Calorimetric Analysis of the Multiple Melting Behavior of Poly(L-lactic acid)

Maria Laura Di Lorenzo

Istituto di Chimica e Tecnologia dei Polimeri (CNR), c/o Comprensorio Olivetti, Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy

ABSTRACT: This article contains a detailed calorimetric analysis of the multiple melting behavior of poly(L-lactic acid) (PLLA) in dependence of crystallization conditions. PLLA crystals formed upon primary crystallization have a greater tendency to reorganize into more stable structures during the heating scan that leads to fusion. Depending on crystallization temperature, one or multiple melting endotherms and/or reorganization exotherms can be evidenced. This complex melting behavior arises from the fusion of a certain amount of the original crystals (already partially perfected during the heating scan), followed by recrystallization and final melting of more perfect crystals, partly grown during primary crystallization, and partly formed through the reorganization processes occurring during the heating scan. A detailed map of the melting behavior of PLLA is described in this contribution. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3145–3151, 2006

Key words: fusion; poly(L-lactic acid); thermal analysis

INTRODUCTION

The recent advances in polymerization technology allow the production of poly(L-lactic acid) (PLLA) with competitive costs, which has led to an increasing interest in the use of PLLA in applications that require disposable and biodegradable materials.[1,2] PLLA can be degraded by simple hydrolysis of the ester bonds, in both the presence or absence of enzymes as catalysts.[3–6] The rate of degradation depends on the size and the shape of the molded product, as well as on D-L isomer ratio, molecular mass, and crystal structure and morphology.[3,7] In addition, PLLA can be used for a wide number of medical applications, including sutures, orthopedic implants, and drug delivery systems, because of its good biocompatibility,[8] and can also be used in food-contact applications.[9]

The crystallization process of PLLA has been investigated by a number of authors. Three structural modifications, characterized by different helix conformations and cell symmetries, have been identified. The α form grows upon melt or cold crystallization, as well as from solution-spinning processes at low drawing temperatures and/or low hot-draw ratios.[10] Its chain conformation is a left-handed 10_3 helix, which packs into an orthorhombic unit cell with parameters $a = 1.06$ nm, $b = 1.737$ nm, and $c = 2.88$ nm.[11] A few more recent analyses report the observation of additional 001 reflections in the α form of PLLA, suggesting some deviation from a "pure" 10_3 helix conformation.[10] The β modification develops upon mechanical stretching of the more stable α form, or from solution-spinning processes conducted at high temperatures or high hot-draw ratios.[10,12,13] The crystal structure of the β form has not been solved yet. Recent studies conducted by Puiggali et al. show that the β phase is indeed a frustrated structure of three three-fold helices in a trigonal unit cell of parameters $a = b = 1.052$ nm and $c = 0.88$ nm, able to accommodate the random up–down orientation of neighbor chains associated with rapid crystallization conditions.[13] A third crystal modification of PLLA, the γ form, has been recently reported to develop upon epitaxial crystallization on hexamethylbenzene substrate; the γ phase has two antiparallel helices packed in an orthorhombic unit cell with $a = 0.995$ nm, $b = 0.625$ nm, and $c = 0.88$ nm.[14]

Crystallization kinetics of PLLA has been analyzed in a wide temperature range, from slightly above the glass transition temperature (T_g) to almost the melting point.[15–21] Some peculiarities have been observed in crystallization behavior of PLLA, as crystallization rate is very high at temperatures between 100 and 118°C, showing a clear deviation from the usual bell-shaped curve. Recent analyses have shown that this discontinuity is due to a sudden acceleration in spherulite growth rate, and is not associated to morphological changes in the appearance of PLLA spherulites.[21]

