

Crystallization of polylactide films: An atomic force microscopy study of the effects of temperature and blending

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Abstract

Surface crystallinity on films of poly(L-lactide), poly(L/D-lactide) and their blends with poly(D-lactide) was studied. The isothermal spherulitic growth rate and its dependence on temperature were studied using tapping mode atomic force microscopy and *ex situ* isothermal crystallization. Using this technique, it is possible to extend spherulitic growth rate measurements to the region of significantly higher supercooling where nucleation concentration makes the use of *in situ* hot stage optical microscopy impossible. It was confirmed that while a poly(L/D-lactide) copolymer exhibits the typical “bell” shaped crystallization rate–temperature dependence, poly(L-lactide) exhibits a nonsymmetrical behavior having two crystallization rate maxima at 105 °C and 130 °C. As expected, the spherulitic growth rate of poly(L-lactide) was significantly higher than that of poly(L/D-lactide). The different types of crystalline formations exhibited at the surface of polylactide films are shown and discussed. The crystalline long spacing of poly(L-lactide) was also measured directly using tapping mode AFM and was found to be 19 nm at 165–170 °C. At low supercooling, several different scenarios of individual crystal formation were observed: purely flat-on stacks, purely edge-on stacks and scenarios where edge-on crystals flip to flat-on crystals and vice versa, where flat-on crystals yield edge-on sprouts. The preferred direction of growth of lamellae of both poly(L-lactide) and poly(D-lactide) was found to be counter-clockwise relative to the free surface.

Finally, the crystallization kinetics of blends of poly(L-lactide) and poly(L/D-lactide) with poly(D-lactide) were studied. In such blends a triclinic stereocomplex crystalline structure forms between chains of opposite chirality and a pseudo-orthorhombic α -crystal structure forms between chains of like chirality. The presence of the stereocomplex crystals affects both the nucleation and the growth of the α -crystals. In fact depending on the stereocomplex content and the crystallization temperature the α -crystallization can either be enhanced or be inhibited. Interestingly it was found that the presence of the stereocomplex had a much stronger effect on the α -crystallization of poly(L/D-lactide) than on the α -crystallization of poly(L-lactide).

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1. Introduction

One of the most promising biodegradable polymers for commodity and speciality applications is polylactide (PLA),

which is synthesized from lactic acid. Despite the fact that polylactide has been known for many decades, many of its properties, especially those related to its crystallization behavior, remain insufficiently explored. In this work we aim to provide certain missing understanding of the crystallization behavior and crystalline morphology of optically pure poly(L-lactide), poly(L/D-lactide) and of blends of these polymers with poly(D-lactide).

Individual optically pure polylactide isomers crystallize in a pseudo-orthorhombic crystalline form with a 10/3 helix

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conformation [1] while chains of different enantiomers form a triclinic stereocomplex with 3/1 helix conformation [2] having a higher melting temperature. The melting point of the stereocomplex is about 230 °C as compared to 180 °C for the pseudo-orthorhombic crystalline form [3]. The stereocomplex forms by the side by side packing mechanism and therefore, has a significantly higher density and melting point than the other crystal form. The stereocomplex can also have a dramatic influence on the rheological behavior of polylactide blends because of its significantly higher melting point as compared to the orthorhombic crystals. In fact, the formation of the stereocomplex can cause *gelation* at the normal melt temperature [4]. The formation of the triclinic stereocomplex in blends of poly(L-lactide) and poly(D-lactide) also strongly affects its crystallization behavior and morphology. Recently it was found that even 0.5 wt% poly(D-lactide) in poly(L-lactide) can result in the formation of stereocomplex [5] which then affects the crystallization. In our experiments we also observed gelation in concentrated dichloromethane solutions of poly(L/D-lactide) and poly(D-lactide) blends when the blend concentration of poly(D-lactide) exceeded 2 wt%. The exact effect of the stereocomplex's presence on the crystallization kinetics of the pseudo-orthorhombic α -crystalline form has not been reported on in detail. In this work we examine this aspect.

The crystallization of polylactides is characterized by fast spherulitic growth and high achievable overall crystallinity up to 87.5% [6]. Unusual isothermal spherulite growth rate data have been reported for poly(L-lactide) [7–10]. Di Lorenzo [9] found that the isothermal spherulite growth rate curve of pure poly(L-lactide) displays two maxima: a broad maximum around 130 °C and another sharper peak at 115 °C. Thus, the G vs. T plot significantly deviates from the typical bell-shaped curve [9]. This peculiar crystallization behavior was also noted by Tsuji et al. [10] who performed an extensive study of crystallization behaviors of the optically pure poly(L-lactide) and of the copolymer poly(L/D-lactide). In particular the unusual crystallization behavior was observed only for essentially pure poly(L-lactide) of intermediate molecular weight (30–100 kg/mol). Interestingly, they observed the typical “bell-shaped” spherulite growth rate dependence for poly(L/D-lactide) copolymers.

One of the most widely used spherulite growth rate measurement techniques is the hot stage polarized light optical microscopy. There are several commercially available setups allowing *in situ* spherulite growth measurements. Being a relatively simple technique, hot stage optical microscopy is precise and reliable only for relatively high crystallization temperatures where spherulite growth rate and especially nucleation density are low. High growth rates and/or high nucleation density significantly decrease the accuracy of *in situ* measurements and make studies impossible at a certain degree of undercooling. The major drawback of *in situ* hot stage optical microscopy is its low cooling rate (maximum 20 °C/min, though some setups allow cooling rate to 100 °C/min) which cannot prevent crystallization from starting before the isothermal treatment temperature of interest is reached [11]. Consequently, a significant range of crystallization temperatures cannot be studied

using an *in situ* hot stage and the applicability of this method is limited to the range of medium to high temperatures. Other techniques have been used to minimize these limitations and increase sample cooling rate. These techniques include using *ex situ* sample melting and two-chamber gas heating and cooling. Non-isothermal techniques similar to those described by Ding and Spruiell, and Wagner and Phillios [12,13] also have been developed. Polylactide exhibits high nucleation density at temperatures below 120 °C which makes difficult to study its crystallization using hot stage optical microscopy. Therefore the unusual crystallization behavior has been studied using indirect measurements making studies of the crystallization behavior of polylactide at high supercooling especially important.

In situ hot stage atomic force microscopy is also a popular tool for studying crystallization [14]. This technique allows not only the study of spherulite growth but also provides valuable information on crystalline morphology at scales inaccessible in optical microscopy. Nevertheless, the *in situ* AFM technique is limited to very low growth rates and very low undercooling crystallization due to the scanning nature of the AFM which makes the time resolution extremely poor. Additionally, it has been shown that the probe tip can itself influence the crystallization being observed during *in situ* AFM studies [15].

Here we study the crystallization behavior and morphology of polylactide films using atomic force microscopy and *ex situ* crystallization. This AFM technique for studying crystallization involves using sufficiently thin polymer films that the crystallization in the surface normal direction is constrained but that in the surface parallel directions proceeds as in the bulk. Because the surface normal crystallization is constrained, peaks are formed at the center of spherulites and troughs are formed at the edges. This aspect of the morphology allows us to measure very accurately the spherulitic dimensions as explained later. We have also developed a technique to locate the same spherulite on a film after removing the sample from the microscope to allow for the *ex situ* thermal treatments. Previous work has showed that from the point of view of orientation of lamellae, the crystallization behavior in polylactide films with thickness down to 30–80 nm is not different from that of the bulk material [15]. For this reason we can extrapolate the results of our studies on films of about 500–700 nm to bulk behavior.

By definition, *ex situ* crystallization studies require intermediate cold periods when the sample is in the glassy state and can be imaged in the absence of ongoing crystallization. We note that polylactide is an excellent candidate for such studies because its glass transition temperature of 60 °C is above room temperature. Therefore crystalline structures are very stable in this polymer at room temperature and different stages of crystallization can easily be “frozen in” and imaged.

We begin by explaining in detail and validating the experimental technique since it is not a standard approach for studying crystallization kinetics (Section 2). Next we consider the kinetics and the morphology of the individual polymers (Sections 3.1 and 3.2) and finally we discuss the kinetics of the blended systems (Section 3.3).

2. Experimental

2.1. Materials and sample preparation

Three polylactide samples were used; the first, supplied by Biomer, was a poly(L/D-lactide) copolymer containing 2% of D-lactide (L 9000). The other two were optically pure resins supplied by PURAC; a poly(L-lactide) (Purasorb PL) and a poly(D-lactide) (Purasorb PD). The molecular weight distributions were analyzed by gel permeation chromatography using a Varian liquid chromatograph equipped with refractive index, UV, light scattering and viscosity detectors. Trichloromethane at 35 °C was used as the eluent and the SEC columns were from Supelco (G6000-4000-2000 HXL). It was found that the poly(L/D-lactide) has a number average molecular weight of 50,000 and a polydispersity index of 2.0. The optically pure PLLA has a number average molecular weight of 59,500 and a polydispersity index of 1.8. The optically pure PDLA has a number average molecular weight of 84,500 and a polydispersity index of 1.7.

