

THE MORPHOLOGY AND STRUCTURE OF POLYETHYLENE TEREPHTHALATE SPHERULITES*

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ABSTRACT

The morphology and structure of three types of normal and abnormal spherulites of polyethylene terephthalate cast from solution in dimethylphthalate were studied by polarizing microscopy, transmission electron microscopy and electron diffraction techniques. In the normal negative spherulites the $[210]^*$ direction is parallel to the radius direction. In the normal positive spherulites the radius direction is parallel to the $[326]^*$. In the abnormal PET spherulites the Maltese cross extinction pattern in the polarizing microscope under crossed polars is oriented at 45° to the polars and there are concentric extinction rings around the center of the spherulite. Electron diffraction pattern indicates that $[212]^*$ is parallel to the radius of the spherulite and this explains the observed extinction pattern in the abnormal spherulite.

INTRODUCTION

Polyethylene terephthalate (PET) is easy to crystallize in the temperature range between the glass transition temperature (69°C) and melting point (264°C), usually spherulites are obtained. There are several types of PET spherulites^[1-3]. Normal spherulites are characterized by their Maltese cross extinction pattern oriented parallel to the polars in the polarizing microscope under crossed polars. The Maltese cross extinction pattern of abnormal spherulites is observed at 45° to the polars. Keller^[2] had studied the molecular orientations of positive and negative normal PET spherulites by X-ray microbeam technique and discussed them theoretically. Because it was difficult to obtain spherulites larger than $60\mu\text{m}$, he did not solve the problem completely. In order to clarify the structure of PET normal spherulites, it is necessary to use spherulites larger than $100\mu\text{m}$ and more suitable techniques, such as electron microscopy and electron diffraction. Abnormal spherulites are often encountered in natural and synthetic macromolecular compounds^[4-10], but have not been studied in detail. Therefore, it is important to well understand the morphology and structure of both normal and abnormal PET spherulites.

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EXPERIMENTAL

1. *Samples used*

PET samples were obtained from Beijing 5th Chemical Plant. The weight average molecular weight is about 17,000.

2. *Spherulitic film preparation*

In order to obtain large size ($100\mu\text{m}$) PET spherulites the solution cast technique was used. PET samples were dried in vacuum at 120°C for 6 h, then the solution of PET in dimethylphthalate with different concentrations (0.05–0.4%) were prepared. A few drops of hot solution ($\sim 240^\circ\text{C}$) were deposited on the bottom of a small covered Petri dish which was previously heated to the crystallization temperature (240°C , 235°C or 220°C), then it was maintained at the crystallization temperature for 4 h and then slowly cooled down to room temperature. The films so prepared were composed of normal positive or normal negative spherulites or abnormal spherulites depending on the crystallization conditions. Most of the spherulites in the films were larger than $100\mu\text{m}$. The film formed on the bottom of the Petri dish was then floated off by 2% HF solution and rinsed several times in distilled water and picked up onto a microscope slide for polarizing microscopy study. A Leitz SM-LUX-POL Polarizing Microscope was used. After careful examination and identification of the spherulites in the polarizing microscope the film was cut into small pieces, subsequently refloated off on distilled water and picked up onto 3 mm copper grids for examination by JEOL JEM-200CX electron microscope with 200KV accelerating voltage and about $5\mu\text{A}$ beam current.

RESULTS AND DISCUSSION

1. *Morphology and structure of PET normal spherulites*

(1) Negative spherulites

Fig. 1 shows the appearance of the spherulites of the film obtained by solution (0.1–0.4%) casting at crystallization temperature 220°C in the polarizing microscope under crossed polars. There are Maltese cross extinction patterns oriented parallel to the polars. After insertion of the compensator (λ plate) the interference colour in the first and third diametrically opposed quadrants of the cross is orange and in the second and fourth ones is blue. This indicates that the spherulites are negative. The size of the spherulites are not uniform in the film. The diameter of large spherulites can be over $120\mu\text{m}$ and that of small ones around the large spherulite are only $\leq 10\mu\text{m}$. There is a ring-like structure which separates the large spherulite from small ones. This indicates that the morphologies of the large and small negative spherulites are different. This has been well confirmed by the electron microscopy. Fig. 2 is a transmission electron micrograph of small negative spherulites, showing a radiating fibrillar morphology. Fig. 3 is a transmission electron micrograph of a large PET negative spherulite, with an electron diffraction pattern overlayed in proper orientation. This figure shows that the spherulite is composed of radiating helical lamellae.

