

THE ORIENTATION AND CRYSTALLIZATION OF POLYETHYLENE TEREPHTHALATE*

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ABSTRACT

The drawing behavior of three types of PET spherulites and PET amorphous samples have been studied. Two different sample preparation techniques were used in this study: (1) The films with normal positive, normal negative or abnormal spherulites were prepared by solution casting techniques, then the films were deformed by uniaxial drawing. The uniaxial drawing behavior of PET spherulites appears to be dependent on the angles between the c-axis and the radius direction of the spherulites and that the deformation of spherulites becomes more difficult the larger the angles. (2) Amorphous films of PET were prepared first, then the films were deformed under uniaxial drawing to achieve c-axis orientation at a temperature near the glass transition temperature. The oriented films were subsequently annealed with fixed length at 215°C. The films prepared in this way exhibit excellent c-axis orientation along the stretching direction. The degree of perfection of the crystalline structure is much greater than that of the spherulites.

INTRODUCTION

In our previous paper^[1] we suggested that polyethylene terephthalate (PET) material with different types of spherulites (normal positive, normal negative or abnormal spherulites) would exhibit different mechanical properties. In order to give the evidence we have prepared films with different types of spherulites and deformed them under uniaxial drawing to obtain fibrous structure and compared their deformation behavior. In addition, we have also prepared amorphous PET films, which were subsequently stretched under uniaxial drawing near the glass transition temperature and then the oriented amorphous films were annealed with fixed length to obtain oriented and crystallized fibrous structure. We compared these two different techniques (1) Crystallization → Orientation (2) Orientation → Crystallization and studied the morphology and structure of these samples by polarizing microscopy, electron microscopy, electron diffraction and DSC techniques. Experimental data indicate that PET films with different types of spherulites really exhibit different drawing behavior and the second technique for preparing samples with fibrous structure (Orientation → Crystallization) is much better than the first one (Crystallization → Orientation).

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EXPERIMENTAL

1. *Material*

PET samples were obtained from Beijing 5th Chemical Plant. The weight average molecular weight is about 17,000. Before use, the PET samples were dried in vacuum at 120°C for 6 h.

2. *Sample Preparation*

(1) Samples prepared by the first technique (Crystallization → Orientation)

(a) Spherulitic film preparation

Films with normal positive, normal negative or abnormal spherulites were prepared from 0.05–2% solutions of PET in dimethylphthalate by solution casting techniques described in our previous paper^[1].

(b) Uniaxial drawing

A small piece of film with positive or negative or abnormal spherulites was clamped in a microstretcher, then it was deformed at 220°C under uniaxial drawing.

(2) Samples prepared by the second technique (Orientation → Crystallization)

(a) Amorphous film preparation

A few drops of a hot solution of 2–8% PET in tetrachloroethane were deposited on a cover glass and allowed to run evenly on it. After the solvent had evaporated a film was formed on the cover glass, then the film was melted in N₂ atmosphere at 275°C and quenched immediately to 15°C in a water bath. The films so prepared were transparent. They were floated off by 2% HF solution and rinsed several times in distilled water, then they were ready for further examination.

(b) Uniaxial drawing

A small piece of film was clamped in a microstretcher and deformed under uniaxial drawing in a water bath at 65°C. The drawing ratio was about 5–7.

(c) Annealing with fixed length

The drawn film in the microstretcher was dried in the atmosphere at room temperature, then it was annealed with fixed length at 215°C for 10 h or 17 h.

Samples prepared by those two different techniques described above were studied by polarizing microscopy (Leitz SM-LUX-POL), electron microscopy, electron diffraction (JEOL JEM-200 CX, accelerating voltage 200 KV, beam current 5 μ A) and DSC (Perkin-Elmer DSC-2, heating rate 20 K/min) techniques.

RESULTS AND DISCUSSION

1. *The orientation of PET spherulites under uniaxial drawing*

(1) Uniaxial drawing of normal positive spherulites

(a) Polarizing microscopy results

The film with normal positive spherulites, as shown in Fig. 1, was deformed in the microstretcher at 220°C.

