Observation of banded spherulites in pure poly(L-lactide) and its miscible blends with amorphous polymers

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Abstract

Banded spherulites of pure poly(L-lactide) (PLLA) were observed via the 'crystallization after annealing' procedure, while only common spherulites were obtained via the 'direct isothermal crystallization' procedure. Wide angle X-ray diffraction revealed that the two types of spherulites had the same crystal lattice of α-modification. Atomic force microscopy demonstrated that the alternative negative and positive birefringent bands resulted from the alternative edge-on and flat-on lamellar orientations in the spherulites. Furthermore, the effect of thermal history on the spherulitic morphology was investigated in details. The PLLA samples melted for longer time or those with lower melting point were more likely to form banded spherulites. The possibility that the change of molecular weight was a determining factor of banding was excluded by the results on differently prepared samples with the same molecular weight. Therefore, we conclude that it was complete melting of the crystalline residues that favored formation of PLLA banded spherulites. Blending of PLLA with atactic poly(D,L-lactide) or poly[(R,S)-3-hydroxybutyrate], led to reduced band spacing. Effect of blending on the chain mobility, spherulite growth kinetics, supercooling and lamellar surface energy was quantitatively studied, which suggests that the blending-reduced band spacing cannot be attributed to the above factors. Therefore, there are other blending-relevant factors leading to the reduced band spacing.
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1. Introduction

Formation mechanism of the banded spherulites is one of very important and interesting topics of semicrystalline polymers, which has been studied for a long time. Banded spherulites have been found in both achiral polymers, including polyethylene [1,2], α-type poly(vinylidene fluoride) (PVDF) [3], poly(ethylene oxide) [4], polyesters [1,5,6], polyamides [7,8], and chiral polymers, such as optically pure poly(propylene oxide) [9], poly(epichlorohydrin) [10], poly(3-hydroxybutyrate) [11], et al. Except for some special cases where rhythmical growth was reported responsible for

the banding texture [12,13], it is generally believed that the periodic bands result from the cooperative lamellar twisting in the radial direction during the crystal growth [1,2,14–16]. However, there are still arguments on how and why the lamellae twist. The banding mechanism spans several levels of structure: Molecular structure [17], lamellar structure [18] and organization of lamellar crystals [19]. In addition, not only thermodynamic [20] but also kinetic factors [21] have been reported responsible for banding. Consequently, banded spherulite has been a hotspot to polymer physicists due to its complexity. Several models have been put forward to reveal the banding mechanism, which was summarized in a recent review [22]. Unbalanced stress at lamellar surface is widely accepted as the drive force of lamellar twisting [18, 22,23]. Lotz and Chen demonstrated the origin of the unbalanced stress from the viewpoint of the structure of lamellar crystals in both chiral and achiral polymers [22]. Nevertheless, up to now evaluation of the stress and

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establishment of a general quantitative equation between the twist period and the physical properties of the polymer system is still an open question. Furthermore, cooperative packing of the twisting lamellae to form regular bands is still poorly understood.

Poly(L-lactide) (PLLA) is also a chiral polymer and has drawn much attention in recent years for its promising physical properties, processability, environmental degradability, which lead to applications in the field of packaging, consumer goods and medical devices [24]. In terms of its chiral molecular structure, PLLA is expected to show banded spherulites [25]. However, up to our knowledge, banding texture of pure PLLA spherulites has only been observed in the solution-cast film [26] and has never been reported in the film crystallized from melt. In fact, it was reported that PLLA showed negative birefringent spherulites when crystallized from quiescent melt [27]. As the super-cooling was reduced, the spherulites demonstrated coarse-grained structure. On the contrary, when PLLA was blended with atactic polylactide [28], atactic poly(3-hydroxybutyrate) [29,30] or poly(ethylene oxide) [31], banded spherulites were observed. It was suggested that incorporation of the second amorphous polymer induced the lamellar twisting.

It has long been known that blending with an amorphous component favors the formation of banded spherulites in poly(ε-caprolactone) (PCL). It was reported that pure PCL grew spherulites with simple extinction crosses below 50 °C; only when crystallized at higher temperatures could the PCL spherulites exhibit banded texture. However, after blending with a compatible amorphous polymer, PCL formed banded spherulites at the temperatures much lower than 50 °C [20,32–35]. It was proposed that the interaction between the two polymer components facilitated the twisting of the PCL lamellae [20,33]. Furthermore, matching between the PCL crystallization rate and the diffusion rate of the non-crystallizable second component was reported to play an important role in the formation of spherulites with regular bands [36]. On the other hand, band spacing is one of the quantitative parameters to investigate the effect of the amorphous component on lamellar twisting. In PCL/poly(styrene-*co*-acrylonitrile) random copolymer (SAN) blends, the band spacing decreased with increase of SAN content, which coincided with the depressed glass transition temperature of the blends [37]. However, why incorporation of an amorphous polymer leads to regular banding is still under discussion and not yet clarified.

In this article, we show for the first time that pure PLLA can form banded spherulites crystallized from melt after sufficient melting. Effects of the thermal history and blending composition on the spherulitic morphology are investigated as well.

