

Isothermal Cold Crystallization and Melting Behaviors of Poly(L-lactic acid)s Prepared by Melt Polycondensation

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ABSTRACT: The isothermal cold crystallization and melting behaviors of poly(L-lactic acid)s (PLLAs, weight average molecular weight, M_w , 6000–80,000) prepared via melt polycondensation were studied with differential scanning calorimeter in this work. It is found that the crystallization rate increased with decreasing M_w , reached a maximum at M_w of ca. 21,000 and then decreased again. The crystallinity of PLLA can be controlled in the range 30–50% by crystallization temperature (T_c) and time to fulfill the requirement of subsequent solid state polycondensation. The melting behavior strongly depends on T_c . The samples crystallized at high T_c melted with a single peak but those crystallized at low T_c melted with double peaks.

The higher melting point (T_{mH}) kept almost constant and the lower melting point (T_{mL}) increased clearly with T_c . But the T_{mL} changed in jumps and a triple melting peak appeared at the vicinity of a characteristic crystallization temperature T_b , possibly because of a change of crystal structure. The equilibrium melting temperature of PLLA with M_w of 21,300 was extrapolated to be 222°C with non-linear Hoffman-Weeks method. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 702–708, 2010

Key words: poly(L-lactic acid); isothermal cold crystallization; melting behavior; biodegradable polymers; melt/solid state polycondensation

INTRODUCTION

Poly(L-lactic acid) (PLLA) is a typical bio-based and biodegradable semicrystalline polymer made from L-lactic acid or its dimer, L-lactide.^{1–3} It exhibits excellent biodegradability and biocompatibility and good physical and mechanical properties and can be thermoplastically processed. Therefore, it is widely researched and applied as commodity plastics, agricultural films, fibers, and biomaterials.^{2–4}

As its crystalline properties have significant influence on its physical and mechanical properties,⁵ the researches on its crystalline structure,^{6–9} morphology,¹⁰ kinetics and spherulite growth,^{7,9,11,12} and their effects on the melting behaviors^{6,8,13,14} have been extensively reported. Most of such researches were based on PLLA prepared by ring opening polymerization (ROP) of L-lactide. This method has been industrialized,² and it is relatively easy to obtain high molecular weight PLLA from it. But the crystallization and melting behaviors of PLLA prepared by melt/solid state polycondensation¹⁵ was rarely reported.^{16,17} This method has not yet

been industrialized currently, but it is very attractive and promising because of its relatively low cost and environmentally benign process in spite of the difficulty involved to obtain high molecular weight. As there are some differences on the microstructure such as optical purity and molecular weight distribution of PLLAs prepared by these two methods, there may be some differences in their crystallization behaviors. More important, the crystalline properties of PLLA prepolymer prepared by melt polycondensation have critical effects for the succeeding solid state polycondensation according to others^{16,17} and our¹⁸ researches. Therefore, studies on the crystallization and melting behaviors of PLLA prepared by melt polycondensation (denoted as mp-PLLA in this study for convenience; for comparison, PLLA prepared with ROP is denoted as rop-PLLA) are significant not only from the viewpoint of fundamental research but also for developing a melt/solid state polycondensation technology.

As one of our series of articles on melt/solid state polymerization of PLLA, this study reports the isothermal cold crystallization at 70–145°C and melting behaviors of mp-PLLAs with weight average molecular weight (M_w) from 6000 to 80,000.

MATERIALS AND METHODS

Seven PLLA samples were prepared via melt polycondensation of L-lactic acid¹⁹ and used in this

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TABLE I
Molecular Characteristic and Optical Purity of PLLA Samples

Sample	t (h)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	$[\alpha]_D^{25}$ (deg)	op (%ee)
PLLA1	2.5	6.2	1.88	-154.2	98.8
PLLA2	3	14.0	1.87	-149.1	95.6
PLLA3	4	21.3	1.83	-148.1	94.9
PLLA4	4.5	27.1	1.82	-149.0	95.5
PLLA5	6	43.1	1.80	-147.0	94.2
PLLA6	7	58.2	1.86	-145.0	92.9
PLLA7	8	79.7	1.77	-141.8	90.9

study. Their molecular weights were controlled by polycondensation time and are shown in Table I. The specific optical rotation ($[\alpha]_D^{25}$) was measured in a chloroform solution of 1.0 g/dL at 25°C using an automatic polarimeter (PE 341LC, Perkin-Elmer Co.) at a wavelength of 589.3 nm. The optical purity (op) was calculated from Eq. (1) based on the fact that the specific optical rotation of pure PLLA is -156° .²⁰