For the crystallization kinetics studies, samples were prepared using the solution casting technique with dichloromethane, supplied by ACROS, as a solvent. The polymer was dissolved in dichloromethane at a concentration of 0.1 wt% and then cast onto a thin glass substrate (a 6 mm by 6 mm piece of microscope slide of 150 μm thickness supplied by Fisher Scientific). The samples were dried at room temperature under controlled evaporation conditions which allowed a film to form over 1–2 h. Dichloromethane has a very high volatility and evaporation of a drop of solution under normal ambient conditions takes less than 40 s resulting in a film with a very rough surface not suitable for subsequent AFM imaging. For this reason, the casting was performed in a closed chamber nearly saturated with solvent vapor. The films cast under these conditions have a smooth surface and are ideally suited for AFM imaging. The thickness of the films was measured by profiling the film surface in the vicinity of a sharp cut using AFM and was found to be in the range of 500–600 nm.

It was established experimentally that heating the film for 3 min at temperature higher than the melting point is enough to erase the effect of the casting process on subsequent surface crystallization. In particular, the concentration of crystallization nuclei is much higher in the cast films than in the films that were melted after casting. By melting the film and evaporating any residual solvent from the surface and immediate subsurface regions, the nuclei density is decreased drastically allowing longer times for spherulite growth before impingement in the subsequent crystallization studies. We refer to this step as “premelting”. The heating and cooling for the premelting step were performed very quickly (method explained in following section) to prevent crystallization during cooling. Additionally, the premelting step was performed under a nitrogen atmosphere to prevent polymer decomposition. The difference between premelted and solution cast film crystallization behavior can be readily seen in Fig. 1. Note the difference in nuclei density in the premelted series as compared to the cast series. Additionally, note that the residual solvent in the

cast films does not significantly affect the spherulite growth rate; the size of the spherulites after 2 min of crystallization is 6.9 ± 0.3 and 7.0 ± 0.3 μm for the premelted and cast films, respectively.

AFM imaging of numerous premelted film surfaces showed no traces of crystallinity validating our quenching procedure which is explained in more detail in the next section. According to the nominal melting temperatures of the polymers under investigation, the premelting temperature was chosen to be 182 °C for poly(L/D-lactide) and its blends and 192 °C for poly(L-lactide) and its blends.

The high nucleation density and high spherulite growth rate in polylactides at high supercooling puts a strict limitation on the crystallization time available before spherulite impingement. The only way to observe isothermal crystallization under these circumstances is to bring the sample to and from the crystallization temperature at a very high heating/cooling rate. Quenching is a well known technique used to “freeze” polymer’s crystalline structure for subsequent studies by using very high cooling rates. It is also possible to perform the opposite fast heating if certain conditions are met. First, the heating environment should be preheated and equilibrated at the target temperature. Second, the weight of the sample should be of several orders less than that of the heating media. Third, the sample must have a high surface to weight ratio for maximum heat exchange rate.

2.2. Heating/cooling of samples

For the crystallization experiments, a preheated and thermally stabilized heating chamber of a modular compact rheometer MCR 500 by Anton Paar was used. Prior to experiments the heating chamber was stabilized at the target temperature with ± 0.1 °C tolerance. Heated nitrogen was flowing into the chamber (1.1 m^3/h) facilitating convective heat transfer with the sample. The preheated gas flow also allows the system to rapidly compensate for the heat loss that occurs during sample insertion. During the experiments, the sample (film and substrate) was placed on a hot surface inside the chamber and after the desired crystallization time it was quickly removed and placed on metallic plate at room temperature for cooling. A heat transfer calculation showed that at 150 °C the sample reaches the heating media temperature in less than 2 s. Such a high heating rate is possible due to the small sample weight (typically less than 9 μg) and the high surface area to weight ratio. The heat transfer to the sample occurs by forced convection from the preheated gas and by conduction from the hot metal surface on which it was sitting. A precisely calibrated thermocouple was placed inside the metal immediately under the sample. After reaching steady state, the temperature was kept constant within ± 0.1 °C by the controller.

During sample insertion some of the hot gas escapes from the heating chamber causing a temporary temperature drop which is compensated for by the controller. The maximum temperature drop ranged from 0.44 °C for a 110 °C set point to 1.05 °C for a 170 °C set point and returned to within ± 0.3 °C in 54 and 82 s, respectively. Note that at the lower

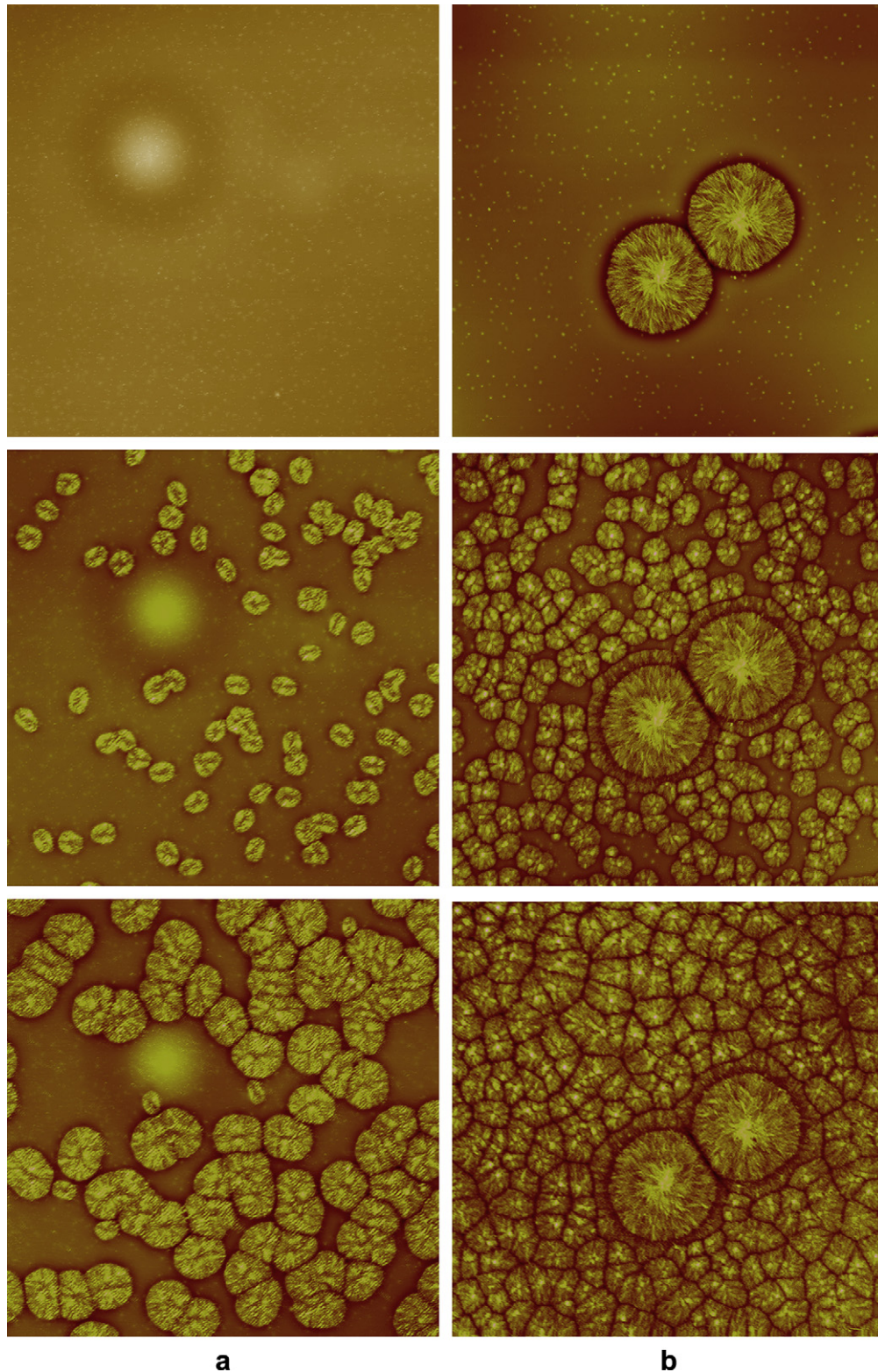


Fig. 1. The development of crystalline structure on the surface of the (a) premelted and (b) solution cast films of poly(L/D-lactide) at 110 °C. The upper row images show the polymer surface prior to isothermal crystallization, the middle and lower rows show the same samples crystallized for 2 and 4 min, respectively. The round elevated area on the left images is an amorphous area remaining after a spherulite formed in the casting step was melted in the premelting step. The 100 μm AFM height images are shown.

temperatures, where we will observe the maximum spherulite growth rate, the temperature drop is the smallest. Additionally the oscillations around the set point approximately

compensate for each other. We therefore consider this temperature drop to be negligible in regards to the overall measurement accuracy.