The melting behavior of PLLA has also been investigated, but has not received the same attention as the crystallization process. AFM analyses of the melting process of PLLA single crystals have been recently published.[22] Sarasua et al. and Abe et al. analyzed the influence of D-L isomer ratio on melting behavior of poly(lactic acid) copolymers.[23,24] Yasuniwa et al. reported the influence of crystallization rate on fusion behavior of PLLA, showing the occurrence of double melting peaks when crystallization is conducted at low cooling rates.[25] The observation of multiple melting endotherms is a common phenomenon for synthetic macromolecules, being observed for several other polyesters, including poly(ethylene terephthalate) (PET),[26] poly(trimethylene terephthalate),[27] poly(butylene terephthalate),[28–30] poly(3-hydroxybutyrate), and its copolymers with 3-hydroxyvalerate.[31] However, a general explanation of such a complex process has not been achieved yet. This behavior can, in principle, be ascribed to a number of factors, such as the presence of more than one crystal modification, molecular weight segregation that accompanies crystallization, different crystal morphologies, orientation effects, or reorganization processes that occur during the DSC heating scan.[32] To better clarify this aspect, a detailed map of the dependence of the multiple melting behavior of PLLA on crystallization conditions is reported in this contribution.

EXPERIMENTAL

Materials

A poly(L-lactic acid) (PLLA) of molecular mass $M_w = 101,000$ Da, produced by Boehringer Ingelheim (Germany) was received in the form of small chips, and was used without further purification.

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 was purged through the cell during all measurements and thermal treatments. A fresh sample was used for each experimental measurement, so as to minimize thermal degradation. Each measurement was repeated three times to improve accuracy.

PLLA was isothermally crystallized at various temperatures, using the following temperature program: each sample was heated from 30 to 200°C at a rate of 20°C/min, melted at 200°C for 2 min, then cooled at a rate of 50°C/min to the desired T_c, and allowed to crystallize. Preliminary investigations showed that the scanning rate used to reach T_c from the melt (50°C/min) was high enough to prevent crystallization during cooling.[19,21] The time (t_c) of residence at T_c was kept constant within groups of temperature ranges, to minimize possible crystal perfection after primary crystallization. For crystallizations conducted in the range 92°C $\leq T_c \leq$ 128°C, t_c was 15 min. For $T_c \leq$ 90°C and $T_c \geq$ 130°C, t_c was increased to 30 min, because of the slower crystallization kinetics. For the experimental conditions used, the effect of a different crystallization time on melting behavior was found to be minor, as detailed in the next section. After isothermal crystallization, the sample was heated from T_c to 210°C using a linear heating rate. For most measurements, the constant heating rate from T_c to complete fusion was set at 20°C/min. Slower heating rates were also used, as detailed in the text.

From the melting endotherms, the crystal fraction (w_c) of PLLA, isothermally crystallized at the various T_c, was calculated, using the value of enthalpy of fusion of the fully crystalline sample $\Delta H = 91$ J/g.[33] Because of the complex melting behavior of PLLA, crystallinities were also determined from the exotherms recorded during isothermal crystallization, which values resulted in excellent agreement with the data measured during heating.

Temperature-modulated DSC analyses (TMDSC) were conducted with a Perkin–Elmer Pyris Diamond DSC. A sawtooth modulated temperature program, with heating-only segments, was built in the standard DSC mode, with the following parameters: the underlying heating rate was set to 1.5°C/min, the modulation amplitude was 1°C, and the modulation period was 4 min.

RESULTS AND DISCUSSION

Polymer melting is affected not only by crystallization temperature (T_c), but also by the time of residence at T_c, as a longer crystallization time may induce a larger occurrence of crystal perfection and/or annealing processes, which influences melting behavior.[32] As mentioned in the experimental section, care was taken to optimize the crystallization conditions of PLLA, to minimize the effect of further structural reorganization after primary crystallization. One possibility to control these processes is to choose a single crystallization time for all the investigated temperature range. However, this results in a much longer annealing at T_c when primary crystallization is very fast. It was instead chosen to keep constant the crystallization time within T_c ranges, so as to minimize the time of residence at T_c after the primary phase transition, using two different crystallization times: $t_c = 30$ min for low and high T_c, and $t_c = 15$ min for the temperature range of fast kinetics.

