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The Crystallization and Melting Processes of Poly(L-lactic acid)

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Summary: A throughout investigation of crystallization and melting behavior of poly(L-lactic acid) is detailed in this contribution. Crystallization analyses, conducted in both isothermal and non-isothermal conditions, revealed the occurrence of a sudden acceleration in phase transition rate in the temperature range between 100 and 118 °C. This unusual increase, due to very high rates of spherulite growth, seems not related to morphological changes of PLLA spherulites, nor to unexpected variations in nucleation rate. DSC analyses disclosed multiple melting behavior of PLLA, depending on crystallization temperature. At low temperatures the very high crystallization rates lead to the achievement of low values of crystalline degree, with formation of small and/or defective crystals, which have a large tendency to reorganize into more stable structures during the heating scan that leads to complete fusion. The multiple melting process of PLLA was also analyzed at different heating rates.

Keywords: crystallization; multiple melting; phase transitions; poly(lactic acid); thermal properties

Introduction

In recent years, relatively low cost monomer synthesis has risen interest in large volume production of fibers and films of poly(L-lactic acid).[1–3] The monomer can be derived from renewable agricultural sources, to obtain biocompatible products that can be biodegraded to non-toxic substances.[4,5] In addition, the mechanical performances of poly(lactide)s are comparable to those of commercial macromolecules of wide use, which led to growing academic and industrial interests in these materials.

The monomer exists in three stereoisomeric configurations: L-lactide, D-lactide, and *meso*-lactide (SS, RR, and RS, respectively). Control over the ultimate stereochemistry in the polymer depends on monomer choice, initiating species, and reaction conditions. As a result, high molecular mass poly(lactic acid) can range from atactic to highly isotactic.

The physical and mechanical properties of stereoregular polymers, like isotactic poly(L-lactic acid) (PLLA), largely depend on solid-state morphology and degree of crystallinity. Due to its rather low crystallization rate, compared to other thermoplastics, it is rather easy to define processing conditions to obtain PLLA products with a wide range of degrees of crystallinity, thus varying product properties. A key factor in both medical and industrial applications of polylactides may lay in a full establishment of degradation rate, which, in turn, strongly depends on crystallinity degree, as crystalline lamellar organization plays a crucial role in the degradation mechanism.[6–9] Therefore, an intense research work is needed to correlate the thermal hystory imparted during processing to the final microstructure.

This article summarizes a throughout investigation carried out by our research

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group on crystallinity development in PLLA,[10–12] including primary crystallization kinetics, as well as structural reorganization of the crystal phase occurring during fusion. Discussion of results has been conducted upon taking into account existing data on thermal properties of PLLA.

Thermodynamic heat capacity data of liquid and solid PLLA have been recently updated, including enthalpy, entropy, and Gibbs functions, as well as temperature and heat of fusion of 100% crystalline material.[13] Crystallization kinetics from the melt has been analyzed by a number of research groups.[14–18] The maximum in crystallization rate is often observed around 100 °C, with a discontinuity in phase change kinetics below 120 °C. A similar sudden variation in crystallization rate was also reported for poly(ethylene adipate).[19] Different hypotheses have been put forward to explain the discontinuity in crystallization kinetics of PLLA, which has been linked to a transition in regime II-III growth of spherulites,[14,18] to a difference in the rates of isothermal thickening and secondary nucleation,[18] and to solidification into a different crystal modification.[20] It will be shown in this contribution that the sudden increase in crystallization rate of PLLA below 120 °C is caused by a sudden acceleration in radial growth rate of PLLA spherulites, and is not associated to variations in nucleation rates, nor to morphological changes in the appearance of PLLA spherulites.