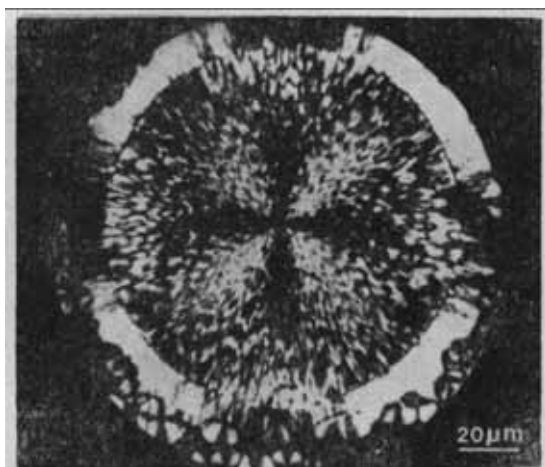


Fig. 1 Optical micrograph of PET negative spherulites (crossed polars)

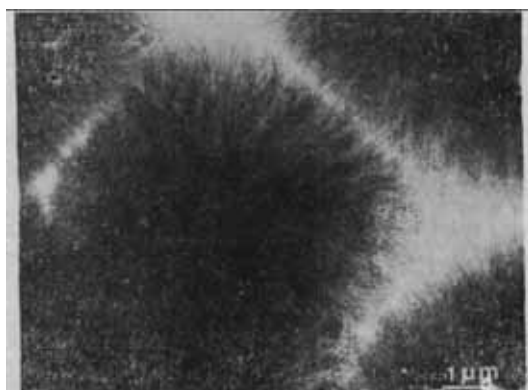


Fig. 2 Electron micrograph of PET small negative spherulites

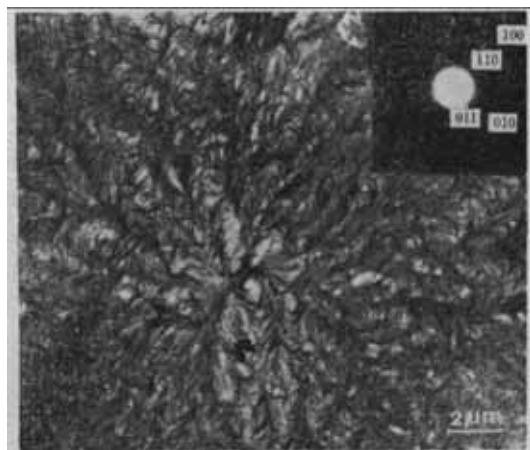


Fig. 3 Electron micrograph of a PET large negative spherulite and a correctly oriented electron diffraction pattern

The electron diffraction pattern, corresponding to a sector of the spherulite, obtained with the selected area diffraction, indicates that the 100 and $\bar{1}\bar{1}0$ ($1\bar{1}0$) reflections are in the region of the meridian (the radius direction of the spherulite). 011 and 010 reflections are in the

region of equator. In order to determine the crystallographic index of the direction of the spherulite radius we studied the reciprocal lattice of PET^[11]. Fig. 4 presents the reciprocal lattice of PET. Three layers of (001) projected along the c-axis direction are represented.

