Structure and Morphology of Poly(tetramethylene succinate) Crystals

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ABSTRACT: Crystals of an aliphatic polyester, poly(tetramethylene succinate) (PBS) are investigated using transmission electron microscopy. Single crystals grown from a 0.01 wt % dichlorobenzene solution show a terrace-like morphology above 65 °C and a leaflike one at lower temperatures. The molecules are packed perpendicular to the basal plane of the single crystals, and twin crystals with a (110) twin plane are frequently observed. The thickness of the single crystal lamellae increases smoothly with increasing crystallization temperature. Lattice parameters of the PBS crystal in the monoclinic unit cell are determined from the electron diffraction patterns of the single crystals and stretched films as a = 0.523 nm, b = 0.908 nm, c = 1.079 nm, and β = 123.87°. The dimension of the c-axis is shorter than the value calculated from a fully extended chain conformation, as has already been found for other aliphatic polyesters. Two types of negative spherulites are observed according to growth temperature.

Introduction

Since aliphatic polyesters were first synthesized by Carothers,[1] a variety of aliphatic polyesters with different carbon numbers in the diol and diacid have been synthesized.[2,3] The aliphatic polyesters are now studied extensively in order to replace some of the common synthetic polymers which present environmental pollution problems because of stable structure.[4−7] The aliphatic polyesters are believed to be able to decompose rather easily into less harmful structures under natural environmental circumstances.

Crystal structures of several polyesters, $-(-O(CH_2)_x-OCO-(CH_2)_{y-2}-CO-)_n^-$, have been studied using X-ray diffractometry.[8−13] Here, x and y denote the number of carbon atoms in the diol and diacid moieties, respectively. The crystal structures of poly(ethylene adipate) (2−6 polyester) and poly(ethylene suberate) (2−8 polyester) were analyzed by Turner-Jones and Bunn,[12] and poly(ethylene succinate) (2−4 polyester) was analyzed by Ueda et al.[13] The dimensions of the c-axis of the aliphatic polyesters shorten from calculated dimensions based on fully extended chains. In other words, chain conformations of the aliphatic polyesters depart from the all-trans zigzag, thus differing from polyethylene[14] and polyamides (nylons)[15,16] possessing planar zigzag chains.

Kanamoto and Tanaka[17] reported the morphology of 2−10, 6−10, and 10−18 aliphatic polyesters. The aliphatic polyesters crystallize in lamellar morphologies as polyethylene, nylon, etc.,[18] but the crystal habits are often not well-defined.[17] With increasing methylene sequence length in the repeating unit, the polyesters crystallize with more regular morphology.[17] The 10−18 polyester crystallizes into true or truncated lozenges with a hollow pyramidal structure,[17] as can be found in the polyethylene single crystals.[19]

The crystallization behavior of aliphatic polyesters is similar to polyethylene: the thickness of the lamellae depends upon the crystallization temperature, and thickening of the lamellae occurs by annealing.[20] The morphology of poly(ethylene adipate) (2−6 polyester) spherulites was investigated by Takayanagi and Yamashita.[21] They observed spherulites with different shapes depending on the growth temperatures.

In the present work, the morphology of an aliphatic polyester, poly(tetramethylene succinate) (4−4 polyester, hereafter PBS) single crystals grown from solutions, is investigated using transmission electron microscopy (TEM). The thickness of PBS lamellae was measured by small angle X-ray scattering (SAXS). Spherulite morphologies were studied by polarizing optical microscopy. The electron diffraction study revealed that the PBS molecules crystallize in the monoclinic crystal lattice: a = 0.523 nm, b = 0.908 nm, c = 1.079 nm, and β = 123.87°.

Experimental Procedures

Polymerization. PBS was synthesized at 240 °C from the polycondensation reaction of bis(4-hydroxybutyl) succinate (BHBS) oligomer with titanium isopropoxide (2×10^{-6} mol/g of oligomer) as a catalyst.[22] The BHBS oligomer was prepared by the direct esterification of succinic acid and 1,4-butanediol without catalyst at 190 °C. The number average molecular weight of the polymer measured by GPC was 70 000, and the melting temperature was 114 °C.