Some investigations of the melting behavior of PLLA have also been reported in the literature.[21–23] The influence of crystallization rate on fusion behavior of PLLA was analyzed by Yasuniwa *et al.*, who showed the occurrence of double melting peaks when crystallization is conducted at low cooling rates.[22] The observation of multiple melting endotherms is a common phenomenon for synthetic macromolecules, being observed for several other polyesters, including poly(ethylene terephthalate) (PET),[24] poly(trimethylene terephthalate),[25] poly(butylene terephthalate),[26–28] poly(3-hydroxybutyrate) and its copolymers with 3-hydroxyvalerate.[29] However, a general explanation of such a complex process has not been achieved yet. For PLLA, a map of the dependence of the multiple melting behavior on crystallization conditions is illustrated in this contribution.

Experimental Part

Material

A poly(L-lactic acid) of molecular mass $M_w = 101{,}000$ Da, produced by Boehringer Ingelheim (Germany) and received in form of small chips, was used without further purification nor thermal treatment.

Calorimetry

The thermal properties of PLLA were measured with a Mettler DSC-30 differential scanning calorimeter. The apparatus was calibrated with pure indium, lead and zinc standards at various scanning rates. Dry nitrogen gas with a flow rate of 20 ml min^{-1} was purged through the cell during all measurements and thermal treatments. A fresh sample was used for each experimental measurement, in order to minimize thermal degradation. Each measurement was repeated three times to improve accuracy.

For the analysis of bulk kinetics of isothermal crystallization, PLLA was heated from 30 to 200 °C at a rate of 20 °C/min, melted at 200 °C for 2 minutes, then rapidly cooled to the desired T_c, and allowed to crystallize. The scanning rate used to reach T_c from the melt (50 °C/min) was high enough to prevent crystallization during cooling, as determined by preliminary analyses. After completion of the phase transition, the sample was heated from T_c to 210 °C using various linear heating rates, as detailed in the text. Crystallization kinetics of PLLA was analyzed also in non-isothermal conditions. The samples were heated from 30 to 200 °C at a scanning rate of 20 °C/min, kept at this temperature for 2 min, then cooled to room temperature at various rates.

Optical Microscopy

A Zeiss polarizing optical microscope equipped with a Linkam TMHS 600 hot stage was used to determine growth rates and morphology of PLLA spherulites. A small piece of PLLA, weighing about 0.3 mg, was squeezed between two microscope slides, then inserted in the hot stage. Isothermal and non-isothermal crystallization analyses were conducted, after melting the sample with the same thermal history detailed above for calorimetry studies. Dry nitrogen gas was purged throughout the hot stage during all measurements and thermal treatments. The radius of growing PLLA crystals was monitored during phase transition by taking photomicrographs with a JVC TK-1085E Video Camera. Spherulite radii were measured with the software Image-Pro Plus 3.0.

WAXS Analysis

Wide-angle X-ray scattering analysis (WAXS) was carried out on a Philips (PW 1050 model) powder diffractometer (CuNi-filtered radiation) equipped with a rotative sample holder device.

Results and Discussion

Figure 1 illustrates the plot of the half time of crystallization ($\tau_{½}$) of poly(L-lactic acid), measured in isothermal conditions after cooling from the melt as a function of temperature (T_c). The $\tau_{½}$ vs. T_c curve presents a broad minimum around 108 °C and a discontinuity around 116–118 °C, evidenced by the arrow in Figure 1. In the same temperature range, an irregular trend can be noticed also in the spherulite growth rate data (G), as exhibited in Figure 2.

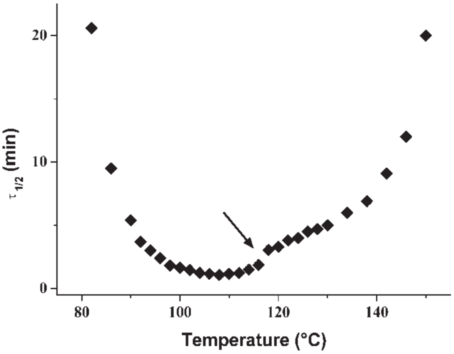

Figure 1.
Half-time of crystallization ($\tau_{½}$) of PLLA as a function of the isothermal crystallization temperature.

