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# ROLE OF THERMAL HISTORY ON THE THERMAL BEHAVIOR OF POLY(*L*-LACTIC ACID) STUDIED BY DSC AND OPTICAL MICROSCOPY

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The thermal behavior of poly(*L*-lactic acid) (PLLA) was studied with differential scanning calorimetry (DSC) and polarized optical microscopy. For amorphous PLLA samples, double cold crystallisation peaks were observed in the DSC traces during heating process, being strongly dependent on heating rates. The observation was discussed based on the assumption that the quenched PLLA sample presented some remaining metastable or a precrystalline phase. A small exothermal peak was observed before the main melting peak at low heating rates. The probable reason was discussed through melt-recrystallisation mechanism. Influence of thermal history on the cold crystallisation and melting behavior was also performed on heating process for PLLA samples.

***Keywords:*** *DSC, optical microscopy, poly(L-lactic acid), thermal behavior, thermal history*

## Introduction

Poly(*L*-lactic acid) (PLLA) is among the most important biodegradable synthetic polymers used in the biomedical field, in applications such as sutures, orthopaedic devices or in supports for drug delivery systems [1]. Thermal behavior is an important aspect characterizing the physical properties of semi-crystalline polymers. Recently, there has been much research on understanding the crystallisation and melting behavior of PLLA [2–12]. Besides crystallisation from the melt, PLLA may crystallise from the glassy state. The cold crystallisation of PLLA has not been appropriately addressed in [13, 14], especially if coupled with previous thermal histories, despite its interest in both academic and industrial points of view. Therefore, a more detailed research on this subject is needed as the information generated will contribute an overall understanding of the thermal behavior of the material. In this work, the non-isothermal cold crystallisation, coupled with previous thermal histories, and subsequently melting behavior were studied using differential scanning calorimetry (DSC). Polarized optical microscopy was also used to follow the development of morphology.

## Experimental

PLLA was from Purac Biochem with inherent viscosity 1.75 dL g$^{-1}$. The molecular mass $M_n$ and $M_w$ of the polymer were 86,000 and 151,000, respectively [14].

A thermal analysis was carried out with a Perkin Elmer DSC 7. Amorphous films of approximately 0.2 mm thickness was prepared by melting the material in a hot plate and quenched in cold water. No crystalline reflection was detected in the WAXS spectra [14]. Two groups of experiments were performed. One group comprised the heating of initially amorphous sample at various rates from 2 to 40 K min$^{-1}$ to obtain information about the cold-crystallisation and melting behavior. For another group experiment, samples were hold in a molten state (200ºC) for 3 min, then, the DSC traces were recorded during cooling at various rates from 2 to 32 K min$^{-1}$, and subsequent heating process at 10 K min$^{-1}$. Separate calibrations for baseline were made for all heating and cooling rates. Calibration for the temperature and energy scale was carried out using a pure indium standard. Separate calibrations were made for all heating rates. Specific and careful precautions were taken for accurate temperature calibration on cooling. 4-Cyano-4'-octyloxi-biphenyl (M24), which was kindly supplied by Prof. Schick (University of Rostock, Germany), was used for the calibration, and the procedure followed that suggested in [15]. To prevent extensive thermal degradation, each sample was used only once and all the runs were carried out under a nitrogen atmosphere.

An Olympus BH-2 polarizing microscope, equipped with a video camera system and a Mettler hot-stage (FP80) was used for morphology observation. The material was melt between microscope glass slides in a hot stage, then, quenched by air to obtain amorphous structure.

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## Results and discussion

Figure 1 shows DSC scans of amorphous PLLA samples at various heating rates from 2 to 40 K min$^{-1}$. Double cold crystallisation peaks are observed at heating rates between 7.5 and 15 K min$^{-1}$. As the heating rate is reduced, the lower temperature peak shifts to lower temperature, while the higher temperature peak is more strongly affected by the heating rate reduction. Finally, the two peaks merged at below 7.5 K min$^{-1}$. However, for the heating rate 20 K min$^{-1}$, only one broad cold crystallisation is observed. For the case of the heating rate 40 K min$^{-1}$, almost no cold crystallisation is observed. This suggests that heating rate can significant influence the cold crystallisation behavior of PLLA.