Single Crystal Preparation. Single crystals of PBS were grown by the self-seeding method[23] in a 0.01 wt % o-dichlorobenzene solution. Crystallization temperatures were 50, 60, and 65 °C.

TEM and X-ray Diffraction. TEM was performed by using a JEOL 2000FX at 200 kV. Aluminum was coated on the TEM specimens in order to calibrate the electron diffraction patterns. TEM samples for the observation of morphology were shadowed with Pt to increase contrast. Sedimented mats of the PBS single crystals crystallized at temperatures between 30 and 65 °C in 0.1 wt % dichlorobenzene solutions were prepared and used to measure the thickness of the lamellae. Ni-filtered Cu Kα radiation from a Rigaku Denki X-ray spectrometer was used.

Film Preparation. PBS cast films were prepared from a 1.0 wt % chloroform solution, and the films were stretched on

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a hot plate in a cylinderical shape heated at 80 °C. Carbon was deposited in vacuum on the surface of the stretched films, and replicas of the stretched film for TEM were prepared using poly(acrylic acid).

Spherulite Preparation. Molten polymer films between two glass slides at 120 °C were transferred quickly onto a hot stage set at the temperature to grow spherulites. Morphologies of the spherulites were observed by a polarizing optical microscope (Nikon HFX-11A).

Results and Discussion

Crystal Structure of PBS. Figure 1a shows the electron diffraction pattern of a stretched PBS film. The draw ratio was approximately 7 at 80 °C. Lattice parameters were determined from this pattern using 13 reflections. More information was obtained from the electron diffraction pattern of a single crystal grown from solution, as shown in Figure 2. The reflections in Figure 2 are the $hk0$ net which correspond to the reflections on the equator of Figure 1a. By analysis of the electron diffraction patterns the lattice parameters of a monoclinic unit cell were determined as $a = 0.523$ nm, $b = 0.908$ nm, $c = 1.079$ nm, and $\beta = 123.87°$. The density of bulk PBS annealed at 90 °C for 48 h was 1.24 g·cm^{-3}, which corresponds to two repeating units in a unit cell. The calculated crystalline density is 1.34 g·cm^{-3}. The calculated density of the PBS crystal is identical with that of the 2−6 polyester crystal,[12] which possesses the same C, H, and O numbers as PBS.

The $h00$ and $0k0$ reflections in Figure 2 are absent when h and k are odd, respectively. The PBS crystal, thus, may have a center of inversion in the repeating unit of the chain and the symmetry of the glide plane between the two chains in the unit cell. From the hkl reflections no further symmetry is found, as indexed in Figure 1b.

Turner-Jones et al.[12] and Ueda et al.[13] have analyzed the crystal structure of 2−4 and 2−8 polyesters and a 2−6 polyester, respectively. Crystal morphologies and lattice parameters have been studied for the 2−10, 4−6, 6−6, 6−10, 10−10, and 10−18 polyesters.[17,20,24,25] The aliphatic polyesters with long repeating units, i.e., 6−10, 10−10, and 10−18 polyesters, have chain lengths nearly the same as that of the fully extended conformation.[17] X-ray studies of polyesters with shorter repeating units have revealed a shortening of c-axis dimensions as compared to calculations based on the all-trans planar zigzag conformation.[17] The differences between measured and calculated c-axis dimensions are approximately 0.05 nm. Gauche as well as trans chain conformations were found in the crystals of 2−4, 2−6, and 2−8 polyesters.[12,13] Liau and Boyd referred to theses as "kinks".[25] The c-axis dimension of PBS is 1.079 nm, that is 0.141 nm shorter than the dimension of an all-trans conformation (1.22 nm). Moreover, the PBS has a 0.093 nm shorter chain than the 2−6 polyester (c-axis of 2−6 polyester is 1.172 nm),[12] which has the same carbon number as PBS. Accordingly, we can conclude that PBS may have a chain conformation deviated from the all-trans zigzag.

Electron diffraction patterns of PBS single crystals frequently show evidence of twinning, as show in Figure 3a. In the pattern, reflections from one domain of the twin crystal are indexed. As indexed in Figure 3a the (110) twin plane exists in the crystal. Figure 3b shows the lattices of PBS with a (110) twin boundary. The dots denote the stems of PBS molecules.

