Unusual Spherulitic Morphology of Poly(propylene fumarate)

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Abstract Spherulites are the most common crystalline morphology and thus the visual expression of crystal structures for polymers. The diversified patterns have provided intuitive morphology probes for various crystallization behaviors, while the correlations between them are still needed to be enriched. In this work, the complicated spherulitic morphology of poly(propylene fumarate) (PPF), which is sensitive to crystallization temperature, is investigated. PPF melt, respectively, crystallizes into rough spherulites, regularly banded spherulites, and spherulites containing both two kinds of morphology at low, high, and mediate temperatures. By systematically assaying, it is clear that the growth axis along the radial direction changes from α-axis to β-axis as the crystallization temperature increases, which leads to the formation of unique crystallization-temperature-dependent spherulites. Based on detailed characterization of Fourier transform infrared spectroscopy, the packing state of the specific hydrogen bonds of “C=C−H−O=−C=C=C” in PPF crystal lattices is determined, and furthermore, the mechanism for temperature-dependent selection of growth axes for PPF spherulites in melt is reasonably speculated.

Keywords Spherulite; Crystallization; Growth axis; Hydrogen bond

INTRODUCTION

Spherulites can be found in small organic molecules, synthetic ceramics, minerals and nearly all crystallizable polymers.[1−3] The spherical structure, a polycrystalline aggregate composed of fine lamellae, is the most common morphology of semi-crystalline polymer,[4] which is often crystallized from viscous melts or solutions at large supercoolings. When detected between orthogonal linear polarizers, the arresting birefringent characteristics originated from anisotropic bodies in quasi-two-dimensional spherulites reflect a number of structural informations. Consequently, spherulites have become essentially important morphological probes to unveil crystal structure of polymer, and thus develop crystallization theory.[4−7]

Morphology of spherulite has been effectively used to reveal the packing state of polymer lamellae. A positive spherulite has its highest refractive index for the light vibrating along the radius, and a negative spherulite has the highest refractive index for the light vibrating tangentially. For example, poly(L-lactide) (PLLA) formed negative nonbanded spherulites, corresponding to the predominately growing of edge-on lamellae along radial directions.[8,9] The signs of the birefringence changed from a positive spherulite to a mixed spherulite and then to a negative spherulite as the counterpart of PLLA, poly(D-lactide) (PDLA) was blended in, which was due to the change of orientation of edge-on lamellae from radial to tangential directions.[9] When crystallized at elevated temperatures close to melting point, the birefringence of as-formed PLLA (or PDLA) spherulites dramatically declined compared to spherulites that grew at lower temperatures, indicating the change of radially grown lamellae from edge-on to flat-on.[10] Banded spherulite, showing rhythmically repeating concentric bands of greater and lesser transmittance consistent with oscillatory linear birefringence along the radii, is a more representative case. The twisted lamellae model for polymers was raised based on the banded spherulitic morphology,[11−14] and also for the further elucidation of twisting mechanism,[15] the anisotropic surface stresses on lamellae.[5,16]

Once a much more complicated spherulitic morphology is captured, more information of crystal structure will be revealed, which is of great benefit for uncovering various polymer crystallization mechanisms. The co-existence of two types of banded regions in one poly(3-hydroxyvalerate) (PHV) spherulite demonstrated that the growth axis is one of the key factors determining the twist handedness of the lamellae of chiral polymers.[17] Observation on the growth behavior of new spherulites on the periphery of other pre-existing spherulites with different crystal modifications is the direct and most used approach to confirm and study the mechanism of polymorphism and cross-nucleation in polymers, such as poly(butylene adipate) (PBA),[18] poly(1,3-dioxolan) (PDOL),[19] and poly(1-butene) (PB-1).[20] In addition, the complicated spherulitic morphology of polymerized cyclic butylene terephthalate (PcBT) was the response to the different regional distributions of polymer molecular weight dur-
ing melt crystallization.\cite{21}