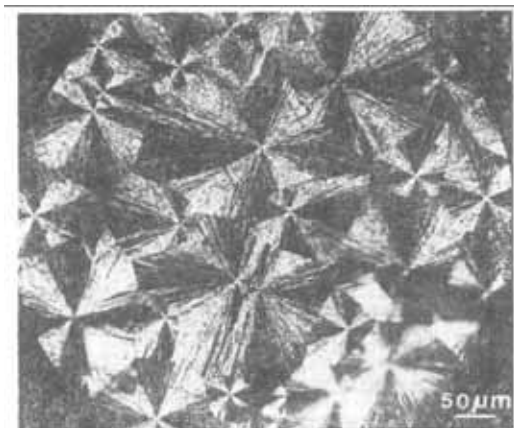


Fig. 1 Optical micrograph of PET normal positive spherulites (crossed polars)

The drawing ratio was 2—4. Fig. 2 shows an optical micrograph of the drawn spherulitic film in the polarizing microscope under crossed polars. The drawing direction is at 45° to the polars. This figure shows that the spherulites are elongated in the drawing direction and instead of the Maltese cross extinction there are two extinction sectors located perpendicularly to the drawing direction in the middle part of each elongated spherulite. The second and fourth

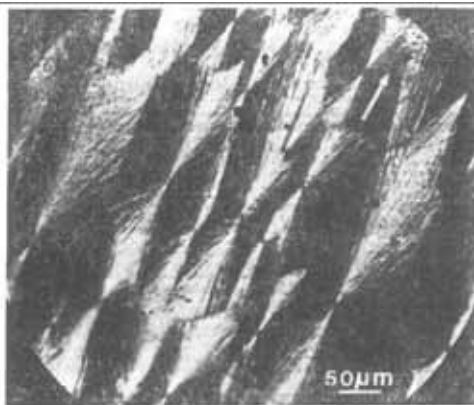


Fig. 2 Optical micrograph of drawn positive spherulites (crossed polars).
The arrow indicates the drawing direction

quadrants of the original spherulite which were bright in the polarizing microscope under crossed polars now are dark. The two axes of indicatrix which aligned at an inclined angle to the polars in the second and fourth quadrants of the spherulite now are nearly parallel to them. This indicates that towards the drawing direction some rotational motion of the helical lamellae has taken place within these two sectors of the spherulite under uniaxial drawing. During further drawing the spherulites become even longer (Fig. 3,4) and finally the two extinction sectors in the elongated spherulite disappear and the whole sample becomes bright in the polarizing microscope under crossed polars when the drawing direction of the film is at 45° to the polars. After insertion of the compensator (λ plate) into the polarizing microscope the inter-

ference colour is blue. This indicates that the sample has achieved c-axis orientation.

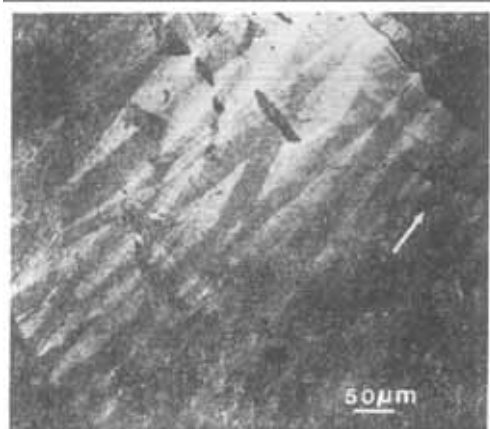


Fig. 3 Optical micrograph of further drawn positive spherulites (crossed polars). The arrow indicates the drawing direction

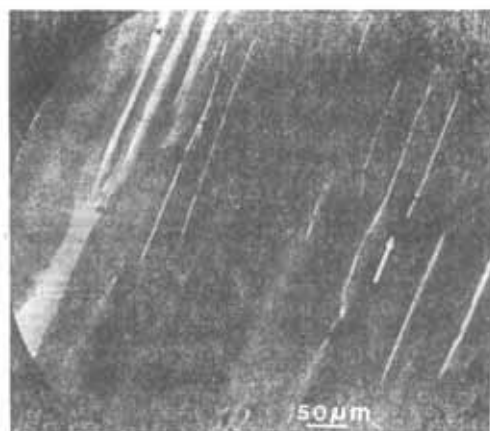


Fig. 4 Optical micrograph of further drawn positive spherulites (crossed polars). The arrow indicates the drawing direction