Single Crystal Morphology. Figure 4 shows an electron micrograph of PBS single crystals grown isothermally at 65 °C from a 0.01 wt % solution in o-dichlorobenzene. The crystals were shadowed with platinum to increase the contrast. The picture shows the spiral growth of single crystal lamellae. The electron diffraction pattern of the single crystal shown

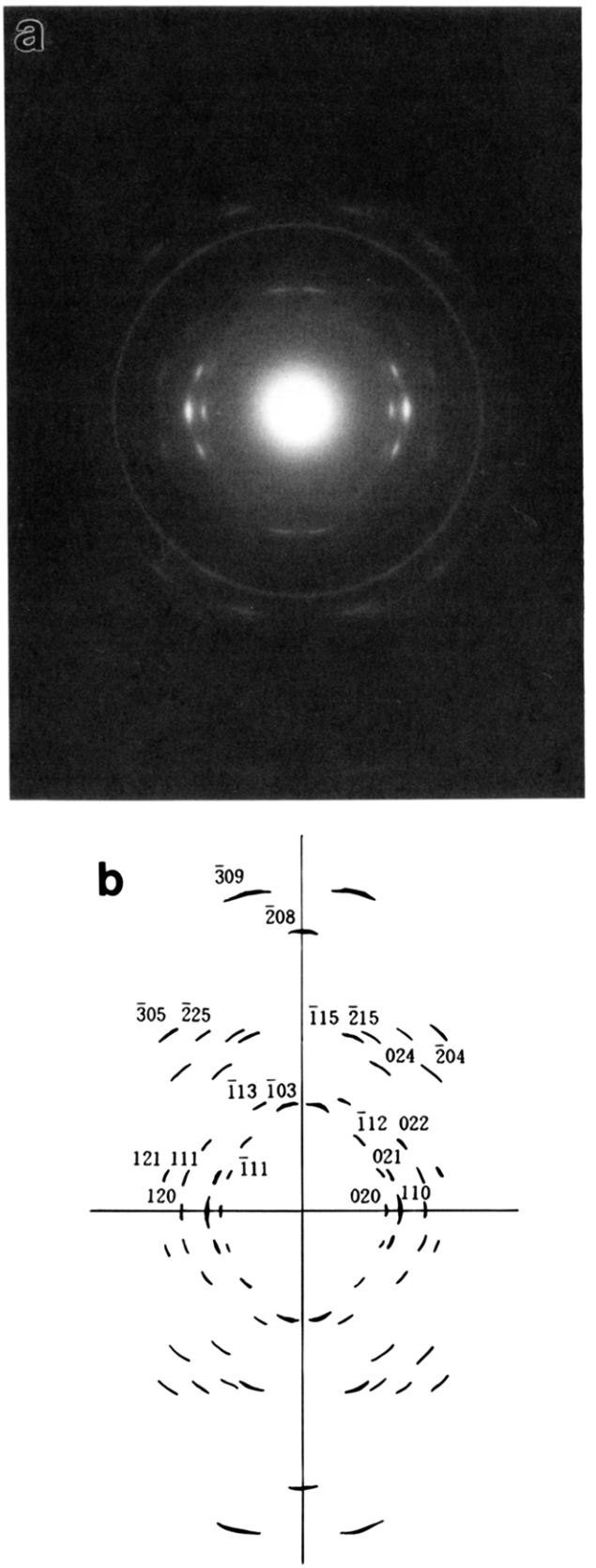


Figure 1. (a) Electron diffraction pattern of the stretched PBS film and (b) corresponding indexes. The draw ratio is 7 at 80 °C.