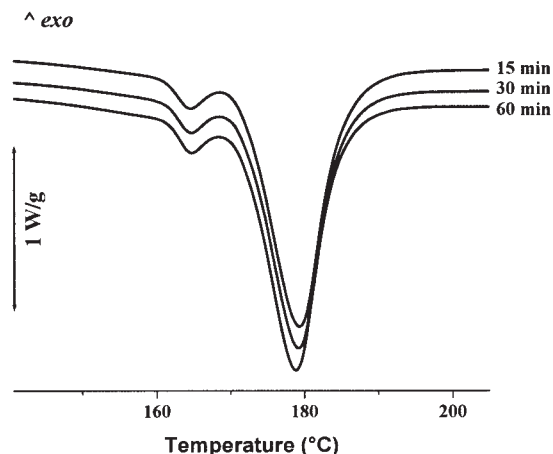Before proceeding with the investigation of melting process, the effect of different crystallization times

Figure 1 Melting behavior of PLLA after isothermal crystallization at 110°C for different times.

was quantified. Figure 1 illustrates the melting behavior of PLLA after crystallization at $T_c = 110°C$ for 15, 30, and 60 min. Multiple transitions can be evidenced after crystallization at this temperature, as detailed later. Some minor differences in melting endotherms can be detected from Figure 1, quantifiable as a shift of less than 1°C in peak position when crystallization time is increased from 10 to 60 min. This small variation falls within the experimental uncertainty of the calorimeter used. In addition, no differences in crystallinity content or in the relative dimensions of the various endotherms and exotherms can be deduced from Figure 1. Similar results were obtained also for crystallization at other temperatures within the crystallization time ranges used in this contribution.

Some different results were instead reported by Abe et al.,[24] who found shifts in crystallization temperature and the appearance of an additional melting endotherm, but no differences in crystallinity content, in a P(L-LA-co-meso-LA) copolymer with 2 mol % of meso content. The data published by Abe et al. were gained at $T_c = 150°C$, for crystallization times ranging from 12 to 120 h, that is, one to three orders of magnitude larger than those used in our study. Considering that the chosen crystallization times were either 15 or 30 min, upon view of results shown in Figure 1, the effect of a different duration of the isothermal crystallization in our experiments was considered negligible.

The melting behavior of PLLA was analyzed as a function of the isothermal crystallization temperature. DSC thermograms, obtained at a heating rate of 20°C/min after isothermal crystallization, are reported in Figure 2 for the various T_c. For the sake of clarity, the thermograms have been grouped within limited ranges of T_c. The DSC curves related to isothermal crystallization in the range 96–108°C, presented in Figure 2(a), display several transitions: a broad and weak exotherm ("Peak I"), a small and narrow endo-

therm ("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. Peak II moves
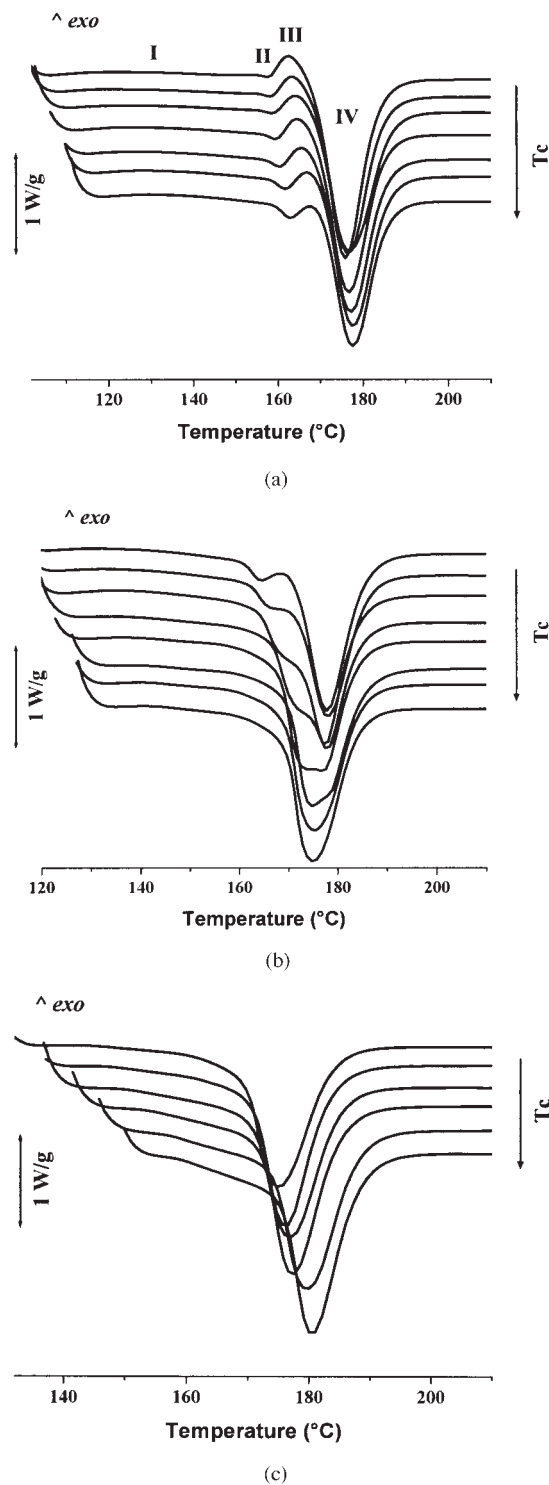