G values of PLLA were measured using both isothermal and non-isothermal methods. With the conventional isothermal method, the growth of a spherulite radius (r) is recorded as a function of time (t), at a fixed crystallization temperature, until solidification is terminated by impingement on neighboring spherulites.[30] In all the analyzed T_c range, for PLLA the plot of r vs. t is linear and its slope gives the value of G at the temperature selected for the measurement. Conversely, in the non-isothermal procedure, the spherulite radius is determined during cooling from the melt at a constant rate, and G is estimated by taking the first derivative of the r vs. T plot at each experimental point, following the procedure detailed in Ref. 31–33.

The non isothermal method was applied with cooling rates ranging from 1 to 5 °C/min, using also a self-nucleation procedure in order to expand the temperature range of experimental data: PLLA was cooled from the melt at 1 °C/min until the first spherulite became visible, then the temperature was raised to just below the melting point and a second cooling at constant rate was performed. The radius of the growing spherulite was monitored during the second cooling as a function of temperature. With the self-nucleation procedure, G data were obtained at temperatures as high as 174 °C. Isothermal G data were also determined at a few selected temperatures, to confirm the reliability of the non-isothermal method, as illustrated in the Figure.

In addition, cold crystallization was exploited to gain data at low temperatures, by quenching a partially crystallized PLLA, containing only one or a few growing crystallites, then heating to the desired T_c, as the high crystallization rate of PLLA prevents the measurement of spherulite

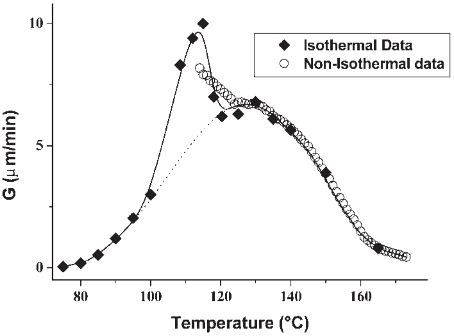

Figure 2.
Spherulite growth rates of PLLA measured in isothermal and non-isothermal conditions. The solid line was drawn as a possible interpolation of spherulite growth rates data.

growth rates at low temperatures after direct cooling from the melt. The combined use of isothermal and non-isothermal methods permitted to measure *G* at temperatures ranging from 75 to 174 °C, as shown in Figure 2, an interval much larger than that obtainable with the traditional isothermal method.[34] The *G* vs. T_c curve displays a broad maximum around 130 °C, and a sharper peak at 115 °C, as the plot diverges from the typical bell-shaped curve below 120 °C, where the rate of spherulite growth becomes much higher. *G* values measured in non-isothermal conditions during cooling at a constant rate, after self-nucleation, also deviate from the bell-shaped curve in the same temperature interval.

The discrepancy below 120 °C in growth rate values obtained during cooling with data measured in isothermal conditions arises from the very high crystallization rate of PLLA in the narrow temperature range below 120 °C. The rapid development of latent heat may cause some local heating and create thermal gradients within the sample, which produces an increase in the experimental uncertainty associated with the experimental determination of *G*, both in isothermal and non-isothermal conditions. The error associated to non-isothermal measurements is even higher, since temperature is continuously reduced during analysis.[35]

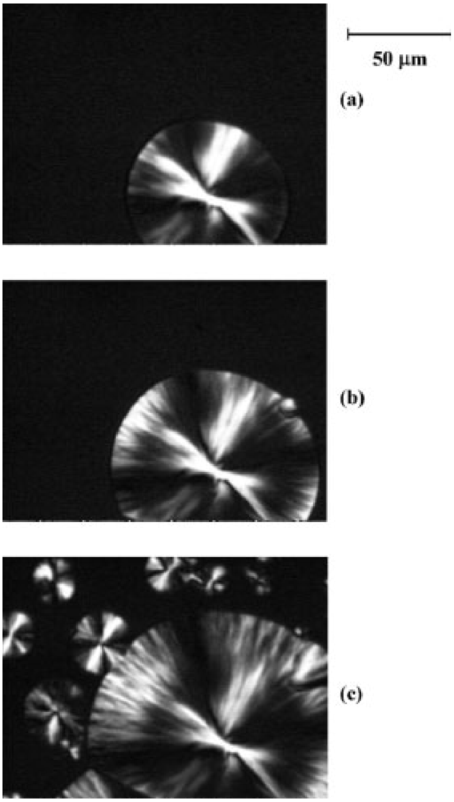

Figure 3.
Optical micrographs of PLLA spherulites grown during cooling from the melt at 5 °C/min: (a) 130 °C; (b) 120 °C; (c) 110 °C.