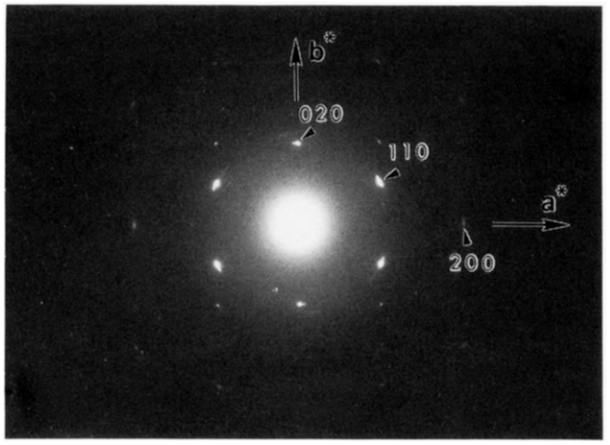
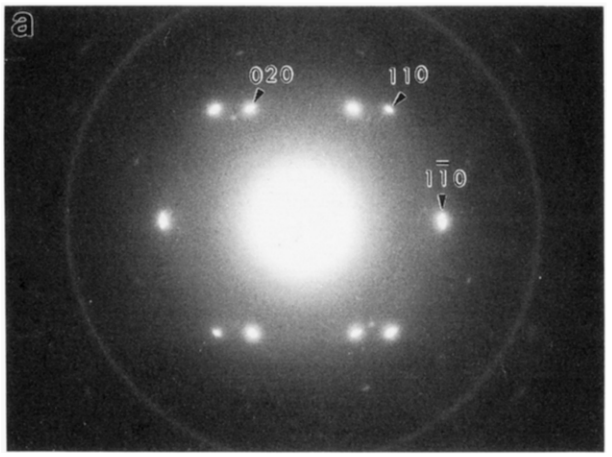


Figure 2. Electron diffraction pattern from a single crystal of PBS. The pattern was obtained from the edge of a monolayer region of the single crystal.



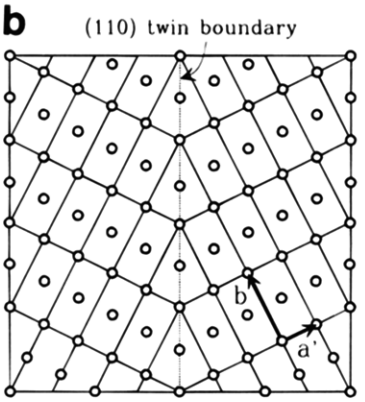


Figure 3. (a) Electron diffraction pattern of a PBS twin crystal and (b) lattices of the (110) twin crystal. The reflections originating from one domain are indexed in (a). The dots in (b) are the projection of the molecular stems in the unit cell.

in Figure 2 was obtained from the monolayer region at the edge of a PBS lamella. The PBS single crystals obtained at 60 °C show a leaflike morphology, as shown in Figure 5. Many overgrown thin layers are observed in the leaflike crystals.

The chains of PBS are oriented perpendicular to the basal plane of the single crystal lamellae, since the corresponding electron diffraction patterns give the $hk0$ net.

A crest of corrugation in the central area of the lamella is observed in the solution grown PBS single crystal, as shown in Figure 5. This reflects the hollow structure of the PBS crystal lamellae and indicates that

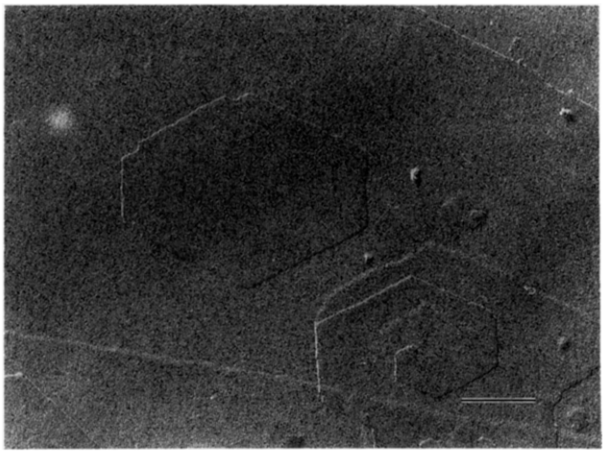


Figure 4. Terrace-like PBS single crystal. The single crystals were grown at 65 °C from 0.01 wt % *o*-dichlorobenzene and shadowed with Pt to increase the contrast for TEM (bar: 0.4 μm).