Poly(propylene fumarate) (PPF) is a typical biodegradable and bio-compatible unsaturated polyester and widely used as tissue engineering scaffolds.\cite{22-24} As far as the authors aware, however, the crystallization behavior and crystal structure of PPF have not been investigated yet. Recently, we employed PPF as an example that could grow very regularly banded spherulites with appropriate band spacings to demonstrate the twist sense distribution in achiral polymers for the first time.\cite{25} Besides, the spherulitic morphology of PPF was crystallization-temperature-dependent, growing non-banded spherulites at 25 °C but regularly banded spherulites at 95 °C. The mechanism for such temperature sensitive spherulitic morphology of PPF is unclear. Therefore, in this work, the interesting, complicated crystalline morphologies of PPF at various temperatures are in detail studied, and the relationship between spherulitic morphology and inter-segment hydrogen-bonding interaction is speculated.

**EXPERIMENTAL**

**Materials**

PPF was synthesized from fumaric acid (FA, AR grade) and 1,3-propylene glycol (PG, AR grade) by a two-step reaction of esterification and polycondensation in melt state. Tetra-n-butyl titanate (TBT) and p-hydroxyanisole (pHA) were utilized as catalyst and free radical inhibitor in polycondensation step. Both TBT and pHA adding contents were 0.5 wt% relative to the total reactant. Detailed synthesis procedure was the same as preparation of poly(butylene fumarate) (PBf)\cite{26} while with shorter polycondensation time for 1 h. All reagents were purchased from Shanghai Aladdin Industrial Inc. and used without further purification.

The product was dissolved in chloroform and centrifuged to remove impurities, then precipitated in an excess amount of cold methanol (at 0 °C). The filtered sample was dried in vacuum at 40 °C for 48 h before use.

**Characterizations**

Molecular weight and polydispersity (Đ) of PPF were determined by Viscotek-M302 TDA Multiple testing gel chromatography system. The measurements were carried out at 40 °C with a Shimadzu GPC-804C column at a flow rate of 1.0 mL/min, and chloroform (HPLC grade) was used as the eluent. The average-number molecular weight (Mn) and Đ of PPF are 8.50×10⁴ g/mol and 1.70, respectively.

Spherulitic morphology and radial growth rate of PPF at different temperatures were obtained by a Leica DM2500P polarized optical microscope (POM) equipped with a Linkam THMS5600 hot-stage. The thickness of sample was ~10 µm.

The thermal properties of samples were measured on a NETZSCH 204F1 differential scanning calorimeter (DSC) equipped with an intercooler system under nitrogen atmosphere. The heating and cooling rates were set at 10 °C/min (Fig. 1). The specimen showed crystallization temperature (Tc), melting point (Tm) and melting enthalpy (ΔHm) as 63.5 °C, 135.7 °C, and 61.1 J/g, respectively.

![Fig 1](image)

The non-isothermal crystallization and subsequent heating DSC thermograms of PPF measured at a rate of 10 °C/min.

Interestingly, PPF was found to display diversified spherulitic morphologies with respect to crystallization temperature (Fig. 2). It crystallized into distinct positive, rough spherulites, and negative, regularly banded spherulites when the melt-crystallization temperature was set below 72 °C or above 82 °C, while could exhibit complicated patterns containing the above two kinds of morphology within one spherulite at temperatures between 72 and 82 °C. The rough morphology turned into very irregularly banded structure with alternating positive and negative birefringence when increasing crystallization temperature. Pitches of both irregular and regular bands increased as the temperature was raised, which is a commonly-observed change of banded spherulitic morphology.\cite{21} The fraction of rough (or very irregularly banded) mor-
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Fig. 2 The typical POM images of PPF samples isothermally crystallized at different temperatures.

