

# Banded Spherulites in Poly(L-lactic acid): Effects of the Crystallization Temperature and Molecular Weight

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**ABSTRACT:** The spherulitic morphology of pure poly(L-lactide) (PLLA) was investigated with polarized optical microscopy as a function of the crystallization temperature and molecular weight. After being melted at 210°C for 3 min, samples were cooled quickly to designated temperatures for isothermal crystallization. It was shown for the first time that a clear banding-to-nonbanding morphological transition took place at a critical temperature for PLLA with a number-average molecular weight of 86,000. With the increasing molecular weight of the material, the spherulite growth rates decreased notably, and the band spacing

decreased significantly. On the basis of the main-chain chirality in PLLA and the observation of a nonbanded spherulitic morphology in a certain temperature region, it was suggested that the crystallization temperature might have an effect on the relationship between the sense of lamellar twisting and the main-chain chiral structure in PLLA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3500–3504, 2007

**Key words:** biodegradable; crystallization; polyesters; spherulites

## INTRODUCTION

Banded spherulites have been observed sometimes in achiral polymers and frequently in chiral polymers.<sup>1</sup> It is commonly accepted that the formation of banded spherulites is attributable to lamellar twisting along the direction of radial growth, although the origin of the twisting is still debated intensively.<sup>1–7</sup> In the case of chiral polymers, earlier studies proposed a correlation between the main-chain chirality and the sense of lamellar twisting in banded spherulites.<sup>2,3,8,9</sup> However, this correlation was proved to be not universal when a series of polymers with the same chiral center but different chain constitutions were considered.<sup>10–13</sup> Nevertheless, banding in the spherulites could be observed for almost all the chiral polymers or even organic and inorganic compounds with a chiral structure.<sup>1,10</sup>

Poly(L-lactide) (PLLA) is a biodegradable and biocompatible polymer with main-chain chirality that is widely used in biomedical and environmental

fields.<sup>14,15</sup> The spherulitic morphology of PLLA is quite debated in the literature. Frequently, morphological evidence for PLLA has shown nonbanded spherulites.<sup>16–20</sup> Furthermore, Gazzano et al.<sup>19</sup> investigated the spherulitic structure of PLLA on the scale of several micrometers, using microfocus X-ray diffraction with synchrotron radiation, and concluded that no lamellar twisting existed in pure PLLA. However, Xu et al.<sup>21</sup> obtained banded spherulites of PLLA recently through a crystallization-after-annealing procedure or through isothermal crystallization after samples were melted at a temperature far above the melting temperature for a longer time, although the authors obtained common spherulites of PLLA via the typical direct isothermal crystallization procedure. Di Lorenzo<sup>22</sup> recently obtained band-like spherulites of PLLA through cooling at 5°C/min from the melt. Tsuji and Ikada<sup>23</sup> even reported a banded texture for a solution-cast PLLA film.<sup>23</sup>

In this work, we have investigated the spherulitic morphology of PLLA as a function of the crystallization temperature ( $T_c$ ) and molecular weight. We show for the first time that a clear banding-to-nonbanding morphological transition takes place at a critical temperature for the PLLA with a lower molecular weight. On the basis of the special nature of main-chain chirality in PLLA and the nonbanded spherulitic morphology observed in a certain temperature region, the role of  $T_c$  in the correlation of the lamellar twisting and main-chain chiral structure of polymers is discussed as well.

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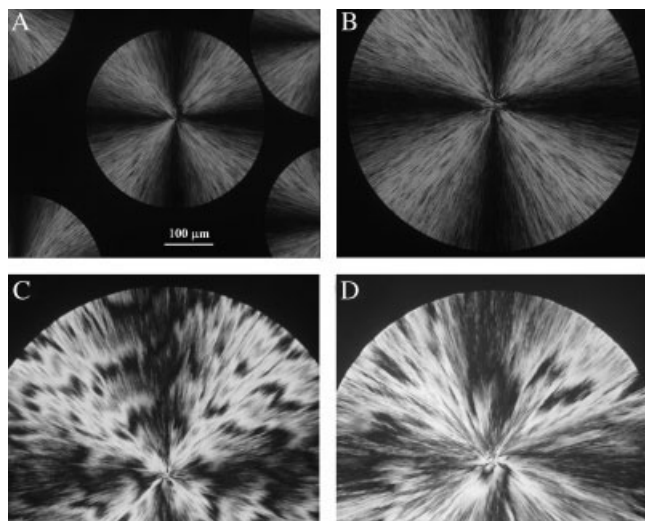
## EXPERIMENTAL

