

Effects of Molecular Weight on the Crystallization and Melting Behaviors of Poly(L-lactide)^{*}

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Abstract In this study, a series of monodispersed poly(L-lactide) (PLLA) were synthesized by the ring-opening polymerization with Schiff base aluminum catalyst, and the effects of the number-average molecular weight (M_n) on the crystallization and melting behaviors of PLLA were investigated by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The total crystallization rate of PLLA was M_n -dependent, which reached the maximum value for PLLA with M_n of 18.6 kg/mol. In addition, when M_n of PLLA was 18.6 kg/mol, the melting enthalpy (ΔH_m) showed a maximum value (87.1 J/g), which was the highest reported value till now. The critical temperature for change of crystal formation from δ -form to α -form crystals increased in the isothermal crystallization process with M_n increasing. In the reheating procedure, high- M_n PLLA demonstrated a small exothermal peak prior to the dominant melting peak, corresponding to crystal transition from δ to α -form, but low- M_n PLLA didn't show the peak of crystal transition. These different crystallization and melting behaviors were attributed to the different chain mobility of PLLA with different M_n .

Keywords: Poly(L-lactide); Crystallization behavior; Melting behavior; Crystal transition.

INTRODUCTION

Poly(L-lactide) (PLLA) is a biodegradable thermoplastic polyester, which can be produced from annually renewable resources, such as corn starch and cane sugar. PLLA boasts excellent modulus, superior strength and favorable clarity, which can be compared with the widely used petroleum-based plastics. In addition, it is nontoxic to human body. As a result, PLLA materials have great potential in academia and industry parts, such as pharmacy, drug delivery, tissue engineering, fibers, films, and packaging^[1–3]. As a semi-crystalline polymeric material, the mechanical and thermal properties of PLLA greatly depend on the crystal structures and morphologies^[4–10]. Furthermore, polymorphism crystalline structures for PLLA were well known. And three different crystal structures of PLLA (α -, β -, and γ -form) have been widely studied, of which the formation depended on the crystallization conditions. Another crystal structure (δ -form) was reported by Zhang *et al.*, which was slightly different from α -form just with a looser and less ordered chain packing^[11]. The δ -form

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crystals formed at temperatures below 120 °C, lower than that of the crystal of α -form^[12]. Therefore, the studies of the crystallization and melting behaviors for PLLA are of importance to enlarge the applications of PLLA.

The crystallization and melting behaviors of PLLA depend on several factors, such as crystallization temperature (T_c) for isothermal crystallization, and cooling rate for nonisothermal crystallization. With varying T_c , the curve of crystallization rate versus T_c showed a clear deviation at around 100–120 °C, which was attributed to the competition between δ - and α -forms of different growth characteristics^[13, 14]. At $T_c < 120$ °C, the double melting behaviors of PLLA were observed, and a small exothermic peak appeared around 160 °C prior to the main melting peak in DSC curves^[15]. With T_c increasing, the small exothermic peak became weak, corresponded to the crystal transition from δ - to α -form and was a solid-solid-phase transition. On the other hand, the nonisothermal crystallization of PLLA and subsequent melting behaviors were also investigated at different cooling rates. The cooling rate affected the nucleation kinetics and morphology of PLLA^[16]. With cooling rate decreasing, the peak crystallization temperature shifted to higher temperatures, the exothermic enthalpy of crystallization increased, and the double-melting behaviors were observed in the reheating DSC scans^[17]. Under fast cooling conditions, a small exothermic peak was also observed prior to the dominant melting peak, which was the signal of crystal transition^[18]. The multiple melting behavior of PLLA usually accounted for the melt-recrystallization and phase transition^[15, 18].

Besides, M_n is one of key factors governing the crystallization and melting behaviors of PLLA, but the effect of M_n on the crystallization and melting behaviors has been little reported in literatures. Miyata *et al.* studied the effect of M_n on the crystallization kinetics of PLLA by polarizing optical microscopy (POM), and revealed that the crystal growth rate reduced greatly with M_n increasing^[19]. He *et al.* investigated isothermal crystallization of PLLA with different molecular weights by DSC, and found that the half-time ($t_{1/2}$) of crystallization increased with M_n decreasing^[20]. Pan *et al.* studied the melting behavior of PLLA with M_n ranging from 15 kg/mol to 219 kg/mol by WAXD and FTIR^[21]. They concluded that both high- M_n and low- M_n PLLA tended to crystallize as δ -form at low T_c , but the melting behaviors were different. For high- M_n PLLA, δ -form crystals transformed into α -form in the heating scan. However, for the low- M_n PLLA, some amounts of δ -form crystals melted directly without transition during the heating process. Although several investigations were reported on the crystallization and melting behaviors of PLLA with different M_n , M_n of samples in those works was almost above 20 kg/mol, and few researchers focused on PLLA specimens with low M_n below 20 kg/mol.