(a)

(b)

(c)

Figure 2 DSC analyses of PLLA, isothermally crystallized at the indicated temperatures. The heat-flow rate curves have been grouped according to the T_c range: (a) 96°C $\leq T_c$ $\leq$ 108°C; (b) 110°C $\leq T_c \leq$ 124°C; (c) 126°C $\leq T_c \leq$ 146°C.
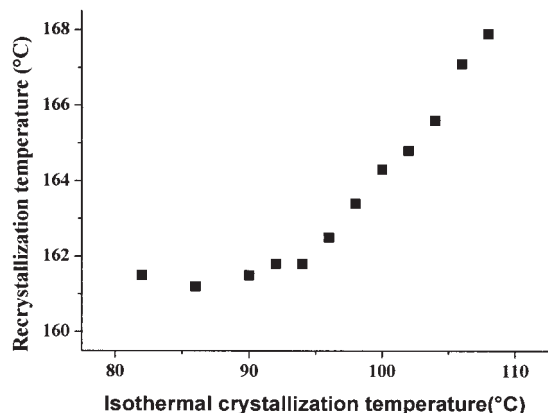
Figure 3 T_c dependence of Peak III, as determined from Figure 2.

to higher temperatures and becomes more pronounced with increasing T_c. Similarly, Peak III increases with T_c, becoming, at the same time, less intense. Also the position of the final endotherm (Peak IV) is affected by crystallization conditions, slightly moving towards higher temperatures with the increase of T_c.

DSC curves measured after isothermal crystallization in the range 110–124°C, presented in Figure 2(b), also display a large influence of T_c on melting behavior. Again, Peak II moves to higher temperatures with the increase of T_c, merging with Peak IV when the crystallization temperature is raised. At the same time, Peak III becomes less pronounced, being recrystallization obscured by the more intense melting.[28] When crystallization is performed at higher temperatures, a single melting peak is always present, and its position is strongly affected by T_c, as illustrated in Figure 2(c), where data gained at T_c from 126 to 146°C are presented.

The influence of isothermal crystallization temperature on multiple melting behavior is summarized in Figures 3 and 4. Peak I is too broad and weak to be measured with sufficient precision. The temperature where the maximum in the major exothermic transition occurs (Peak III) is reported in Figure 3 as a function of the isothermal crystallization temperature. Figure 3 shows that the position of Peak III is roughly constant with temperature up to $T_c = 94$°C, then linearly increases. The variation of the endotherms with crystallization temperature, illustrated in Figure 4, reveals an overall, but not continuous increase of T_m with T_c. The lower endotherm monotonously increases 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 4. Such a decrease in melting point has also been reported in

the literature for PLLA samples isothermally cold crystallized after heating from room temperature.[34]

The very high crystallization rates of PLLA, typical of $T_c < 120$°C,[21] may lead to largely imperfect 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 2 (Peaks I and III), as well as by the partial melting addressed as Peak II. For $T_c > 120$°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 $T_c < 120$°C, the measured final endotherm is due to the crystals largely perfected during the heating scan, that melt as Peak IV, whereas the final melting peak for $T_c > 120$°C is due to Peak II. In other words, the apparent decrease of melting point for $120° < T_c < 130$°C, shown in Figure 4, is due to the lower extent of recrystallization/crystal perfection processes, during heating, as when PLLA is crystallized at $T_c > 120$°C, the observed melting endotherm is Peak II, and not Peak IV, as it occurs for crystals grown at lower T_c.