The materials were from Purac Biochem (Netherlands) and had two inherent viscosities: 1.75 (PLLA1) and 5.87 dL/g (PLLA2). The number-average molecular weights and weight-average molecular weights of the polymers were evaluated with gel permeation chromatography (LC 10A, Shimadzu, Japan) using polystyrene as a standard and chloroform as a solvent. For PLLA1, the number-average molecular weight and weight-average molecular weight were 86,000 and 151,000, respectively, and for PLLA2, the number-average molecular weight and weight-average molecular weight were 269,000 and 301,000, respectively. The melting peak temperatures were about 178°C for PLLA1 and 180°C for PLLA2, as measured with a PerkinElmer (Waltham, MA) DSC7 during a heating run (2°C/min) of the melt-quenched specimens.<sup>24</sup>

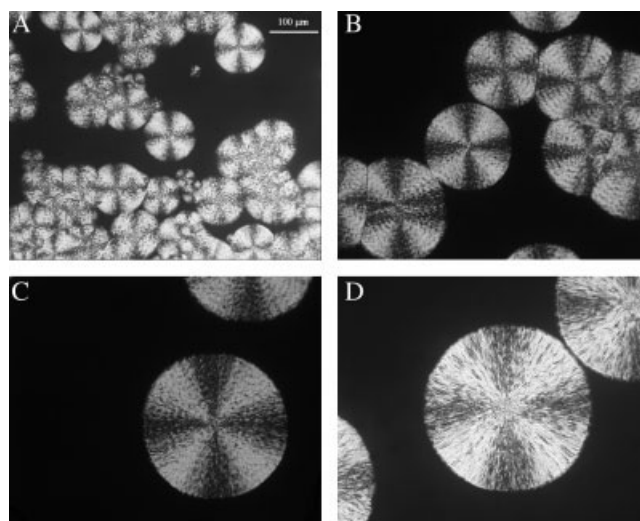
The samples for optical microscopy were melted between two glass slides at 210°C, and gentle pressure was applied to the upper glass to squeeze the melt into a very thin film. The prepared slides were moved onto a Mettler (Columbus, OH) FP80 hot stage and kept at 210°C for 3 min under a nitrogen atmosphere, cooled quickly to a designated  $T_c$ , and then held at that  $T_c$  for isothermal crystallization. The morphology was observed with an Olympus (Center Valley, PA) BH-2 polarizing microscope equipped with a digital camera system.

## RESULTS AND DISCUSSION

Figures 1 and 2 show a series of polarized optical micrographs for PLLA1 and PLLA2 samples isothermally crystallized at various  $T_c$  values. In PLLA1,



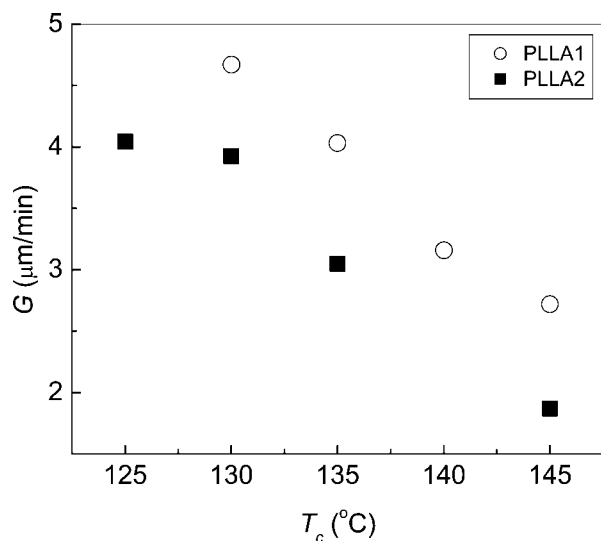
**Figure 1** Spherulitic morphology of PLLA1 partially crystallized at various  $T_c$  values: (a) 130, (b) 135, (c) 140, and (d) 145°C. The scales for all the graphs are the same as that of image a.



**Figure 2** Spherulitic morphologies of PLLA2 partially crystallized at various  $T_c$  values: (a) 125, (b) 130, (c) 135, and (d) 145°C. The scales for all the graphs are the same as that of image a.