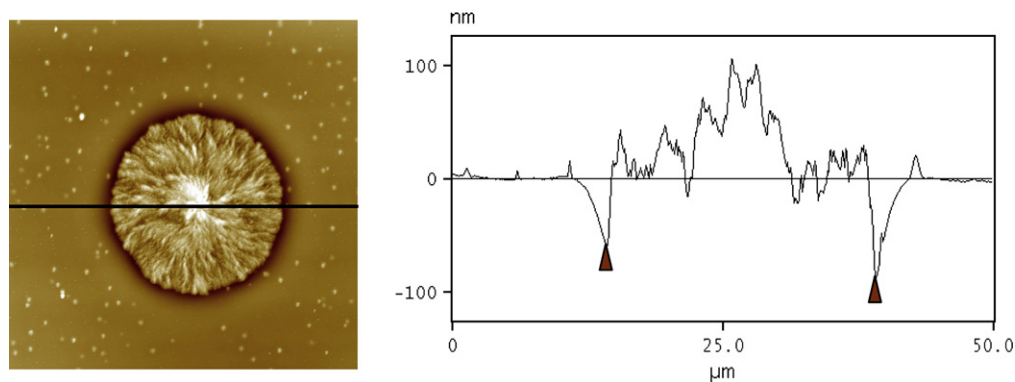


Fig. 2. AFM height image of solution cast poly(L/D-lactide) film (left) and spherulite cross-section (right). These spherulites are about 25 μm in size and are typical for both the polylactides under investigation in solution cast films. Image size is 50 μm . Note the clearly distinguishable spherulite borders which make the accurate size measurements possible.

It was found that, for small samples, cooling in air at room temperature on the surface of a room temperature metal plate gives cooling rates comparable to our heating rates. In such conditions, the sample cools to below the glass transition temperature ($\sim 60^\circ\text{C}$) in less than 2 s.

2.3. Technique for the measurement of spherulite size

A Digital Instrument's Nanoscope IIIa MultiMode SPM atomic force microscope was used in tapping mode for these studies. The ultra sharp NSC15/AIBS cantilevers used for scanning were obtained from MikroMash. The typical resonance frequency of the tips was approximately 300 kHz and the characteristic force constant was approximately 40 N/m. The small radius of the tips ($R < 10\text{ nm}$) allowed scanning with high image resolution. Image analysis was then performed to measure the sizes of the crystalline features. Prior to the experiments, the dimensional precision of the AFM was calibrated and verified using a reference silicon grid with 10 μm mesh (supplied by Digital Instruments Company). The scan rate ranged from 0.5 Hz to 1.0 Hz. For all scans only the highest 512 by 512 resolution was used.

The crystalline sizes in polymer films can be conveniently measured using cross-sectional analysis of height images (Fig. 2) because of the trough that surrounds each spherulite in thin films. We found that in films thicker than about 1.5–2 μm this interface becomes increasingly blurred thus decreasing the precision of the spherulite size measurement. Additionally it was almost impossible even to find surface crystallinity in films thicker than 5–8 μm as the crystalline structure tends to be submerged under a layer of amorphous polymer at these thicknesses.

For each temperature at each crystallization time at least 14–30 crystalline features were measured and averaged. In the case of spherulites, the radius was determined from the diameter measurement and used in the calculation of the growth rates. For the axialitic crystalline structures, size measurements were taken along lamellae, i.e. along the growth directions, and half of this dimension was used in the calculation of the growth rate. For the high-temperature crystalline structures, growth rate measurements were determined from the

radius of the circle inside which the crystalline structure was inscribed. To determine the variation in spherulite size over time at least three different crystallization times were used. In order to increase the reliability of our data, the measurements of spherulite size were performed on 3–5 AFM images obtained from different locations on each sample. Even our small samples had a surface more than thousand times larger AFM scan area. Since scanning is performed on stable, already crystallized samples below the glass transition temperature; this method allows enough time and surface area to perform numerous measurements thus increasing measurement accuracy. Even for the high supercooling range where the nucleation density is very high, it is possible to find enough unconstrained crystalline structures to perform accurate measurements.

2.4. Influence of the heating/cooling cycle on spherulite growth measurements

The most important issue in *ex situ* crystallization studies such as ours is whether or not the exposure to multiple heating and cooling cycles affects the crystallization rates. In order to evaluate this we undertook 3 series of experiments (1 series at each of the temperatures 110, 130, and 150 $^\circ\text{C}$) under 2 conditions (single cycle and multiple cycles). Samples were subjected to repeated fast heating/cooling cycles according to the techniques described above and then compared to samples subjected only to 1 cycle. The difference in the spherulite sizes and morphology of these samples provides key information on the effects of each cycle on polylactide crystallization. Images of the series of experiments at 130 $^\circ\text{C}$ are shown in Fig. 3. The numerical results for this study are presented in Fig. 4.

In order to improve the precision of this study we used an in-house developed technique to repeatedly find the same region on the film for the AFM scanning. All multiple cycle measurements were performed on the same set of spherulites and in the same growth directions. We consider first the sequence of images presented in Fig. 3 all collected at 130 $^\circ\text{C}$. The first four images (a–d) show the development of the same spherulites over 1 through 4 heating and cooling cycles reaching in Fig. 3(d) a total crystallization time of 250 s. It is apparent that demarcations exist in the spherulites for each

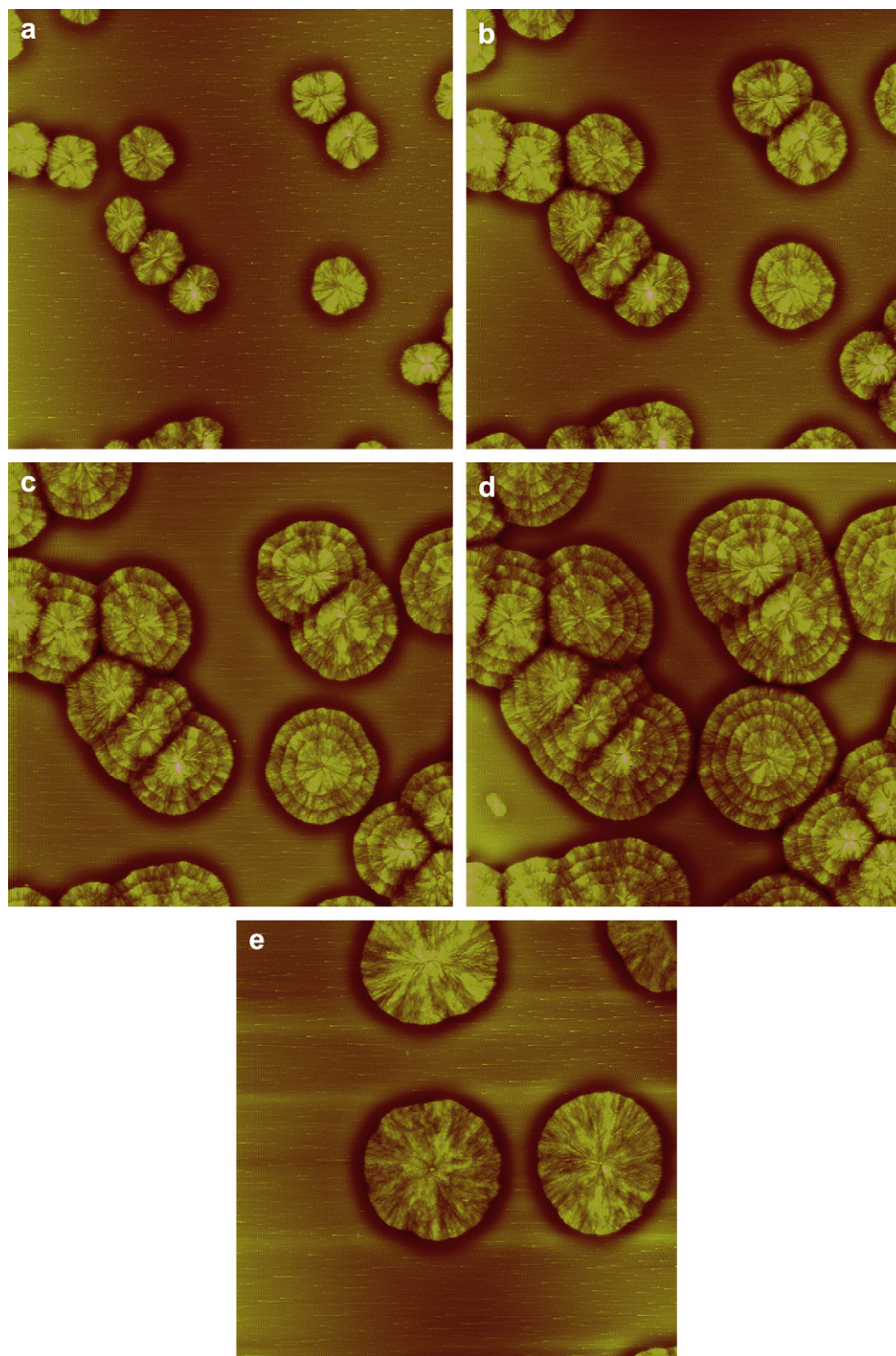


Fig. 3. The AFM height images of the same area of the same poly(L-lactide) sample subjected to crystallization at 130 °C in (a) one fast heating/cooling cycle for 100 s; (b) two cycles (150 s in total); (c) three cycles (200 s in total) and (d) four cycles (250 s in total). (e) Sample crystallized at 130 °C in one cycle for 250 s is considered to be the reference point. All images are 100 μm scans.

crystallization cycle. This phenomenon is relatively common in samples exposed to such fast heating/cooling cycles as explained by Frascini et al. [16]. Fig. 3(e) shows another sample which was exposed to only 1 cycle with a total crystallization time of 250 s. By visual inspection we can see that the sizes of the spherulites in Fig. 3(d) and (e) are very similar.

