Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 6152–6161
polymer
www.elsevier.com/locate/polymer

Structural analysis of poly(butylene adipate) banded spherulites from their biodegradation behavior

Lifen Zhao [a,b], Xiaohong Wang [b,c], Lin Li [c], Zhihua Gan [a,*]

[a] The CAS Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100080, China
[b] The Graduate School of Chinese Academy of Sciences, Beijing 100049, China
[c] State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 3 May 2007; received in revised form 15 July 2007; accepted 19 July 2007
Available online 29 July 2007

Abstract

Poly(butylene adipate) (PBA) has been reported to have polymorphic crystal structures and only the mixture of two crystal modifications (α and β crystals) forms banded spherulites. However, how the two crystals coexist in banded spherulites remains to be solved. In this work, the morphological structure of PBA banded spherulites was analyzed from their biodegradation behavior by means of polarized optical microscopy (POM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and wide-angle X-ray diffraction (WAXD). It was found that the banded spherulites were made up of alternate flat-on and edge-on domains in lamellar crystals along the radiating direction. To determine the distribution of two crystal modifications in banded spherulites and the interrelationships between the alternate domains with polymorphic crystal structures, the relative contents of two crystal modifications in banded spherulites were first quantified, and their changes were then correlated to the morphological changes of banded spherulites in the course of biodegradation in terms of the difference in biodegradation kinetics of two crystal modifications. It was found that the flat-on domains show a slower crystal growth rate but a faster biodegradation rate than the edge-on domains. The analysis indicates that the flat-on domains in spherulites are composed of α crystals, while the edge-on domains are composed of β crystals. The primary growth mechanism of PBA banded spherulite was proposed based on the difference in crystallization heat and kinetics of two crystal modifications.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Banded spherulite; Polymorphic crystals; Enzymatic degradation

1. Introduction

Banded spherulites, which show regular concentric bands along the radiating direction under a polarized optical microscope, are common morphological features for many crystalline polymers. These polymers can be divided into two types of systems according to the composition. One system consists of the semicrystalline homopolymers, such as polyethylene [1–4], isotactic polystyrene [5], poly(ethylene oxide) [6], poly(propylene oxide) [7], poly(3-hydroxybutyrate) [8], polylactide [9,10] and poly(butylene terephthalate) [11]. Another system consists of polymer blends, such as poly(ε-caprolactone)/poly(ethylene oxide) [12], poly(ε-caprolactone)/poly(styrene-*co*-acrylonitrile) copolymer [13], liquid crystalline poly(aryl ether ketone)/poly(aryl ether ether ketone) [14], and poly(vinylidene fluoride)/poly(vinyl acetate) [15]. In 1950s, Keith and Padden [1], Price [16] and Keller [17], respectively, proposed models of lamellar twisting. From then on, a large amount of work has been performed to build theoretical models to explain the formation of banded spherulites. There are two typical models that are widely accepted. The first model is based on the stress induced lamellar crystal twisting [4,18–21]. Recently, Lotz and Cheng gave a comprehensive review on the lamellar twisting by the unbalanced surface

---

* Corresponding author. Tel./fax: +86 10 62529194.
E-mail address: zhgan@iccas.ac.cn (Z. Gan).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.07.055

stress [22]. Keith and Padden proposed another typical model of structural discontinuities caused by rhythmic crystal growth [1,23]. This model has been proved in some works [14,24] and simulated by Kyu et al. using nonlinear diffusion equations [25]. Although it has been studied for decades, the growth mechanism of banded spherulites is still a controversial topic in the research field of polymer crystallization and morphology.

Apart from those reported crystalline polymers, poly(butylene adipate) (PBA) shows a very special crystallization mechanism of banded spherulites. It has been reported that PBA is a polymorphic polymer with two crystal modifications (α and β crystals) and their formation depends on crystallization conditions and thermal treatment [26]. In our previous work, simply changing crystallization temperatures results in the formation of polymorphic crystals. α and β crystals grow at the temperatures above 32 °C and below 27 °C, respectively. Interestingly, two crystal modifications grow simultaneously at the temperatures between 27 and 32 °C to form a mixture of two crystal forms. The morphological investigations on PBA samples indicate that neither α crystal nor β crystal shows banded spherulites. However, when the two crystal modifications grow simultaneously, they show banded spherulite morphology [27]. This is a new phenomenon that the formation of banded spherulites depends on crystal structure. So the relationship between the mixed crystal structure and the banded spherulite morphology as well as the growth mechanism of this kind of banded spherulite will be of great interest to investigate.

To demonstrate the crystallization mechanism of PBA banded spherulites, the first step is to analyze the morphological microstructure of PBA banded spherulites, or in other words, to determine the distribution of α and β crystals in the banded spherulites. Electron diffraction is an ideal method to determine crystal structure [28]. Especially nanobeam electron diffraction is a powerful method to analyze the banded structures of spherulites because the diffraction area is able to be converged to several nanometers in domain [29]. However, radiation damage on PBA samples is a limiting factor due to the lower melting temperature (∼50 °C) and poor radiation resistance of aliphatic PBA. Furthermore, the mixed crystals of PBA are very sensitive to temperature fluctuation. The β crystal is a thermodynamically metastable phase which is able to transform into α crystal at an elevated temperature [30]. When the electron beam hits the PBA sample, it may cause a quick rise in the local temperature. Thus, the data of electron diffraction may not reflect the real crystal structure of sample. Recently, the microbeam X-ray diffraction with synchrotron radiation was used to study the microstructure of banded spherulites [31]. However, at present it is difficult to obtain direct data on the crystal structure of microdomains in PBA banded spherulites from electron or X-ray diffraction.

The biodegradability of PBA provides us a novel way to study the morphological structure of PBA banded spherulites. Our previous work has revealed that the two crystal modifications show different biodegradation kinetics [27]. The α crystal shows a faster degradation rate than the β crystal, and the degradation rate of the mixed crystals increases with the content of α crystal. It can be predicted that the faster degradation of α crystal should cause the corresponding morphological changes of banded spherulites. So the difference in biodegradation kinetics of two crystal modifications may enable us to reveal the crystal structures of PBA banded spherulites from their biodegradation behavior.

The purpose of this work is to determine the microstructure of PBA banded spherulites, or in other words, to determine the distribution of two crystal modifications in spherulites. We characterized the crystal structures and morphologies of PBA banded spherulites in the course of enzymatic degradation by means of wide-angle X-ray diffraction (WAXD), polarized optical microscopy (POM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Based on the quantitative analysis of the relative contents of two crystal modifications in banded spherulites and the interrelation between polymorphic crystal contents and morphological changes, the morphological structure and the distribution of two crystal modifications in banded spherulites were determined.