$$\text{op}(\%ee) = \frac{[\alpha]_D^{25}}{-156} \times 100 \quad (1)$$

The isothermal cold crystallization and melting behaviors were studied with a differential scanning calorimeter (DSC7, Perkin-Elmer Co.), which was calibrated using the melting temperature and enthalpy of indium. The sample was first heated from 40 to 200°C at 10°C/min and maintained at 200°C for 3 min, then cooled to 40°C at $-80^\circ\text{C}/\text{min}$ and maintained at 40°C from 3 min, and finally heated at 80°C/min from 40°C to a predetermined isothermal crystallization temperature (T_c , 70–145°C) to perform isothermal cold crystallization for 10–60 min. After the crystallization was completed, the sample was reheated to 200°C at 10°C/min to observe the melting behavior.

RESULTS AND DISCUSSION

Isothermal cold crystallization

For melt/solid state polycondensation of PLLA, the M_w of PLLA prepolymer prepared by melt polycondensation is usually controlled to be 10,000–30,000, and the prepolymer is often pretreated by cold crystallization to reach certain crystallinity to avoid adhesion among the prepolymer particles during solid state polycondensation.^{15–18} So a sample with M_w of 21,300, PLLA3, was studied with emphasis. For comparison, the samples with lower and higher M_w were also examined.

Figure 1 shows the crystallization isotherms of PLLA3 at the indicated T_c 's from 70 to 145°C. The crystallization exhibited a maximum rate at 115°C and was completed in 5–6 min. The crystallization

rate decreased at lower and higher temperatures. The crystallization was completed in over 40 min at 70°C and 145°C. The crystallization rate depends on the nucleation rate and growth rate. As both the nucleation rate at high T_c , and the growth rate at low T_c are slow, a maximum crystallization rate appeared at a moderate temperature, $T_{c,\text{max}}$.

The relative crystallinity x_t was calculated from Eq. (2), where dH/dt is the heat flow during the crystallization process. The relationship between x_t and crystallization time is shown in Eq. (3) according to well-known Avrami equation,²¹ where K is the Avrami crystallization rate constant, and n is the Avrami exponent. The half time of crystallization $t_{1/2}$ was calculated from n and K according to Eq. (4). The reciprocal of $t_{1/2}$ ($t_{1/2}^{-1}$) is defined as the crystallization rate. Its dependence on T_c for the seven samples is shown in Figure 2. For a given sample, the crystallization rate at $T_{c,\text{max}}$ is denoted as maximum crystallization rate, $(t_{1/2}^{-1})_{\text{max}}$. The effects of M_w on $(t_{1/2}^{-1})_{\text{max}}$ and $T_{c,\text{max}}$ are shown in Figure 3.

$$x(t) = \frac{\int_0^t \left(\frac{dH}{dt}\right) dt}{\int_0^\infty \left(\frac{dH}{dt}\right) dt} \quad (2)$$

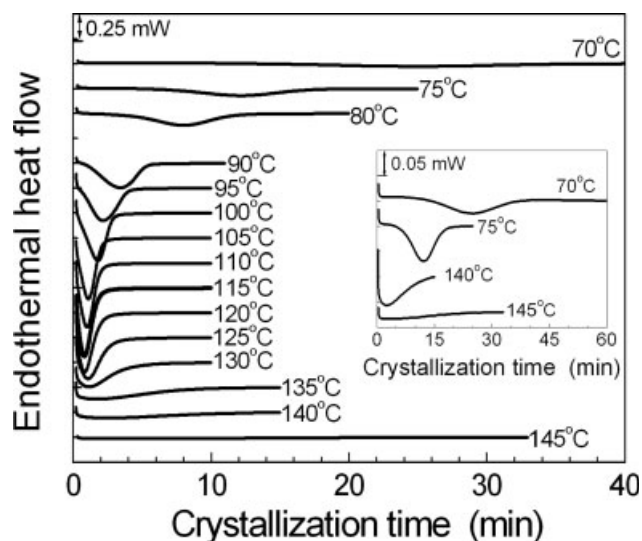


Figure 1 DSC curves of PLLA3 crystallized isothermally at various temperatures.