In this work, the nearly monodispersed PLLA, with different M_n ranging from 5.5 kg/mol to 58.9 kg/mol, were synthesized by using Schiff base aluminum as a catalyst^[22]. And the crystallization and melting behaviors of PLLA were studied by DSC and WAXD in the non-isothermal and isothermal crystallization process. It was found that the curves of total crystallization rate and crystallization enthalpy versus M_n were bell-shaped. In the reheating procedure, M_n greatly influenced the melting behavior and crystal transition. And this investigation would provide a deeper understanding relationship between melt-crystallization behaviors and M_n of PLLA in non-isothermal or isothermal process, especially for M_n below 20 kg/mol.

EXPERIMENTAL

Materials

L-lactide (L-LA) (L content $\geq 99.5\%$) was kindly supplied by Hisun Biomaterials Co., Ltd., and purified by recrystallization with dried ethylacetate. PLLAs were synthesized by the ring-opening polymerization (ROP) in toluene at 70 °C, and the Schiff base aluminum (SB-2d)AlOⁱPr[(SB-2d)-2,2-dimethyl-1,3-propylenebis-(3,5-di-*tert*-butylsalicylideneiminato)] was used as catalyst according to reference^[22]. The molecular weights of PLLA were controlled by the ratios of catalyst to L-LA, and the end group of PLLA chains was isopropoxycarbonyl group. The polymers were purified by reprecipitation method using dichloromethane as solvent and cold methanol as precipitant, then dried in a vacuum oven at 50 °C to constant weight.

Characterization

The molecular weight and polydispersity indexes were obtained in chloroform at 35 °C by gel permeation chromatography (GPC), using a Waters liquid chromatograph equipped with two Styragel HR gel columns (HR2 and HR4) and refractive index detection (Waters 2414 RI Detector). Polystyrene was used as the standard reference. All PLLA samples were almost monodisperse with polydispersity indexes ($PDI = M_w/M_n$) in the range of 1.12–1.26, as shown in Table 1.

Table 1. Molecular weights and polydispersity indexes of PLLA Samples

Code	M_n (kg/mol)	M_w (kg/mol)	PDI
PLLA5.5	5.5	6.9	1.26
PLLA10.6	10.6	12.5	1.18
PLLA18.6	18.6	21.0	1.13
PLLA38.2	38.2	42.8	1.12
PLLA58.9	58.9	69.5	1.18

The thermal behaviors of PLLA were performed with a DSC Q100 (TA Instruments, USA) apparatus under nitrogen atmosphere. The sample of about 5 mg was sealed into an aluminum pan. The calibrations of temperature and heat flow were conducted with standard Indium. To study the nonisothermal crystallization, the samples were heated to 200 °C at first, then were cooled from 200 °C to 25 °C at different cooling rates (*i.e.*, 1, 2.5, 5, 10, 20, 50 K/min), and were reheated to 200 °C at 10 K/min. To study the isothermal crystallization, the samples were directly quenched from 200 °C to the isothermal crystallization temperature (T_c), and held for 60 min, then reheated to 200 °C at 10 K/min. T_c was set from 90 °C to 140 °C, respectively.

Wide angle X-ray diffraction (WAXD) measurements were carried out with a Bruker D8 Advance X-ray diffractometer as reported^[23]. The X-ray beam used was Cu K α radiation. The X-ray diffraction patterns were measured in the 2θ range of 10°–30°.