For a given cooling rate, *G* data were taken from the same spherulite during its growth. As shown in Figure 3, morphology of the growing spherulite does not vary in the whole explored temperature range, at least within the resolution power of optical microscopy, even during the very rapid increase of linear growth rate below 120 °C, as shown in Figure 3. This probes that that the sudden increase in crystallization rate is not due to a varied spherulitic morphology. Figure 3 gives also indications on the effects of temperature on nucleation rate of PLLA spherulites. Besides the large spherulite, smaller ones continuously appear when temperature is decreased, as illustrated in Figures 3-b and 3-c. No sudden increase in nucleation rate can be drawn from optical microscopy analyses, hence the abrupt variation in crystallization rate cannot be not linked to changes in nucleation behavior.

The sudden change in the rate of phase transition may be caused by crystal growth in a different structural modification, favored at temperatures below 120 °C. PLLA is a polymorph polymer that can solidify in three crystal modifications, identified as α, β, and γ.[36–41] WAXS analyses conducted after isothermal crystallization at various temperatures indicate that, after the thermal treatments used to follow the crystallization kinetics, only the α form was present. However, this does not exclude the possibility that a different crystal modification may initially develop, then transform into the more stable α form. The different modification might be characterized by a faster crystal growth, thus explaining the sudden jump in phase transition rate below 120 °C.

In the same temperature range, a discontinuity can be observed also in the temperature dependence of degree of crystallinity. The crystal fraction (w_c) of PLLA after isothermal crystallization, determined using the heat of fusion of 100% crystalline PLLA in the α form, $\Delta H = 91$ J g^{-1},[13] was found to be strongly dependent on temperature, as illustrated in Figure 4, that reports a monotonous increase of w_c with T_c in all the analyzed crystallization range. The variation of w_c with T_c is quite large, as it raises from 41 to 67% when T_c is increased from 82 to 146 °C. The experimental w_c values seem to follow two different trends with temperature, with a slope ratio quite close to 2. The break in the plot around 120 °C might be correlated to the sudden acceleration in phase transition rate detailed above, as the very high crystallization rates in this temperature range, lead to very poor crystallization.

The melting process of PLLA after isothermal crystallization was analyzed as a function of T_c. DSC thermograms, obtained at a heating rate of 20 °C/min after isothermal crystallization, are reported in Figure 5 for a few selected T_c. The DSC curves display several transitions: a broad and weak exotherm (''Peak I''), a small and narrow endotherm (''Peak II''), a second sharper exotherm (Peak III), and a final large fusion endotherm (Peak IV). Position and dimension of the various peaks strongly depend on crystallization temperature. For $T_c < 120$ °C, upon increase of T_c, both Peak II and Peak III move to higher temperatures, Peak II becoming more pronounced and Peak III less intense. Also the position of the final endotherm (Peak IV) is affected by crystallization conditions, as it slightly moves towards higher temperatures with T_c. For $T_c > 120$ °C, Peak II merges with Peak IV, and Peak III becomes less pronounced with the increase of T_c, being recrystallization

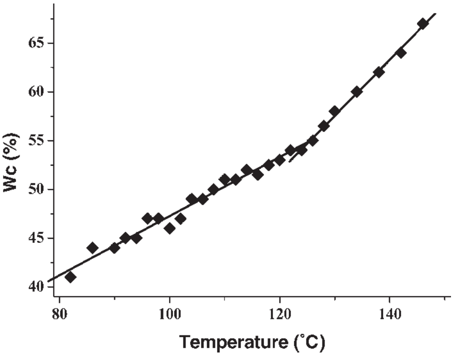

Figure 4.
Dependence of crystal content (w_c) on crystallization temperature.