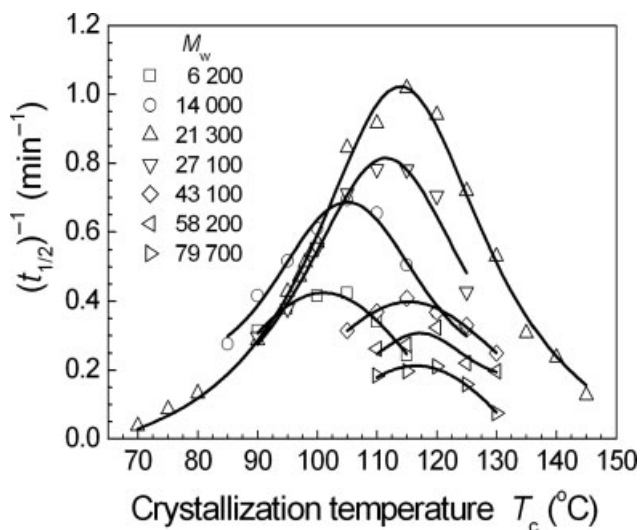


Figure 2 The crystallization rate ($t_{1/2}^{-1}$) as function of crystallization temperature T_c of PLLAs with various molecular weights

$$\log[-\ln(1 - x_t)] = \log K + n \log(t) \quad (3)$$

$$t_{1/2} = (\ln 2/K)^{1/n} \quad (4)$$

The crystallization exhibited strong dependence on molecular weight in M_w range of 6000–60,000. The maximum crystallization rate increased with decreasing M_w , reached a maximum at M_w of about 21,000 and then decreased again. The $T_{c,max}$ increased gradually with increasing molecular weight. But the effects of molecular weight leveled off when M_w was over 60,000.

As compared with rop-PLLAs with comparable molecular weight,¹³ the mp-PLLAs exhibited lower crystallization rate. The difference may be attributed to their discrepancy in microstructures. PLLA racemized unavoidably during melt polycondensation at high temperature as the molecular weight developed. As can be seen from Table I, the optical purity of PLLA decreased from 98.8 to 90.9% when the M_w increased from 6000 to 80,000. The decrease in optical purity resulted in low crystallinity.²² The high racemization resulted in the weak dependence of crystallization rate on M_w at M_w higher than 60,000. On the other hand, rop-PLLAs usually have narrow molecular weight distribution ($M_w/M_n \sim 1.3$ – 1.4) because of the living ROP characteristic, but the mp-PLLAs exhibited broader molecular weight distribution ($M_w/M_n \sim 1.8$, Table I), which may also be responsible for the lower crystallization rate.

The effect of molecular weight on the crystallization rate is related to its effect on both nucleation and diffusion of PLLA chains. During crystallization, the crystals grew up when the polymer chains diffused to and arrayed onto the surface of crystal

nuclei. High molecular weight PLLA had enough nucleation ability but its diffusion ability depended on its molecular weight. As the molecular weight decreased, its viscosity reduced clearly and therefore, it was easy to diffuse to the crystallization site, leading to rapid crystallization rate. Such results have been reported for rop-PLLAs with relatively high molecular weight by many researchers^{6,10,13} since it is easy for ROP to produce high molecular weight PLLA. When the molecular weight is too low, the nucleation ability reduced obviously and therefore, the total crystallization rate decreased again in spite of its high diffusion ability. Therefore, a maximum crystallization rate was observed at a certain molecular weight. We found in this study for the first time that the M_w for the maximum crystallization rate of mp-PLLAs is about 21,000.

The crystallinity of PLLAs was calculated with Eq. (5) (where ΔH_m^0 is the melting enthalpy of 100% crystalline PLLA, 93.6 J/g).²² Figure 4 shows the evolution of the crystallinity of PLLA3 with crystallization time at various T_c 's. These results can tell how to control the crystallinity of PLLA prepolymer with crystallization temperature and time before solid state polycondensation. To avoid adhesion among PLLA prepolymer particles, the crystallization should be conducted below the low melt temperatures, 130°C (Fig. 6). Due to the too rapid crystallization rate, it is in fact not a good choice to crystallize around $T_{c,max}$. To obtain a predetermined crystallinity easily and precisely, it is better to crystallize at relatively low temperature at 70–90°C thanks to the relatively slow crystallization rate and sufficient final crystallinity (γ_{cf}) enough for solid state polycondensation. Further study demonstrates that it is easier to get high molecular weight PLLA