RESULTS AND DISCUSSION

Nonisothermal Crystallization

To reveal the effect of molecular weight on the crystallization kinetics of PLLA systematically, the non-isothermal crystallization behaviors of PLLA at various cooling rates were investigated by DSC. At different cooling rates, the effects of M_n on the crystallization enthalpy (ΔH_c) and the peak crystallization temperature (T_p) are presented in Fig. 1. With the increase of M_n , the crystallization enthalpy reached a maximum value for PLLA with $M_n = 18.6$ kg/mol, and then decreased, as shown in Fig. 1(a). T_p relates to the nucleation characteristics and the overall crystallization kinetics, and is dependent on M_n , as shown in Fig. 1(b). With the increase of molecular weight, T_p and ΔH_c reached the maximum for PLLA18.6, regardless of cooling rate. These results manifest evidently that the crystallization ability of PLLA is dependent on M_n .

Figure 2 shows the second heating DSC scans after cooling at the rates of 1 and 50 K/min, respectively. The melting peaks shift to higher temperatures with M_n increasing. At lower cooling of 1 K/min, the exothermic peaks are absent prior to the melting peak (Fig. 2a). When the cooling rate is 50 K/min, as shown in Fig. 2(b), two exothermic peaks (T_{ccI} and T_{ccII}) are observed prior to the main melting peak for PLLA38.2 and PLLA58.9 specimens, and weak T_{ccI} is observed for PLLA18.6. While T_{ccI} and T_{ccII} are not shown for PLLA5.5 and PLLA10.6 samples. The DSC curves show that the T_{ccI} peak shifts to higher temperatures with M_n increasing. According to references, the two exothermic peaks were respectively attributed to the cold-crystallization (T_{ccI}) and the crystal transition (T_{ccII})^[15]. For low chain mobility, high- M_n PLLAs crystallize incompletely during fast cooling process. T_{ccII} formed a shoulder at the lower-temperature side of the mainly endothermic peak, due to the transformation from δ - to α -form. The variation of T_{ccII} suggests that the crystal transition is affected by M_n .

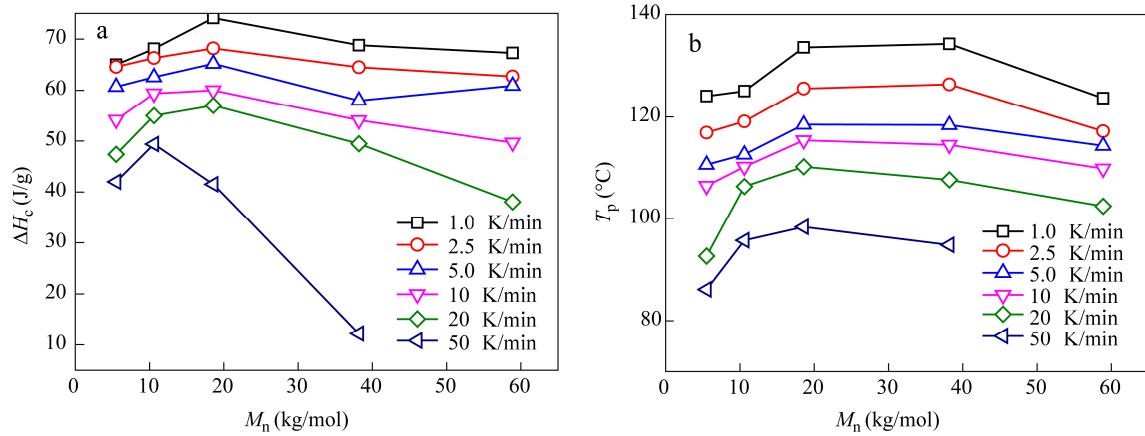


Fig. 1 Effects of M_n on the crystallization behavior of PLLA revealed by DSC during the cooling process: (a) the crystallization enthalpy (ΔH_c) against M_n and (b) the peak crystallization temperature (T_p) against M_n

