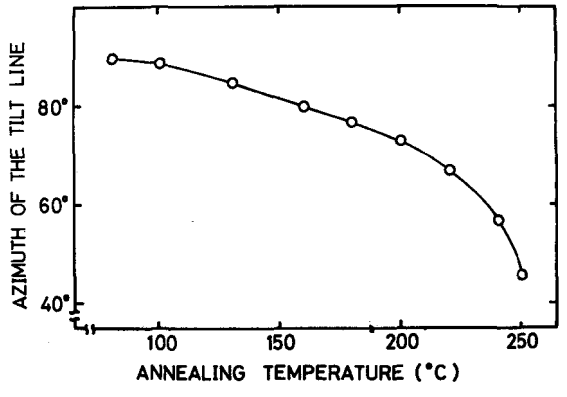


FIGURE 3. Plots of azimuth of tilt line vs. annealing temperature.

TABLE 1. The change of tilt angle for annealing temperature.

Annealing temperature (°C)	Tilt angle (degree)
80	8.6
100	6.9
130	6.5
160	5.7
180	5.9
200	5.1
220	4.3
240	4.6
250	4.3

3. The Feature of Chain Packing and Layer Structure in Cold Drawn PET

In the previous paper(4,5), we suggested a new realistic model for the glassy amorphous PET. In our model the molecular conformation of glassy PET is chain folded one and its glassy structure is one phase. We considered that this structure is formed owing to the irregular foldings of PET chains which disturb the three dimensional arrangements of chain sequence adjacent to the folds. Such situation was confirmed to be reasonable from the estimation of chain folding energy in PET and from the feature of defects in glassy PET revealed by means of infrared spectroscopy. Figure 4 shows our new model for the structure of glassy PET.

When the glassy PET is drawn through the necking stage at room temperature, the wide angle x-ray diffraction pattern shows very broad scattering peaks on the equator which indicate an uniaxial orientation of chains. At present, the morphology of cold drawn PET has not enoughly been studied. However, we can speculate that does not occur by the drastic changes of chain conformation in glassy state but occurs by the rotation of the blocks of irregularly folded chains similar to crystalline polymers.

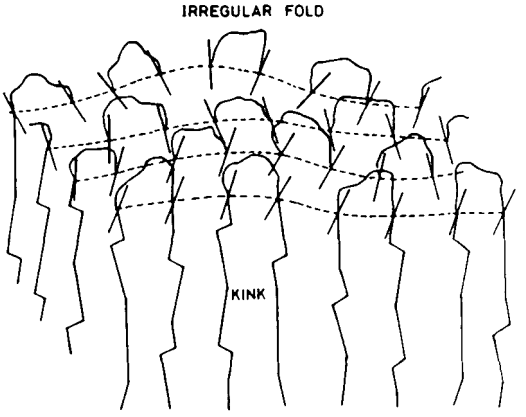


FIGURE 4. A new model proposed for the structure of PET in the glassy state.

On the other hand, Yeh and Geil(6) have observed that the small angle x-ray pattern of cold drawn PET shows four distinct maxima occurring at about 70° to the meridian. This fact show that the inclined layer structure is formed in the texture of cold drawn PET. Therefore, we believe that this layer structure consists of stacking of the blocks of irregularly folded chains.

4. The Ordering Process from the Cold Drawn State of Glassy PET

In this section, we investigated the ordering process of cold drawn PET in the course of annealing. In the previous paper(7), we reported that the paracrystalline monoclinic unit cell was found for the cold

drawn specimens annealed at temperatures below T_g. This structure is different from that reported by Asano and Seto(3). Their structure was suggested from the x-ray spacings of 4.3 A and 4.6 A in equator and the spacing of 10.3 A in the meridian. However, the appearing of the spots of 4.3 A and 4.6 A in the diffuse reflections could not be reproduced with our careful experiments. Therefore, we felt their unit cell to be questionable. On the contrary, our proposed unit cell is based on the well defined crystalline spots, although our observed spots are only three. The appearance of only three reflections can be explained with the paracrystalline structure in which the (0kl) reflections give sharp peaks and the (hkl) reflections ($h \neq 0$) give diffuse halos. The formation of such paracrystalline structure is reasonably explained with the anisotropic ordering in chain packing of cold drawn PET which results from the remaining of irregular foldings because of poor thermal motions of chains at low temperature. Furthermore, it should be noted that the chain tilt occurs in the course of the formation of this paracrystalline structure.

On annealing at temperatures above T_g, the ordinary triclinic structure are formed. In order to examine the ordering process from the cold drawn state, the spacings of the triclinic reflections were measured from fiber patterns of annealed specimens at various temperatures. Figure 5 shows the changes of the (010), ($\bar{1}$10) and (100) spacings with annealing temperatures. From the observed spacings, c axis projection of real lattice is visualized in Figure 6. The results of Figure 6 clearly show that the lattice is changed with annealing temperature. The lattice contraction occurs mainly in the direction perpendicular to the (100) plane with annealing temperature and γ' made with a' and b' axis