Growth Rates in PPF Spherulites

...the occurrence of cross-nucleation from one crystal modification to another. To present the change more clearly, PPF melt was sequentially crystallized at different temperatures (Fig. 4). When PPF sample being crystallized at 95 °C was switched to 72 °C, the spherulites first continued to form regular bands but with much smaller pitch (region 1). After 1–2 min, rough structure grew and fanned out some regions at the growing front (e.g., region 2). After being re-placed at 95 °C, the regularly banded structure with wider spacing recovered at both fronts of narrow regular bands and rough regions, while the rough morphology could grow a little more at the high temperature before changing. The lag in morphology change for rough to regularly banded should respond to the alternating process of growing axes along radii.

Fig. 4 POM image of PPF sequentially crystallized at 95, 72 and 95 °C for appropriate times.

Growth Axes in Spherulite

The PPF spherulitic film samples isothermally crystallized at low temperatures (e.g., 50 °C) and high temperatures (e.g., 95 °C) exhibited similar diffractograms as shown in Fig. 5(A), ensuring that the complicated spherulite morphology was not originated from polymorphism. And, the difference between two diffractograms reflected distinct crystal orientations in the spherulite plane. Since the crystal lattice structure of PPF has not been reported, the single crystal of PPF was prepared (Fig. 5B) and assayed by electron diffraction (Fig. 5C). The electron diffraction pattern defined a rectangular unit cell, suggesting the formation

https://doi.org/10.1007/s10118-021-2518-y
of orthorhombic or monoclinic unit cell. The pattern allowed a molecular chain orientation perpendicular to the crystal basal plane to be postulated, and some lattice parameters were directly calculated, i.e., \( a = 0.994 \text{ nm} \) and \( b = 1.481 \text{ nm} \) (\( \beta = 90^\circ \) in orthorhombic unit cell and other values in monoclinic unit cell). Yet the information of unit cell was not completely clear; the diffraction peaks at \( 2\theta = 17.85^\circ \) and \( 23.96^\circ \) respectively corresponding to interplanar spacings of 0.496 and 0.371 nm, intriguingly, agreed well with the (200) and (040) planes. Considering the geometry during WAXD measurement and the quasi-two-dimensional film structure, the diffraction intensity of (200) plane will be stronger for PPF spherulites consisting of radially grown lamellae along \( a \)-axis than those along \( a \)-axis, and in verse for the intensity of (040) plane. Thus, it is suggested that the radial growth direction of rough spherulites (e.g., formed at 50 °C) was \( a \)-axis, while that of regularly banded spherulites (e.g., formed at 95 °C) was \( b \)-axis.

**FTIR Investigation**

To study packing behavior of PPF stems in crystals, the in situ FTIR spectra of crystallizing PPF were investigated (Fig. 6). During crystallization the absorption intensity of stretching vibration of \( \text{C} = \text{O} \) bonds decreased at 1723 cm\(^{-1}\) and increased at 1701 cm\(^{-1}\), respectively. The FTIR band at 1723 cm\(^{-1}\) was ascribed to the amorphous phase, and FTIR band at 1701 cm\(^{-1}\) was ascribed to the crystal phase. Moreover, the sharp raising of band at 3071 cm\(^{-1}\) assigned to the stretching vibrations of \( \text{C} = \text{H} \) bonds in \( \text{C} = \text{C} = \text{H} \) groups confirmed the formation of the specific \( \text{C} = \text{C} = \text{H} = \text{O} \) hydrogen-bonding in crystal phase.\(^{[28-30]}\)

It is apparent to note that the area crystalline \( \text{C} = \text{O} \) band (i.e., at 1701 cm\(^{-1}\)) for PPF crystallized at 50 °C was higher than that at 95 °C. The relative crystallinities \( \chi_{\text{c,FTIR}} \) were respectively calculated out as 37.4% and 28.5% for these two samples isothermally crystallized at the low and high temperatures by using the conventional deconvolution method.\(^{[31,32]}\) However, occurrence of such significantly different crystallinities for PPF samples by changing crystallization temperature was obviously perverse as the crystal modification kept the same. DSC measurement showed that the two samples possessed almost the same melting enthalpy, 62.7 J/g versus 63.9 J/g. Consequently, the difference on as-calculated \( \chi_{\text{c,FTIR}} \) here from FTIR could not be in reality, but, rather reflect response of IR absorption to the difference of lamellar orientation (geometric effect) in spherulites of the two film samples (about 10 \( \mu \text{m} \) in thickness). Some evidences of geometry-dependency for crystallinity measured by spectroscopy methods, such as FTIR and Raman, have been revealed in polymer samples.\(^{[32-34]}\)