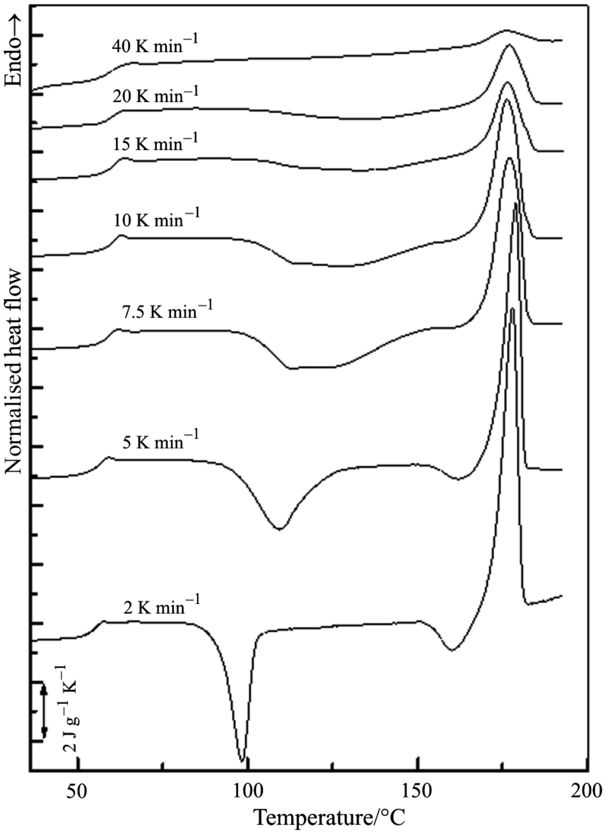

**Fig. 1** DSC traces of previous quenched PLLA heated from amorphous state at indicated rates

Similar double cold crystallisation peaks were reported from DSC curves for poorly crystallised poly(ethylene terephthalate) (PET) [16], and quenched poly(ethylene-*co*-butylene naphthalene-2,6-dicarboxylate)s (PEBN copolyesters) [17]. However, the nature of double crystallisation peaks is still unclear. Zhu and Ma [16] suggested that two kinds of amorphous regions existed for the properly treated PET samples: inter-spherulites amorphous region and inter-lamellar amorphous region. Further, the nature of the lower temperature peak was explained as the crystallisation of amorphous chains of inter-lamellae, and the higher temperature one was from the crystallisation of inter-spherulitic amorphous chains. Other probable reasons were attempted by Papageorgiou and Karayannidis [17] to explain the appearance of double peaks for PEBN copolyesters. Based on Keller and Cheng [18], it was suggested that the lower temperature peak might be related to the formation of original metastable crystals, and the higher one related to the formation of a more stable phase. The polymer crystal growth or secondary nucleation kinetics theory introduced by Lauritzen and Hoffman [19–21] was also attempted to understand the origin of the double peaks.

It was reported that thermal history played an important role on the quiescent cold crystallisation of PET [22]. For the melt quenched samples of PET at cooling rates beyond about 120 K min$^{-1}$, no crystalline reflections were detected in the WAXS spectra. However, the cold crystallisation rate was still strongly dependent on the cooling rate used to quench the samples from the melt. It was further suggested that a metastable or a precrystalline phase still remained after quenched [22]. Follow this, even though no crystalline reflection are detected in the WAXS spectra, the amorphous PLLA samples obtained in this study may be not completely amorphous, that is, a metastable or precrystalline phase remained. The metastable or precrystalline phase may act as self-nuclei. Besides this, a slow spontaneous nucleation from completely amorphous phase will also take place, which usually is thermal type. Therefore, the two competitive nucleation processes may be responsible for the double crystallisation peaks observed. The lower temperature peak is from the growth of initial nuclei, while the higher one is from the formation of new nuclei and crystal growth.