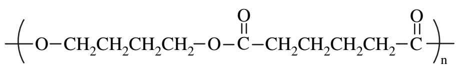
2. Experimental

2.1. Materials

Poly(butylene adipate) (IUPAC name: poly(1,4-butylene adipate)) (PBA) homopolymer was synthesized by melt polycondensation of 1,4-butanediol (CAS No. 110-63-4, supplied by BASF) and adipic acid (CAS No. 124-04-9, supplied by BASF) with tetrabutylorthotitanate (TBOT, CAS No. 5593-70-4, supplied by Fluka) as catalyst [32]. The chemical structure of PBA is shown in Scheme 1. PBA was purified by first dissolving in chloroform, then precipitating from methanol, and finally dried under vacuum before investigation. The glass transition temperature of PBA measured by differential scanning calorimetry at a heating rate of 20 °C is −60 °C. The number-average molecular weight M_n and polydispersity M_w/M_n were 40,000 and 1.7, respectively, measured by gel permeation chromatography (GPC) at 40 °C with narrow-distributed polystyrenes as standards and with chloroform as an eluant.

2.2. Morphological observation of banded spherulites

The PBA samples for polarized optical microscope (POM) were prepared on cover glass (20 × 20 mm in size) by casting from PBA chloroform solution (10 mg/mL). After the solvent was removed, the samples were melted on a hot stage at 75 °C for 2 min and then transferred onto another hot stage at a specific temperature for isothermal crystallization. The morphological observation and growth process of the spherulites



$$\left(\!-O-CH_2CH_2CH_2CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\right)_n$$

Scheme 1. The chemical structure of poly(butylene adipate) (PBA).

were performed by a Leica DMLP microscope (Germany) with a CCD record system.

For observation of morphology of banded spherulites by atomic force microscopes (AFM), the PBA films were prepared on a cover glass (12 × 12 mm) by first spin casting from a dilute PBA chloroform solution (1 mg/mL) and then melt-crystallizing at 31 °C. For comparison, the morphologies of PBA thin films after melt-crystallized at 25, 35, and 45 °C were also observed by AFM. All the AFM observations were carried out under tapping mode by using a Nanoscope III MultiMode AFM (Digital Instruments). Both the height and the phase images were recorded simultaneously. Typical values for the set-point amplitude ratio (r_{sp} is defined as the ratio of the cantilever's oscillating amplitude to its freely oscillating amplitude) were 0.7–0.9. The amplitude of the freely oscillating cantilever was approximately 40 nm. TESP tips with a resonance frequency of approximately 300 kHz and a spring constant of about 30 N/m were used.

2.3. Biodegradation of banded spherulites

For determining the biodegradation rate, crystal structure and morphology by means of gravity, WAXD and SEM, the PBA films with a thickness of 0.1 mm were prepared by first sandwiching the polymer samples between two Teflon sheets with another Teflon film (0.1 mm in thickness) as a spacer and then compressing the samples on a hot plate at 70 °C for 2 min under a pressure of 50 kg cm^{-2}. After that, the sandwiched polymer films were transferred rapidly into a water bath at a designated temperature for isothermal crystallization. After completion of crystallization, the polymer films were separated for enzymatic degradation experiments.

The enzymatic degradation experiments of PBA films were carried out at 37 °C in phosphate buffered solution containing the lipase from *Pseudomonas* sp. (Sigma). Briefly, 20 μL of lipase solution (1 mg/mL in 0.1 M phosphate buffered solution) was added into the vial with a piece of PBA film (10 × 10 × 0.1 mm in dimension) in 1 mL phosphate buffered solution. After every 3-h interval, some of the polymer films were taken out, washed with distilled water and then dried under vacuum for analysis. For the samples exposed for longer degradation times, the phosphate buffered solution in the vial was replaced with fresh buffer solution. After degradation for different time lengths, all of the PBA films were dried thoroughly for weight loss measurement and WAXD characterization. The morphological changes of banded spherulites after biodegradation were observed on a HITACHI S-530 scanning electron microscope (Japan) after being coated with gold under vacuum. In addition, to observe the morphological changes of lamellar crystals in banded spherulites, the PBA thin films on the cover glass were put into the phosphate buffered solution containing lipase for enzymatic degradation. After a certain time interval, the PBA thin films were taken out from the cover glass, washed with distilled water and finally dried under vacuum. The surface morphology of these films was observed by AFM.

2.4. Crystallization heat of polymorphic crystals

The isothermal crystallization of PBA was performed on a Pyris Diamond DSC (Perkin–Elmer instrument) which is equipped with a CryoFill liquid nitrogen cooling system and operated under nitrogen atmosphere at a flow rate of 20 mL/min. The instrument was carefully calibrated by using standard materials before measurement. For exothermic measurement during isothermal crystallization process, ca. 5 mg PBA sample encapsulated in the DSC aluminum pan was first heated to 70 °C, held there 3 min for melting, and then quenched at a rate of 200 °C/min to a given temperature for isothermal crystallization. The heat flow curves at a given temperature as a function of time were recorded to calculate the exothermic heat of PBA polymorphic crystals during isothermal crystallization process.

3. Results and discussion

3.1. Crystal structure and morphology of banded spherulite

Fig. 1 shows typical polarized optical micrographs of PBA spherulites with different polymorphic crystal structures. Different morphologies were found for spherulites with polymorphic crystal structures. Very interestingly, the banded spherulites were found when the crystallization temperature was 31 °C (see Fig. 1b and the inset). The WAXD analysis indicates that the crystal structure of banded spherulites is a mixture of α and β crystal modifications. On the other hand, the pure PBA β crystal and α crystal have the similar and non-banded spherulite morphology, as seen in Fig. 1a and c. The different sizes of spherulites are due to their different degrees of supercooling from the melt.

It was found that every spherulite with the mixed structure of two crystal modifications consisted of the banded spherulite morphology. In consideration of the fact that neither PBA α crystal nor β crystal exhibits banded spherulite over their crystallization temperature ranges, we can exclude the possibility that the PBA mixed crystal structures are a mixture of the spherulites with α and β crystal structures. The α and β crystals should coexist inside every banded spherulite. Because lamellae are the basic constitutional units of spherulites, two models of PBA banded spherulites are possible: (1) spherulites are composed of the lamellae with α and β crystal structures; or (2) each lamella is composed of α and β crystal domains, and these distinct lamellae constitute the banded spherulites. To examine the possibility, the lamellar crystal morphology of spherulites with the structure of α crystal, β crystal, and the mixture of two crystals was observed one by one by AFM.