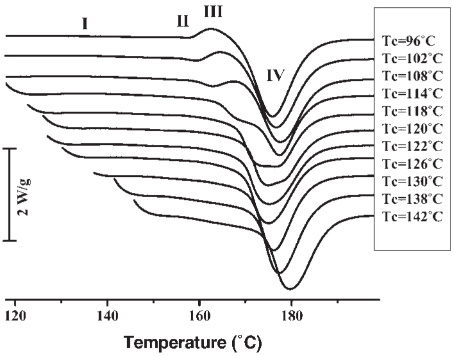

Figure 5.
DSC thermoanalytical curves of PLLA, isothermally crystallized at the indicated temperatures; heating rate 20 °C/min.

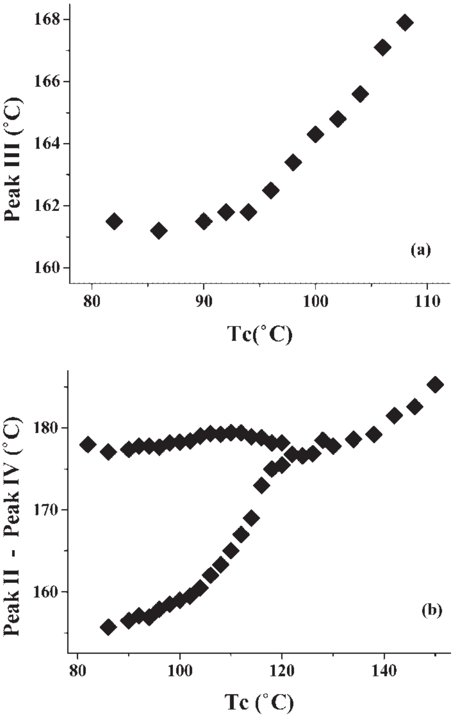

Figure 6.

T_c dependence of (a) main reorganization exotherm, and (b) endothermic peaks, as determined from Figure 5.

obscured by the more intense melting.[26] When crystallization is performed at higher temperatures, a single melting peak is always present, and its position is strongly affected by T_c.

The influence of isothermal crystallization temperature on recrystallization and partial and final melting is depicted in Figures 6-a and 6-b. The temperature where the maximum in the major exothermic transition occurs (Peak III) is reported in Figure 6-a as a function of the isothermal crystallization temperature. Peak III remains roughly constant with temperature up to $T_c = 94\,°C$, then linearly increases. The variation of the endotherms with crystallization temperature, illustrated in Figure 6-b, reveals an overall, but not continuous increase of T_m with T_c. The lower endotherm monotonously raises with T_c in all the analyzed temperature range, whereas the final endotherm remains roughly constant with T_c up to about $T_c = 130\,°C$, then increases with T_c. For T_c ranging from 118 to 130 °C, a slight drop of T_m with T_c can also be inferred from Figure 6-b.

To better clarify the structural reorganization of the crystal phase of PLLA that leads to multiple melting, the effect of a low heating rate on melting behavior was determined, as summarized in Figure 7, that the reports DSC curves obtained at a 2 °C/min after isothermal crystallization at various T_c. Again, one or multiple endotherms, sometimes interrupted by exotherms, can be observed, depending on crystallization temperature, and peak positions are strongly affected by crystallization temperature. Peak II increases with T_c in all the analyzed temperature range. Also the temperature of the final endotherm raises with T_c, but only up to $T_c = 130\,°C$, as the final melting point for $T_c > 130\,°C$ occurs at lower temperatures, as exampled in Figure 7 for $T_c = 142\,°C$. In addition, compared to Figure 5, for $T_c = 130\,°C$, an additional endotherm becomes visible, with the peak centered around 180 °C.