The experimental T_m versus T_c data reported in Figure 4 allow to determine the equilibrium melting point (T_m^o) of PLLA, using Hoffman–Weeks equation,[35] which is based on the assumption of a linear dependence of T_c and T_m:

$$T_m^o = T_m\left(1 - \frac{1}{\beta}\right) + \frac{T_c}{\beta} \tag{1}$$

and T_m^o can be easily obtained by plotting the experimental melting temperatures as a function of the isothermal crystallization temperatures and extrapolating at $T_m = T_c$. However, it has been shown that the latter assumption is valid only in limited temperature ranges, generally at low undercooling.[36] At high
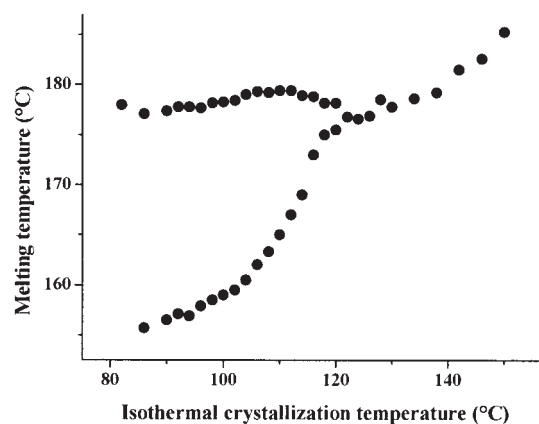

Figure 4 T_c dependence of Peak II and Peak IV, as determined from Figure 2.
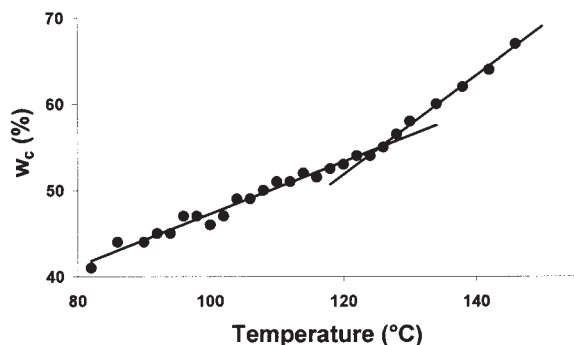
Figure 5 Crystal fraction (w_c) of PLLA as a function of crystallization temperature.

and/or moderate undercooling, a region where T_m is constant with T_c has been often observed.[36,37] A similar relationship between T_m and T_c is evident also for PLLA, as shown in Figure 4, where the final melting temperature remains constant for T_c values up to about 120–130°C, then gradually increases with T_c. Extrapolation of melting temperatures at $T_m = T_c$, using data gained at high T_c, leads to an equilibrium melting point of 204°C, quite close to the value of $T_m^o = 207$°C reported in the literature.[17,33]

The crystal fraction (w_c) of PLLA was also found to be strongly dependent on crystallization temperature, as shown in Figure 5, 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 w_c varies from 41 to 67% when T_c is raised from 82 to 146°C. The experimental values seem to follow two different trends with temperature, with a slope ratio quite close to 2. A similar break in the w_c versus T_c plot has also been reported by other authors, and attributed to a regime II–III transition in crystal growth.[16] At temperatures below 120°C, PLLA displays an unusual crystallization behavior, due to a sudden acceleration in phase transition rate when crystallization is conducted at temperatures below 120°C, because of the very high crystal growth rates. The break in the trend of crystalline fraction with crystallization temperature, which can be inferred from Figure 5, might be correlated to the very high crystal growth rates in this temperature range, that lead to poor crystallization.

To better clarify the structural reorganization of the crystal phase of PLLA that leads to multiple melting, the effect of heating rate (q) was determined. Figure 6 reports the fusion thermograms, acquired at different scanning rates, of PLLA samples crystallized at two representative temperatures ($T_c = 90$°C in Fig. 6(a) and $T_c = 120$°C in Fig. 6(b)). For $T_c = 90$°C, upon decreasing the heating rate, the position of both Peak II and Peak III move towards higher temperatures, and smaller effects of q can be observed also on Peak