Fig. 2 shows the AFM images of lamellar crystal morphologies with pure β and α crystal structures. It was found that the spherulites of β crystal structure are composed of edge-on lamellar crystals (Fig. 2a and b), while those spherulites of α crystal structure are composed of lath-like flat-on lamellar crystals (Fig. 2c), which are much clearer at higher

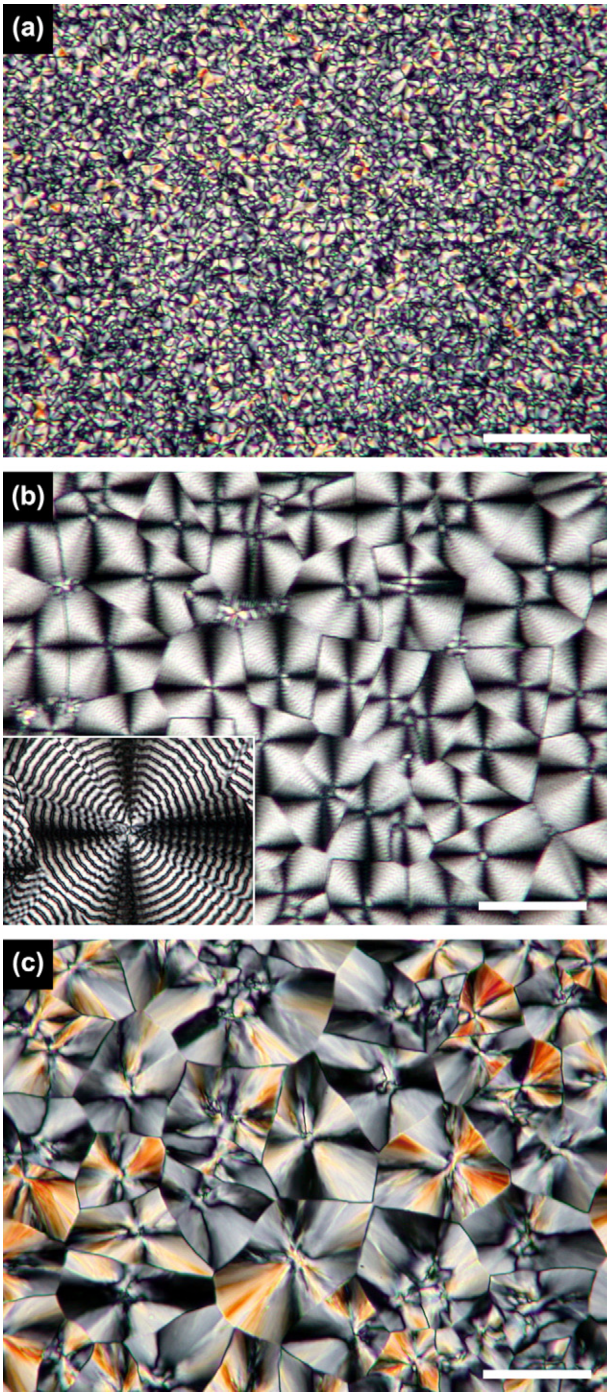


Fig. 1. The polarized optical micrographs of PBA spherulites with different crystal structures after isothermal crystallization from the melt. (a) Crystallization temperature $T_c = 25$ °C, β crystal structure; (b) $T_c = 31$ °C, mixed α and β crystal structures, the inset is the enlarged picture of banded spherulite; (c) $T_c = 35$ °C, α crystal structure. The scale bar is 50 μm.

crystallization temperature of 45 °C (Fig. 2d). Therefore, it can be concluded that the characteristic morphology of α crystal is flat-on lamellar crystals and that of β crystal is edge-on lamellar crystals. This conclusion is helpful for us to analyze the morphological structure of banded spherulites.

Fig. 3 shows the AFM images with different magnitudes of banded spherulites after melt-crystallization at 31 °C. Fig. 3a is the AFM height image at a scale of 20 × 20 μm. Fig. 3b is the enlarged AFM phase images (3 × 3 μm), denoted as the square part in Fig. 3a. It can be clearly seen that the PBA banded spherulite is made up of the alternate array of flat-on domains and edge-on domains along radiating direction of spherulite. When combined the POM pictures and AFM images, it has been clear that the dark ringed ribbons of banded spherulites under polarized light in Fig. 1b are composed of flat-on lamellae while the bright ribbons are composed of edge-on lamellae.

Now it is clear that the PBA banded spherulites are made up of alternate domains of flat-on and edge-on in lamellae along spherulite radiating direction. It will be of interest to know the correlations between these domains and polymorphic crystal structures. The morphological characters of pure α lamellar crystals and pure β lamellar crystals as shown in Fig. 2 suggest that the alternate flat-on and edge-on domains in banded spherulites may correspond to the structures of α and β crystals, respectively. To prove this suggestion, we need evidences, which may come from the biodegradation behavior of PBA banded spherulites in terms of the different biodegradation kinetics of two crystal modifications. Before that, we must first determine the relative contents of the two crystal modifications in banded spherulites and then correlate the contents to the morphological changes of PBA banded spherulites during biodegradation process.

3.2. The relative contents of polymorphic crystals in banded spherulites

Fig. 4 is a typical WAXD pattern of PBA with mixed two crystal modifications. The diffraction pattern is composed of two β crystal diffraction peaks ($\beta_{(110)}$ and $\beta_{(020)}$) and three α crystal diffraction peaks ($\alpha_{(110)}$, $\alpha_{(020)}$ and $\alpha_{(021)}$). It has been known that the integral area of WAXD diffraction patterns is the sum of crystalline and amorphous parts, and the degree of crystallinity is able to be calculated from the percentage of crystalline part contribution [33]. Based on this, we utilized Gaussian functions to separate the diffraction patterns of PBA mixed crystals and to fit them with an amorphous peak and five crystalline peaks. The peak separating and fitting results have been represented by the lines in Fig. 4.

Because two crystal modifications are different only in crystalline region, the relative content of α crystal in the mixture could be simply calculated from the integration of crystalline diffraction peaks according to Eq. (1):

$$\alpha\% = \frac{S_{\alpha(110)} + S_{\alpha(020)} + S_{\alpha(021)}}{S_{\alpha(110)} + S_{\alpha(020)} + S_{\alpha(021)} + S_{\beta(110)} + S_{\beta(020)}} \quad (1)$$

where $S_{\alpha(110)}$, $S_{\alpha(020)}$ and $S_{\alpha(021)}$ are the integral area of diffraction peaks $\alpha_{(110)}$, $\alpha_{(020)}$ and $\alpha_{(021)}$, respectively, while $S_{\beta(110)}$ and $S_{\beta(020)}$ are the integral area of diffraction peaks $\beta_{(110)}$ and $\beta_{(020)}$, respectively.