(b) Electron microscopy results

In order to obtain more detailed information on the deformation of positive spherulites under uniaxial drawing we have studied them by electron microscopy and electron diffraction techniques. Fig. 5 is an electron micrograph of a sector of a positive spherulite, with an electron diffraction pattern overlaid in proper orientation. This figure shows the appearance of the helical lamellae of the spherulite. Electron diffraction pattern indicates that $[326]^*$ is the radius direction of the spherulite^[1]. Fig. 6 is an electron micrograph of a deformed spherulite and a correctly oriented electron diffraction pattern. This figure shows that instead of the helical lamellae there are only some "debris" remained. Electron diffraction pattern shows that the 010 reflection has its maximum on the equator and is much sharper than that of the spherulite; the $0\bar{1}1$ reflection of the spherulite has split into two located on each side of the equator and the $\bar{1}05$ reflection has appeared

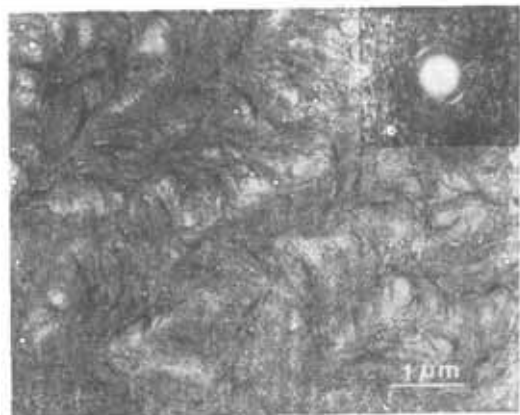


Fig. 5 Electron micrograph of a sector of a positive spherulite, with an electron diffraction pattern overlaid in proper orientation

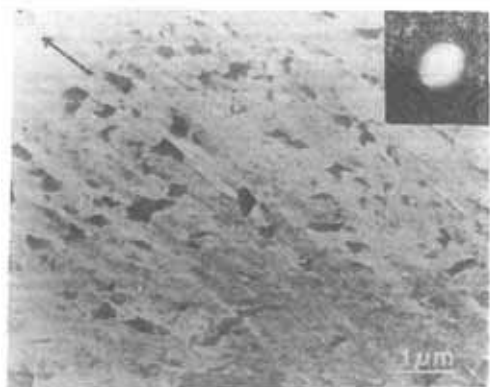


Fig. 6 Electron micrograph of a drawn positive spherulite and a correctly oriented electron diffraction pattern. The arrow indicates the drawing direction

in the meridional region. All of these indicate that the c -axes of PET tend to be oriented along the stretching direction under uniaxial drawing, though the degree of orientation now is not high. Fig. 7 is an electron micrograph of a further draw PET positive spherulite and an electron diffraction pattern overlaid in proper orientation. This figure shows that there are no more "debris" of lamellae but microfibrils^[2,3,4] are formed along the drawing direction. Electron diffraction pattern shows that 010 , $\bar{1}10$ and 100 reflections are on the equator; $0\bar{1}1$, $\bar{1}11$ reflections are on the layer line of $N=1$. In the meridional region $\bar{1}05$ reflection splits into two at an angle of $\sim 10^\circ$ with the meridian. This indicates that the c -axes of the sample are highly oriented in the drawing direction.

(2) Uniaxial drawing of normal negative spherulites

When the film with normal negative spherulites was drawn in the microstretcher at temperature 150°C and 220°C , it tended to break at the beginning of drawing and almost no deformation took place.

(3) Uniaxial drawing of abnormal spherulites

When the film with abnormal spherulites was drawn in the microstretcher, it was just like

that in the case of negative spherulites, the film tended to break and nearly no deformation took place.