Microscope observations (Fig. 2) show that the nuclei concentration decreases with the increase of heating rate, and a spherulitic morphology is formed upon cold crystallisation process.

Apart from cold crystallisation peaks, the curves in Fig. 1, for heating rates from 2 to 5 K min$^{-1}$, show an apparent exothermal peak before the main melting peak. With increasing heating rate, the depth of the exothermal peak decreases, and finally disappears at heating rates higher than 15 K min$^{-1}$. The area of the main melting peak also decreases with increasing heating rates. The melt-recrystallisation model [23] can be used to explain this effect. This model suggests that, with the increase in temperature, the small and imperfect crystals will change successively into more stable crystals. That is, the melting and recrystallisation are competitive in the heating process. Since the recrystallisation is a time-consuming process, the quantity of the recrystallised crystals decreases with increasing

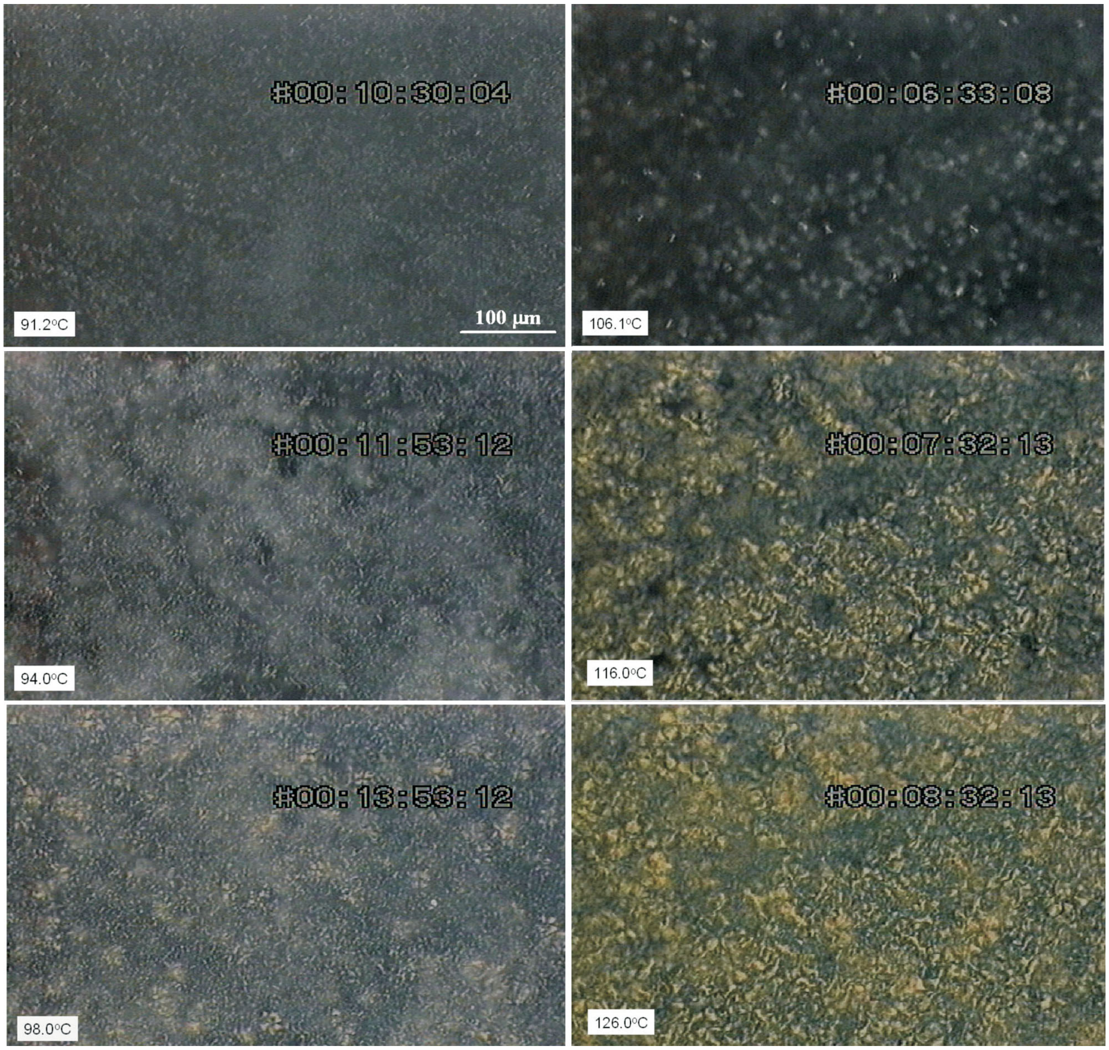

**Fig. 2** Microscope observation of PLLA heated from amorphous state at indicated rates, a – 2 K $\text{min}^{-1}$, b – 10 K $\text{min}^{-1}$

heating rate, which is in agreement with the observation that the depth of the exothermal peak decreases with increasing heating rate. This melt-recrystallisation behavior has also been observed by Yasuniwa *et al.* [12] through measurements performed at different heating rates from 0.5 to 20 K $\text{min}^{-1}$ for melt crystallised PLLA samples at 1 K $\text{min}^{-1}$. Besides the contribution of heating rate, the morphology developed before melting could also influence the melting behavior of PLLA [6]. For PLLA, a regime II to regime III transition was detected at 115ºC by Iannace *et al.