We now consider the final results of this study which are shown in Fig. 4. The difference between the final spherulite size in the multicycle sample and the one cycle sample is in each case less than 5%, which is lower than the standard deviation of our results (10%). Therefore we consider that the effect of multiple heating/cooling cycles on the spherulite

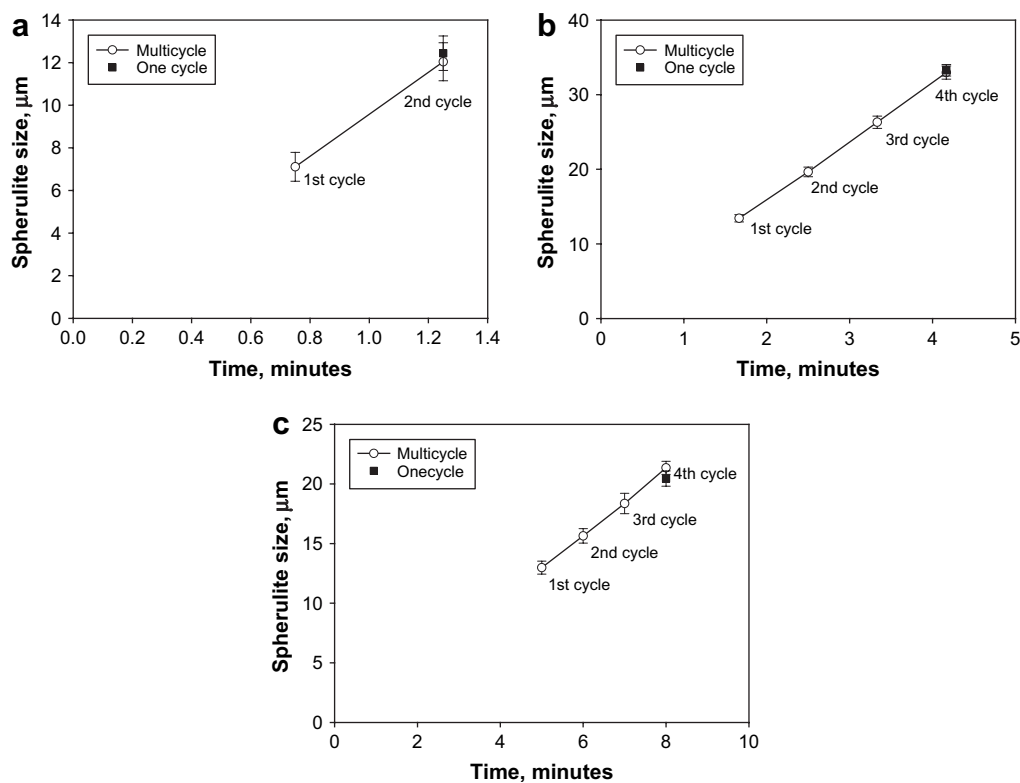


Fig. 4. Influence of fast heating/cooling cycle on spherulite size and growth rate measurements of poly(L-lactide). The comparison of the spherulite sizes of the samples subjected to multiple fast heating/cooling cycle with those of the samples subjected to only one cycle at (a) 110 °C; (b) 130 °C and (c) 150 °C.

size is negligible. Additionally based on these results, we consider that the intermediate glassy periods do not affect the crystallization which will proceed in essentially the same manner as crystallization from the melt. All of the following kinetics studies were done using multiple heating/cooling cycles on the same sample.

2.5. Generality of experimental technique

At this point it is important to consider whether or not our experimental technique for studying crystallization kinetics is generally applicable or if it depends upon the nucleation behavior of polylactide. Therefore we have performed a limited study with isotactic polystyrene of $M_N = 400 \text{ kg/mol}$ to ensure that sufficient nucleation would occur over the entire crystallization range and that spherulites would grow from nucleation from the same time. The casting, premelting and *ex situ* crystallization were performed in exactly the same manner as with the polylactide. The only procedural difference was that PS was melted at 250 °C and quenched to room temperature before dissolution in dichloromethane at 0.84 wt%. Crystallization was performed for 65 min at 130, 135, 140, 150, 160, 170 and 178 °C. At all temperatures there was sufficient nucleation such that many spherulites could be identified. In fact for 135 °C and above the entire surface was covered with spherulites. Also, it was clear that all of the spherulites were nucleated at the same time leading to equal diameters. As an example, the morphology of the sample crystallized at

170 °C is presented in Fig. 5. Presumably, since the high degree of nucleation occurs in both polylactide and polystyrene, it is caused by residual solvent which may be increasing the chain mobility and/or acting as heterogeneous nucleation centers.

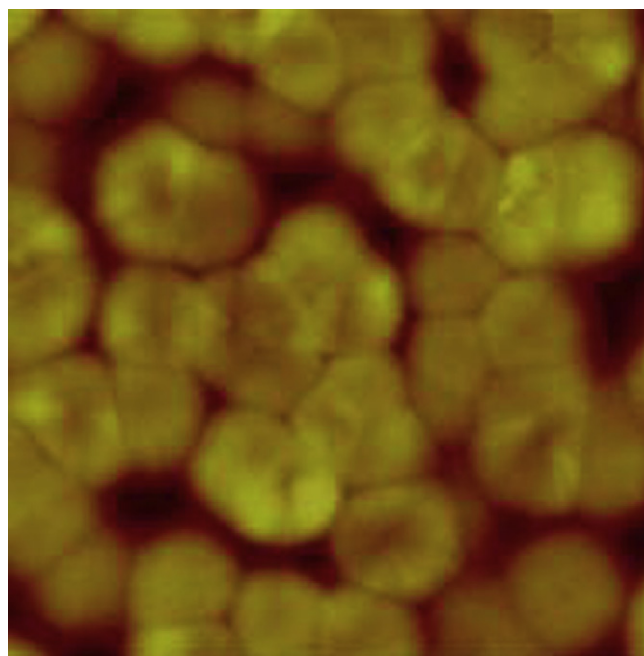


Fig. 5. Morphology of isotactic polystyrene crystallized at 170 °C for 65 min.

3. Results and discussion

3.1. Isothermal spherulite growth rate

We measured spherulite growth rates of poly(L/D-lactide) in the range of 100–160 °C and of poly(L-lactide) in the range of 100–170 °C. The growth rate curves were constructed from the spherulite size measurements as shown in Figs. 6 and 7. A relatively small standard deviation rarely exceeding 10% in spherulite size was present in our data. Generally, it can be noted that the intersections of the lines are very close to the origin meaning both very short nucleation time in all poly-lactide samples and a very fast heating allowing crystallization without delay. This extremely short induction time was also observed by Tsuji et al. [10] for poly(L-lactide) and poly(L/D-lactide).

Previous studies show that the maximum spherulite growth rate of poly(L-lactide) is around 110–130 °C, and that it exhibits a most peculiar, bimodal shape (observed by Di Lorenzo [9] and by Tsuji et al. [10]). The lower temperature peak (at about 110 °C) has been correlated to a transition in spherulitic growth regimes II to III that was observed in the same temperature range [17] although other explanations of the unusual crystallization behavior of poly(L-lactide) exist as well. Our results perfectly match the results obtained by Tsuji et al. [10]. For the optically pure poly(L-lactide) they reported a spherulite growth rate curve of a similar shape to ours. There is very nice accordance between our data and those from Tsuji et al. [10] in that the peaks occur at the

same temperatures for both polymers. We note that our study covers a temperature range that is broader by 20 °C than that of Tsuji et al. [10] providing additional information at high temperatures. If we now consider the data of Baratian et al. [18] we can observe that their study did not cover the low temperature where the second peak occurs therefore missing the unexpected second peak. This data set indicates the importance of the lower temperature range accessible by the *ex situ* crystallization techniques used in this study and that of Tsuji et al. [10].

Following Abe et al. [17], Tsuji et al. [10] attributed the transition zone between the two peaks to a regime II–regime III transition. According to Abe et al. [17] this effect is related to a change in the isothermal thickening coefficient at the regime transition which favors an accelerated growth rate in regime II under certain conditions. This was first observed and explained for long-chain *n*-alkanes by Alamo et al. [19]. Note that the transition from regime II to III is not accompanied by any transformations in spherulite morphology. Rather, the most dramatic changes in crystallization morphology of poly(L-lactide) are observed at low supercooling at temperatures of 160 °C and above.