2. Experimental

Poly(L-lactide) (PLLA) and atactic poly(D,L-lactide) (PDLLA) was purchased from Birmingham Polymers Inc.,

which have inherent viscosity of 0.70 and 0.63 dL/g, respectively, in 1 mg/mL chloroform at 30 °C. Atactic poly[(*R,S*)-3-hydroxybutyrate] (atactic PHB or a-PHB) was synthesized by anionic ring-opening polymerization of racemic β-butyrolactone (from Aldrich) with KOH/18-crown-6 complexes as initiator, as described previously [38]. The polymerization was carried out in bulk at room temperature, and the extent of the reaction was monitored by FT-IR spectroscopy. After completion of the reaction, the polymer was dissolved in chloroform, and the ion-exchange resin in acid form was added as the termination agent and 18-crown-6 adsorber. Then, the ion-exchange resin was filtered off, the polymer was precipitated into cold hexane and dried under vacuum. The atactic structure of polymer was confirmed by ^{1}H NMR spectroscopy (Varian VCR-300 multinuclear spectrometer), thus showing, that the syndiotactic diad fraction was equal to the isotactic diad fraction [39]. Number average molecular mass $(M_n) =$ 18,000 and polydispersity index $(M_w/M_n) = 1.27$ were estimated by gel permeation chromatography (GPC) experiments.

PLLA pellets received were termed as the as-received PLLA. Solution-cast PLLA film was obtained from 1% chloroform solution of the as-received PLLA. Thermally degraded PLLA was prepared via thermal degradation of the as-received PLLA in air at 240 °C for 15 min. The PLLA/lactic acid mixture, PLLA/PDLLA and PLLA/a-PHB blends were prepared via casting from 1% chloroform solution in a polytetrafluoroethylene boat. After visible evaporation of the solvent, the samples were kept in vacuum over night to completely remove the residual solvent.

The samples for optical microscopy were melted between two glass slides to eliminate the thermal history. If not specially mentioned, the melting was kept at 240 °C for 2 min. Two types of temperature control procedures were adopted for crystallization. In the first procedure, the melted specimen was quickly removed onto the thermal stage in the polarized light microscope (less than 1 s), which was preset at temperatures of 110, 120, 130 and 140 °C, respectively, for isothermal crystallization. This procedure is termed as 'directly isothermal crystallization', in which the thin film was obtained via manual pressing after melting, with thickness around 5–10 μm. In another procedure, which is termed as 'crystallization after annealing', the melted specimen was removed onto the thermal stage preset at 160 °C and remained for 2 h, then the stage was cooled at a rate of 0.5 °C/min to 110, 120, 130 and 140 °C, respectively, kept at the crystallization temperature until all the spherulites impinged with each other. The sample thickness was the same as that in the 'directly isothermal crystallization' procedure. After kept at 160 °C for 2 h, PLLA sample showed only several spherulites at the edges of the film. The spherulites showed weak birefringence and were easy to distinguish from the strong-birefringent spherulites formed at 110–140 °C. During the slow cooling process, few primary nuclei appeared when the temperature

was higher than 120 °C. The special treatment considerably depressed the nuclei density, leading to large spherulites containing several bands in each spherulite. The crystallization process was monitored with a computer controlled charge coupled detector (Tota, Japan) to capture digital images of spherulitic morphology. To obtain qualitative information of birefringence, a first order tint plate (530 nm) was inserted.

After observation under optical microscope, the cover slide was gently detached from the crystallized PLLA film. Wide-angle X-ray diffraction (WAXD) spectra of the films with thickness around 100 μm were collected with a Bruker D8 advance powder diffractometer, using nickel filtered Cu Kα radiation ($\lambda = 0.1542$ nm).

The samples for atomic force microscopy (AFM) study were specially prepared. After complete melting of the PLLA pellet between two glass slides, the cover slide was quickly removed to obtain a smooth film of melt remained on the bottom slide. After isothermal crystallization, the film was observed directly under a Nanoscope III MultiMode AFM (Digital Instruments) at room temperature. Both height and phase images were recorded simultaneously with tapping mode. Typical values for the RMS amplitude and the set-point amplitude ratio (r_{sp} is defined as the ratio of the cantilever's oscillating amplitude to its freely oscillating amplitude) were 2.0 and 0.7–0.9 V, respectively. The amplitude of the free-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.

Gel permeation chromatography (GPC) experiments were conducted in THF solution at 35 °C, at a flow rate of 1 mL/min using a Spectra-Physics 8800 solvent delivery system with a two Mixed C Styragel columns in series and a Shodex SE 61 refractive index detector. Polystyrene standards with low polydispersities were used to generate a calibration curve.

DSC analysis was performed to study the thermal behavior of PLLA and its blends, on a DSC-60 (Shimadzu) differential scanning calorimeter. The equipment was calibrated with indium standard and nitrogen atmosphere was used throughout. In the first heat run, the specimens with weight around 2 mg sealed in an aluminum pan were heated from room temperature to 220 °C at a rate of 10 °C/min. After remained at the melting temperature for 2 min, the samples were quenched with liquid nitrogen until they reached the temperature below −60 °C. At the second heat run, they were heated to 220 °C at the same rate as the first heat run. Melting point (T_m) was determined from the first heat run and glass transition temperature (T_g) was determined from the second heat run.

3. Results and discussion

3.1. Banding in pure PLLA

In the 'directly isothermal crystallization' procedure, the

PLLA sample was quickly transferred from the melt stage onto the crystallization stage preset at the isothermal crystallization temperature (in less than 1 s). When the crystallization temperature was not higher than 140 °C, the spherulites showed the appearance of negative birefringence, as shown in the left column of Fig. 1, which agrees with the literature [27]. When the crystallized samples were cooled to room temperature, cracks propagated along the circumferential direction of the spherulites, forming concentric circles, as indicated by an arrow in Fig. 1(c). Formation of the circumferential crack is proposed to result from the difference of the thermal expansion coefficients in the radial and the circumferential direction [40].