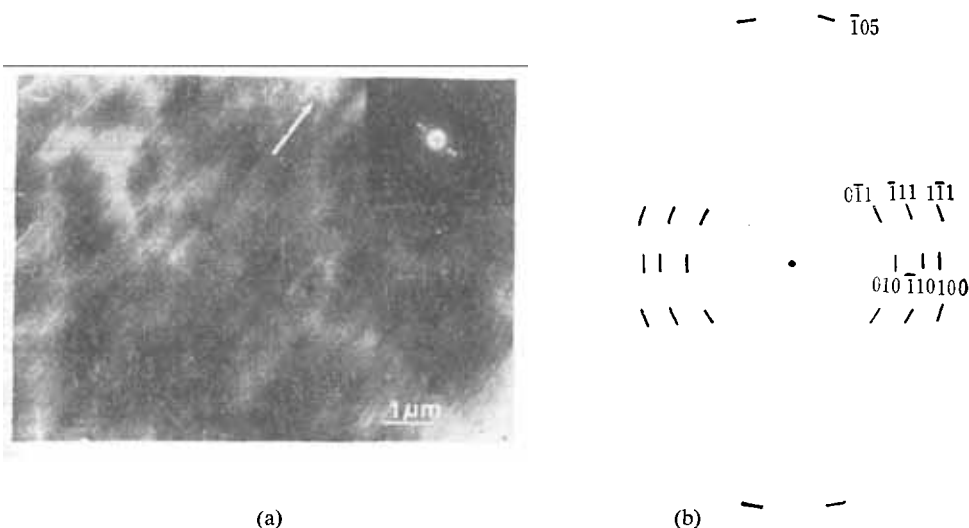
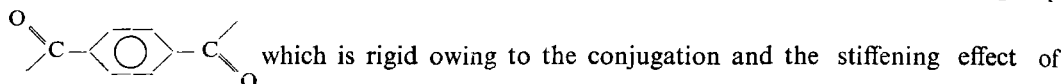


Fig. 7 (a) Electron micrograph of a further drawn positive spherulite and an electron diffraction pattern overlaid in proper orientation
(b) Schematic diagram showing electron diffraction pattern with indexes

Based on the experimental data of uniaxial drawing of positive, negative and abnormal spherulites, the deformation of PET films, just as we predicted, is dependent on the types of spherulites. Only films with positive spherulites can be deformed under uniaxial drawing.

Because the c -axes are aligned parallel to the drawing direction in the highly oriented films, it is very important to know which direction in the spherulite the c -axes are in. It is known from the structural analysis of PET spherulites^[1] that $[\bar{3}26]^*$ is the radius direction of the positive spherulite and the angle between the c -axis and the radius is 42° . In the case of negative spherulite the $[\bar{2}10]^*$ is the radius direction and the angle between the c -axis and the radius is 90° and $[\bar{2}12]^*$ is the radius direction of abnormal spherulites and the angle between the c -axis and the radius is 65° . The radius directions of a spherulite are in the plane of the spherulitic film. During uniaxial drawing the c -axes must rotate to the drawing direction in the plane of the film, therefore, the larger the angle between the c -axis and the radius direction of the spherulite the more difficult the rotation of the c -axis to the drawing direction. This is probably the reason for the fracture of the films with negative and abnormal spherulites at the beginning of drawing. Even in the case of positive spherulites the angle between the c -axis and the radius direction of the spherulite is only 42° , the drawing is not easy to be carried out, usually it must be performed at higher temperature, e.g. 220°C . In addition, the helical lamellae located in a different region of a spherulite have different azimuth angle with respect to the drawing direction and even in the same lamella of a spherulite the unit cells rotated around the radius of the spherulite are oriented differently, therefore, the angles between the c -axes and the drawing direction are different. Because of these reasons the deformation of spherulites

is always not uniform. As shown in Fig. 6 there are still some undeformed debris of lamellae remained. It is well known that polyethylene spherulite is negative,^[5,6] the radius direction of the spherulite is b-axis direction and the angle between the c-axis and the radius direction is 90°. Why can PE spherulites be easily deformed under uniaxial drawing? This is probably because the chain of PE is much more flexible than that of PET. Though the PE chain segments can easily rotate and translate during uniaxial drawing, the deformation of spherulites is not uniform either, usually along the drawing direction the middle part of the spherulite deforms first^[2]. This is because the lamellae of the middle part of the spherulite are located at an azimuth angle favorable with respect to the drawing direction. In the case of PET the chain contains O—CH₂ bonds, which permit easy rotation, but the chain also contains the group



these parts of the chain is more stronger than the opposite effect of the O—CH₂ bonds^[7]. Therefore it is difficult for the chain segment to rotate and translate during uniaxial drawing.

Based on the evidence described above we may conclude that the deformation of spherulites appears to depend upon two factors: (1) The flexibility of the chain; (2) The angle between the c-axis and the radius of the spherulite.