IV, as illustrated in Figure 6(a). Isothermal crystallization at $T_c = 90$°C leads to a crystal fraction of $w_c = 44$%. The low value of initial crystallinity is responsible for the wide occurrence of structural reorganization of the crystal phase during heating, which is highly affected by the heating rate. For a larger initial crystallinity, the occurrence of reorganization is smaller, as illustrated in Figure 6(b), that shows the influence of scanning rate on multiple melting for a PLLA sample isothermally crystallized at $T_c = 120$°C, with an initial crystallinity of $w_c = 54$%. For $T_c = 120$°C, heating at different rates results in minor effects on melting temperatures. Conversely, different heights of the two endothermic peaks can be observed, because of the varied amount of high melting crystals that have been perfected during the heating scans at low rates that leads to an increased size of Peak IV and a smaller Peak II when the heating rate is reduced.
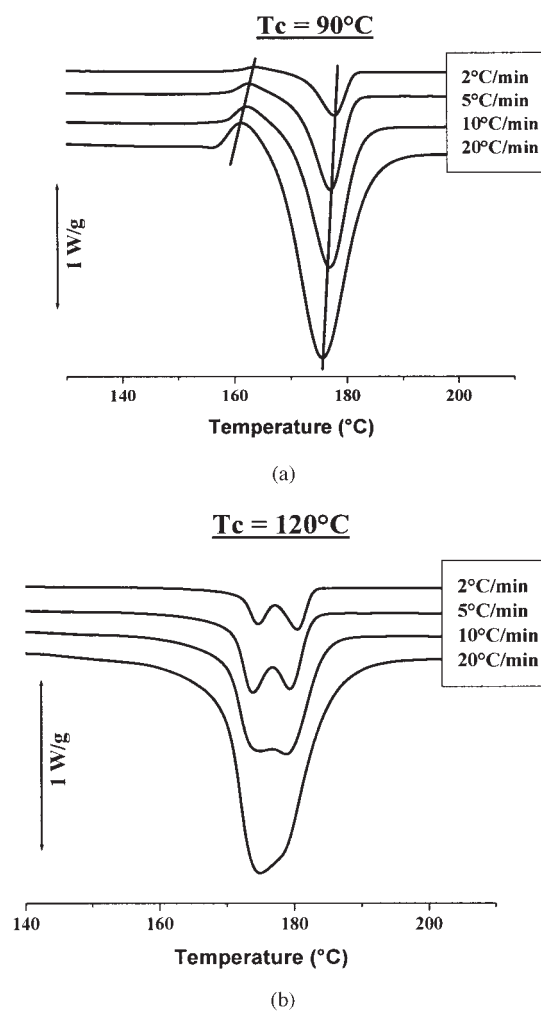

(a)

(b)

Figure 6 DSC analyses of isothermally crystallized PLLA, conducted at various scanning rates: (a) $T_c = 90$°C; (b) $T_c = 120$°C. The straight lines in (a) highlight the trend of Peak III and Peak IV.
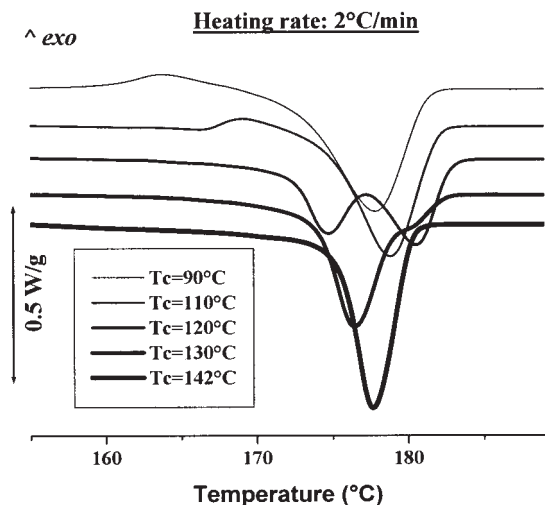
Figure 7 DSC analyses of PLLA, isothermally crystallized at the indicated temperatures; the heating rate was set at 2°C/min.