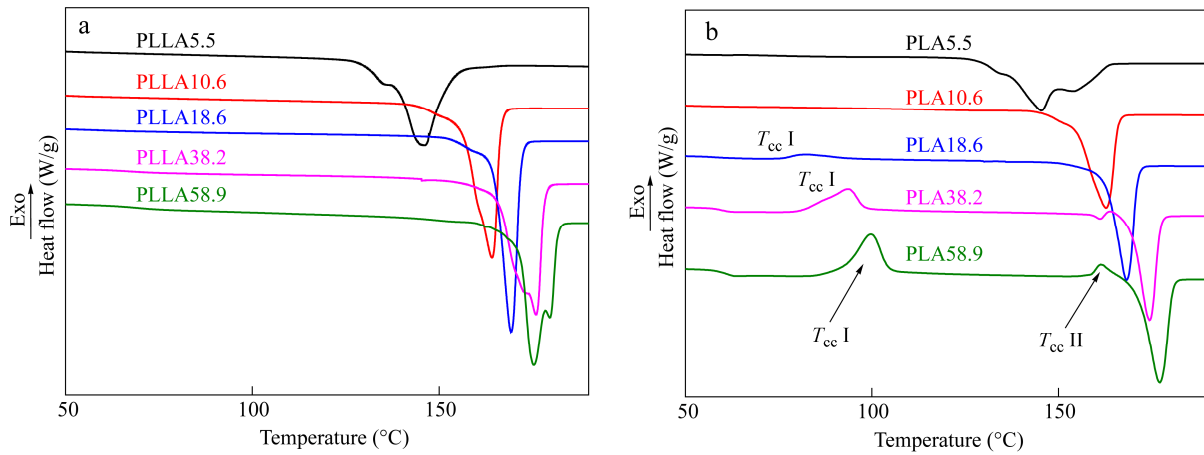


Fig. 2 Second heating DSC scans of different M_n PLLA at different rates: (a) 1 K/min, and (b) 50 K/min

At different cooling rates, the melting DSC thermograms for PLLA18.6 and PLLA58.9 are shown in Fig. 3. For PLLA18.6 (Fig. 3a), a weak T_{cc} I is observed at cooling rate for 50 K/min. At the cooling rate of 1.0 K/min, T_{cc} II is not observed for PLLA18.6, and a single melting peak presents in the heating process. For PLLA58.9 (Fig. 3b), T_{cc} II shifts to higher temperatures with cooling rate decreasing, and the intensity of T_{cc} II becomes weaker, which moves to the position between T_{m} I and T_{m} II. When the cooling rate is 5.0 K/min, the peaks of T_{cc} I and T_{cc} II are indistinct in the second heating DSC thermograms, while T_{m} I and T_{m} II are observed evidently. The peaks of T_{cc} I and T_{cc} II disappear under low cooling rate condition, which means the PLLA58.9 form stable crystal structure (α -form). The intensity of peak T_{m} I increases, while the intensity of T_{m} II peak decreases at lower cooling rate. When PLLA58.9 is cooled at 1.0 K/min, the T_{m} I peak becomes stronger than that of T_{m} II, and the double melting peaks (T_{m} I and T_{m} II) tend to overlap, and the T_{m} II peak becomes a shoulder peak of the T_{m} I peak.

As shown in Fig. 2 and Fig. 3, the crystal transition (T_{cc} II) is not observed for low- M_n PLLA, regardless of cooling rate. However, the crystal transition (T_{cc} II) and the multiple melting peaks are observed for high- M_n samples. In order to investigate the effect of M_n on the crystallization and melting behaviors of PLLA in details, the isothermal crystallization process was analyzed by DSC and WAXD.

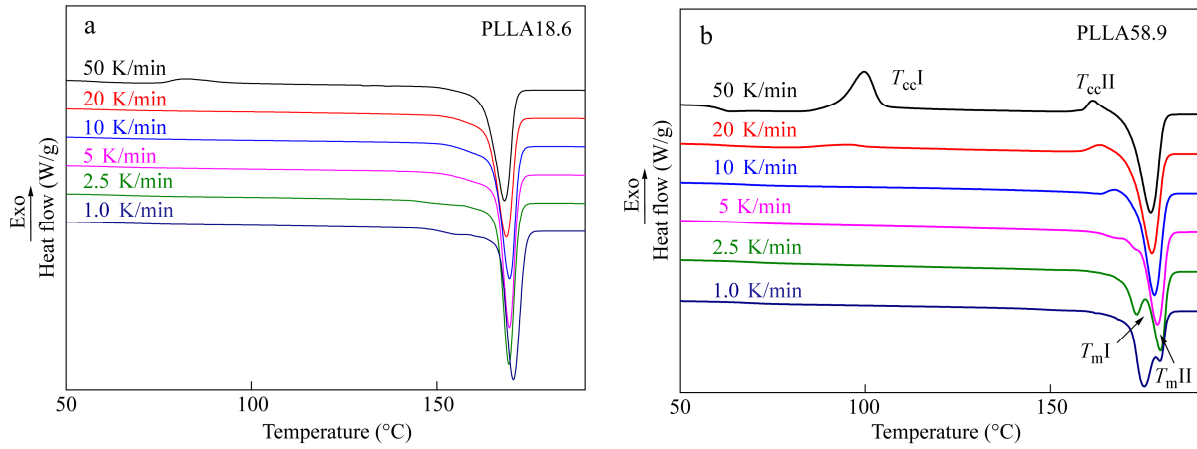


Fig. 3 DSC reheating scans of PLLA after nonisothermal crystallization at various cooling rates for (a) PLLA18.6 and (b) PLLA58.9