Fig. 5 shows the calculated contents of two crystal modifications in PBA mixed crystals at different crystallization temperatures. It reveals that the content of α crystal in the mixture

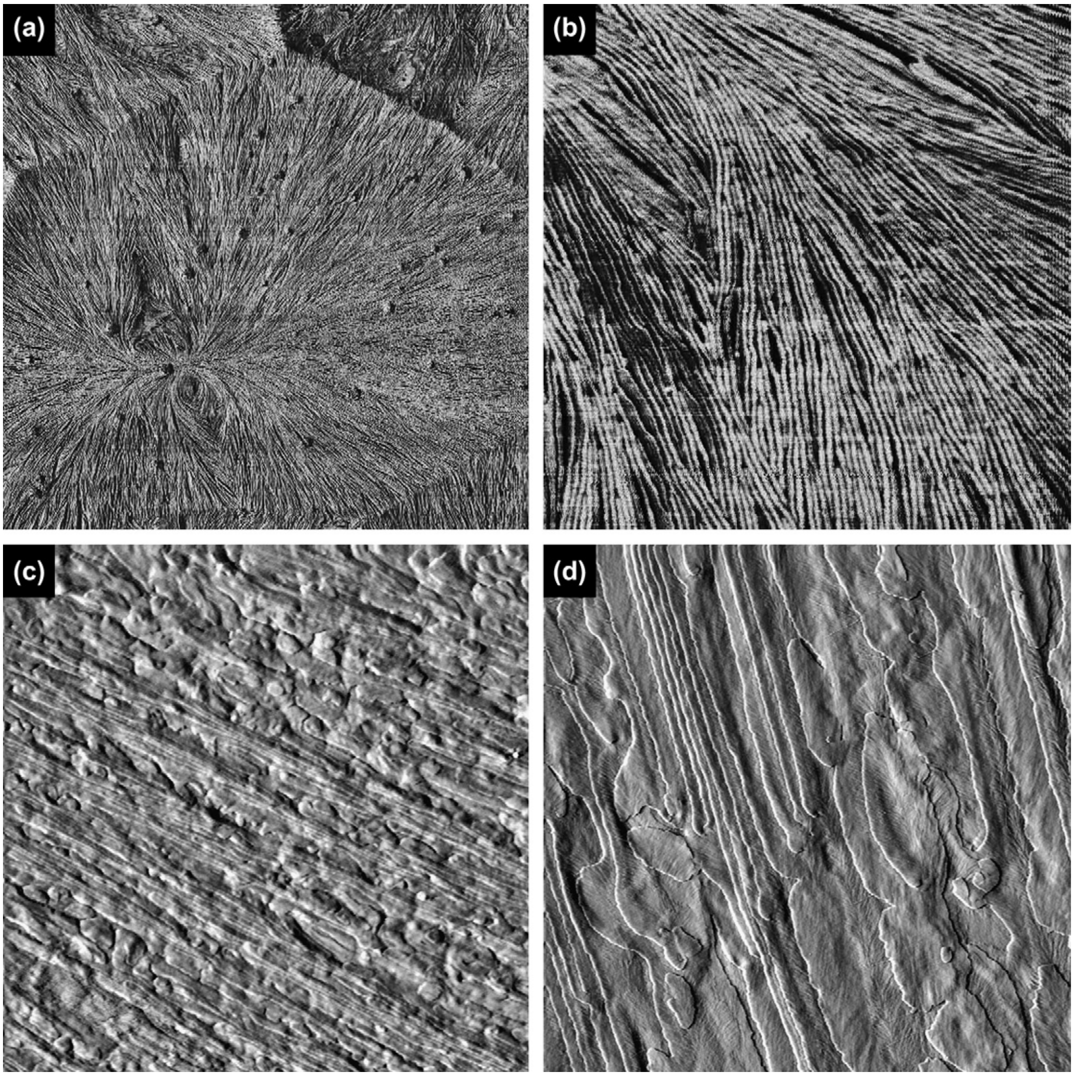


Fig. 2. AFM images of PBA spherulites and lamellar crystals with pure β and pure α crystal structures. (a) $T_c = 25$ °C, β crystal structure, 12 × 12 μm in dimension; (b) $T_c = 25$ °C, β crystal structure, 1 × 1 μm; (c) $T_c = 35$ °C, α crystal structure, 15 × 15 μm; (d) $T_c = 45$ °C, α crystal structure, 15 × 15 μm.

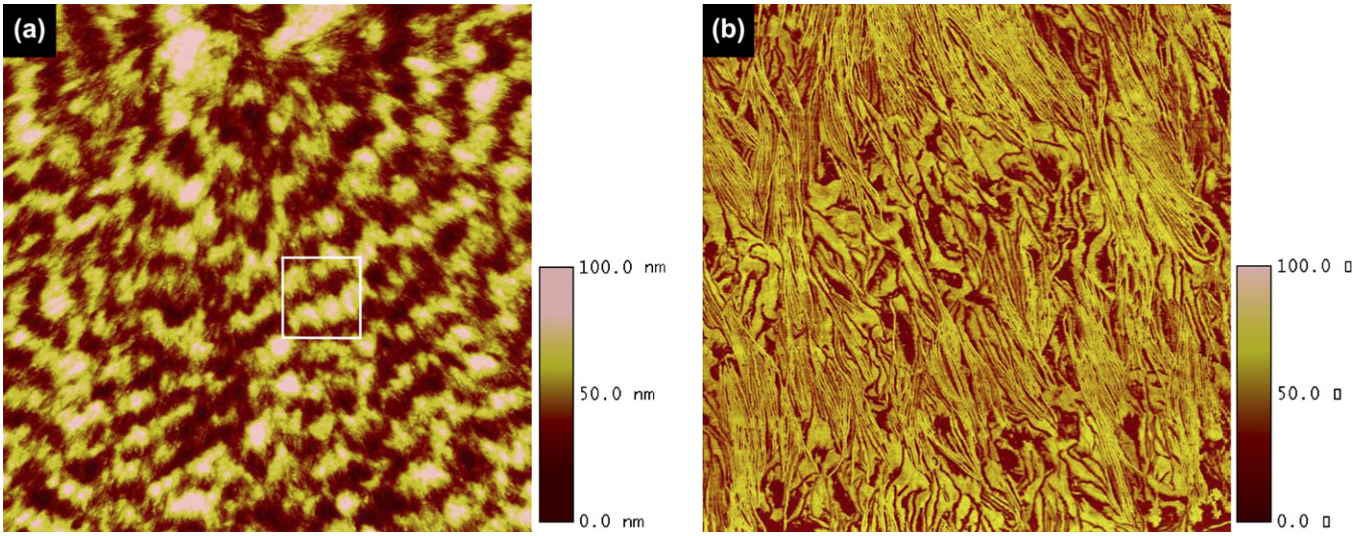


Fig. 3. AFM images of PBA banded spherulites after melt-crystallization at 31 °C. (a) Height image with dimension of 20 × 20 μm; (b) enlarged phase image with dimension of 3 × 3 μm, as denoted by the square in (a).