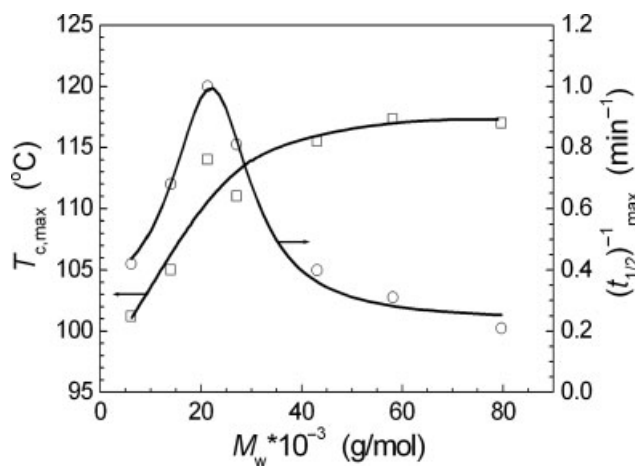


Figure 3 Dependences of the maximum crystallization rate $(t_{1/2}^{-1})_{max}$ and the temperature $T_{c,max}$ at which it appeared on the weight average molecular weight M_w of PLLAs

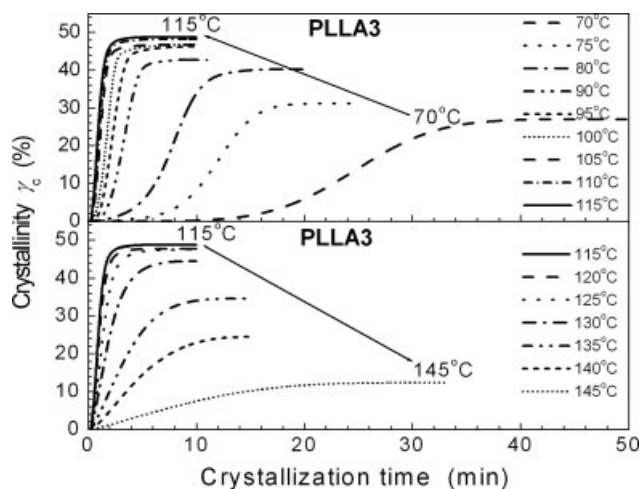


Figure 4 Crystallinity (γ_c)-time curves of PLLA3 during isothermal cold crystallization at various T_c 's.

from solid state polycondensation of thus crystallized samples.¹⁸

$$\gamma_c(t) = \frac{\int_0^t \left(\frac{dH}{dt}\right) dt}{\Delta H_m^0} \quad (5)$$

Figure 5 illustrates the dependences of the final crystallinity of PLLAs (γ_{cf}) after the crystallization was completed on the crystallization temperature and molecular weight. It can be seen that there is a clear effect of T_c on the γ_{cf} though the γ_{cf} 's at very high and low T_c 's may be underestimated to a little extent because of the very slow crystallization rates and possible uncompleted crystallization. With increasing T_c , the γ_{cf} increased rapidly at low T_c ,

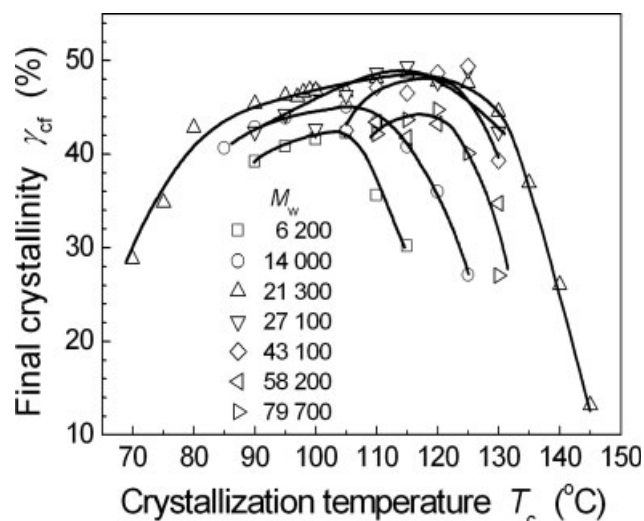


Figure 5 The final crystallinity (γ_{cf}) of PLLAs after isothermal cold crystallization at various temperatures.

then increased slowly to a maximum, and finally decreased rapidly at high T_c . The temperatures at which γ_{cf} reached the maxima are equal to or a little higher than $T_{c,max}$. The effect of molecular weight on γ_{cf} is similar to but less than its effect on the crystallization rate. It can be seen from Figures 2 and 5 that higher crystallization rate resulted in higher γ_{cf} .