In the 'crystallization after annealing' procedure, the PLLA melt was annealed at 160 °C for 2 h and then slowly cooled to the crystallization temperature at a rate of 0.5 °C/min. In contrast to the 'directly isothermal crystallization' procedure, banded spherulites with alternative negative and positive birefringence were observed, as demonstrated by the right column images in Fig. 1. The band spacing increases with crystallization temperature, ranging from 66 μm at 110 °C to 500 μm at 140 °C. Up to our knowledge, they are among the polymeric banded spherulites that have the largest band spacing. Apparently, to clearly observe the bands, it is required that the spherulites consist of cooperatively twisting lamellae. Consequently, in the 'crystallization after annealing' procedure, the formed spherulites consisted of lamellae twisting in phase. In the 'directly isothermal crystallization' procedure, the formed spherulites still contained twisting lamellae. In Fig. 1(a), the arrow points to a region with change of birefringence, which indicates change of lamellar orientation, implying lamellar twisting in the spherulites as well. However, in the spherulites formed during the direct isothermal crystallization, the lamellae did not twist in phase. As a result, regular bands were not observed.

3.2. Mechanism of PLLA banding

In the polymers forming several crystalline polymorphs, can only a certain crystalline modification form banded spherulites, such as β-modification of isotactic polypropylene [41] and α-modification of PVDF [42]. PLLA can form three crystal modifications depending on the formation conditions: α-Form with a 10_3 helical chain conformation [43,44], β-form with a 3_1 helical conformation [45,46] and γ-form modification [47]. The most common polymorph of PLLA is the α-form, which is generally obtained via crystallization from the melt or solutions. To examine whether the banded spherulites of PLLA resulted from a different crystalline modification, the X-ray diffractograms of the crystalline films were recorded with 2θ in the range from 5 to 50°. Fig. 2 shows the WAXD plots of the two types of spherulites. The banded spherulites exhibited the same WAXD profile as the usual non-banded spherulites, both with the characteristic diffraction pattern of the
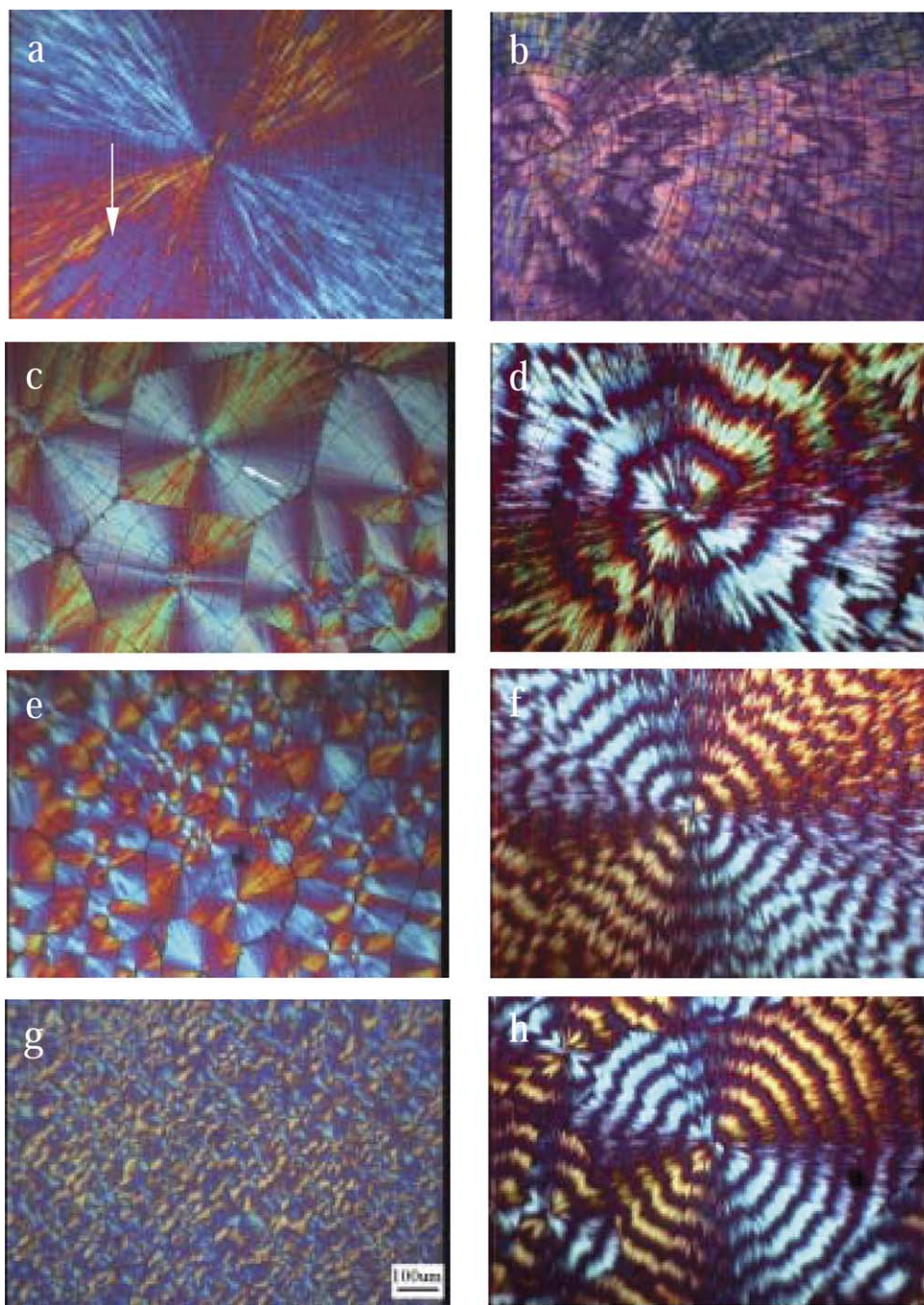
Fig. 1. Morphology of PLLA spherulites after direct crystallization at different temperatures (left column) and annealing at 160 °C for 2 h followed by slow cooling to the crystallization temperatures (right column), respectively. The spherulites were obtained via crystallization at 140 °C (a) and (b), 130 °C (c) and (d), 120 °C (e) and (f) and 110 °C (g) and (h), respectively. The arrow in figure (a) indicates change of lamellar orientation, however, due to the irregular packing of the twisting lamellae, bands do not appear. The circular line indicated by the arrow in (c) is a crack.