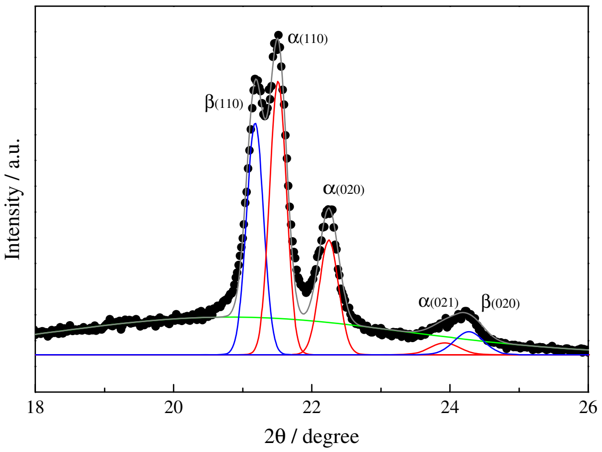


Fig. 4. Typical WAXD patterns of PBA films with mixed two crystal structures after melt-crystallization at 31 °C. The (●) is the experimental data, while the lines are the simulated results to fit the diffraction peaks on the basis of Gaussian functions.

increases with crystallization temperatures. This result indicates that the peak fitting method of WAXD diffraction patterns is a quantitative method to calculate the relative contents of two crystal modifications in the mixture. By following the change of diffraction patterns of PBA films in the course of biodegradation, it is possible to correlate the content changes of two crystal modifications to the weight loss and to the morphological changes of PBA banded spherulites, and further to determine the distribution of polymorphic crystals in the spherulites.

3.3. Enzymatic degradation and structural analysis of banded spherulites

In our previous work, we found that each of the pure α and β crystals shows the dependence of degradation rate R_d on lamellar thickness, *i.e.* R_d decreases with increase of lamellar thickness [27]. However, the α crystal shows a faster degradation rate than the β crystal when their crystallization temperatures are near 30 °C. These results indicate that not only the lamellar thickness but also the polymorphic crystal structure are the important factor to influence degradation rate. As shown in Fig. 5, the enzymatic degradation rate of the films with mixed crystal structures increases with increasing α crystal content in the mixture. Therefore for a given PBA sample with mixed crystal structures, the α crystal region has a faster biodegradation rate than the β crystal region. The faster degradation of α crystal region should lead to corresponding morphological changes of banded spherulites. Therefore, obviously morphological changes of PBA sample with higher α crystal content are favorable for the clear observation on morphological changes of banded spherulites by means of AFM and SEM. Here the PBA sample with 74% α crystal content after melt-crystallization at 31 °C was chosen for the study of morphological structure of banded spherulites.

Fig. 6 shows the changes of α crystal contents and weight loss of PBA films with mixed crystal structures during enzymatic degradation process. Within 12 h of enzymatic degradation, the weight loss of the films increases linearly with time. Notable is the change tendency of α crystal contents, which was found to decrease rapidly within the first 3 h, and then to keep almost unchanged with longer degradation time. The drastic loss of α crystal content within the first 3 h can be attributed to the fast degradation of α crystals in banded spherulites.

The dominant biodegradation of α crystal at beginning and the simultaneous biodegradation of both crystal modifications afterwards should cause the corresponding morphological changes of PBA banded spherulites. Fig. 7 shows SEM pictures of PBA films with banded spherulite structures during enzymatic degradation process. After degradation for 1.5 h, banded spherulites appear on the surface of PBA films (Fig. 7a). This is because of the fast degradation of amorphous regions. As revealed by the enlarged picture (Fig. 7b), enzymatic degradation leads to the formation of some lath-like holes in the ringed ribbons. After degradation for 3 h, the ringed ribbons became much clearer than before (Fig. 7c), and the enlarged picture (Fig. 7d) indicates that both the amount and the size of the holes increase with the degradation time. However, the other ringed ribbons between these degraded ones do not show obviously morphological

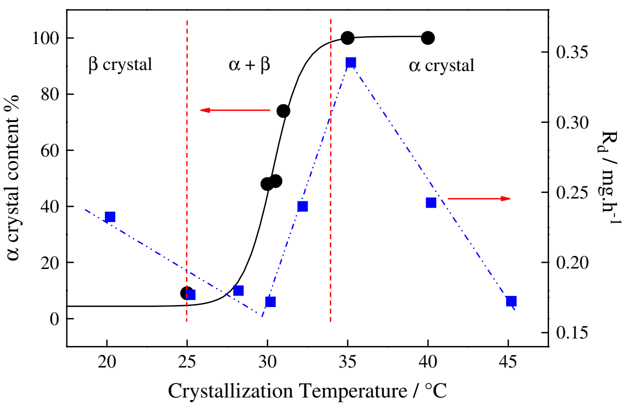


Fig. 5. The α crystal contents and biodegradation rates of PBA samples after melt-crystallization at different temperatures.

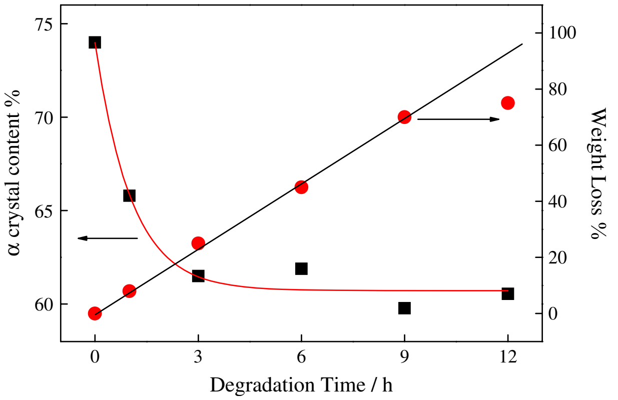


Fig. 6. The changes of α crystal content and weight loss of melt-crystallized PBA films ($T_c = 31$ °C) with mixed crystal modifications during enzymatic biodegradation.