2. The orientation and crystallization of amorphous PET films

Since it is very difficult to obtain fibrous structure with highly oriented c-axis along the drawing direction from the spherulitic films, we have considered to take another route, that is to prepare amorphous films first, then they were stretched to obtain c-axis orientation and subsequently annealed. This is probably the better technique to obtain fibrous structure for semi-rigid chain polymers. The following experiments have been performed:

(1) Uniaxial drawing of amorphous PET films

Amorphous PET films prepared by the techniques described above are transparent. Fig. 8 is an optical micrograph of a piece of such films in the polarizing microscope under crossed polars and an electron diffraction pattern. It can be seen that the film is completely dark except a few bright lines at the edge of the film, which were obtained by scratching with a needle

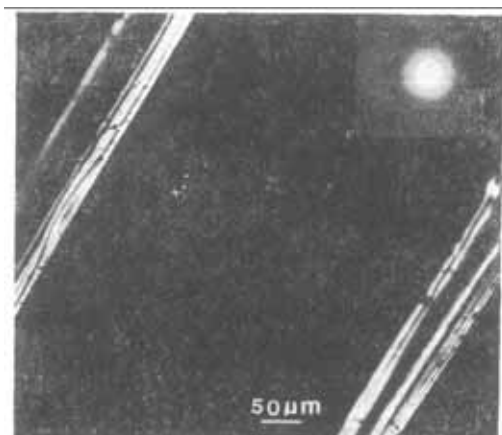


Fig. 8 Optical micrograph of an amorphous film (crossed polars) and an electron diffraction pattern

on purpose. This figure indicates that there is no birefringence and the film is optically isotropic. Electron diffraction pattern shows two halos indicating the amorphous structure of the film. Then the amorphous film was clamped in a microstretcher and drawn 5—7 times. Fig. 9 is an optical micrograph of a stretched amorphous film in the polarizing microscope under crossed polars with the drawing direction at 45° to the polars and an electron diffraction pattern overlaid in proper orientation. This figure shows that the film is bright. When the drawing direction of the film is parallel or perpendicular to the polarizer or the analyzer by rotating the specimen stage, extinction takes place. This indicates that there is birefringence and the film possesses c-axis orientation. Electron diffraction pattern shows two diffuse spots on the equator instead of the original halo and in the meridional region a spread reflection can also be seen. This indicates that the film has preferential uniaxial orientation.

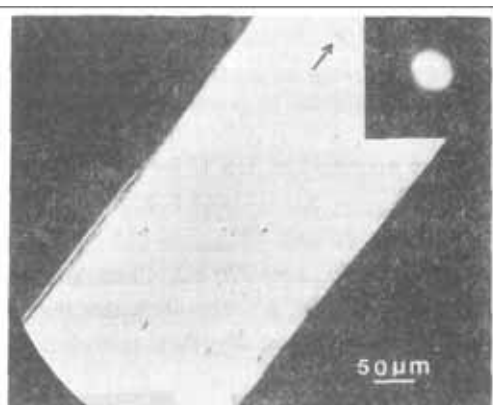


Fig. 9 Optical micrograph of a drawn amorphous film (crossed polars) and an electron diffraction pattern overlaid in proper orientation. The arrow indicates the drawing direction

(2) Crystallization by annealing

The oriented amorphous film was annealed with fixed length at 215°C for 10 h. After annealing the film is still transparent. Fig. 10 is a transmission electron micrograph of an annealed film with an electron diffraction pattern overlaid in proper orientation. This figure shows a few cracks along the drawing direction. Electron diffraction pattern clearly shows the layer lines and the 010 , $\bar{1}\bar{1}0$ ($1\bar{1}0$), 100 reflections are on the equator; $0\bar{1}1$, $\bar{1}11$ and $1\bar{1}\bar{1}$ reflections are on the $N=1$ layer line and $\bar{1}05$ reflection splits into two on the both side of the meridian. The angle between the $[\bar{1}05]^*$ and the meridian is $\sim 10^\circ$. This electron diffraction pattern indicates that the film is highly crystallized with c-axis oriented perfectly along the drawing direction.

Because the amorphous oriented films already have one dimensional order along the drawing direction, it can be expected that during annealing the three dimensional order would occur easily in the films.