α-modification of PLLA. The strongest diffraction peak at $2\theta = 16.7°$ corresponds to the (200,110) reflection of the α-form crystals. The other remarkable diffraction peaks were found at $2\theta = 14.8°$ (010 reflection) and $2\theta = 19.0°$ (203 reflection) [48].

AFM study was carried out to observe the lamellar orientation in the spherulite. It revealed that the alteration of birefringence was caused by the alternative lamellar orientation, as demonstrated in Fig. 3. The negative birefringent bands consisted of edge-on lamellae (Fig. 3(a)), while the positive birefringent ones consisted of flat-on lamellae (Fig. 3(b)). Consequently, the periodical bands in the PLLA do result from lamellar twisting, which is similar to the AFM results on α-type poly(vinylidene fluoride) [42], poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [49], poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

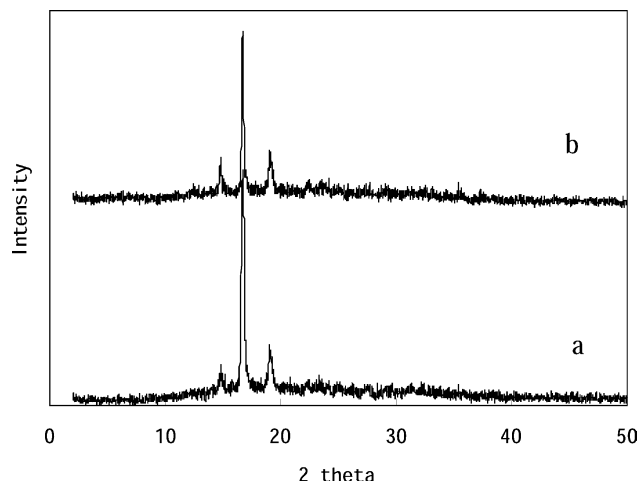Fig. 2. WAXD spectra of the crystallized PLLA samples via direct quenching to 120 °C (a) and slow cooling to 120 °C after annealing (b).
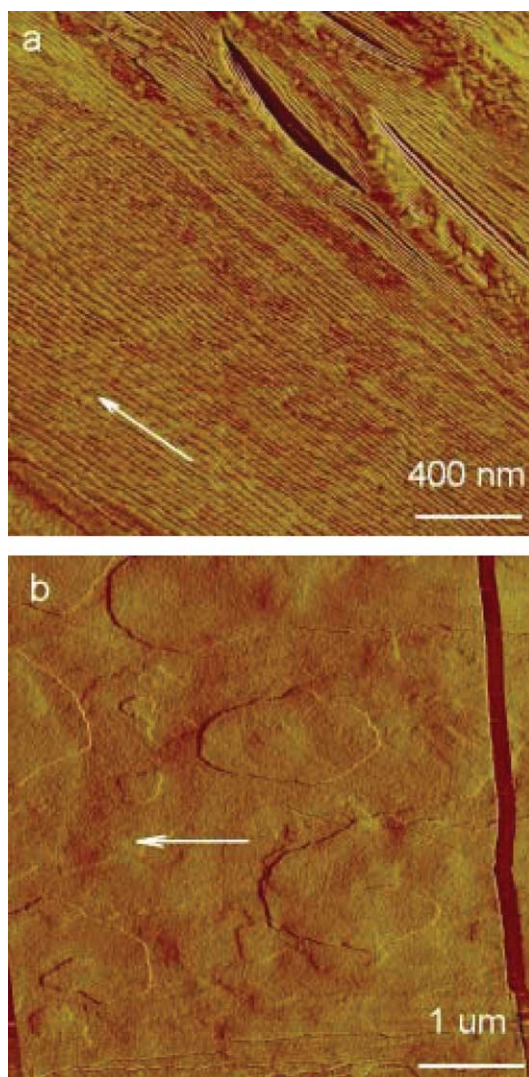
[50], poly(trimethylene terephthalate) [51], and *S*-poly (propylene oxide) [52], etc.

The large width of the bright and dark bands makes it convenient to measure the radial growth rate of the two types of bands. Fig. 4 shows the growth profile of a PLLA spherulite crystallized at 135 °C. The radial propagation rate of the bright band was 9.6 μm/min, almost the same as that of the dark band, 10.0 μm/min, provided the measuring error was taken into account. This further supports that the birefringent bands in PLLA spherulites result from lamellar twisting rather than alteration of the lamellar growth direction.