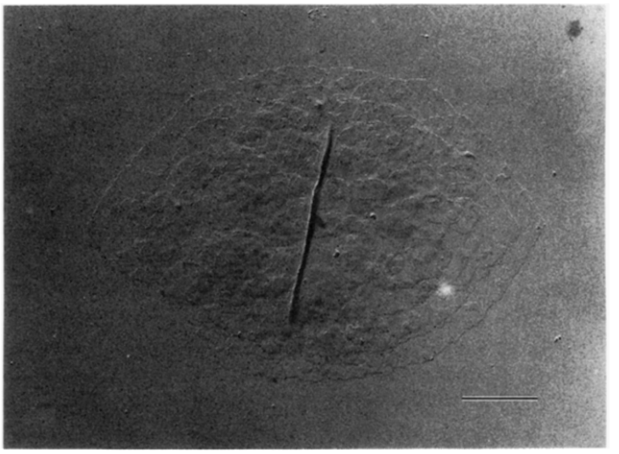


Figure 5. Leaflike PBS single crystal. Conditions are the same as for Figure 4 but at 60 °C. A crest of corrugation in the center of the crystal is observed, indicating a hollow crystal (bar: 1 μm).

lamellar surfaces were inclined to the basal plane before sedimentation onto the substrate. Kanamoto[20] reported such collapse features for single crystals of the 10−18 polyester which have a lozenge or truncated shape. The morphology is quite similar to that of the collapsed hollow pyramid of polyethylene single crystals.[18,19]

Lamellar Thickness. Lamellar thickening behavior for polymers with long repeating units such as aliphatic polyesters and polyamides is not well-defined. Some of the polymers show lamellar thicknesses related with multiples of the repeating unit dimensions, but some are not. Kanamoto[20] reported the relationship between the lamellar thickness and crystallization temperature or annealing temperature for several aliphatic polyesters. The lamellar thickness of the 2−10 and 10−18 polyesters increased continuously with an increase of the crystallization temperature, i.e. did not show a stepwise increase. This smooth change of thickness was also observed in annealed samples. On the contrary, Mnyukh et al.[26] reported that the long periods of oligomeric decamethylene glycol and dodecamethylene glycol polyesters precipitated by cooling from solution were equivalent to multiples of the repeating unit dimensions. For nylons, Dreyfuss and Keller[27] reported that the thickness of unusually thin lamellar crystals is approximately equal to a small integral multiple of the (001) spacing. Atkins et al.[28] also reported for the

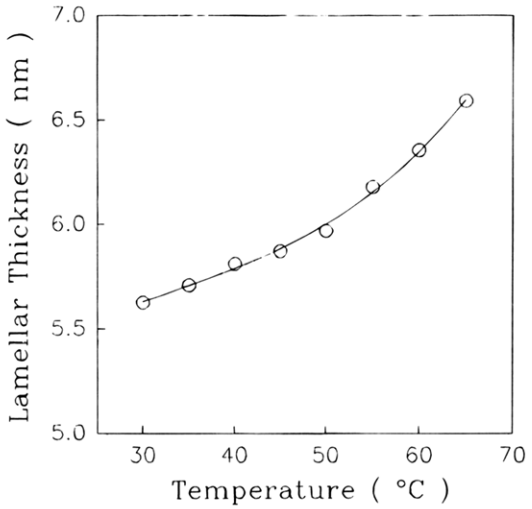


Figure 6. Lamellar thickness of PBS as a function of growth temperature.

46 nylon that the lamellar thickness is sufficient to accommodate four structural repeats of the chain.

The relationship of lamellar thickness and crystallizing temperature of solution grown PBS crystal lamellae is shown in Figure 6. The figure shows a smooth increase of lamellar thickness with temperature that is consistent with the results of Kanamoto.[20] This result suggests that the surface of PBS lamellae might consist irregularly of methylene or ester bonds in order to accommodate the chains to smoothly increasing thickness of the lameallae.

Surface decoration studies of nylon crystals[28] gave ordered structure and indicated chain-folding parallel to the hydrogen bonds. The chemical structures of polyesters and polyamides are quite similar, because they have long methylene units with ester and amide bonds, respectively. Since the polyamides have strong hydrogen bonds between amide bonds, the polyamide crystals have a planar structure of the molecules parallel to the hydrogen bonds. The 2–4, 2–6, and 2–8 aliphatic polyesters show no such planar structure in the crystal. Accordingly, the molecules of the two polymers behave in different manners to form the crystals.