The occurrence of multiple melting behavior in PLLA can be linked to crystal reorganization during heating. The very high crystallization rates, typical of $T_c < 120\,°C$, may lead to largely imperfect

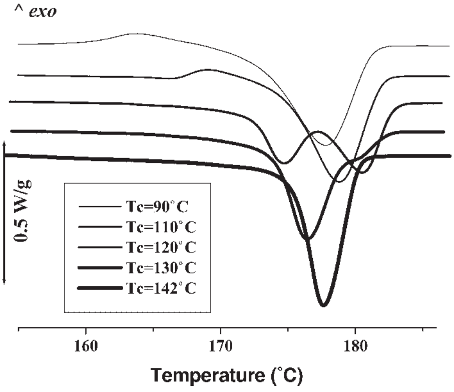

Figure 7.

DSC thermoanalytical curves of PLLA, isothermally crystallized at the indicated temperatures; the heating rate was 2 °C/min.

crystals, which have a high tendency to reorganize into more stable structures during the heating scan that follows the isothermal crystallization. Reorganization during heating can be inferred from the two recrystallization exotherms displayed in Figure 5 (Peaks I and III), as well as by the partial melting addressed as Peak II. For $T_c > 120\,^\circ$C, Peaks II, III, and IV merge into a single endothermic transition when the sample is heated at 20 °C/min after isothermal crystallization. With the experimental conditions used, when $T_c < 120\,^\circ$C, the measured final endotherm is ascribed to the crystals largely perfected during the heating scan, that melt as Peak IV, whereas the final melting peak for $T_c > 120\,^\circ$C is attributed to Peak II. In other words, the apparent decrease of melting point for $120 < T_c < 130\,^\circ$C, shown in Figure 7, is due to the lower extent of recrystallization/crystal perfection processes during heating, as when PLLA is crystallized at Tc > 120 °C, the observed melting endotherm is Peak II, and not Peak IV, as it occurs for crystals grown at lower T_c. Similarly, the use of a low scanning rate induces a larger extent of structural reorganization, which results in the appearance of Peak IV for $T_c = 130\,^\circ$C when a heating rate of 2 °C/min is used instead of 20 °C/min. For $T_c = 142\,^\circ$C, the thermal stability of the initial crystals is much higher. This leads to a lower occurrence of partial melting and subsequent recrystallization process, involving poorer crystal perfection during heating, which results in a lower temperature of final melting (Peak II) when low heating rates are used.

Conclusions

The analysis of crystallization and melting processes of poly(L-lactic acid) has evidenced a series of peculiarities. Crystallization rate of PLLA is unusually high at temperatures between 100 and 118 °C. This behavior has to be ascribed to the high rate of radial growth of PLLA spherulites, whose origin has still to be clarified, but seems not be associated to morphological changes of PLLA spherulites. No particular increase of nucleation rate has been evidenced in this temperature range.

PLLA crystals have a large tendency to reorganize into more stable structures, through continuous partial melting/recrystallization/crystal perfection processes that occur during the subsequent heating scan that leads to fusion. When crystallization is conducted at low temperatures, small and/or defective crystals develop, and low values of crystallinity are attained. The large reorganization of the crystal phase results in a multiple melting behavior. Conversely, when high crystallization rates are used, only one single endotherm is detectable from calorimetric analyses.

The broad exotherm named Peak I arises from further crystallization of polymer chains, that becomes possible when temperature is raised above T_c. The initial endotherm (Peak II) is due to fusion of PLLA crystals with a low thermal stability, formed at T_c and/or in the temperature range of Peak I. Successive structural reorganization may result in the appearance of an exotherm (Peak III), and a final endotherm (Peak IV). In all cases, the final melting temperature does not refer to the initial crystals as grown at T_c, but to the perfected ones. For a heating rate of 20 °C/min, Peaks II, III, and IV merge into a single endothermic transition when isothermal crystallization is conducted at $T_c > 120\,^\circ$C. When lower heating rates are used, an additional endothermic peak (Peak IV) appears also at $T_c > 120\,^\circ$C, because of the longer time available for the structural reorganization.

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