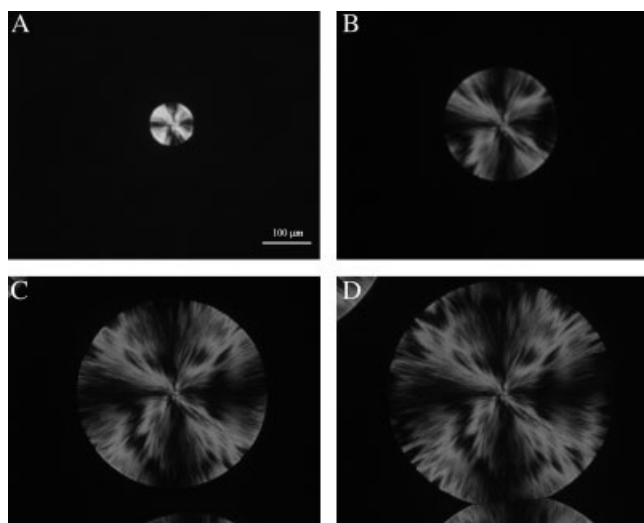
banded spherulites appear at 140 and 145°C, whereas at lower  $T_c$  values (135 and 130°C), non-banded spherulites appear. In PLLA2, banded spherulites appear at 135 and 130°C, whereas at 125 and 145°C, it is not easy to distinguish whether the spherulites are banded or not. The average band spacing of the spherulites for PLLA1, obtained at 140°C, is  $\sim 130 \mu\text{m}$ , whereas the band spacings of the spherulites for PLLA2, obtained at 130 and 135°C, are  $\sim 14 \mu\text{m}$ . The band spacing of the PLLA spherulites significantly decreases with increasing molecular weight, as observed in other polymers.<sup>3</sup> The crystal growth rates of the PLLA spherulites were derived from the slopes of the lines obtained through the plotting of the spherulite radius against time. The obtained crystal growth rates are plotted as a function of  $T_c$  in Figure 3. In this temperature range, the spherulite growth rate decreases with increasing  $T_c$  for both PLLA1 and PLLA2. Moreover, the crystal growth rate of PLLA decreases with an increase in the molecular weight, as observed by other authors.<sup>25,26</sup> There is no simple correlation between the spherulite growth rate and the corresponding band spacing when different polymers are compared. For instance, spacings in the range of 1–10  $\mu\text{m}$  were found both with a very rapid rate of 1–250  $\mu\text{m/s}$  in polyethylene and with a very slow rate of  $10^{-4}$ – $10^{-2} \mu\text{m/s}$  in  $\alpha$ -poly(vinylidene fluoride), whereas bands with large spacings around 100  $\mu\text{m}$  appeared at 1.5  $\mu\text{m/s}$  in poly(ethylene oxide) and at 0.1  $\mu\text{m/s}$  in  $\beta$ -polypropylene.<sup>3</sup>

The observations from Figures 1 and 2 clearly show that banded spherulites of PLLA can be observed via direct isothermal crystallization from the melt. These results do not contradict the mor-



**Figure 3** Spherulite growth rate ( $G$ ) as a function of  $T_c$  for PLLA samples with different molecular weights.

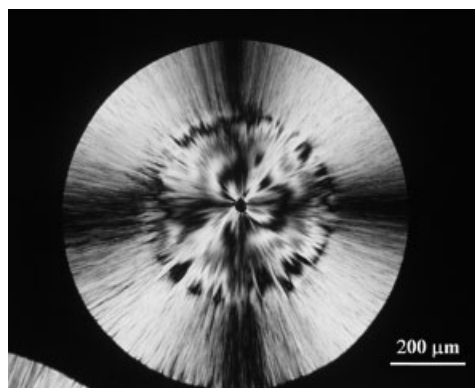
phological evidence of nonbanded spherulites in PLLA, which has been frequently reported in literature.<sup>16–20</sup> One possibility for the observations of nonbanded spherulites is that the apparent nonbanded spherulites might actually contain crystals that twist with a period larger than the spherulite radius or with a too short period, depending on the molecular weight of PLLA. For example, as shown in Figure 4, only a nonbanded spherulitic morphology can be seen at the early crystallization stage of PLLA1, whereas a banded morphology appears gradually with the further development of crystallization. Another possibility is that the samples were isothermally crystallized in a temperature region in which



**Figure 4** Polarized optical micrographs of PLLA1 spherulites isothermally crystallized at 140°C from the melt for different times: (a) 16.4, (b) 37.4, (c) 65.6, and (d) 73.6 min. The scales for all the graphs are the same as that of image a.

no lamellar twisting occurs. For instance, Gazzano et al.<sup>19</sup> performed an excellent investigation of the spherulites of PLLA, using microfocuss X-rays from synchrotron radiation, which has been shown to be a powerful technique for obtaining direct evidence of a gradual change in a unit cell's orientation along the spherulite radius on the scale of several micrometers.<sup>27,28</sup> A sample of PLLA (viscosity-average molecular weight = 140,000) was prepared by isothermal crystallization at 135°C from the melt. The graph of the sample from polarized optical microscopy showed a nonbanded spherulitic morphology, whereas the unit cell from microfocuss X-rays lacked any twisting.<sup>19</sup>