Micro-FTIR spectra of the rough and the regularly banded structures in a spherulite (Fig. 7A) show, again, that more hydrogen bonds were orientated parallel to the quasi-two-dimensional film in rough region than regularly banded region. In order to further assay the direction of hydrogen bonds, micro-polarized-FTIR (MP-FTIR) was employed to detect the IR dichroism \( (R = A_P/A_V, A_P \text{ and } A_V \text{ are the absorption areas of crystalline } \text{C} = \text{O} \text{ bands when the polarized IR was respectively parallel to and perpendicular to the radial directions}) \) of the three regions that localized similarly along the radial direction as the sequent regions 1–3 marked in Fig. 4. The anisotropy of hydrogen bonds is clearly presented in Fig. 7(B). The value of \( R \) was calculated as 0.67 for the region 1 of regularly banded structure, demonstrating the preferential orientation of hydrogen bonds in crystal phase was along the tangential directions of spherulite. The value of \( R \) increased to 1.35 in the region 2 of rough structure, which revealed the change of preferential orientation of hydrogen bonds to the radius of spherulite. And, the preferential orientation of hydrogen bonds recovered to the tangential directions in the region 3 of regularly banded structure, showing a value of \( R \) as 0.65.

By combining the growth axes of spherulites and the dominant orientation directions of hydrogen bonds in crystal phase, PPF lamellae, growing along \( a \)-axis in rough morphology and \( b \)-axis in regularly banded morphology, are schemed in Fig. 7(C). The inter-stem hydrogen bonds in flat-on and edge-on lamellae both contributed to the absorption intensity of stretching vibration band of \( \text{C} = \text{O} \) groups at 1701 cm\(^{-1}\) when the radial direction was selected as \( a \)-axis. But, only the flat-on lamellae participated in the FTIR signal at 1701 cm\(^{-1}\) when the radial direction was \( b \)-axis, which led to a much lower absorption intensity, and thus induced a smaller value of \( \chi_{\text{c,FTIR}} \) for the as-grown, quasi-two-dimensional spherulites at high temperatures.

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*Fig. 5* Wide angle X-ray diffractograms of PPF crystallized at different temperatures (A), TEM image (B) and the corresponding electron diffraction pattern of a PPF single crystal (C).
Discussion

A growth model for co-existence of two kinds of morphological regions in a spherulite showing only one crystal modification has been well demonstrated in earlier study. In the early growth stage of spherulite, the primary nuclei contain one or several layered lamellae, designated as baby lamellae. The relative position between baby lamellae and substrate (glass was used here) will determine the spherulitic morphology observed. When the baby lamellae are edge-on against the glass slide, spherulite growth will only find the way along one axis (a-axis or b-axis) due to thickness restriction between two glass slides. In other cases, flat-on or tilting state, the spherulites can grow along both a-axis and b-axis, leading to the obvious formation of complicated morphology with two kinds of regions if the growth rates along these two axes are competitive. Therefore, besides the state of baby lamellae, the differential in growth ability along different axes is a key factor for PPF to present such complicated morphology or not. The mismatching ratio of spherulite growth rates along two axes for PPF was less than 10% in the crystallization temperature range of 72–80 °C (see Fig. 3). However, what determines the growth rates along different axes needs further investigation.