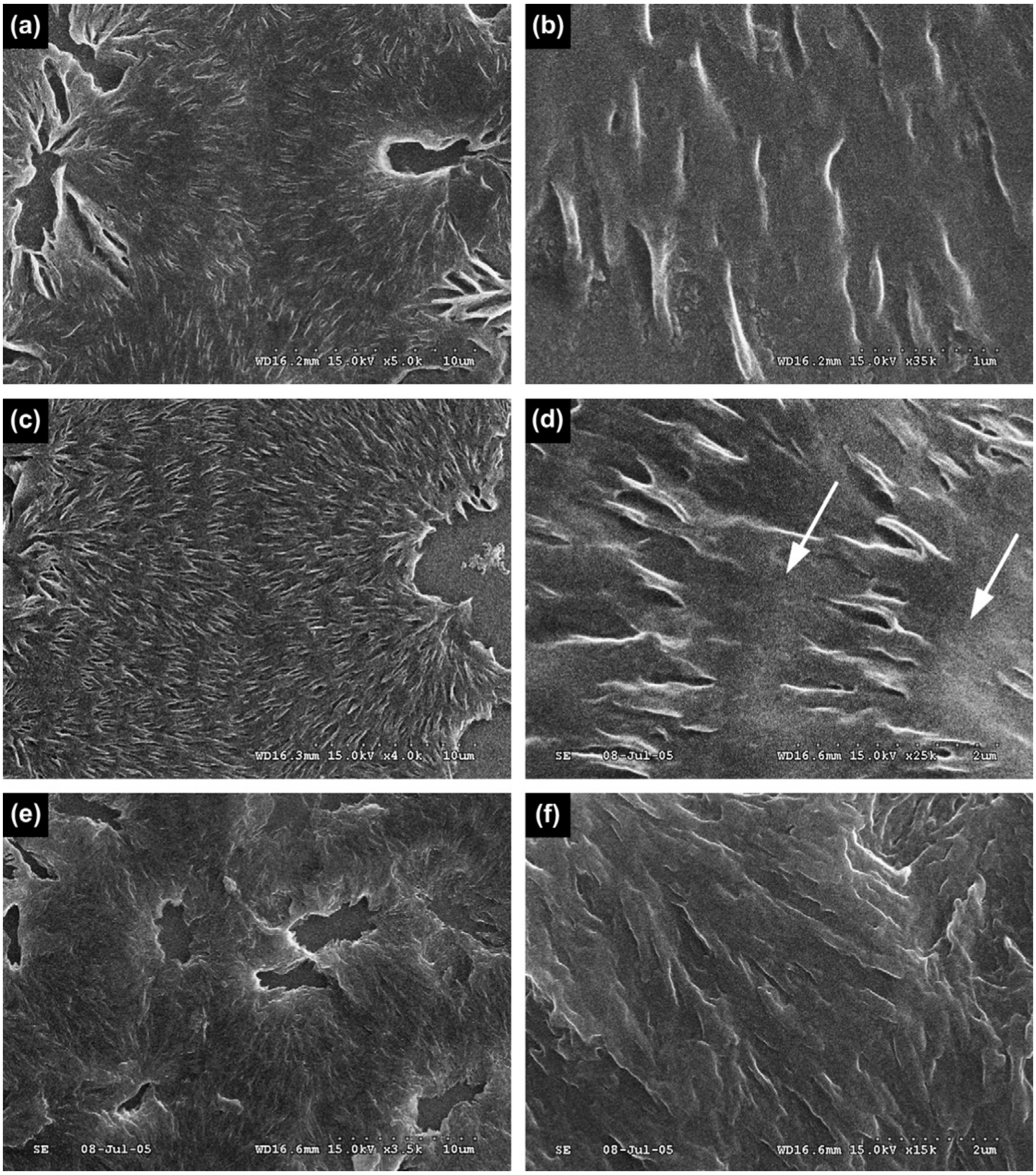


Fig. 7. SEM pictures of morphological change of PBA film surface after biodegradation for 1.5 h (a and b), 3 h (c and d) and 6 h (e and f). The films were prepared after isothermal crystallization at 31 °C.

changes (see the arrows in Fig. 7d). Combined the analysis of relative contents of two crystal modifications in Fig. 6 that the degradation of α crystals in banded spherulites is dominant in the first 3 h, it could be concluded that the degraded ringed ribbons are composed of the lamellae with α crystal structure. With further biodegradation for 6 h, the ringed ribbons in banded spherulites disappeared, as shown in Fig. 7e and f. This is due to the simultaneous biodegradation of α and β crystals in their corresponding ringed ribbons. Therefore, the morphological changes of banded spherulites at different time length are in well accordance to the enzymatic degradation kinetics of α crystals and β crystals as shown in Fig. 6.

Fig. 8 shows the AFM analysis on the morphological changes of lamellar crystals in banded spherulites after biodegradation for 3 h. Compared to the lamellar crystal morphology before degradation as shown in Fig. 3b, it was found that the flat-on lamellae with relatively large size and smooth surface degraded into many small fragments which were denoted by the arrow in Fig. 8, while the edge-on lamellar crystals still keep the entireness even though cracks could be seen between them. These morphological changes in lamellar crystals clearly reveal that the enzymatic degradation of lamellar crystals takes place firstly on the flat-on domains. Combined with the results in Fig. 6 that the dominant degradation within the first 3 h takes place in α crystal domains, it could be concluded that the flat-on domains in lamellar crystals are composed of α crystals.

Based on the morphology and slower degradation rate of edge-on domains in banded spherulites, it could be concluded

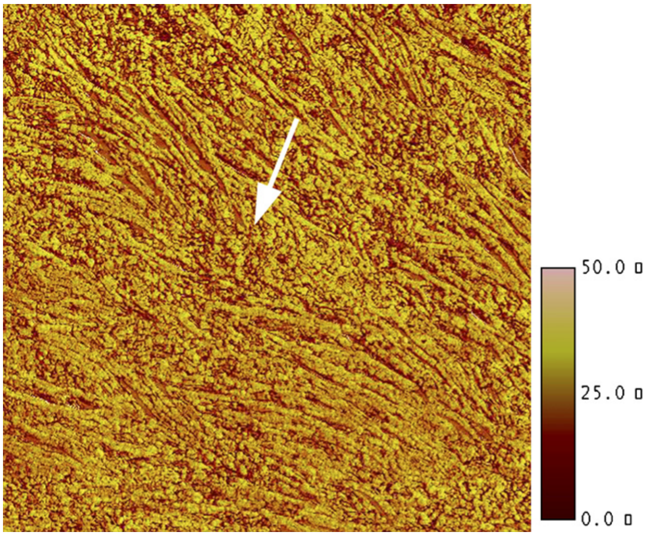


Fig. 8. AFM phase image with dimension of 5 × 5 μm for melt-crystallized PBA films ($T_c = 31$ °C) after biodegradation for 3 h. The arrow indicates the degraded flat-on crystals.

that the edge-on domains in banded spherulites are composed of β crystals.

3.4. The crystallization mechanism of banded spherulites

Fig. 9 shows the radius of banded spherulites during crystallization process. The radius is the distance from the spherulite center to the boundary edge between bright ringed ribbons (edge-on lamellar crystals) and dark ringed ribbons (flat-on lamellar crystals). Therefore, the slope of line connecting two adjacent points in Fig. 9 reflects the growth rate of lamellar crystals in flat-on or edge-on domains. It was found that the banded spherulites show rhythmical growth kinetics, and the rhythm comes from the lamellar crystals with different structures (α or β) and/or spatial orientation (flat-on or edge-on). The crystals in bright ringed ribbons show a faster growth rate than those in dark ringed ribbons. This result further confirms that the bright ringed ribbons are composed of β crystals, because our previous kinetic analysis has revealed that β crystals are kinetically preferential and show a faster crystallization rate than the α crystals [30].