Melting behaviors after crystallization

The PLLA samples after isothermal crystallization were heated again from T_c to observe the melting behaviors. The crystallization temperature exhibited significant effect on the melting behaviors. As shown in Figure 6, there appeared double melt peaks for

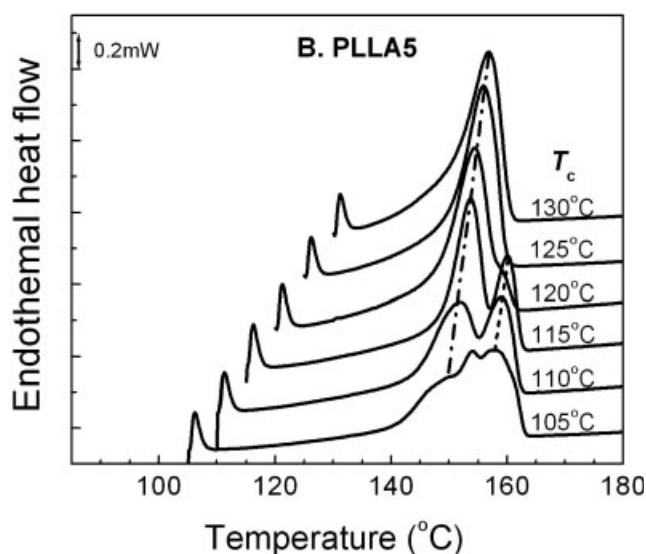
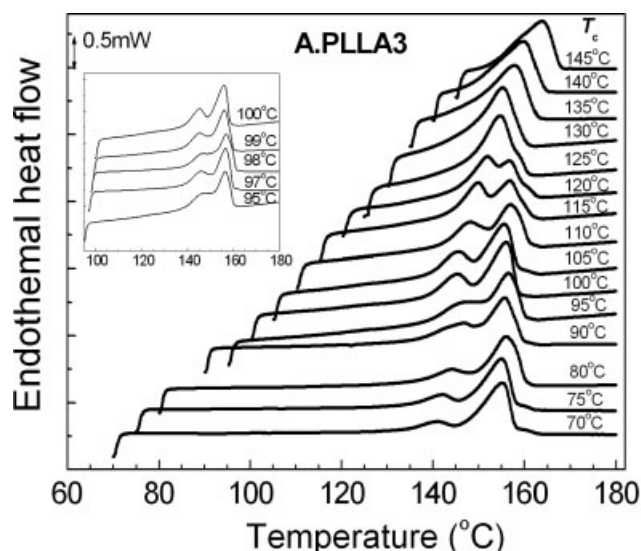


Figure 6 DSC curves for PLLA3 (A) and PLLA5 (B) after cold isothermal crystallization at indicated crystallization temperatures.

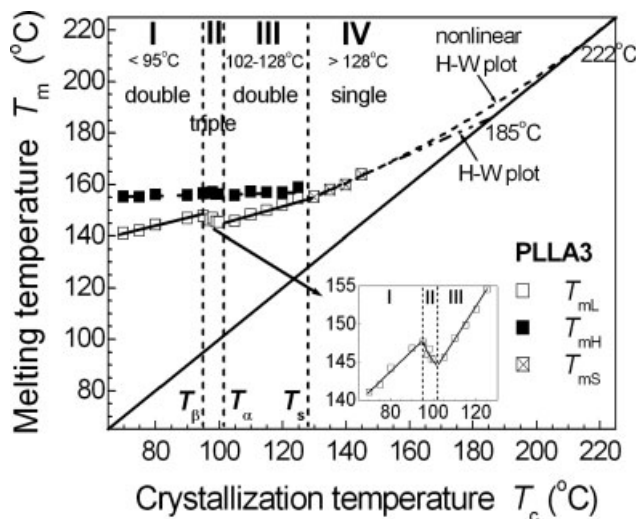


Figure 7 Dependences of T_{mL} , T_{mS} , and T_{mH} on the crystallization temperature T_c of PLLA3. The T_m - T_c change was divided into three regions with two characteristic temperatures T_b and T_d . Linear and nonlinear Hoffmann-Weeks extrapolations of the T_{mS} - T_c data was conducted to determine the equilibrium melt temperature.