Poly(L-lactide) exhibited a spherulite growth rate about two times higher than that of poly(L/D-lactide). It is the 2% D-lactide repeat unit content in the poly(L/D-lactide) which causes this decrease of the spherulite growth rate. The randomly distributed D-lactide repeat units create steric impediments during crystallization thus decreasing the overall spherulite growth rate. This effect is well known and has

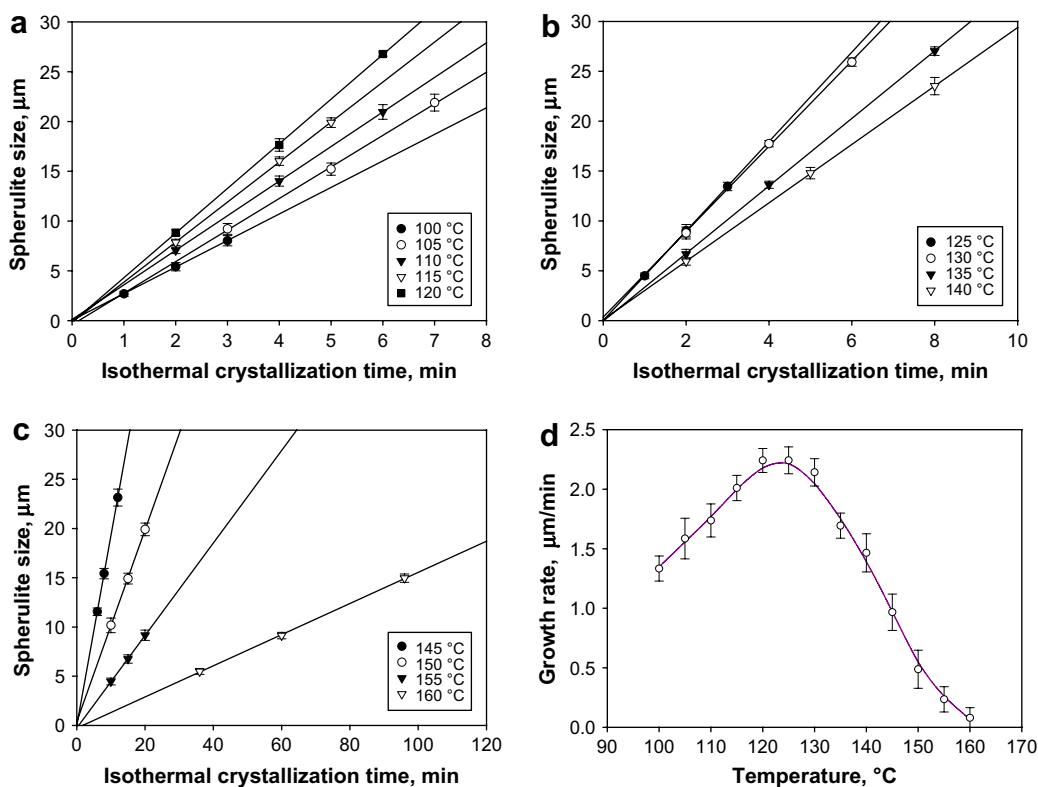


Fig. 6. Spherulite size vs. isothermal crystallization time for poly(L/D-lactide) at various temperatures (a)–(c). Error bars indicate one standard deviation. (d) Spherulite radius growth rate vs. isothermal crystallization temperature. Error bars indicate standard error in the slope from least squares regression of data in (a)–(c).

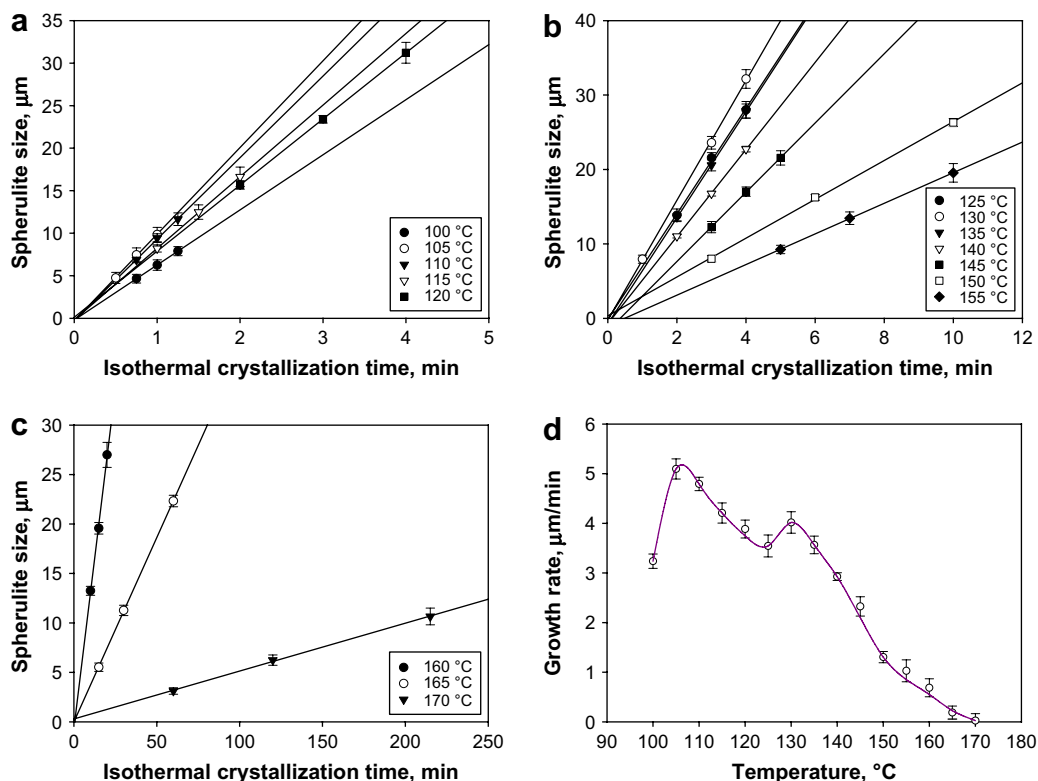


Fig. 7. Spherulite size vs. isothermal crystallization time for poly(L-lactide) at various temperatures (a)–(c). Error bars indicate one standard deviation. (d) Spherulite radius growth rate vs. isothermal crystallization temperature. Error bars indicate standard error in the slope from least squares regression of data in (a)–(c).

been quantified by Tsuji et al. [10] for polylactide. The poly(L/D-lactide) copolymers that they studied exhibited crystallization behavior very similar to our sample. We also note that the growth rate curve for our poly(L/D-lactide) exhibited only one maximum again in accordance with the observations of Tsuji et al. [10]. It is clear that the unusually fast spherulite growth at low temperatures is entirely suppressed by even very small amounts of D-lactide units in the chain. Since this unusual behavior has been observed only with optically pure polylactides of $17,000 \leq M_N \leq 104,000$ [10,17] it is likely that L-lactyl sequence lengths of at least 230 (or $17,000/M_0$) units are necessary for its occurrence.

3.2. The crystalline morphology of polylactides

The morphology observed naturally depends on the crystallization temperature. Generally, four typical crystalline forms can be distinguished (Figs. 8 and 9). As expected, at low temperatures the nucleation concentration is very high and crystallization proceeds in the form of non-oriented lamellae stacks (Fig. 8(a)), making direct measurements of the crystalline features very difficult at temperatures below 100 °C. At intermediate temperatures, clearly distinguishable spherulitic structures can be observed (Fig. 8(b)). Despite the fact that some researchers reported that they were not able to observe the formation of the high-

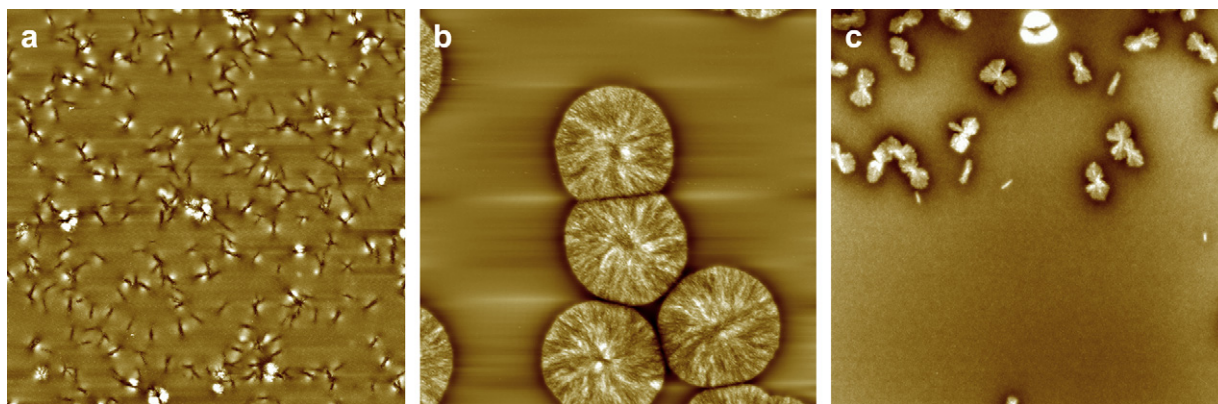


Fig. 8. Morphology of surface crystallinity of poly(L-lactide) formed (a) at 90 °C for 1.5 min (50 μm height image); (b) at 120 °C for 4 min (100 μm height image) and (c) morphology of surface crystallinity of poly(L/D-lactide) formed at 160 °C for 60 min (100 μm height image).