* [6] and 120ºC by Di Lorenzo [9]. Therefore, for the experiments performed at lower heating rates, crystallisation developes at regime III, that is, the larger nucleation rates results in a larger number of crystals and finally to small and imperfect crystals. For experiments performed at higher heating rates, crystallisation developes at regime II, where crystals are more perfect than that developed at regime III. Therefore, the morphology differences formed at different heating rates may also be partly responsible for the observations above.

When PLLA is cooled from the melt, one crystallisation peak is observed at each run (Fig. 3a). The final degrees of crystallinity decrease from 0.300 to 0.002 and the onset temperatures of crystallisation (defined as the intersection temperature point of the extrapolated baseline and the line of the leading edge of the crystallization curve) decrease from 122.9 to 109.5ºC with an increase of cooling rate from 2 to 32 K $\text{min}^{-1}$ (Fig. 4). The degree of crystallinity above is obtained by comparing the enthalpy of melt crystallisation with the value of an infinitely large crystal 81.3 J $\text{g}^{-1}$ [2]. On subsequently heating at 10 K $\text{min}^{-1}$ (Fig. 3b), one cold crystallisation peak is observed for the samples cooled down at 2 K $\text{min}^{-1}$, while double peaks are observed for the samples cooled down between 4 and 32 K $\text{min}^{-1}$. It also can be seen that, with the increase of cooling rate, during the subsequently heating process, the peak area ratio of the higher temperature peak to the lower one increases. It can be explained that, with increasing cooling rate, the fully amorphous fraction in the samples increases, result-