3.3. Effect of thermal history on spherulitic morphology of PLLA

It is of interest that PLLA can show non-banded or banded spherulites, depending on the thermal history before crystallization. Annealing then crystallization led to the regular banded spherulites while the direct isothermal crystallization produced only non-banded spherulites. What happened during the annealing? Two possible changes may be expected: Complete melting of the crystalline residues or degradation of PLLA. To examine whether regular banding might result from the degradation products, we investigated the 60/40 (wt/wt) mixture of PLLA and lactic acid. The mixture crystallized at 110, 120 and 130 °C after melted at 240 °C for 2 min exhibited non-banded spherulites, as presented in Fig. 5(a). Thus, we conclude that the possible low molecular weight compound was not the major factor causing regular banding.

Molecular weight distribution of the as-received and the thermally degraded PLLA was measured via GPC. The as-received PLLA had a M_n of 8400 and M_w of 20,200, while

Fig. 3. AFM phase images of the lamellae located in the negative (a) and positive (b) birefringent bands, respectively. The arrows show the radial direction pointing toward the spherulitic boundary.
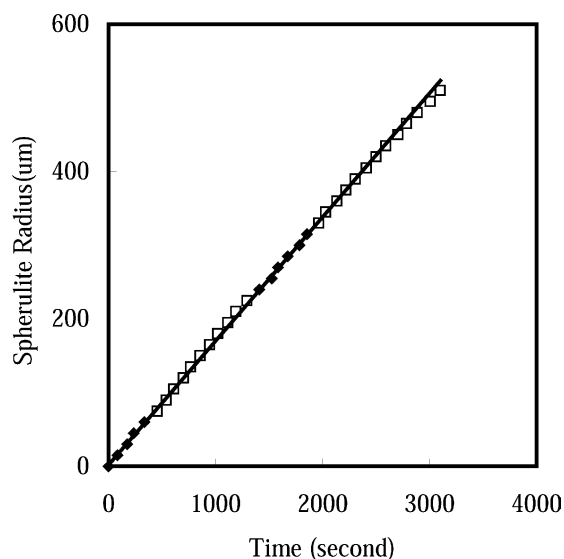

Fig. 4. Growth profile of a PLLA banded spherulite crystallized at 135 °C. The open data points indicate the bright bands and the closed points indicate the dark bands.
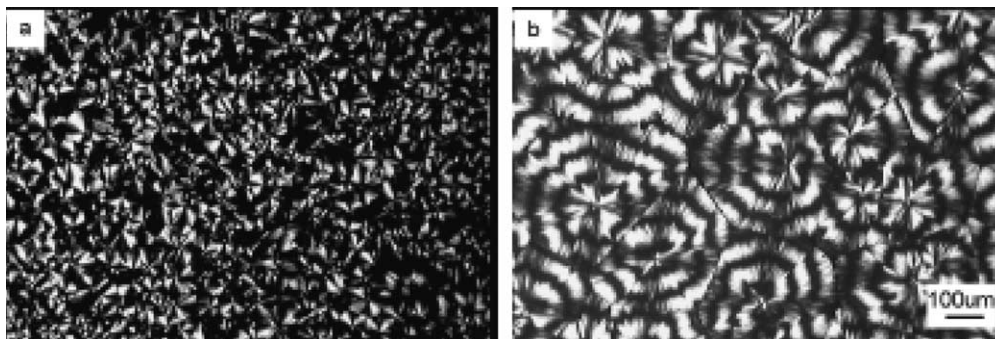
Fig. 5. Spherulitic morphology of different PLLA samples crystallized at 120 °C: (a) PLLA/Lactic acid=60/40 wt/wt; (b) solution-cast PLLA.

the degraded PLLA showed a M_n of 5100 and M_w of 8900. Both the GPC, ^{13}C and ^{1}H NMR experiments did not indicate the presence of low molecular weight PLLA oligomers. Thus, the thermal treatment may cause some scission of PLLA chains (which may be expected), but rather random, i.e. with no preference for low molecular weight PLLA oligomers formation. Thermal degradation also led to a lower polydispersity index, with M_w/M_n decreasing from 2.4 to 1.7.

Now another question arises: Does the depressed molecular weight favor banded spherulite formation? We prepared a solution cast PLLA from the chloroform solution of the as-received PLLA. Since no thermal process was involved, the solution cast PLLA had the same molecular weight as the as-received PLLA. However, the former but not the latter produced banded spherulites during the direct isothermal crystallization (Fig. 5(b)). Thus, the change of molecular weight is not a determining factor for formation of the banded spherulites.

Therefore, we speculate that complete melting of the crystalline residues may play an important role. To validate the assumption, the as-received PLLA was melted at 240 °C for different periods of time, then directly crystallized at 120 °C. It was observed that longer melting time led to lower density of the primary nuclei, as shown in Fig. 6. When the melting time was not longer than 5 min, only common non-banded spherulites were observed (Fig. 6(a) and (b)). On the contrary, the PLLA melted for longer than 10 min produced regular banded spherulites (Fig. 6(c) and (d)). We suggest that when melted at 240 °C, 15 min was a sufficient time to remove most of the crystalline residues in the studied PLLA, so as to produce banded spherulites during the following crystallization; while after melting for 2 min a few crystalline residues survived, leading to formation of the non-banded spherulites. This is also reflected from the higher nucleation density of the spherulites formed in the PLLA melted only for 2 min (Fig. 6(a)).