Isothermal Crystallization

To further demonstrate the effect of M_n on the crystallization and melting behaviors of PLLA, isothermal crystallization processes were investigated. The peak crystallization time (t_p) is defined as the time spent from the onset to the point, where the exothermic peak appears in the isothermal treatment. Since t_p is determined from the exothermic heat flow in the whole process, so t_p can be considered to express the overall rate of crystallization like $t_{1/2}$ ^[24]. In Fig. 4, the crystallization rate (t_p^{-1}) is plotted against M_n . The bell-shaped curve is observed for the dependence of t_p^{-1} on M_n , and the maximum crystallization rate appears for PLLA18.6. All the phenomena suggest that crystallization behaviors are affected by M_n .

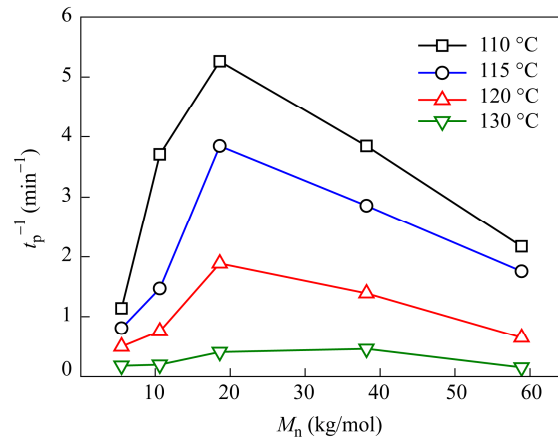


Fig. 4 Relationship between crystallization rate (t_p^{-1}) and M_n in isothermal experiments, at different isothermal crystallization temperatures (T_c)

The WAXD patterns of PLLA specimens, crystallized at various T_c , were measured at room temperature, as shown in Fig. 5. For α -form crystals, many X-ray diffraction peaks appear, including (110/200), (203), (210), (116), and (207) planes which correspond to the Bragg angles 2θ of 16.7°, 19.1°, 22.5°, 24.5°, and 27.4°, respectively^[7]. However, for δ -form crystals, diffraction peaks appear at 16.4°, 18.7° and 24.5°. Accordingly, the difference in α - and δ -form can be identified by the diffraction patterns with characteristic diffraction peaks. As shown in Fig. 5, the two strong diffraction peaks of (200/110) and (203) are observed for the samples. Therefore, the characteristic diffraction of PLLA α -form crystals exhibits at 22.5°, the change of intensity of which is used to confirm transition from δ -form to α -form for PLLA18.6 and PLLA58.9. For PLLA18.6, the sample

crystallized at $T_c > 100$ °C, the diffraction peak of α -form crystals at 22.5° appears in Fig. 5(a), which is predominantly developed at high T_c (> 100 °C), but disappear in the pattern of δ -form crystals produced at low T_c (< 100 °C). For PLLA58.9, the samples crystallized at $T_c < 110$ °C, and $T_c > 110$ °C show the typical WAXD profiles of the PLLA δ -form and α -form crystals, respectively. As M_n decreases, the mobility of PLLA chains is improved, inducing the much easier arranging into crystalline lattices during the crystallization process. Accordingly, as for the lower M_n samples, PLLA tends to format stable phase at lower temperatures because of high chain mobility. On the other hand, as for the higher M_n samples, the molecular chain is so long that it is difficult to arrange orderly as perfect crystals. Thus, the critical T_c for change of crystal formation from δ -form to α -form increases as M_n increasing.