PLLA3 when T_c was lower than 125°C. The melt points for the low and high melt peaks are denoted as T_{mL} and T_{mH} , respectively. T_{mL} increased clearly with increasing T_c , but T_{mH} kept almost constant or slightly increased. For the samples crystallized at low T_c , the high melt peak is predominant; then the area of the high melt peak decreased but that of the low melt peak increased gradually with increasing T_c and the two peaks got close to each other; and finally, they became a single peak at T_c of 125°C. The melt temperature of the single peaks increased continuously with T_c . Other samples exhibited similar melting behaviors. However, triple peaks appeared for PLLA5-7, namely, a middle peak appeared clearly at T_c around 110°C between the

low and high melting peaks, as shown in Figure 6B. For PLLAs 1-4, no clear middle peak was observed when a 5-10°C T_c interval was used, but when the T_c was changed at 1°C T_c interval from 95°C to 100°C, a weak middle peak was also observed for PLLA3 at 98°C, as shown in the inserted diagram in Figure 6A. The melting temperatures for PLLA3 are plotted as functions of T_c and illustrated in Figure 7, and those for other PLLAs are shown in Table II.

It can be seen from Figure 7, that there appeared different T_m - T_c dependencies for PLLA3 in different T_c ranges. T_{mL} increased almost linearly when T_c was lower than ~95°C. Then, there appeared a 4°C decrease of T_{mL} at T_c from 95°C to 102°C, and after that, T_{mL} increased again. Finally, single melting peak appeared at T_c above 128°C and the T_{mS} increased with T_c at an enhanced slope.

Yasuniwa et al.⁸ even reported that the melting behaviors of rop-PLLA with M_w of 90,000 differs in three temperature regions of T_c divided by two characteristic temperatures, T_b (113°C) and T_d (135°C) in addition, they found triple melting peaks and a discrete T_{mL} increase at T_b , which are attributed to the fact that there is a change of crystalline-form at T_b .^{8,9} Trigonal b crystal and orthorhombic α crystal are formed at T_c 's lower and higher than 113°C, respectively, and both crystals are formed simultaneously around 113°C.^{8,9} So, the low and middle melting peaks result from the melting off β and α crystals formed during isothermal crystallization, respectively. The high melting peak indicates the melting of the α crystals formed originally and/or after recrystallization.

Figure 7 shows that the T_{mL} changed in an interesting "Z-shape" manner rather than a discrete manner reported by Yasuniwa et al.⁹ It decreased suddenly in a narrow T_c range (95°C-102°C) though it increased with T_c in lower or higher T_c range. So, the whole T_c range for PLLA3 can be divided into

TABLE II
The Dependences of the Melt Temperatures, T_{mL} , T_{mS} , and T_{mH} of PLLAs on their Crystallization Temperature, T_c

T_c (°C)	PLLA1		PLLA2		PLLA4		PLLA5		PLLA6		PLLA7	
	T_{mL} (°C)	T_{mH} (°C)	T_{mL} (°C)	T_{mH} (°C)	T_{mL} (°C)	T_{mH} (°C)	T_{mL} (°C)	T_{mH} (°C)	T_{mL} (°C)	T_{mH} (°C)	T_{mL} (°C)	T_{mH} (°C)
85	nd ^a	nd	125	145.6	nd	nd	nd	nd	nd	nd	nd	nd
90	123.4	141.8	127.5	144.8	141.7	153.4	nd	nd	nd	nd	nd	nd
95	126.5	142.2	129.4	145.0	142.0	153.3	nd	nd	nd	nd	nd	nd
100	127.6	141.5	133.5	146.4	144.3	155.0	nd	nd	nd	nd	nd	nd
105	131.2	141.9	135.5	146.7	145.0	153.8	nd	nd	nd	nd	nd	nd
110	133.2	141.6	138.6	146.9	146.9	154.0	151.9/ 154.0 ^d	159.0	149.7/ 154.0 ^d	157.2	148.7/ 152.0 ^d	156.1
115	136.6	142.48	139.8	146.5	150.9	154.6	153.7	160.0	153.4	158.9	nd	nd
120	nd	nd	142.6	148.8	151.9 ^b	/ ^c	154.4	159.6	151.4	155.9	152.4 ^b	/ ^c
125	nd	nd	144.8 ^b	/ ^c	152.8 ^b	/ ^c	155.9 ^b	/ ^c	155.9 ^b	/ ^c	154.3 ^b	/ ^c
130	nd	nd	nd	nd	nd	nd	156.8 ^b	/ ^c	155.3 ^b	/ ^c	155.9 ^b	/ ^c