Furthermore, we investigated the change of melting point after different treatment. In the above text, three types of PLLA samples were examined, including the as-received PLLA, thermally degraded PLLA and solution-cast PLLA.

Melting point of these samples was determined via DSC, as shown in Fig. 7. Under the same melting condition, e.g. 240 °C for 2 min, PLLA with different T_m has different spherulitic morphology in the crystallized film. Among these samples the as-received PLLA exhibited the highest T_m at around 182 °C (Fig. 7(a)), and it was the most difficult one to obtain regular banded spherulites, as shown in the left column of Fig. 1. The crystallized PLLA after annealed at 160 °C had a lower T_m around 158 °C (Fig. 7(b)), produced banded spherulites during isothermal crystallization, as demonstrated in the right column of Fig. 1. The PLLA sample degraded at 240 °C for 15 min had a T_m at 154 °C (Fig. 7(c)) and produced banded spherulites as well (Fig. 6(d)). It is worth noting that the solution-cast PLLA with the lowest T_m at 151 °C (Fig. 7(d)) also exhibited banded spherulites (Fig. 5(b)).

All the above results demonstrate that PLLAs melted for longer time or those with lower T_m, are more likely to form banded spherulites during the following crystallization. That is to say, complete melting of the crystalline residues in PLLA favors formation of the banded spherulites. Investigation on the reason why complete melting of PLLA produced cooperatively twisting lamellae while incomplete melting led to misaligned twisting lamellae is still in progress, which may shed some light on the organization mechanism of twisting lamellae in polymer banded spherulites.

3.4. Effect of blending with an amorphous polymer on banding

To further investigate the effect of an amorphous polymer on the formation of banded spherulites, the crystallization behaviors of the blends comprising PLLA and an amorphous polymer, PDLLA or a-PHB, were investigated. It has been reported that PLLA was miscible with PDLLA [28] and miscible or partly miscible with a-PHB, depending on the molecular weight of a-PHB [29, 30]. In our case, the PLLA/PDLLA blends showed a single T_g at around 50 °C, almost the same as that of pure PLLA. Because PLLA and PDLLA has almost the same T_g, we cannot determine the miscibility from the single T_g.
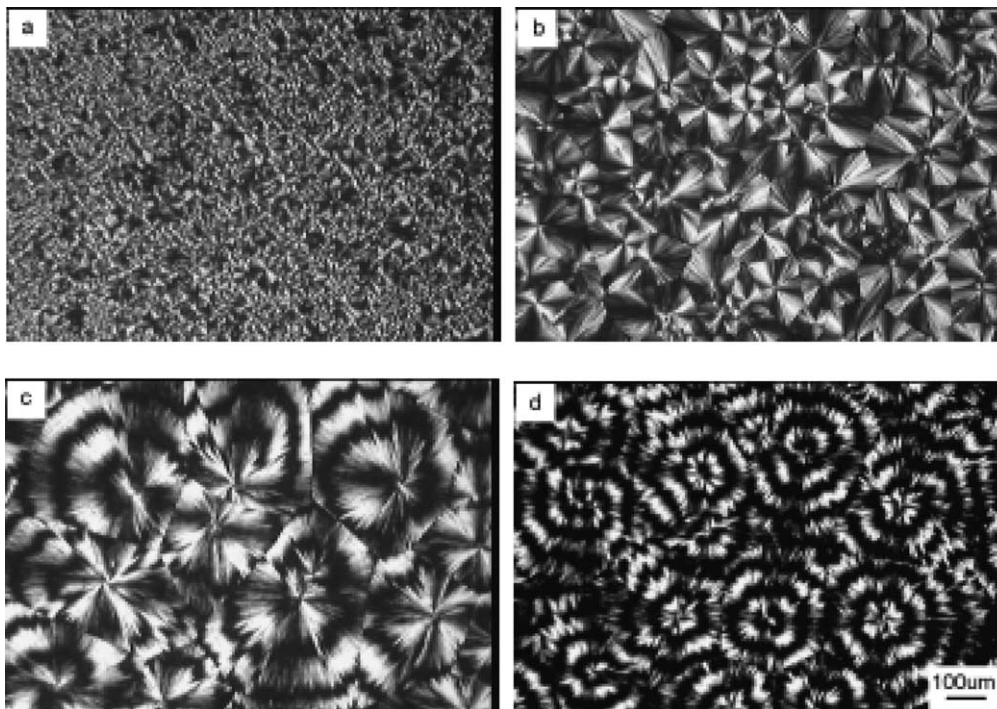
Fig. 6. Effect of melting time on the morphology of PLLA spherulites. The spherulites were obtained via crystallization at 120 °C after melted at 240 °C for different periods of time: (a) 2 min; (b) 5 min; (c) 10 min; (d) 15 min.

However, from the decreased growth rate of spherulitic growth and no macroscopic phase separation, we can draw a conclusion that PLLA/PDLLA are miscible to some extent in the studied composition range. On the contrary, with increase of a-PHB content from 0 to 60 wt%, the single T_g of the PLLA/a-PHB blends decreased steadily from 51 to 4 °C, which indicates miscibility. In this article, the effect of blending on the band spacing was particularly concerned.