The effect of a low scanning rate on fusion behavior of PLLA is summarized in Figure 7, which reports DSC curves obtained at a q = 2°C/min after isothermal crystallization at various temperatures. Similarly to the data shown with Figure 2, one or multiple endotherms, sometimes interrupted by exotherms, can be observed, depending on crystallization temperature. Again, peak positions strongly vary with 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. In fact, compared with Figure 2, for T_c = 130°C, an additional endotherm (Peak IV) becomes visible, the peak being centered around 180°C. 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°C when a heating rate of 2°C/min is used instead of 20°C/min. For T_c = 142°C, the thermal stability of the initial crystals is much higher. This leads to a lower occurrence of partial melting and subsequent recrystallization process, which results in a lower temperature of final melting (Peak II).

The large structural reorganization of the crystal phase during heating was also probed by temperature-modulated calorimetry (TMDSC). Figure 8 presents the TMDSC analysis of a PLLA sample isothermally crystallized at 90°C, then heated with a modulated sawtooth temperature program made of heating-only segments, as detailed in the experimental section. Experimental raw data were not analyzed with the common procedures used for TMDSC data treatment, because of their failure in providing quantitative data for polymer melting, because of overlapping endothermic and exothermic events.[39] Conversely, the shape of the modulated heat flow-rate profile, exhib-

ited in Figure 8, was closely examined, following the method proposed by Righetti et al.[28] Above 180°C, melting of PLLA is complete, and oscillation of the heat-flow rate is determined only by the thermodynamic heat capacity of the sample. In the temperature range between 160 and 180°C, repeated partial melting and recrystallization/crystal perfection occur, as highlighted by the arrows in the figure. In some cases, like in the area indicated by the large arrow, the initial endotherm is followed by an exotherm, then by a second endotherm, all taking place within the same half-cycle of modulation, indicating the simultaneous occurrence of partial fusion and recrystallization/crystal perfection. In other words, the various transitions named Peak I to Peak IV do not have to be taken as distinct processes, since endothermic and exothermic events simultaneously occur. These reorganization processes are not induced by temperature modulation, because of the continuous heating during analysis. The intermittent variation of heating rate in TMDSC allows to evidence that the various processes take place at the same time, because of the rather long semiperiod used (120 s).

CONCLUSIONS

Isothermally grown 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, one single endotherm is detectable from calorimetric analyses.
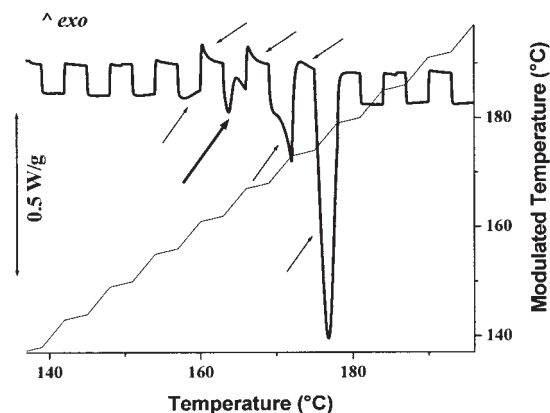

Figure 8 TMDSC analysis of a PLLA sample, after isothermal crystallization at 90°C. The thick line is the modulated heat-flow rate, and the thin line represents the modulated temperature.

The broad exotherm named Peak I arises from further crystallization of polymer chains, which 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 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.

TMDSC revealed that the partial melting of PLLA crystals is immediately followed by exothermic processes, like recrystallization into more stable structures and further crystal perfection. These events are not induced by modulation of the temperature, but take place also when the sample temperature is continuously raised during analysis, like in the conventional DSC analyses. The continuous partial melting/recrystallization/crystal perfection processes are affected by the scanning rate used. 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 $T_c > 120$°C. When lower heating rates are used, an additional endothermic peak (Peak IV) appears also at $T_c > 120$°C, because of the longer time available for the structural reorganization.