PBS Spherulites. Parts a and b of Figure 7 show polarizing optical micrographs of PBS spherulites grown at 70 and 95 °C, respectively. In addition to a Maltese cross Figure 7a shows a banded structure with regularly spaced concentric rings, and Figure 7b shows an irregular pattern. The irregular pattern of extinction of Figure 7b appears at temperatures above 92 °C. Many polymeric spherulites show these features, e.g., polyamides, aromatic polyesters, etc.[18,19,21]

By the insertion of a first-order red plate between the crossed polars, it was found that the PBS spherulites are negative. This result indicates the strong reflective index located along the tangential direction, possibly parallel to the chain direction. The chain orientation in the spherulites was confirmed by observing the color change of a thin stretched PBS film in the polarizing optical microscope using a first-order red plate. When the chain direction of the stretched film was parallel to the tangential of the PBS spherulite, the raised (blue) or lowered (yellow) color was observed. The optical properties of banded structure and the irregular patterns of extinction in Figure 7a,b have been well explored earlier.[29,30] Especially, the chain orientation

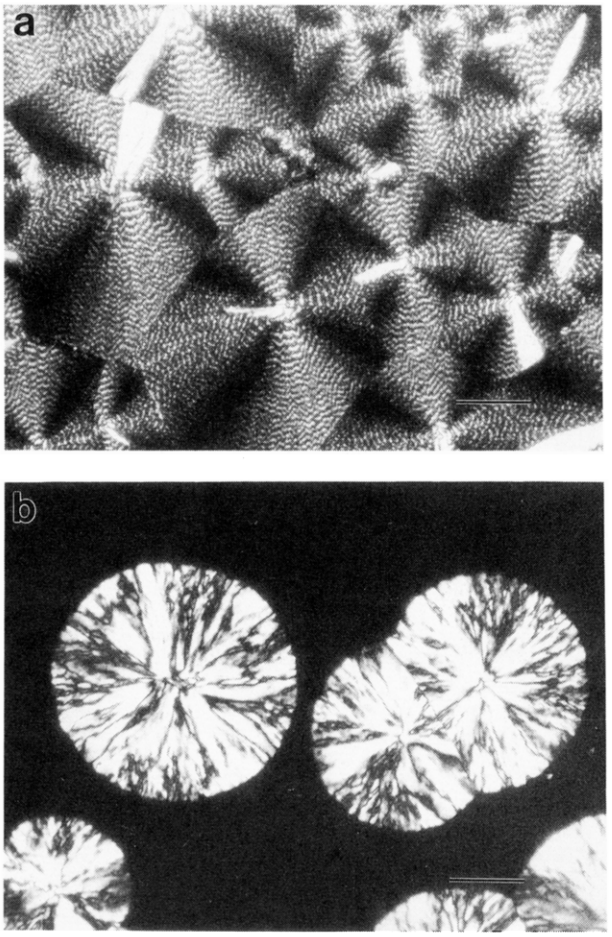


Figure 7. Polarizing optical micrographs of PBS spherulites grown at (a) 70 °C and (b) 95 °C. Spherulites with irregular pattern of extinction (b) were observed above 92 °C. The spherulites are negative, and the chains orient in a tangential direction. The bar on (a) is 20 μm and on (b) is 30 μm.

of the spherulites in Figure 7a should be quite similar to that of polyethylene spherulites of banded structure: the molecules orient in a tangential direction and the lamellae have a regular twist as they grow in the radial direction.

Conclusions

PBS single crystals grown from solution show terrace-like and leaflike shapes depending upon growth temperature. The PBS chains are oriented normal to the basal plane of the lamellae, as shown by electron diffraction. SAXS shows the lamellar thickness increases smoothly with temperature, but not stepwisely, to accommodate the repeating units. This suggests lamellar surfaces composed irregularly of both ester bonds and methylene units.

For PBS a monoclinic unit cell was determined from electron diffraction patterns: $a = 0.523$ nm, $b = 0.908$ nm, $c = 1.079$ nm, and $\beta = 123.87°$. Since the c-axis dimension of PBS is shorter than that of the fully extended chain, the PBS chain includes trans conformations as well as gauche.

Spherulites grown above 92 °C show irregular patterns, and banded patterns in the radial direction at lower temperature. The polarizing optical microscopy using a first-order red plate revealed the spherulites are optically negative, with tangential chain orientation in the spherulites.

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