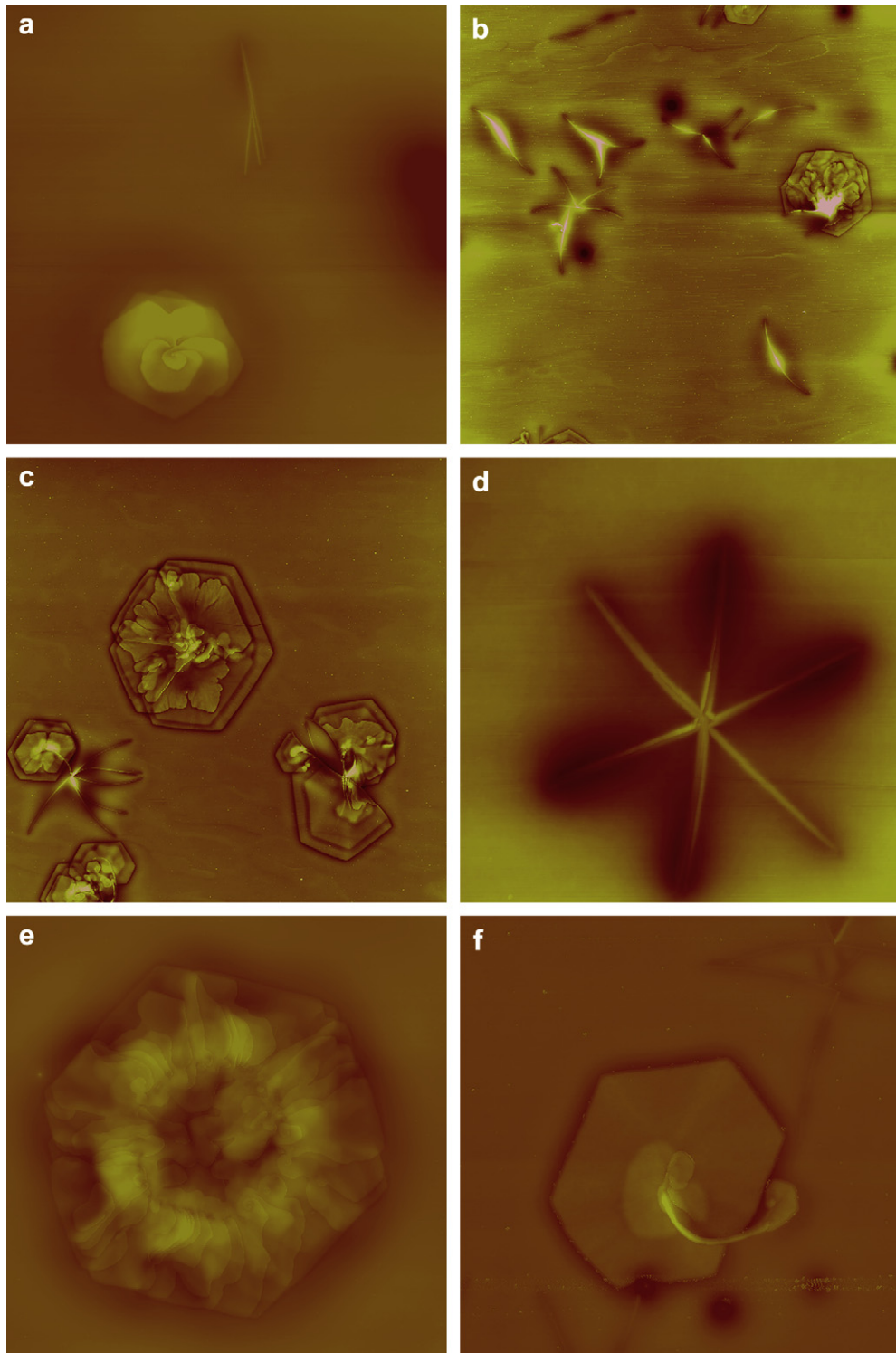


Fig. 9. The crystalline morphology of the poly(L-lactide) samples crystallized at low supercooling. Crystallization temperatures, times and AFM height image scales are: (a) 170 °C, 120 min, 20 μm ; (b) 165 °C, 30 min, 50 μm ; (c) 165 °C, 90 min, 100 μm ; (d) 170 °C, 120 min, 8 μm ; (e) 165 °C, 60 min, 30 μm and (f) 165 °C, 25 min, 15 μm .

temperature axialites for polylactide [20], in our experiments we observed them at temperatures around 160 °C (Fig. 8(c)). At higher temperatures crystalline structures having “truncated lozenge” morphology with distinguishable lamellar structure were observed (Fig. 9(a)–(f)). The transformations between the different morphologies take place gradually as isothermal

crystallization temperature changes and no specific transformation temperatures were observed. Nevertheless perfectly round spherulites were observed in the temperature range of 110–130 °C which is the zone of the highest spherulite growth rate.

As expected, nucleation density rapidly decreases at higher temperatures; the nucleation density for the poly(L-lactide)

samples crystallized at 170 °C was estimated to be $4.2 \pm 1.6 \times 10^{14} \text{ m}^{-3}$. Under these low supercooling conditions, polylactide forms stacked, flat-on and edge-on crystalline structures (Fig. 9(a)). The nucleation density increases to $3.3 \pm 1.4 \times 10^{15} \text{ m}^{-3}$ at 130 °C and reaches $1.3 \pm 0.4 \times 10^{17} \text{ m}^{-3}$ at 110 °C.

Kikkawa et al. [15] proposed that crystallization of polylactide takes place as edge-on crystals only, which can flip later during their growth to a flat-on crystal by a defect obstacle mechanism. We found that at low supercooling this is not the only possible crystallization behavior and in fact different scenarios of individual crystalline structure formation are possible. The crystallization can proceed in the form of a purely flat-on stack (Fig. 9(a), (c) and (e)), purely a edge-on stack (Fig. 9(a), (b) and (d)) and scenarios where edge-on crystals flip to flat-on crystals (Fig. 9(c)) and the opposite, where flat-on crystals yield edge-on sprouts (Fig. 9(f)). Interestingly, at 170 °C no transitions between edge-on and flat-on crystals were observed (Fig. 9(a)) and crystallization took place in the form of completely flat-on and edge-on lamellae in an approximately equal ratio. At slightly lower crystallization temperatures (165 °C) the edge-on orientation seemed to be preferable (Fig. 9(b)). It is interesting that in some cases edge-on stacks also maintained hexagonal symmetry (Fig. 9(d)). We note that it is possible that the lamellar orientation transitions observed by Kikkawa et al. [15] were caused by the interaction of the AFM tip and growing lamellae during *in situ* scanning since it has been proven that the AFM tip can cause additional nucleation [15]. This is another benefit of the *ex situ* crystallization technique as the imaging takes place below the glass transition where it is certain that no spurious artifacts will be caused.

An important crystallization parameter is the lamellar thickness l_g^* which can be related to thermodynamic properties such as supercooling. Normally, the lamellar thickness decreases with increasing degree of supercooling [21]. The clearly distinguishable lamellar structure of the crystalline formations observed at low supercooling allows the direct measurement of long spacing which is the sum of lamellar and amorphous layer thickness. It was found that for poly(L-lactide) the average long spacing in the range of 165–170 °C is $19 \pm 2 \text{ nm}$. These values correlate well with experimental SAXS lamellar thickness measurements of 15–20 nm [18] for polylactides at this temperature.

3.3. Stereocomplexation phenomenon in polylactide blends and its influence on spherulite growth

The stereocomplex forms when sequences of different optical isomers are present in a system. It can form in a blend of two optically pure polymers and also in a single poly(L/D-lactide) polymer if sequences of sufficient length of both optical isomers exist. This crystalline form is interesting because its presence can have significant effects on many aspects of the dynamic behavior of polylactide. The stereocomplex melts at about 230 °C and therefore can be present under conditions when the α -crystals are molten (above 170 °C) and when they are crystallizing (between 70 and 170 °C). In those situations the stereocomplex particles act as crosslinks which

hinder the whole chain coordinated motions required for crystallization and melt flow. Here we are looking at the effect of the stereocomplex particles on the spherulitic growth rates of the α -crystals.

We begin by confirming the presence of the stereocomplex in the blends of our polylactides from a series of DSC analyses. These analyses were performed on blends containing 2, 5, 10, 20 and 50% poly(D-lactide) in poly(L/D-lactide) and 5, 10, 20 and 50% poly(D-lactide) in poly(L-lactide) (Fig. 10). In both the first and the second runs, the blends containing poly(D-lactide) showed a small peak at about 220–230 °C that does not exist for the pure polymers. The area under this peak increases as the poly(D-lactide) content increases (up to a maximum) confirming the presence of the stereocomplex as shown in Fig. 11. Note that the stereocomplex melting peak is not visible in Fig. 10(a) for the 2% PDLA blend. This is simply a result of the low vertical resolution on the graph and there is actually a very small peak in the data. The heat of fusion of the pure stereocomplex is 142 J/g, indicating that the maximum stereocomplex content observed in our blends is about 10% by weight. Interestingly, the maximum stereocomplex content occurs at 20% PDLA in both systems with the maximum being significantly lower in the poly(L/D-lactide) based system. We note that the amounts of