four regions, I, II, III and IV with three characteristic temperatures T_b ($\sim 95^\circ\text{C}$), T_a ($\sim 102^\circ\text{C}$), and T_s ($\sim 128^\circ\text{C}$) according to the different melting behaviors shown in Figure 7. The crystallization and melting behaviors differ in each region. When PLLA was crystallized in region I, only trigonal β crystals were formed and then melted to form the low melting peak. During melt-recrystallization, the β crystal was transformed to the α form. Melting of thus formed α crystals led to the high melting peak. When PLLA was crystallized in region II, both β and α crystals were formed. They and the recrystallized α crystals are responsible for the low, middle and high peaks in the triple melting peaks, respectively. As this region locates in a narrow T_c range and the middle melt peak is sometime very weak, it can be regarded as a transitional region. In region III, only α crystals formed and the melting of the originally formed and recrystallized α crystals contributed to the low and high peaks, respectively. There was no crystal form transform during melt-recrystallization in this region. In region IV, only α crystals were formed and no clear melt-recrystallization happened, therefore only single melting peak appeared during the melting process.

Finally, the equilibrium melting temperature T_m° of PLLA3 was calculated from the $T_{ms} - T_c$ data in region IV according to linear [Eq. (6)] and nonlinear [Eq. (7)] Hoffman-Weeks extrapolation methods.²⁵ the equations, γ is the thickening ratio defined as $\gamma = l/l^*$, where l^* and l are the lamellar thickness at the time zero and t during melting; and a is a constant defined as

$$a = \frac{C_2 \Delta H_f}{2\sigma_e^1},$$

where C_2 is a constant, ΔH_f is the fusion enthalpy, and σ_e^1 the fold surface free energy.

The result from linear extrapolation, 185°C , is much lower than the literature value 207°C .²⁶ But the result from nonlinear extrapolation, 222°C , is close to the value (224.8°C)¹⁰ previously reported for rop-PLLA with comparable molecular weight (M_w 22 000). It seems that it can obtain better result from nonlinear Hoffman-Weeks extrapolation, and it should be noted that the equilibrium melting point corresponds to the melting of the orthorhombic α crystalline structure. The constants γ and α in Eq. (7) are regressed to be 1.0 and 0.90, respectively.

$$T_m = T_c/\gamma + T_m^\circ(1 - 1/\gamma) \quad (6)$$

$$\frac{T_m^\circ}{T_m^\circ - T_m} = \gamma \left(\frac{T_m^\circ}{T_m^\circ - T_c} + a \right) \quad (7)$$

CONCLUSIONS

The isothermal cold crystallization and melting behaviors of mp-PLLAs with M_w of 6000–80,000 were studied with DSC and the following conclusions are drawn. (1) The crystallization rate of PLLA increases with decreasing M_w , reached a maximum at M_w of 21,000 and then decreases again. (2) The temperature $T_{c,max}$ at which the maximum crystallization rate appears increases with molecular weight. (3) The crystallization rate is slightly slower than that of rop-PLLAs with comparable molecular weight, possibly because of certain degree of racemization and broader molecular weight distribution of mp-PLLA. (4) The PLLAs with typical molecular weight can be coldly crystallized at relatively low temperature to reach crystallinity of 30–50% to fulfill the requirement of the subsequent solid state polycondensation. (5) Different crystal structures are formed at different T_c ranges, as a result, different melting behaviors appear. So the $T_m - T_c$ change is divided into four regions by three characteristic crystallization temperatures T_β ($\sim 95^\circ\text{C}$), T_α ($\sim 102^\circ\text{C}$), and T_s ($\sim 128^\circ\text{C}$) for PLLA3. Trigonal β crystal structure is formed in region I, orthorhombic α crystal structure is formed in regions III and IV, and both β and α crystal structures are formed in region II. Melt-recrystallization occurs in the regions I–III, but not in region IV. Therefore, double, triple, double and single melt peaks appear in the four regions successively, and the T_{mL} changed in a “Z-shape” manner. (6) The equilibrium melting temperature of PLLA3 is extrapolated to be 222°C from nonlinear Hoffman-Weeks method.

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