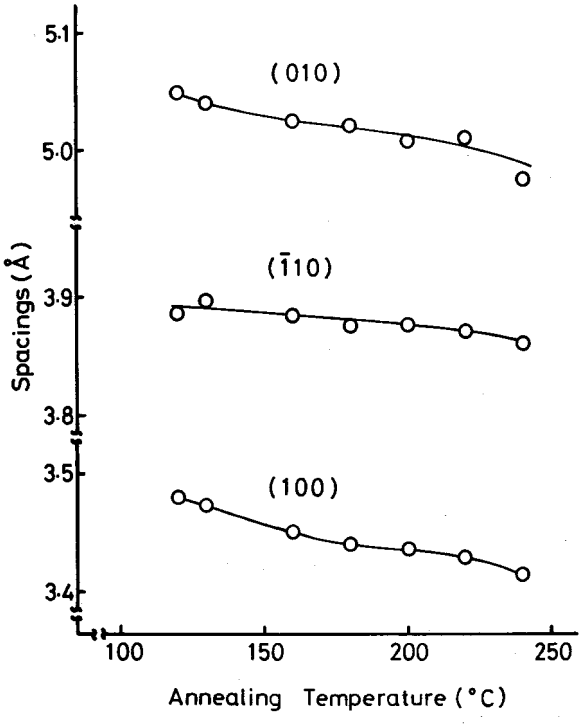


FIGURE 5. Plots of the (010), ($\bar{1}$10) and (100) spacings vs. annealing temperature.

slightly increases with annealing temperature. Such ordering process in cold drawn PET at temperatures above T_g is also explained with our proposed chain packing of glassy state. Irregular foldings in glassy PET disturb the three dimensional arrangements of segments in chain packings of the paracrystalline state and the cold drawn state. The regularization of irregular foldings is easily achieved, as the chain mobility at temperatures above T_g is higher. We can suggest that the preferred lattice contraction of the direction perpendicular to the (100) plane occurs by such regularization of chain foldings which exist in only the normal direction of the molecular plane (nealy parallel to the (100) plane).

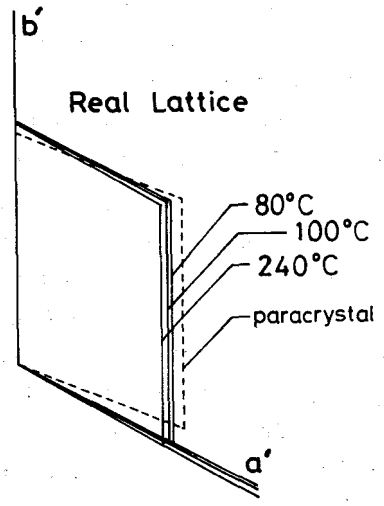


FIGURE 6. Variation in the real lattice with annealing temperature.

5. The Molecular Mechanism of Chain Tilt in PET Fibers

The x-ray diffraction studies showed that the crystallites in PET fibers are tilted in a precisely defined direction. The azimuth of chain tilt varied with annealing temperature. Furthermore, we showed that the lateral ordering in chain packing from cold drawn state of glassy PET occurs firstly by anisotropic ordering to the perpendicular direction of chain folds and in succession by large ordering to the direction of chain folds. It is apparent that such ordering in chain packing changes the direction of the maximum contraction from b* in paracrystalline lattice to a* in triclinic lattice. The directions of the maximum contraction varied with annealing temperature qualitatively agree with the azimuth of chain tilt.

On the other hand, on the ordering of chain packing the expansion to the direction of molecular chains is caused by the transition of kink conformation in glassy structure to crystalline conformation. We can consider that in the stacking structure of irregularly folded chain blocks of cold drawn PET, the expansion to the chain direction and the contraction to the lateral direction yield the compressive stress and tensile stress, respectively. The stress revealed as the

result of the ordering from the glassy structure to crystalline structure can be relaxed by the rotation of the resulting crystallites. Therefore, we can suggest that the chain tilt is caused by the relaxation process of the stress. Figure 7 shows schematically the molecular mechanism of chain tilting. At present, this mechanism can not be checked quantitatively, as the sufficient information on the chain packing and the layer structure in cold drawn PET is absent. However, we believe that our mechanism basing on the presently found structural evidences in cold drawn PET is more reasonable than those of Bonart and Asano et al.

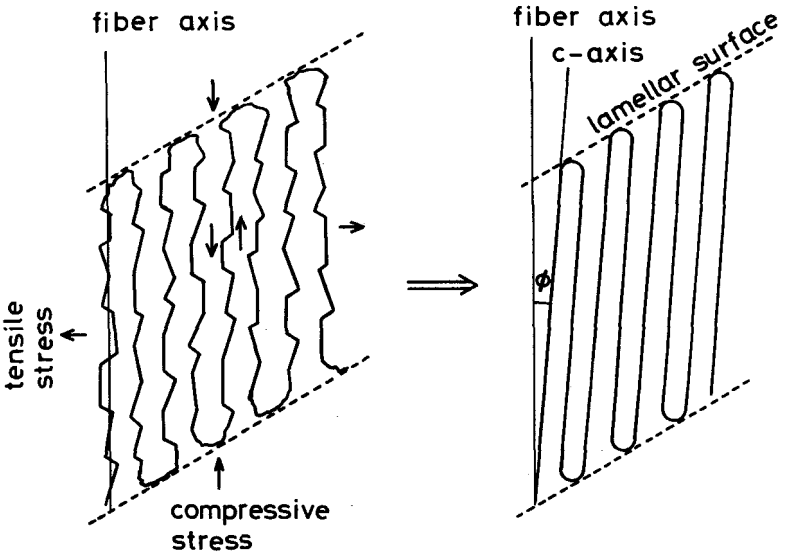


FIGURE 7. Schematical representation of the molecular mechanism of chain tilting.

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