As shown in Figure 1, a banding-to-nonbanding morphological transition takes place in PLLA1 at a critical  $T_c$ , being in line with the observations in several other systems.<sup>29–32</sup> To confirm this morphological transition, we performed a two-step isothermal crystallization experiment, and the graph is illustrated in Figure 5. The center of the spherulite shows a banded spherulite at 138°C, and then a nonbanded morphology is formed at 130°C. This observation is in agreement with what has been observed in poly(trimethylene terephthalate)<sup>32</sup> but is contrary to observations by Rego Lopez and Gedde,<sup>33</sup> who observed a nonbanding-to-banding morphological transition in binary linear polyethylene blends with decreasing  $T_c$ . Poly(trimethylene terephthalate) and the binary linear polyethylene blends are both achiral polymers. One may relate the morphological transition in PLLA to the regime transition because a transition from regime II to regime III has been reported in PLLA in almost this temperature region.<sup>34</sup> However, this may be a coincidence only because it is a common phenomenon in many systems that the variation in the temperature dependence of the crystallization rate leads to a change in the crystallite morphology.<sup>35–37</sup> Recently, Di



**Figure 5** Polarized optical micrograph of a PLLA1 spherulite successively crystallized under two-step isothermal crystallization (138–130°C).

Lorenzo<sup>22</sup> dealt with the crystallization behavior of PLLA over a very wide range of  $T_c$  values (75–165°C) and showed an unusual bell-shaped crystallization rate curve with a discontinuity that was not associated with morphological changes in PLLA spherulites observed by optical microscopy.<sup>22</sup> Other mechanisms, such as a second-order transition<sup>35,38</sup> and a nonequilibrium phase transition,<sup>32</sup> have been proposed also. Nevertheless, it seems that the origin of the morphological transition is still somewhat unclear, and further investigation is required.

For the present, however, we focus on the observation of nonbanded spherulites in PLLA1 samples at lower  $T_c$  values and the main-chain chiral structure of PLLA. Earlier studies presented a strong correlation between the main-chain chirality and the sense of lamellar twisting in banded spherulites in several chiral polymers, such as silk fibroin,<sup>39</sup> the (*R*)- and (*S*)-enantiomers of polyepichlorohydrin and of poly(propylene oxide),<sup>8,9</sup> and poly(3-hydroxybutyrate).<sup>2,3,9</sup> However, exceptions could still be found when more chiral polymers were considered.<sup>10–13</sup> For example, in a series of synthetic liquid-crystalline main-chain nonracemic chiral polyesters, the lamellar twist sense depends on the odd or even numbers of atoms in the aliphatic segment.<sup>12,13</sup> It is noteworthy that, although previous studies attempted to relate the main-chain chiral structure to the lamellar twisting sense in banded spherulites, they did not consider other external contributing factors, such as  $T_c$ . In fact, it has been reported that in certain macromolecules, chain conformations can be changed between plus and minus, a so-called helix-helix transition, with only a change in the temperature.<sup>40,41</sup> As presented in Figures 1 and 5,  $T_c$  plays a critical role in banding or nonbanding in spherulites of PLLA1. Nonbanded spherulites could be clearly observed in PLLA1 at a lower  $T_c$ . Next, it is very important to judge whether the nonbanded spherulites (in Fig. 1) lack any lamellar twisting. We note that the radius of the nonbanded spherulite obtained at 135°C is around 300 μm, which is much higher than the banding spacings of the banded spherulites obtained at 140°C. Because the temperature difference between 135 and 140°C is very small, it is hard to think that the nonbanded spherulites obtained at 135°C actually contain crystals that twist with a period larger than the spherulite radius or with a too short period. Hence, it is reasonable to presume that the nonbanded spherulites obtained at 135°C lack any twisting. The investigation performed by Gazzano et al.<sup>19</sup> could also give strong support for the assumption. The authors indeed revealed the existence of nonbanded spherulites lacking any lamellar twisting in PLLA. This implies that, at the special  $T_c$ , the correlation between the sense of lamellar twisting and the main-chain chiral structure for PLLA is

lost. Thus, further attention is required to check any universal behavior of the possible role of  $T_c$  in the correlation between the sense of lamellar twisting and the main-chain chiral structure in other chiral polymers.

## CONCLUSIONS

It has been shown for the first time that a clear banding-to-nonbanding morphological transition in PLLA takes place at a critical temperature. The band spacing of PLLA spherulites significantly decreases with increasing molecular weight. It is also possible that  $T_c$  may have an effect on the relationship between the sense of lamellar twisting and the main-chain chiral structure in PLLA.

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