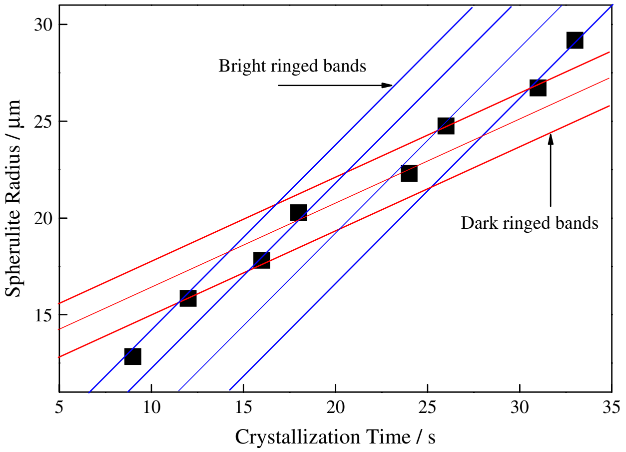


Fig. 9. The radius of PBA banded spherulite as a function of crystallization time during isothermal crystallization at 31 °C. Every point represents the distance from spherulite center to the boundary edge of bright and dark ringed ribbons of banded spherulites.

Generally the rhythmical growth of lamellar crystals is related to the changing of local environment in the crystal growth front. In the case of PBA polymorphic crystals which are sensitive to temperatures, temperature fluctuation may be the key factor for rhythmical growth of lamellar crystals. However, it is difficult to directly measure the temperature fluctuation at crystal growth front from experiments. Nevertheless, the temperature fluctuation can be associated to the exothermic heat of PBA polymorphic crystals during crystallization process.

Fig. 10 shows the exothermic heats (ΔH_cs) of PBA α and β crystals as a function of crystallization temperatures (T_cs). Good linear relationship between ΔH_c and T_c was found for each of two crystal modifications, but the slopes are different. If we extrapolate the fitting lines of ΔH_c *vs* T_c to the temperature of 31 °C, the crystallization heats of α and β crystals at 31 °C were obtained as 23 and 72 J/g, respectively. The β crystal was found to release much more heat than the α crystal when they crystallized at 31 °C. Therefore, it can be imaged that when β crystal grows at 31 °C, the release of large crystallization heat at crystal growth front could raise the local temperature which is favorable for the formation of α crystal. During the growth of α crystal, the local temperature falls down after rise due to the slower growth rate and the lower crystallization heat of α crystal, resulting in the transition from α to β crystal growth. Thus, the difference of α and β crystals in crystallization heats causes the rhythmical fluctuation of temperature, which results in the alternate growth of edge-on and flat-on domains in banded spherulites.

Fig. 11 is the AFM images of nucleating center of PBA spherulite formed at 25 °C (β crystal structure), 31 °C (mixed α and β crystal structure) and 45 °C (α crystal structure). Sheaf-like structure with edge-on crystals is clearly seen in the nucleating center of PBA spherulite with β crystal

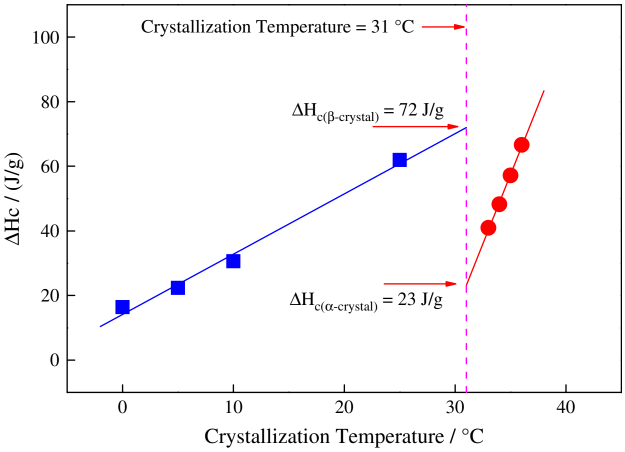


Fig. 10. The crystallization heat of PBA with pure α and pure β crystal structures as a function of crystallization temperatures.

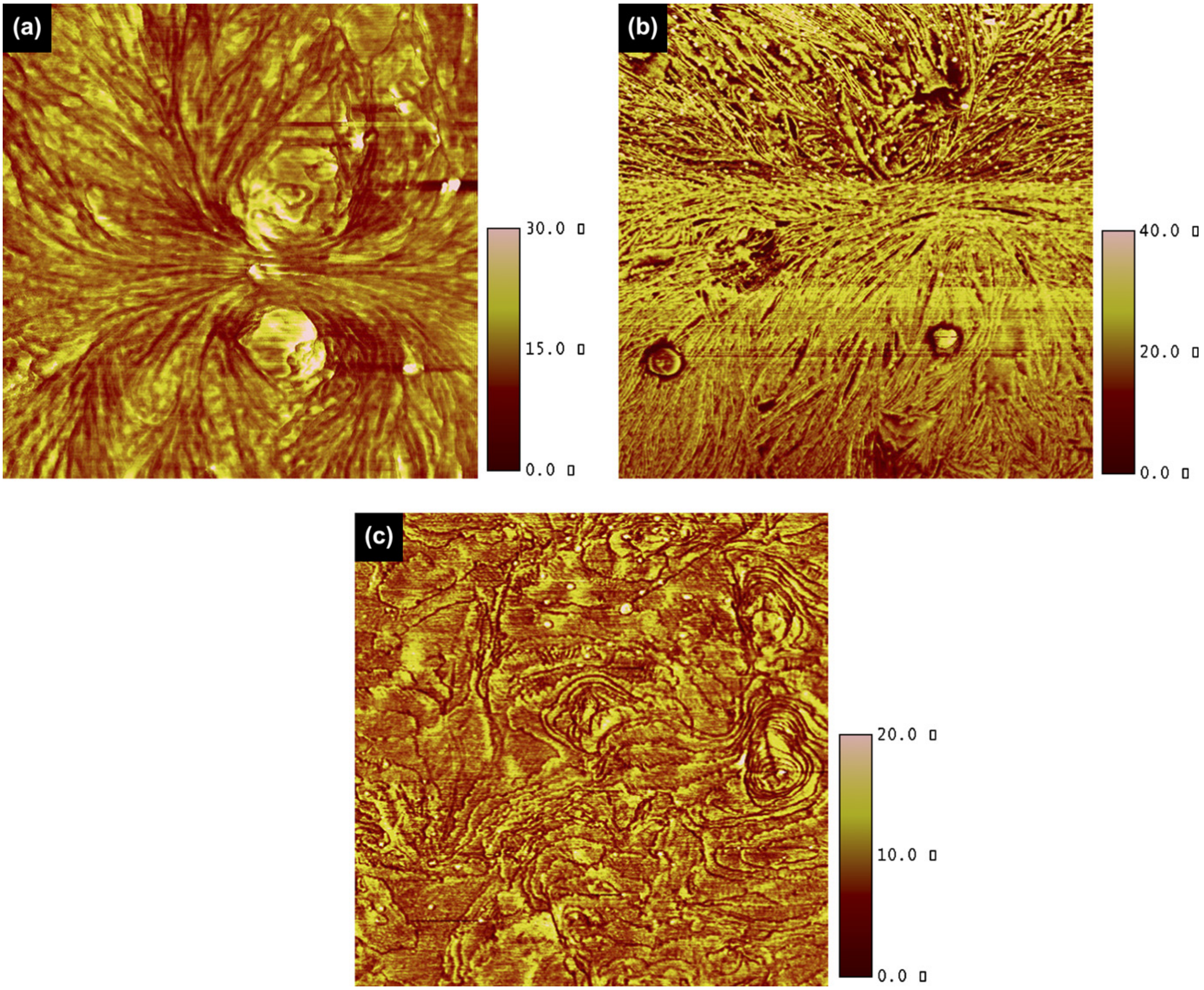


Fig. 11. AFM phase images of central part of PBA spherulites with different crystal structures. (a) Crystallization at 25 °C (β crystal structure), image size 3 × 3 μm; (b) crystallization at 31 °C (mixed α and β crystal structure), 3 × 3 μm; (c) crystallization at 45 °C (α crystal structure), 10 × 10 μm.