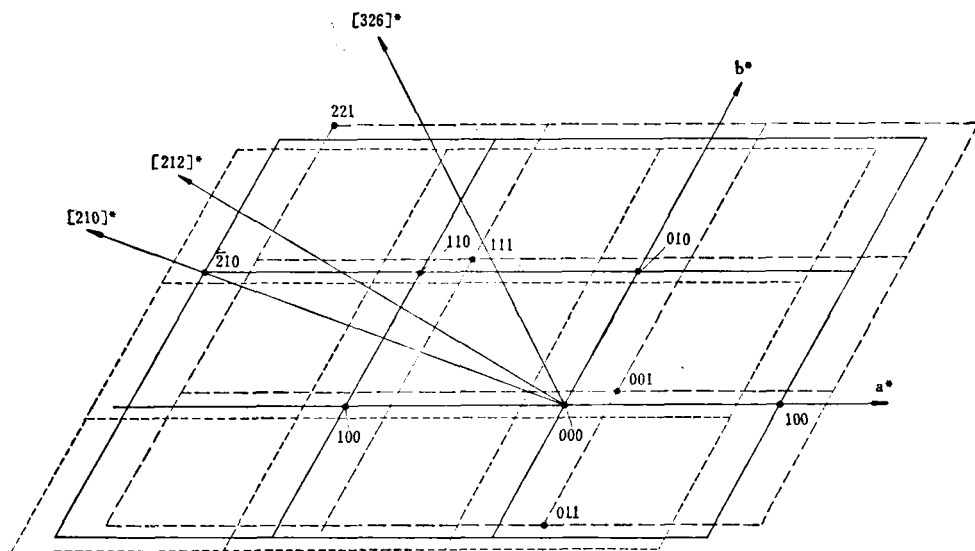


Fig. 4 Reciprocal lattice of PET crystal structure, showing three (001) layers and the $[210]^*$, $[212]^*$ and $[326]^*$ directions, projected along the c-axis

In addition, the angle between each crystallographic plane of interest and a particular plane, assumed perpendicular to the spherulite radius, was calculated using the classical equations of crystallography. Table 1 presents some of the calculated values. These values were then compared directly with the azimuthal angles of the reflections measured on the diffraction pattern. A very good correspondence was found for the radius direction taken to be parallel to $[210]^*$. Kunigi et al.^[12] calculated the polarizabilities of the PET crystal and obtained 2.27×10^{-27} and $2.15 \times 10^{-27} \text{cm}^3$, respectively, for the polarizabilities along the chain and perpendicular to it in the plane of the terephthalate residue and the polarizability perpendicular to the plane is smaller. Because the plane of the terephthalate residue is located nearly to the (100) plane, $[100]^*$ is the direction of the smallest polarizability. The angle between $[210]^*$ and $[100]^*$ is about 20° and the c-axis is perpendicular to $[210]^*$. When the unit cell of PET rotates around the $[210]^*$ direction the sections of indicatrix (cutting in the

Table 1

	$\bar{1}11$	$\bar{1}10$	100	$0\bar{1}1$	010
$\bar{2}10$	42.39	22.50	160.3	96.13	100.9
$\bar{3}26$	25.17	49.79	111.1	92.02	72.37
$\bar{2}12$	24.34	27.75	141.8	91.14	90.64

direction parallel to the spherulitic film plane containing $[\bar{2}10]^*$ are ellipses. The longer axis of each ellipse is nearly perpendicular to the $[\bar{2}10]^*$ and the shorter one is nearly parallel to it, therefore, $n_{\parallel} < n_{\perp}$ ($n_{\parallel}$ is the refractive index parallel, and $n_{\perp}$ the one perpendicular, to the radius of the spherulite), the spherulite is negative. In addition, the two axes of the ellipses of the lamellae near the direction of the crossed polars are nearly parallel to the polars, so there is a Maltese cross extinction pattern oriented parallel to the crossed polars.

(2) Positive spherulites

The spherulitic film obtained by solution (0.1–0.4%) casting technique at the crystallization temperature 240°C exhibits a Maltese cross in each spherulite also parallel to the polars (Fig. 5). After insertion of the compensator (λ plate) the interference colour in the