When going through structure features inside crystal lattices of polymers that exhibit the similarly specific spherulitic morphology like PPF, both of whose a-axis and b-axis can be available as the growth axis along radial direction, including PHV, PES, PBS, cellulose/ionic liquid system, it is interesting to note the usual existence of stronger inter-segment interaction than just van der Waals force, that is, hydrogen-bonding interaction (“C—H···O” or “O—H···O”). Since hydrogen bond is of directional characteristic and sensitive to temperature, it may play an important role in determining the growth ability along different axes, and thus impact the final microstructural morphology. The absorption FTIR bands of C=O of PPF melt-quenched to different temperatures were immediately measured (ahead of the occurrence of crystallization) and presented in Fig. 8(a). It is clear that the FTIR bands shifted toward lower wavenumber position as the temperature set for the quenched amorphous PPF was decreased. The lower position of band revealed the stronger inter-segment hydrogen-bonding interaction of “C—H···O=C—C”. When the peaks of C=O absorption bands were plotted with quenched temperatures (Fig. 8b), it is intriguing to find an inflection between 70 and 80 °C. The temperature-dependent shifting degree of C=O absorption band was much steeper in lower temperature range (<70 °C) than higher temperature range (>80 °C). The abrupt and more obvious change of relying law of shifting on temperature should be a hint for the formation a kind of stronger inter-segment hydrogen-bonding interaction, though the exact structure information was not clear yet.

The quite well overlapping temperature range for the existence of complicated spherulitic morphology (Fig. 2) and the
abruption of relying law of hydrogen-bonding interaction (Fig. 8b) indicate the correlation between morphology and hydrogen bond. Very recently, a relationship between the pre-formed hydrogen bonds in melt and the final optical properties of spherulites for polyamide 56 (PA56) was revealed and the direction of the hydrogen bonding plane between the chains parallel to the spherulite radius direction and the chains becomes vertical, making the positive optical spherulite transformation to negative optical characteristics.\[38\]

Based on the growth habit of polymer lamella, a growth mechanism at the lamellar front was, then, speculated for PPF. For simplicity, only hydrogen-bonded chain segment pairs were considered.

As schemed in Fig. 9, during crystallization the pre-formed segment pair with hydrogen-bonding interaction in amorphous attaches on the lamellar frontier and then regulates its conformation to transform into part of crystal. When crystallized at lower temperatures (i.e., \(<72^\circ\text{C}\) ), the interaction bet-
When crystallized at higher temperatures (i.e., >82 °C), the inter-segment hydrogen-bonding interaction is changed and weakened (Fig. 8), resulting in the disappearance of advantage for growing along a-axis. Instead, it is more conductive to growth along b-axis, because the attachment of segment pair could be more stable than single segment, which declines the dynamically detaching process of segment from lamellar frontier. Thus, PPF lamellae prefer to growth along the b-axis.

Once located at mediate temperatures (i.e., 72–82 °C), the two kinds of growth behavior speculated above are competitive, that is, the growth abilities of PPF spherulite along a-axis and b-axis are comparable, then the complicated morphology containing two distinct regions in one spherulite is produced.

CONCLUSIONS

In summary, we present a new case for polymer spherulites with complicated morphology in PPF, whose crystal structure and crystallization behavior are waiting to be investigated. PPF melt, respectively, crystallizes into rough spherulites, regularly banded spherulites, and spherulites containing both two kinds of morphologies at low, high, and mediate temperatures. Based on the data assayed by DSC, WAXD and FTIR, it is clear that the change of spherulitic morphology relies on the temperature-dependent growth axis along radial direction. The growth axis changes from a-axis to b-axis as the crystallization temperature increases, and the spherulites could grow along both axes at mediate temperatures. The packing state of specific hydrogen bonds of \( -C\,\ldots\,H\,-O\,-=\,C\,-\ldots\,C\,-\ldots\,C\,) in crystal lattices is determined from the obvious difference on apparent crystallinities of the two kinds of spherulitic morphologies, which are evaluated from FTIR spectra. And furthermore, the mechanism for temperature-dependent selection of growth axis for PPF spherulite in melt is reasonably speculated.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 21674128) and Science Foundation of China University of Petroleum, Beijing (No. ZK20200097).

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https://doi.org/10.1007/s10118-021-2518-y