structure (Fig. 11a) and with mixed crystal structure (Fig. 11b), while only the flat-on crystals are seen in the nucleating center of spherulite with α crystal structure (Fig. 11c). These results indicate that the nucleus of PBA banded spherulites with mixed crystal structures is made up of edge-on β crystals.

Based on the above analyses, a primary crystallization mechanism is proposed for PBA banded spherulites. When PBA melt-crystallizes at temperatures between 27 and 32 °C, the kinetically preferred β crystal forms the nucleus firstly and then starts the growth of spherulites. The relatively fast crystal growth rate as well as the large crystallization heat of β crystal may cause local temperature rising at the crystal growth front, resulting in the transition of crystal growth from β crystal to α crystal. During the growth of α crystal, its relatively slow growth rate and low crystallization heat lead to the system temperature fall down, so the β crystal begins to form once again. The recycle of temperature fluctuation at crystal growth front leads to the formation of alternate α and β crystal domains along lamellar crystals and subsequently to the formation of banded spherulites.

It should be pointed out that the crystallization mechanism of two crystal modifications in PBA banded spherulites is much complicated due to the simultaneous changes in crystal structure (α and β) and spatial orientation (flat-on and edge-on) during crystal growth process. Many questions still remain to be solved. For example, why the relative contents of two crystal modifications keep unchanged after degradation for 3 h, as shown in Fig. 6? What are the mutual influences of two crystal modifications during biodegradation process? How the two crystal modifications transit their growth at the interface of flat-on and edge-on domains when temperature fluctuates? All these questions need our further investigations. However, the determination of two crystal modifications in alternate flat-on and edge-on domains of banded spherulites in this work is undoubtedly the first important step for the next investigation to clarify the crystallization mechanism of PBA banded spherulites.

4. Conclusions

By correlating the morphological changes to the relative content of two crystal modifications in PBA banded spherulites in the course of enzymatic degradation, the distribution and morphological structure of two crystal modifications in banded spherulites have been determined. The two polymorphic crystals are mixed in each of lamellar crystals. These lamellar crystals are distributed with alternate flat-on and edge-on domains along the radiating direction. The flat-on domains are composed of α crystals, while the edge-on domains are composed of β crystals. The alternate growth of α and β crystal domains along radiating direction is caused by temperature fluctuation at crystal growth front and the crystallization kinetics of two crystal modifications.

Acknowledgment

This work was supported by the National Science Foundation of China (Nos. 20474072, 20634050), and the Hundreds Talents Project of Chinese Academy of Science (CAS).

References

[1] Keith HD, Padden Jr FJ. J Polym Sci 1959;39:123.
[2] Keith HD, Padden Jr FJ. Macromolecules 1996;29:7776.
[3] Janimak JJ, Markey L, Stevens GC. Polymer 2001;42:4675.
[4] Keith HD, Padden Jr FJ. Polymer 1984;25:28.
[5] Duan Y, Jiang Y, Jiang S, Li L, Yan S. Macromolecules 2004;37:9283.
[6] Yang H, Yin W, Zhang X, Cai Z, Wang Z, Cheng R. J Appl Polym Sci 2005;96:2454.
[7] Beekmans LGM, Hempenius MA, Vancso GJ. Eur Polym J 2004;40:893.
[8] Xu J, Guo B, Chen E, Zhang Z. J Polym Sci Part B Polym Phys 2003;41:2128.
[9] Xu J, Guo B, Chen E, Zhou J, Li L, Wu J, et al. Polymer 2005;46:9176.
[10] Kikkawa Y, Abe H, Fujita M, Iwata T, Inoue Y, Doi Y. Macromol Chem Phys 2003;204:1822.
[11] Hong P, Chung W, Hsu C. Polymer 2002;43:3335.
[12] Jiang S, He C, An L, Chen X, Jiang B. Macromol Chem Phys 2004;205:2229.
[13] Wang Z, An L, Jiang W, Jiang B, Wang X. J Polym Sci Part B Polym Phys 1999;37:2682.
[14] Chen J, Yang D. Macromol Rapid Commun 2004;25:1425.
[15] Okabe Y, Kyu T, Saito H, Inoue T. Macromolecules 1998;31:5823.
[16] Price F. J Polym Sci 1959;39:139.
[17] Keller A. J Polym Sci 1959;39:151.
[18] Schultz JM. Polymer 2003;44:433.
[19] Bassett DC, Hodge AM. Polymer 1978;19:469.
[20] Toda A, Arita T, Hikosaka M. Polymer 2001;42:2223.
[21] Keith HD. Polymer 2001;42:9987.
[22] Lotz B, Cheng SZD. Polymer 2005;46:577.
[23] Keith HD, Padden Jr FJ. J Appl Phys 1963;34:2409.
[24] Wang Z, An L, Jiang B, Wang X. Macromol Rapid Commun 1998;19:131.
[25] Kyu T, Chin HW, Guenther A, Okada Y, Saito H, Inoue T. Phys Rev Lett 1999;83:2749.
[26] Gan Z, Abe H, Doi Y. Macromol Chem Phys 2002;203:2369.
[27] Gan Z, Kuwabara K, Abe H, Iwata T, Doi Y. Polym Degrad Stab 2005;87:191.
[28] Sawyer LC, Grubb DT. Polymer microscopy. London, UK: Chapman & Hall; 1996. p. 331.
[29] Fujiwara T, Miyamoto M, Kimura Y, Iwata T, Doi Y. Macromolecules 2001;34:4043.
[30] Gan Z, Kuwabara K, Abe H, Iwata T, Doi Y. Biomacromolecules 2004;5:371.
[31] Tanaka T, Fujita M, Takeuchi A, Suzuki Y, Uesugi K, Doi Y, et al. Polymer 2005;46:5673.
[32] Gan Z, Kuwabara K, Yamamoto M, Abe H, Doi Y. Polym Degrad Stab 2004;83:289.
[33] Mo Z, Zhang H. In: Mo Z, Zhang H, editors. Structure of crystalline polymers by X-ray diffraction. Science Press; 2003. p. 186.