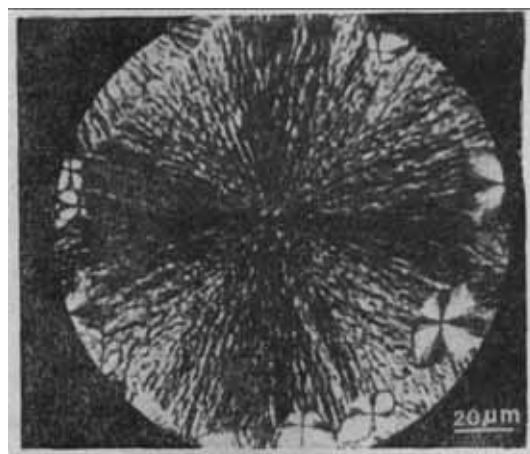


Fig. 5 Optical micrograph of PET positive spherulites (crossed polars)

first and third quadrants of the cross is blue and in the second and fourth ones is orange. This indicates that the spherulites are positive. The diameters of most spherulites are over 140 μm and there are some small spherulites 20 μm in diameter located between the large spherulites. Electron microscopy indicates that the morphology of the positive spherulites is very similar to that of the negative spherulites. They are also composed of radiating helical lamellae, but the orientation of the unit cell around the radius of the spherulites is different from that of the negative spherulites (Fig. 6). The electron diffraction pattern in Fig. 6 is correctly oriented with respect to the micrograph. It shows that $\bar{1}11$ and $\bar{1}10$ reflections are in the region of meridian and the angle between $\bar{1}11$ reflection and the meridian direction is about 25° and the angle between $\bar{1}10$ and the meridian is about 44°. $0\bar{1}1$ and 010 reflections are in the region of equator. According to the reciprocal lattice of PET (Fig. 4) and the values of the angles between planes (Table 1) we found that $[\bar{3}26]^*$ is in the direction of the radius of positive spherulites. The angle between $[\bar{3}26]^*$ and c-axis is about 42°, while the angle between the same direction and $[\bar{1}00]^*$ is about 69°. When the unit cell of PET rotates around the $[\bar{3}26]^*$ direction, the sections of indicatrix (in the plane of the spherulitic film containing $[\bar{3}26]^*$) are ellipses, those longer axes are nearly parallel to the $[\bar{3}26]^*$ and the shorter ones are nearly perpendicular to it, therefore $n_{\parallel} > n_{\perp}$. the spherulites are positive.

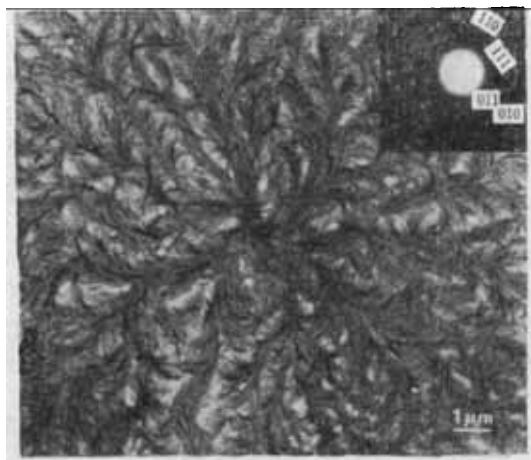


Fig. 6 Electron micrograph of a PET positive spherulite and a correctly oriented electron diffraction pattern

Because the two axes of the ellipses of the lamellae located in the direction close to the crossed polars are nearly parallel to the polars, the Maltese cross extinction pattern is normal i.e. parallel to the polars.

2. Morphology and structure of PET abnormal spherulites

The films prepared by solution (0.05%) casting technique at crystallization temperature 235°C exhibit a spherulitic morphology (Fig. 7). It can be seen that the diameters of these spherulites range from $65\mu\text{m}$ to $300\mu\text{m}$. The Maltese cross extinction pattern of each spherulite is not oriented along the polars, but rotated 45° to them and there are a series of concentric extinction rings around the center of each spherulite. After insertion of the compensator (λ plate) the alternative blue and orange rings around the center of each spherulite were observed, showing a periodic radial structure in the spherulite. This indicates that when the unit cell of PET rotates regularly around the direction of the radius the indexes varied