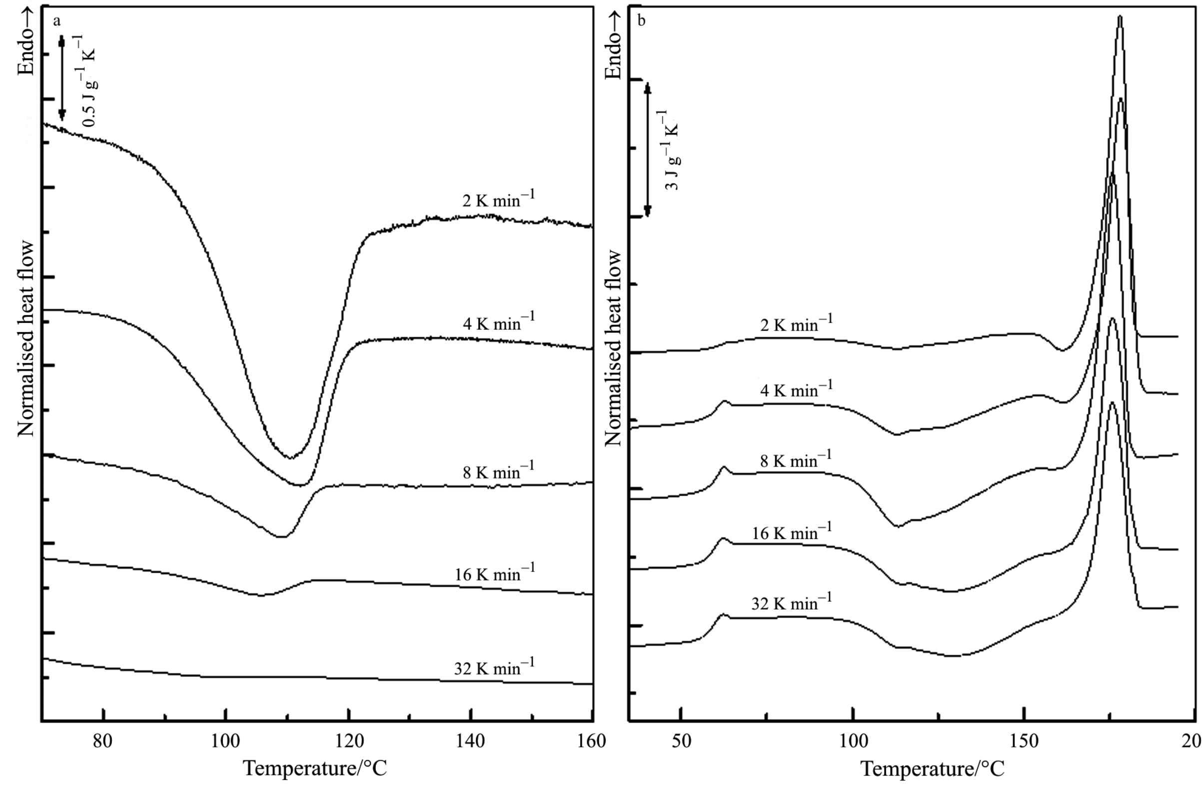

**Fig. 3** DSC traces of PLLA during a – cooling from the melt at indicated rates and b – subsequently heating process at 10 K min$^{-1}$

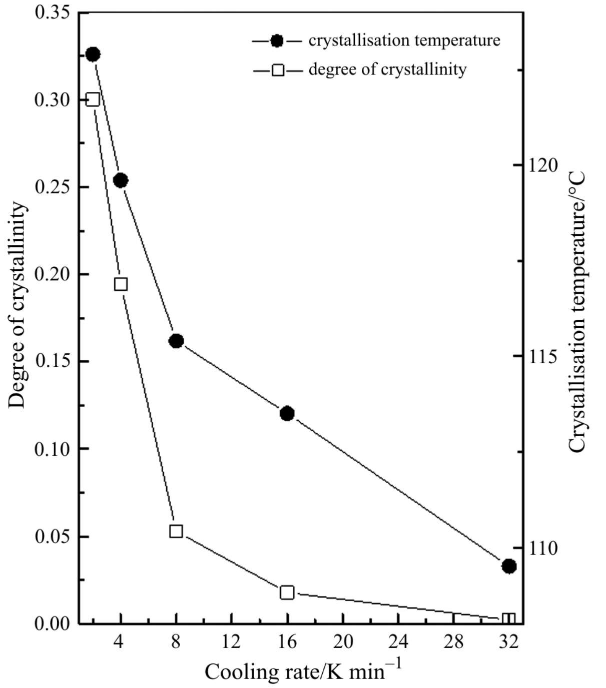

**Fig. 4** Degree of crystallinity and onset temperature of crystallisation *vs*. cooling rate, obtained from the data in Fig. 3a

ing in a higher contribution of spontaneous nucleation and growth during the subsequently heating process.