References

1. Lunt, J. Polym Degrad Stab 1998, 59, 145.
2. Jacobsen, S.; Degée, P.; Fritz, H.; Dubois, P.; Jérome, R. Polym Eng Sci 1999, 39, 1311.
3. Garlotta, D. J Polym Environ 2001, 9, 63.
4. Fisher, E. W.; Sterzel, H. J.; Wegner, G. Kolloid Z Z Polym 1973, 251, 980.
5. Iwata, T.; Doi, Y. Macromolecules 1998, 31, 2461.
6. Reeve, M. S.; McCarthy, S. P.; Downey, M. J.; Gross, R. A. Macromolecules 1994, 27, 825.
7. Turner, J. F.; Riga, A.; O'Connor, A.; Zhang, J.; Collins, J. J Therm Anal Calor 2004, 75, 257.
8. Leenslag, J. W.; Pennings, A. J.; Bos, R. R. M.; Rozema, F. R.; Boering, G. Biomaterials 1987, 8, 311.
9. Cohn, R. E.; Kolstad, J. J.; Borzellecca, J. F.; Dixler, D. S.; Filer, L. J.; Du, B. N.; Pariza, W. Food Chem Toxicol 1995, 33, 273.
10. Hoogsteen, W.; Postema, A. R.; Pennings, A. J.; Ten Brinke, G.; Zugenmaier, P. Macromolecules 1990, 23, 634.
11. De Sanctis, P.; Kovacs, A. J. Biopolymers 1968, 6, 299.
12. Eling, B.; Gogolewski, S.; Pennings, A. J. Polymer 1982, 23, 1587.
13. Puiggali, J.; Ikada, Y.; Tsuji, H.; Cartier, L.; Okihara, T.; Lotz, B. Polymer 2000, 41, 8921.
14. Cartier, L.; Okihara, T.; Ikada, Y.; Tsuji, H.; Puiggali, J.; Lotz, B. Polymer 2000, 41, 8909.
15. Marega, C.; Marigo, A.; Di Noto, V.; Zannetti, R. Makromol Chem 1992, 193, 1599.
16. Iannace, S.; Nicolais, L. J Appl Polym Sci 1997, 64, 911.
17. Vasanthakumari, R.; Pennings, A. J. Polymer 1983, 24, 175.
18. Myiata, T.; Masuko, T. Polymer 1998, 39, 22.
19. Di Lorenzo, M. L. Polymer 2001, 42, 9441.
20. Abe, H.; Kikkawa, Y.; Inoue, Y.; Doi, Y. Biomacromolecules 2001, 2, 1007.
21. Di Lorenzo, M. L. Eur Polym J 2005, 41, 569.
22. Fujita, M.; Doi, Y. Biomacromolecules 2003, 4, 1301.
23. Sarasua, J. R.; Prud'homme, R. E.; Wisniewski, M.; Le Borgne, A.; Spassky, N. Macromolecules 1998, 31, 3895.
24. Abe, H.; Harigaya, M.; Kikkawa, Y.; Tsuge, T.; Doi, Y. Biomacromolecules 2005, 6, 457.
25. Yasuniwa, M.; Tsubakihara, S.; Sugimoto, Y.; Nakafuku, C. J Polym Sci Part B: Polym Phys 2004, 42, 25.
26. Mehta, A.; Wunderlich, B. J Polym Sci Polym Phys Ed 1978, 16, 289.
27. Pyda, M.; Wunderlich, B. J Polym Sci Part B: Polym Phys 2000, 38, 622.
28. Righetti, M. C.; Di Lorenzo, M. L. J Polym Sci Part B: Polym Phys 2004, 42, 2191.
29. Righetti, M. C.; Di Lorenzo, M. L.; Angiuli, M.; Tombari, E. Macromolecules 2004, 37, 9027.
30. Righetti, M. C.; Di Lorenzo, M. L. Polym Bull 2004, 53, 53.
31. Di Lorenzo, M. L.; Raimo, M.; Cascone, E.; Martuscelli, E. J Macromol Sci Phys 2001, 40, 639.
32. Wunderlich, B. Macromolecular Physics, Vol. 3: Crystal Melting; Academic Press: New York, 1980.
33. Pyda, M.; Bopp, R. C.; Wunderlich, B. J Chem Thermodyn 2004, 36, 731.
34. Ohtani, Y.; Okumura, K.; Kawaguchi, A. J Macromol Sci Phys 2003, 42, 875.
35. Hoffman, J. D.; Weeks, J. J. J Res Natl Bur Stand Sect A 1962, 66, 13.
36. Hoffman, J. D.; Miller, R. L. Polymer 1997, 38, 3151.
37. Cimmino, S.; Di Lorenzo, M. L.; Silvestre, C. Thermochim Acta 1998, 321, 99.
38. Di Lorenzo, M. L.; Wunderlich, B. Thermochim Acta 2003, 405, 255.