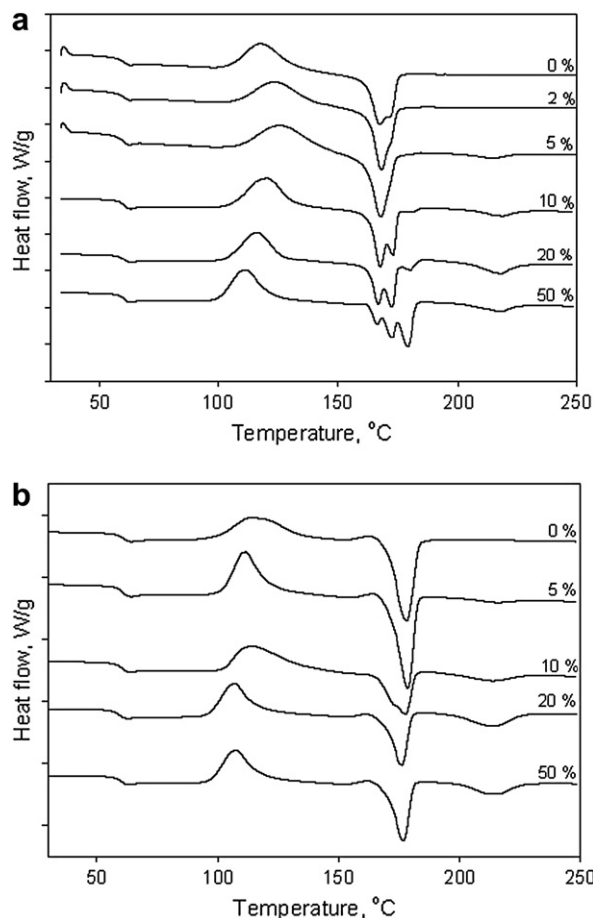


Fig. 10. Second runs DSC curves for the blends of (a) poly(L/D-lactide) and (b) poly(L-lactide) with varying poly(D-lactide) content. Heating rate is 5 °C/min. Curves were shifted vertically for clarity.

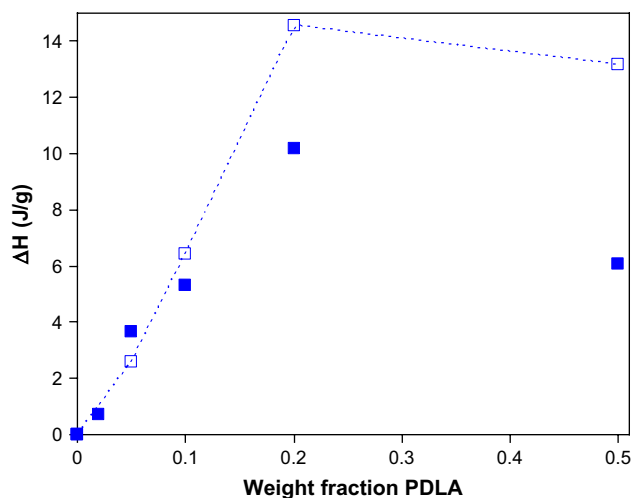


Fig. 11. Enthalpy of stereocomplex melting for the polylactide blends. Filled symbols are for blends of poly(L/D-lactide) with poly(D-lactide) and open symbols are for blends of poly(L-lactide) with poly(D-lactide). Extracted from data in Fig. 10.

stereocomplex observed in the first DSC runs were very similar to those observed in the second runs (Fig. 10). Therefore we propose that during the following crystallization kinetic studies for the blends the stereocomplex content is given approximately by the data in Fig. 10 and is likely not changing while the α -crystallization is taking place.

Additionally, for blends containing 10% or less PDLA there is very little difference between the stereocomplex content in the poly(L/D-lactide) based systems as compared to that of the poly(L-lactide) based systems. This indicates that the formation of stereocomplex is not significantly hindered by the presence of the D-lactide units in the copolymer at these PDLA contents. This is particularly interesting as the presence of a small amount of D-lactide units in a L/D copolymer has an enormous effect on the formation of the α -crystal. We will come back to this issue later with an explanation for this behavior.

We note that the multiple α -crystal melting peaks on the DSC curves for blends of poly(D-lactide) in poly(L/D-lactide) are related to the difference in the melting temperatures of the two pure polymers and also perhaps to structural reorganization caused by the low heating rate [22]. Since we are using the DSC scans only to observe the stereocomplex melting, these multiple peaks can safely be neglected.

In order to study the influence of stereocomplexation on the spherulite growth rate, we have studied the crystallization kinetics of the blends of polylactides using the techniques described earlier. Note that since our premelting step is performed at 182 °C (blends of poly(L/D-lactide) with PDLA) and 192 °C (blends of PLLA with PDLA) all of the stereocomplex that is formed during the casting processes remains intact. Also, during the “premelting” step it is possible that additional stereocomplex forms. As explained previously, based upon the DSC studies we assume that during the crystallization studies the stereocomplex content is not changing significantly. Therefore, we can observe the effect of the presence of stereocomplex particles on the crystallization of the α form separate from any potential effects of the competing crystallization

mechanisms occurring at the same time. This work is complementary to that of Anderson and Hillmyer [5] who showed that small amounts of stereocomplex can act as very effective primary nucleating agents and that of Yamane and Sasai [4] who demonstrated unequivocally that the stereocomplex acts as a primary nucleating agent and that it increases the spherulite growth rate at 120 °C. Yamane and Sasai did not study this effect at other temperatures, nor did they examine the differences between poly(L-lactide) and poly(L/D-lactide). Now by examining in detail its effect on the spherulite growth rate at all temperatures in both polymers we can complete the picture.

One would expect that the addition of the poly(D-lactide) to the poly(L/D-lactide) would lower the spherulite growth rate of the α -crystals because of the reduction in whole chain mobility caused by the stereocomplex crystals. However, a blend containing 2% poly(D-lactide) showed a significantly higher maximum spherulite growth rate than the pure poly(L/D-lactide) while the blend with 5% poly(D-lactide) showed significantly lower growth rate at all temperatures (see Fig. 12). Additionally crystallization was almost completely suppressed in the blend with 10% poly(D-lactide).

For the optically pure poly(L-lactide) and its blends with poly(D-lactide) (Fig. 13), it was found that the shape of the spherulite growth rate curves were significantly different from the poly(L/D-lactide)’s “bell” shape and had two maxima as explained previously. It is especially interesting that the shapes of the curves for these systems are similar, with the spherulite growth rate for most of the blends being lower than that of the pure poly(L-lactide) at all temperatures. The blend containing 2 wt% poly(D-lactide) showed a peculiar crystallization behavior; in that its spherulite growth rate at 120 °C was slightly higher than that for pure poly(L-lactide). This is somewhat similar to the observed increased maximum growth rate for the blend of poly(L/D-lactide) with 2% poly(D-lactide) although not as marked. It was found that the global spherulite growth rate maximum is around 110 °C and the second local maximum is around 130 °C for all poly(L-lactide) with poly(D-lactide) blends. The lines in Figs. 12 and 13 represent cubic spline interpolations of the experimental spherulite growth rate data.

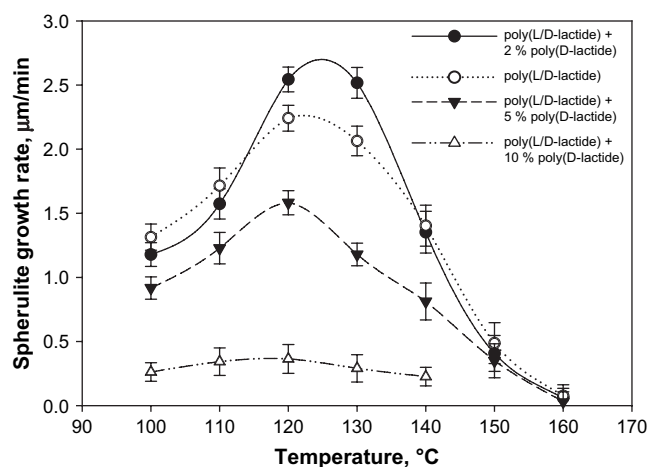


Fig. 12. Isothermal spherulite radius growth rates for poly(L/D-lactide) and its blends with poly(D-lactide).

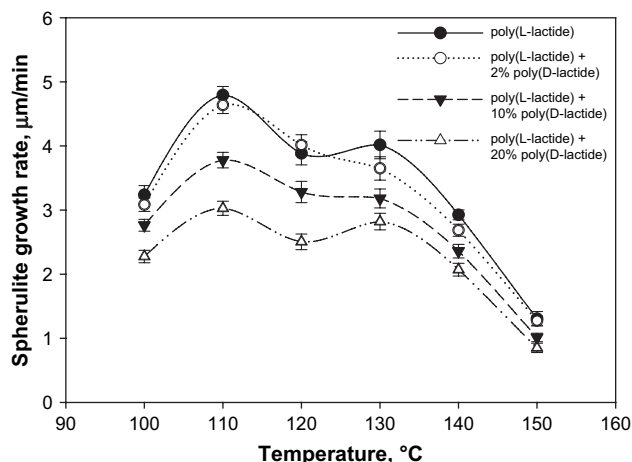


Fig. 13. Isothermal spherulite radius growth rates for poly(L-lactide) and its blends with poly(D-lactide).

In order to compare the effect of the added PDLA on the spherulite growth rate of poly(L/D-lactide) to its effect on the spherulite growth rate of poly(L-lactide) we consider a reduced growth rate, $G_{x,T}/G_{0,T}$, at temperature T . Here x refers to PDLA content in the blend and the subscript 0 indicates the pure matrix material. The reduced growth rate at 110 and 120 °C is plotted in Fig. 14 for both series of blends where we can see clearly the very different impact of PDLA on these two systems. These two temperatures were chosen specifically to illustrate the different effect of the stereocomplex on the growth rate in regime II (120 °C) and regime III (110 °C).