Microscope observation (Fig. 5) shows that the fully inter-spherulitic amorphous fraction of the sample significantly increases with increasing cooling rate. The initial structural differences should be responsible for the differences of cold crystallisation during heating process. Note that a considerable fraction of the amorphous phase will be present within the spherulites, with a completely different dynamics than that of the inter-spherulitic amorphous phase [24].

Again in Fig. 3b, during heating process at 10 K min$^{-1}$ after cooled from the melt at various rates, a small exothermal peak can be observed before the main melting peak. The depth of the exothermal peak decreases with increasing the previous cooling rate. This further suggests that the initial structure developed on melt crystallisation and the subsequently cold crystallisation can significantly influence the melting behaviour of PLLA. As mentioned before, the melt crystallisation of PLLA occurs mainly below 120ºC at all studied cooling rates, that is, crystallisation develops at regime III, resulting in small and imperfect crystals. During subsequently heating process, cold crystallisation develops mainly at regime II, resulting in more perfect crystals formed. Therefore, the higher of the previous heating rate, the more perfect crystals developed before melting, which may be responsible for the observations above.

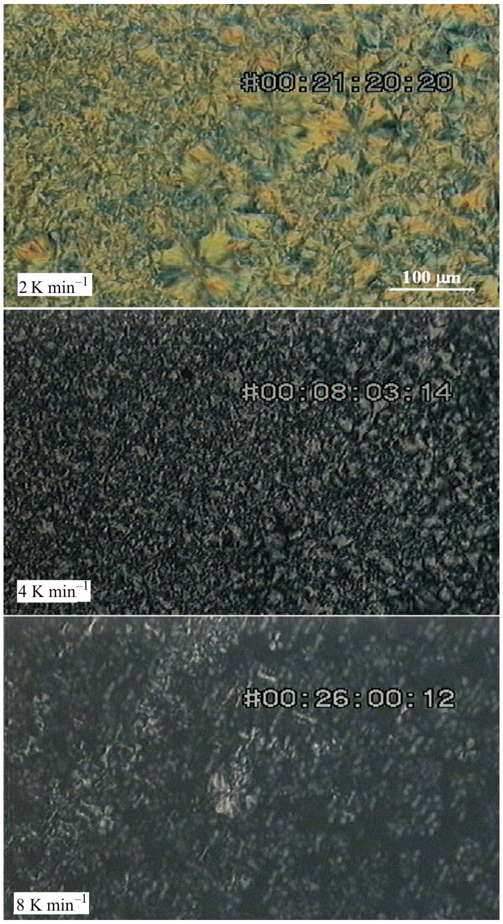

**Fig. 5** Microscope observation at room temperature of the final morphology of PLLA after cooling down from melt at indicated rates

## Conclusions

Double cold crystallisation peaks are observed in the DSC traces during heating process for amorphous PLLA samples. It is probable that the initial amorphous PLLA sample is not completely amorphous, that is, a metastable or a precrystalline phase remains. Therefore, the competition between the crystallisation from the initial nuclei and the crystallization from spontaneous nucleation may be responsible for the appearance of double peaks. For the curves of heating rates from 2 to 5 K min$^{-1}$, an apparent exothermal peak is observed before the main melting peak. With increasing heating rate, the depth of the exothermal peak decreases, and finally disappears at heating rates higher than 15 K min$^{-1}$. It is probable that with increasing temperature, the small and imperfect crystals will change successively into more stable crystals through the melt-recrystallisation mechanism, giving rise to the exothermic signal before the melting peak. Since the recrystallisation is a time-consuming process, the quantity of the recrystallised crystals decreases with increasing heating rate, which is in agreement with the observation that the depth of the exothermal peak decreases with increasing heating rate.

One crystallisation peak is observed for PLLA during cooling from the melt. The obtained degrees of crystallinity dramatically decrease from 0.300 to 0.002 with an increase of cooling rate from 2 to 32 K min$^{-1}$. The initial structural differences can significantly influence the subsequent cold crystallisation and melting behavior.

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