Both the blends exhibited the similar trends: The band spacing decreased considerably with increase of the amorphous polymer content from 0 to 60 wt%, whatever the glass transition temperature of the blends, as shown in Fig. 8. The reduced banding spacing in PLLA/a-PHB blends agrees with the result reported by Gazzano et al. [53]. The effect of crystallization temperature on the band spacing was studied as well. In pure PLLA and its blends, the band spacing of the spherulites increased with crystallization temperature; however, pure PLLA and its blends containing 20 wt% of the amorphous component showed strong temperature dependence, while that of the blends containing 60 wt% of the amorphous component exhibited weak temperature dependence. Microfocus X-ray diffraction has confirmed that the banding in PLLA/a-PHB blends resulted
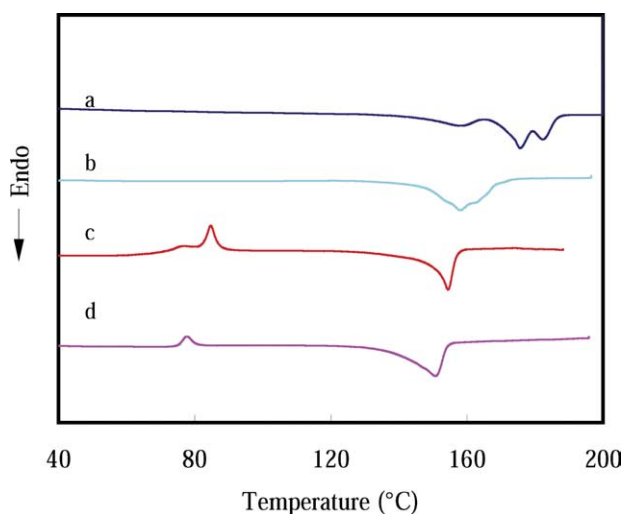

Fig. 7. DSC curves of the different PLLAs during the first heat run. (a) As-received PLLA; (b) PLLA after melt annealing of the as-received sample at 160 °C for 2 h; (c) PLLA after degradation of the as-received sample at 240 °C for 15 min; (d) film cast from the chloroform solution of the as-received PLLA.
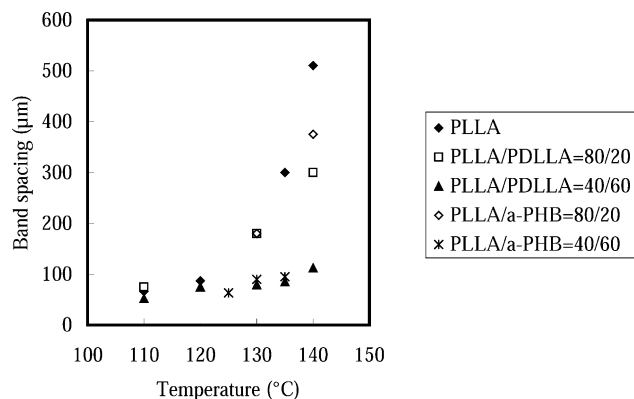

Fig. 8. Band spacing of the spherulites of pure PLLA and its blends.

from cooperative lamellar twisting [53], the same as that in pure PLLA; so it is not arbitrary to attribute banding in PLLA/PDLLA to lamellar twisting.

The results reported here do not contradict to the previous studies on the spherulitic morphology of PLLA [27,30]. We note that in the literature melting was carried out at a temperature not higher than 200 °C. According to the above analysis, melting at this temperature could not sufficiently remove the crystalline residues in pure PLLA, so regular banded spherulites were not observed; however, solution blending with a miscible amorphous polymer depressed the melting point of PLLA, from 182 °C in the pure PLLA to 167 °C in PLLA/PDLLA 40/60 blend and 169 °C in PLLA/a-PHB 40/60 blend. Thus it is possible to destroy most of the PLLA crystalline residues after melting the blends at 200 °C so as to obtain banded spherulites.

Blending reduced band spacing in the blends has been observed in PVDF/poly(methyl methacrylate) [54], PCL/SAN [37], PCL/hydroxyethyl cellulose acetate [55] and PCL/ethyl cellulose [56] blends. However, why blending causes narrower band spacing is still unclear. It is known that in pure crystalline polymer band spacing may depend on the following factors: Chain mobility, radial growth rate of the spherulite, degree of super-cooling, surface free energy, lamellar thickness, etc. Here, we will examine whether the blending effect can be attributed to these factors. From the T_g values, the mobility of PLLA segments in PLLA/a-PHB blend was higher than that in PLLA/PDLLA blend. This is also reflected by the fact that the spherulites demonstrated higher radial growth rate in PLLA/a-PHB blend than in PLLA/PDLLA blend (Fig. 9). If the effect of crystallization kinetics (chain mobility and radial growth rate of spherulite) prevailed on the band spacing, it should show different trend with increase of the amorphous component in PLLA/a-PHB and PLLA/PDLLA blend. However, both the blends exhibited the same trend: The band spacing decreased considerably with increase of the amorphous polymer content from 0 to 60 wt%. For a certain
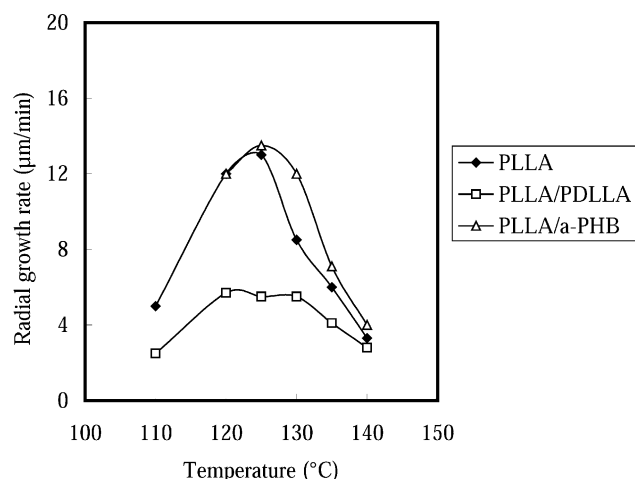
polymer system, the band spacing usually increased with decreased ΔT. Dilution results in a lower super-cooling (ΔT) of PLLA in the blends, since the equilibrium melting point was decreased (data not shown here). If super-cooling determined the band spacing in the blends, the decreased ΔT should tend to increase the banding spacing. However, the PLLA blends showed the opposite trend in band spacing: It decreased with increased content of the amorphous component, namely with decrease of ΔT. In the blends, the surface free energy of the lamellar crystals can be obtained from the nucleation parameter K_g, which is determined from the spherulitic growth kinetics [57–59]:

$$A = \ln G_{PLLA} - \ln \Phi_2 + \frac{U^*}{R(T_c - T_\infty)} - \frac{0.2 T_m^0 \ln \Phi_2}{(T_m^0 - T_c)}$$

$$= \ln G_0 - \frac{K_g}{T_{cf}(T_m^0 - T_c)} \tag{1}$$

From the curves plotted in Fig. 10, K_g of PLLA, PLLA/PDLLA and PLLA/a-PHB was determined to be 294,000, 224,000 and 264,000 K^2, respectively. Since $K_g = (2b_0\sigma\sigma_e T_m^0)/(k\Delta H_f)$ and b_0, T_m^0 and ΔH_f varied little with blending ratio, the lamellar surface free energy in the blends was lower than that in pure PLLA. Owen derived a quantitative equation [60] applicable to the banded spherulites of pure polymer:

$$P \propto \left(\frac{E}{\sigma}\right)^{1/2} t^{3/2} \tag{2}$$

where E, σ and t indicates the elastic modulus, surface energy density and thickness of the lamellae. Eq. (2) suggests that the band spacing should increase with decreased lamellar surface energy density. If the equation could be further applied to the PLLA blends, the band spacing should be predicted to increase with decreased surface energy. However, this is just the opposite of the experimental result. Consequently, the above analysis demonstrates that the blending-reduced band spacing
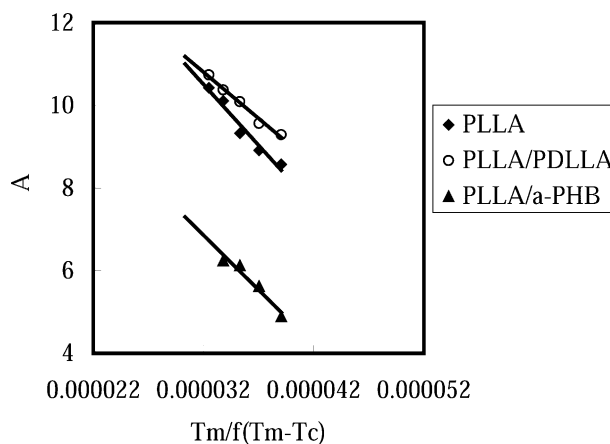

Fig. 9. Radial growth rate of the spherulites in pure PLLA and its blends.

Fig. 10. Plots of the spherulitic growth kinetics of PLLA and its blends. The slope of the line gives the nucleation parameter K_g.

could not be attributed to the aforementioned factors, namely there are other blending-relevant factors that affect lamellar twisting. It seems that the effect of crystallization dynamics and kinetics on band spacing is a complicated issue and deserves further study. Though now we are not yet able to establish a quantitative link between the band spacing and the dynamic and/or kinetic factors during crystallization, we propose here a qualitative method to study the effect of each of these factors, which we believe will help to reveal the banding mechanism.

4. Conclusions

Banded spherulites in pure PLLA were obtained via slow cooling to the crystallization temperature after annealing at 160 °C, while isothermal crystallization after fast cooling from the melt led to formation of the common non-banded spherulites. WAXD study confirmed that the crystal lattice of the banded spherulites and the common spherulites of PLLA were both the α-modification. AFM study revealed that the alternative negative and positive birefringent bands observed under polarized light corresponded to the edge-on and flat-on lamellar orientations, respectively. The thermal history of PLLA before crystallization was demonstrated to play an important role in formation of the regular banded spherulites. The PLLA samples melted for longer time and those with lower melting point were more likely to form banded spherulites. Meanwhile, during crystallization after melted for 2 min the solution-cast PLLA formed banded spherulites while the as-received PLLA exhibited non-banded spherulites, though they had the same molecular weight distribution. Therefore, we exclude the possibility that change of molecular weight is a determining factor of banding and propose that complete melting of the crystalline residues favors formation of banded spherulites, while the impurity in the melt is not a decisive factor for lamellar twisting.

Banded spherulites also appeared in the miscible blends of PLLA and another amorphous polymer, PDLLA or atactic PHB during crystallization. We quantitatively investigated the effect of both kinetic and dynamic factors during crystallization, such as chain mobility, radial growth rate of the spherulite, degree of super-cooling and lamellar surface energy on the band spacing. Band spacing decreased with the amount of the amorphous component at the studied crystallization temperatures, whatever the T_g of the blend was decreased or leveled off. The spherulite growth kinetics was determined via isothermal crystallization at different temperatures, which showed that blending led to decreased K_g, implying lower surface energy of the lamellar crystals. Therefore, the blending effect cannot be attributed to the aforementioned factors, namely, other factors relevant to blending should be responsible for the reduced band spacing.

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