At low PDLA content (2%), the reduced growth rate at 120 °C is enhanced (i.e. higher than 1) in both systems with a much larger degree of enhancement in the poly(L/D-lactide) system. This can be compared to the behavior at 110 °C where the reduced growth rate is lower than 1 for both systems, again with the impact of the PDLA being larger on the poly(L/D-lactide) system. According to Abe et al. [17] the transition between crystallization regime III (limited by the diffusion of individual chains) to regime II (secondary nucleation rate is

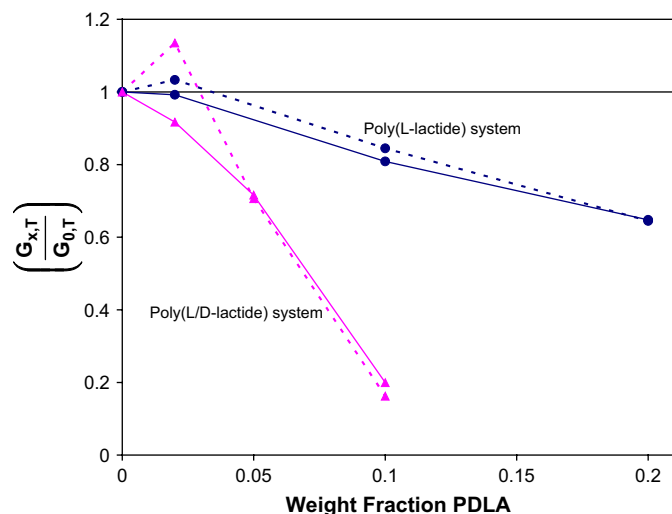


Fig. 14. Reduced spherulite growth rate at 110 °C (solid lines) and 120 °C (dashed lines). Note that 110 °C is in regime III and 120 °C is in regime II.

larger than rate of diffusion) occurs at about 120 °C for poly-lactide and regime II lasts until about 145 °C [17]. Clearly the rate of diffusion of individual chains is decreased by the presence of stereocomplex crystals (as is discussed in more depth in the following paragraphs) explaining the observed reduction in spherulite growth rate at 110 °C where diffusion is an important factor. Now at 120 °C and slightly above, it is possible that the stereocomplex crystallites are increasing the rate of growth nucleation of α -crystals sufficiently to overcome the effect of the reduced diffusion and enhance the overall spherulite growth rate. This effect is only observable at low stereocomplex contents since the reduction in the diffusion rates at higher stereocomplex contents is very large. We note that secondary or growth nucleation is often unaffected by agents which enhance primary nucleation although in some cases there is an effect. For example, Jang et al. [23] have demonstrated that the presence of sodium benzoate in polypropylene increases both primary nucleation and spherulite growth. Additionally, Kim et al. [24] have demonstrated that silica nanoparticles in poly(ethylene 2,6-naphthalate) act as both a primary nucleating agent and an enhancer of spherulitic growth rate. Most importantly, Yamane and Sasai [4] did show that the stereocomplex acts to enhance the spherulitic growth rate at 120 °C. We propose that this increase of growth rate is a direct result of enhanced secondary nucleation. Additionally, since the increase in 120 °C growth rate is much larger in the poly(L/D-lactide) system than that observed in the poly(L-lactide) system we can conclude that there are more stereocomplex particles present in the poly(L/D-lactide) system.

At higher contents, we observe a much stronger reduction in the reduced growth rate of the poly(L/D-lactide) system as compared to the poly(L-lactide) system. These results can be understood by noting that the D-lactide units in the poly(L/D-lactide) chains will disrupt the formation of the stereocomplex. Therefore in this system, for the same PDLA content, we expect to have more but smaller stereocomplex crystals than in the poly(L-lactide) system. The reduction in chain mobility due to a network of stereocomplex particles is dependant on the number of particles and not just the overall mass fraction of stereocomplex. (We recall that according to the DSC results, the mass fraction of stereocomplex present in these two systems is similar at PDLA contents up to 10%.) Therefore we expect that the chain mobility in the poly(L/D-lactide) blend containing 5% PDLA is significantly lower than in the poly(L-lactide) at 5% PDLA. This reduction in chain mobility (as compared to the mobility in the absence of stereocomplex particles) results in the lower average, reduced growth rate.

A sparse network of stereocomplex particles would have a significant effect on whole chain coordinated motions, such as reptation, which are required in the crystallization process while having a negligible effect on the local movements associated with the glass transition. In order to illustrate the difference between the separate effects of stereocomplex particles on α -crystallization and glass transition we consider a hypothetical system in which each of the chains was taking part in a single stereocomplex particle, reptation would be

entirely suppressed and the dominant mechanism of large scale motion would be contour length fluctuations (CLF). The time scales associated with reptation and CLF are proportional to $(M/M_e)^3$ and $\exp(\nu M/M_e)$, respectively [25]. Here M is the molecular weight of the chain of interest and, M_e is the entanglement molecular weight (~ 4000 g/mol for PLA [26]) and ν is a coefficient of order 1. Clearly CLF is a much slower process than reptation for chains of significant length (e.g. if $M = 50$ kg/mol then CLF is 2 orders of magnitude slower than reptation) and therefore crystallization would proceed much more slowly in our hypothetical system than in a system free of stereocomplex particles. Now we consider the effect of this number of stereocomplex particles on the glass transition by using the following semi-empirical equation [27]:

$$\frac{T_g(\chi) - T_g(0)}{T_g(0)} = \frac{\chi K(M/\gamma)}{1 - \chi K(M/\gamma)}$$

Here χ is the number of crosslinks per gram, K is a constant of order 10^{-23} and M/γ is the molecular weight per flexible backbone bond (24 for polylactide). Note that $T_g(0)$ refers to the T_g in the absence of crosslinks. For our hypothetical system described above if the $M_N = 50$ kg/mol and the density is of order 1 g/mol then the number of crosslinks per gram is of order 10^{19} . With a T_g of 60 °C in the absence of crosslinks we expect our hypothetical system to have a T_g of about 60.8 °C. For the blend of 20% PDLA in poly(L/D-lactide) we have observed a T_g of 60.5 °C as compared to the T_g of the pure poly(L/D-lactide) which is 60 °C. We recall that in this blend the crystallization rate is about 5 times lower than in the pure poly(L/D-lactide). Therefore we conclude that our observation of significantly affected crystal growth rates in the absence of significant changes in the glass transition temperature is consistent for our systems. At this point we compare our results to those of Tsuji and Ikada [28] who studied the thermal properties of a series of 50/50 blends of optically pure PLLA and PDLA of varying molecular weight. They found that for $M_w < 10^5$ and stereocomplex contents of 40 wt% and above an augmentation in T_g of up to 5 °C occurs and no α -crystallization occurs. Our study demonstrates that at much lower stereocomplex contents and in the absence of significant augmentation of T_g , the spherulite growth rate can be enormously reduced.

4. Conclusions

A flexible technique for studying the isothermal crystallization behavior of polylactide was developed. This technique which uses *ex situ* isothermal crystallization is applicable to any polymer amenable to solution casting with a glass transition above room temperature. The efficacy of this technique was demonstrated and the sources and magnitudes of experimental errors were investigated.

Using this technique, we confirmed that while poly(L/D-lactide) copolymers have typical bell-shaped spherulite growth rate temperature dependencies, poly(L-lactide)s deviate from this pattern and show significantly higher spherulite growth rate in the low temperature region. Thus, the poly(L-lactide)

spherulite growth rate curve has two maxima: one is higher and sharper at 110 °C and a second flatter one at 130 °C. This behavior, previously attributed to a regime II–regime III transition, is not accompanied by any changes in morphology.

The spherulite growth rate in blends of poly(L/D-lactide) and poly(D-lactide) is much more affected by poly(D-lactide) content than in blends of poly(L-lactide) and poly(D-lactide). We have attributed this to the likely presence of more but smaller stereocomplex particles in the poly(L/D-lactide) systems than in the poly(L-lactide). Our hypothesis is that the presence of 2% D-lactide units in the copolymer chain disrupts the formation of large continuous stereocomplex crystallites but does not hinder the nucleation and initial growth of these crystallites. In a system with more, smaller stereocomplex particles we expect the chain mobility and therefore the spherulite growth rate to be reduced. Additionally in a system with more stereocomplex particles we expect the rate of primary and growth nucleation rates to be increased. In crystallization regimes I and III the presence of stereocomplex particles tends to reduce the spherulite growth rate because of the reduced chain mobility. In crystallization regime II the presence of many small stereocomplex particles tends to enhance the spherulite growth rate because of enhanced growth nucleation.

The development of the crystalline morphology of polylactides was also investigated and discussed. The long spacing of poly(L-lactide) crystallized at high temperature was found to be 19 ± 2 nm in the 165–170 °C temperature range. It was also found that the screw dislocations in hedritic structures in polylactides at low supercooling occurred predominantly in the clockwise direction relative to the surface of the film. Finally we have found that flat-on and edge-on crystallites form at 170 °C but transitions between the two types do not occur at this temperature contrary to 165 °C where edge-on is the preferred orientation and transitions do occur.

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