(3) Thermal behavior of the oriented and annealed PET films

In order to evaluate these two techniques for obtaining fibrous crystalline structure in PET samples we studied the DSC curve of the oriented and annealed films in the vicinity of PET melting point (Fig. 11a) and compared the melting curve with that of the positive spherulites

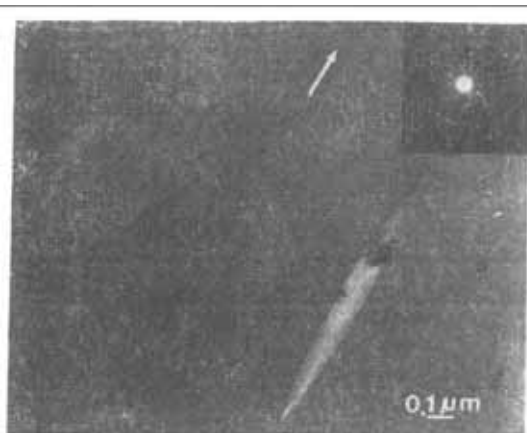


Fig. 10 Transmission electron micrograph of an oriented and annealed film with an electron diffraction pattern overlaid in proper orientation. The arrow indicates the drawing direction

(Fig. 11b). Both samples used were annealed at 215°C for 17 h. It can be seen that the melting peak temperature of Fig. 11a ($T_{\text{peak}} \sim 529$ K) is 15 K higher than that of Fig. 11b ($T_{\text{peak}} \sim 514$ K) and the melting range of the former ($T_{\text{start}} \sim 515$ K, $T_{\text{end}} \sim 535$ K) is narrower than that of the latter ($T_{\text{start}} \sim 469$ K, $T_{\text{end}} \sim 526$ K). The peak area of the former is 15.086 cal/g while the latter is only 8.367 cal/g. This indicates that the degree of perfection of the crystalline structure in the sample oriented first then annealed is much greater than that of the spherulites.

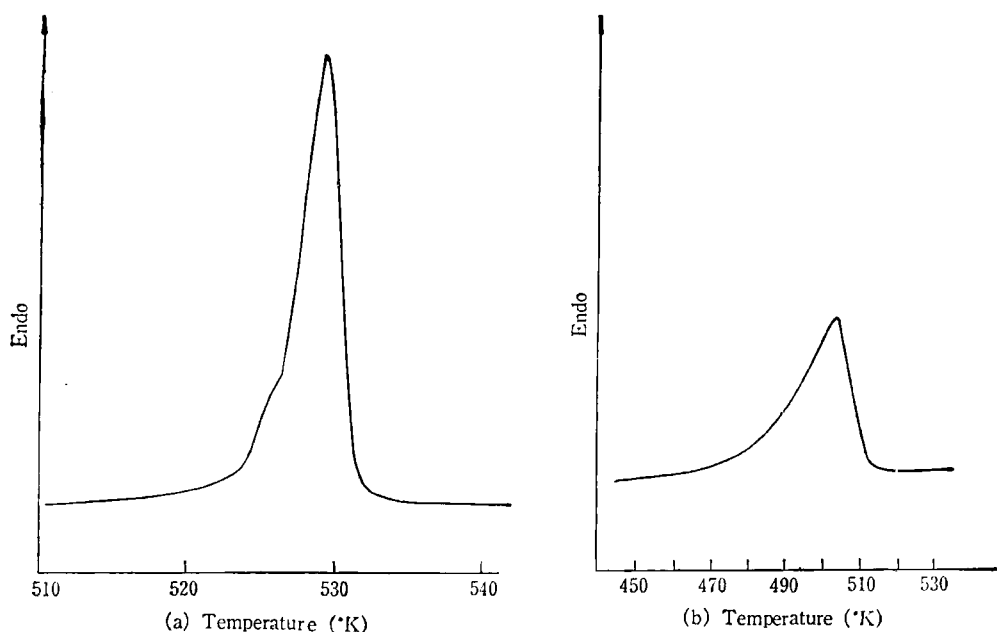


Fig. 11(a) DSC curve of the film oriented first and then annealed in the vicinity of PET melting point
(b) DSC curve of the positive spherulites in the vicinity of PET melting point

Based on all of these experimental results it can be suggested that in the case of linear polymers with stiff groups in the main chain the technique —“orientation of the amorphous samples first, then annealing them with fixed length or under tension” is probably a better method for obtaining materials with fibrous crystalline structure.

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