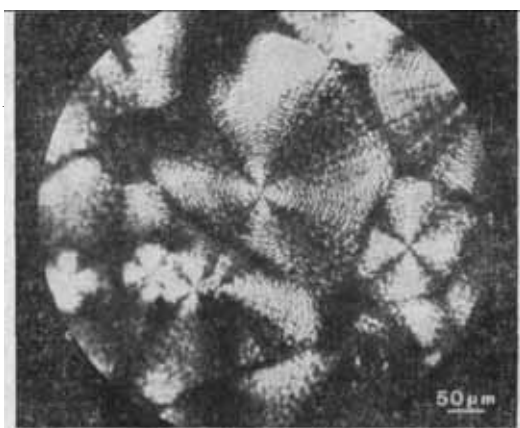


Fig. 7 Optical micrograph of PET abnormal spherulites (crossed polars)

periodically from $n_{\parallel} > n_{\perp}$ (or $n_{\parallel} < n_{\perp}$) through $n_{\parallel} = n_{\perp}$ to $n_{\parallel} < n_{\perp}$ (or $n_{\parallel} > n_{\perp}$) along the center to the periphery of the spherulite, when $n_{\parallel} = n_{\perp}$ extinction takes place. Fig. 8 is a transmission electron micrograph of an abnormal PET spherulite, with an electron diffraction pattern overlayed in proper orientation. This spherulite shows radiating fibrillar morphology. The electron diffraction pattern indicates that the $\bar{1}11$, $\bar{1}10$ and 100 reflections are in the region of meridian. The angles between the meridian and the $\bar{1}11$, $\bar{1}10$ and 100 reflections are $\sim 25^{\circ}$, $\sim 32^{\circ}$ and $\sim 38^{\circ}$, respectively. The $0\bar{1}1$ and 010 reflections are in the equator.

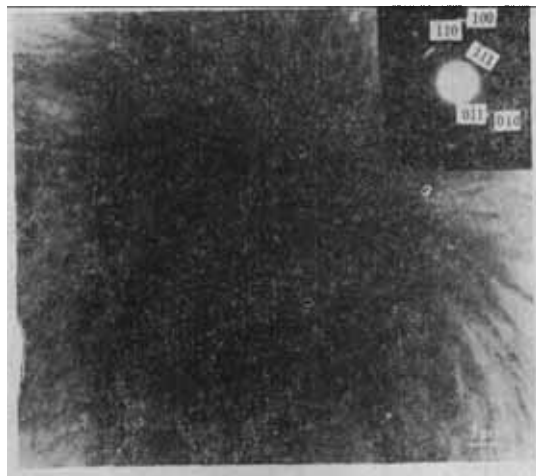


Fig. 8 Electron micrograph of a PET abnormal spherulite and a correctly oriented electron diffraction pattern

According to the reciprocal lattice of PET (Fig. 4) and the values of angles between planes (Table 1) $[\bar{2}12]^*$ is the direction of the abnormal PET spherulites. The angle between the $[\bar{2}12]^*$ and $[\bar{1}00]^*$ is about 38° , while the angle between $[\bar{2}12]^*$ and the chain axis c is about 65° . When the unit cell of PET rotates around $[\bar{2}12]^*$ the two axes of each section of indicatrix (in the plane of spherulitic film containing the $[\bar{2}12]^*$) are tilted at an angle to the $[\bar{2}12]^*$ direction and from the center of the spherulite to the periphery the refractive indexes $n_{\parallel}$ and $n_{\perp}$ change regularly. When $n_{\parallel} = n_{\perp}$ the extinction takes place and one of the two optic axes is parallel to the light at this point in the spherulite. Because the axes of the sections of indicatrix of the crystalline lamellae located at about 45° to the polars are parallel to the polars the Maltese cross extinction pattern, therefore, rotates about 45° to the polars.

The structure of PET spherulites with triclinic unit cell is quite complicated. The directions of the radius of the three types of spherulites investigated are neither parallel to the direction of the largest polarizability nor to that of the smaller and smallest ones. Different types of normal (including positive and negative) and abnormal spherulites can be obtained depending on the crystallization conditions, e.g. crystallization temperature, concentration of the solution etc. Because the orientation of the unit cell around the radius of distinct types of spherulites is different, it can be expected that the mechanical properties will be different in the PET materials with different types of spherulites.

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