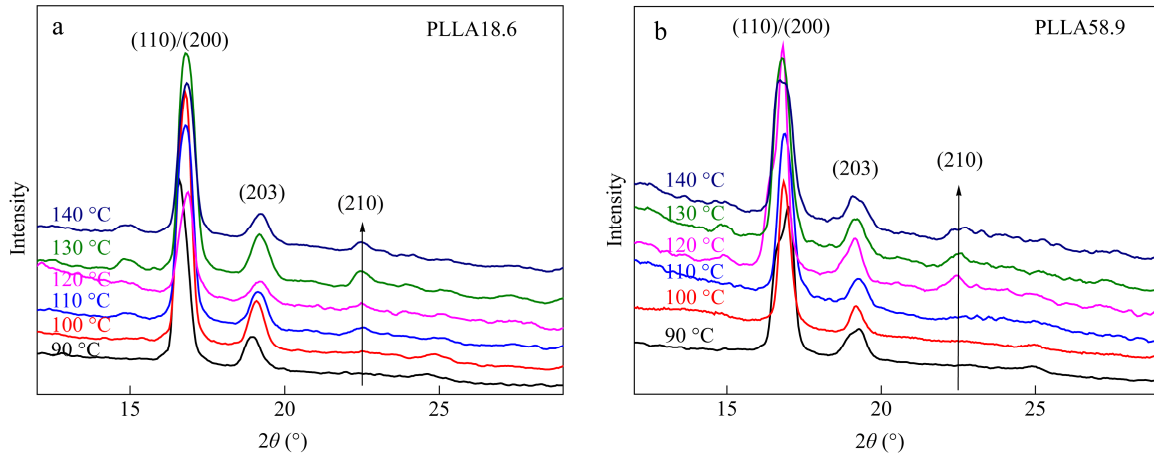


Fig. 5 WAXD patterns for PLLA samples isothermally melt-crystallized at T_c ranging from 90 °C to 140 °C: (a) PLLA18.6 and (b) PLLA58.9

When the isothermal crystallization was over, the samples were reheated to 200 °C at the rate of 10 K/min. The dependence of melting behaviors of PLLA on M_n was analyzed at various T_c , as shown in Fig. 6. The dependence of melting enthalpy (ΔH_m) on M_n is presented in Fig. 6(a). For PLLA5.5 and PLLA10.6, their melting temperatures are below 160 °C, as shown in Fig. 2. At 140 °C, the formation of crystallite is difficult because of low degree of supercooling, so the temperature is raised above 120 °C, the ΔH_m values of PLLA5.5 and PLLA10.6 decrease. When M_n is above 18.6 kg/mol, the ΔH_m values decrease with the M_n increment. For moderate molecular mobility, the ΔH_m value of PLLA18.6 is higher than that of other samples, compared at the same T_c . Especially, the value of ΔH_m reaches 87.1 J/g for PLLA18.6 at 140 °C, and this value is very close to the equilibrium melting enthalpy 93.6 J/g. The melting enthalpy of PLLA18.6 specimen is the highest value reported until now^[2, 6].

In all range of T_c , the phenomena of T_{ccII} and the double melting peaks do not appear in subsequent DSC scans of PLLA18.6 (Fig. 6b). As shown in Fig. 5(a), δ -form is mainly produced in PLLA18.6 isothermally crystallized below 100 °C, and α -form is produced above 100 °C. For crystallization temperature below 100 °C, the temperature of single melting peak for PLLA18.6 remains constant, the peak T_{ccII} is not observed. However, the crystal transition of PLLA18.6 develops fast, the signal of crystal transition is not detected. When PLLA18.6 crystallizes at above 100 °C, the single melting peak of temperature rises up. On the contrary, the melting curves of PLLA58.9 (Fig. 6c) display several differences. The T_{ccII} is observed prior to the single melting peak in the temperature range of $T_c \leq 110$ °C, and the corresponding intensity of T_{ccII} shows a significant decrease with crystallization temperature increasing, while the location of the main melting peak is almost independent of T_c . All these results indicate that the δ -form crystals transform into α -form crystals during the heating. Secondly, in the range of 110 °C $< T_c \leq 130$ °C, PLLA tends to form coexistence of δ - and α -crystals. The enthalpy of melting peak T_{mI} increases, and the T_{mII} peak area drops in enthalpy, and the double melting peaks overlap

severely. These are due to melt-recrystallization and crystal transition process. At 130 °C, only one melting peak is observed. When the crystallization temperature is over 130 °C, both T_{ccII} and the double melting peaks disappear in DSC curves. The single melting peak shifts to higher temperatures. In generally, crystallization rate and melting behavior are affected by M_n .

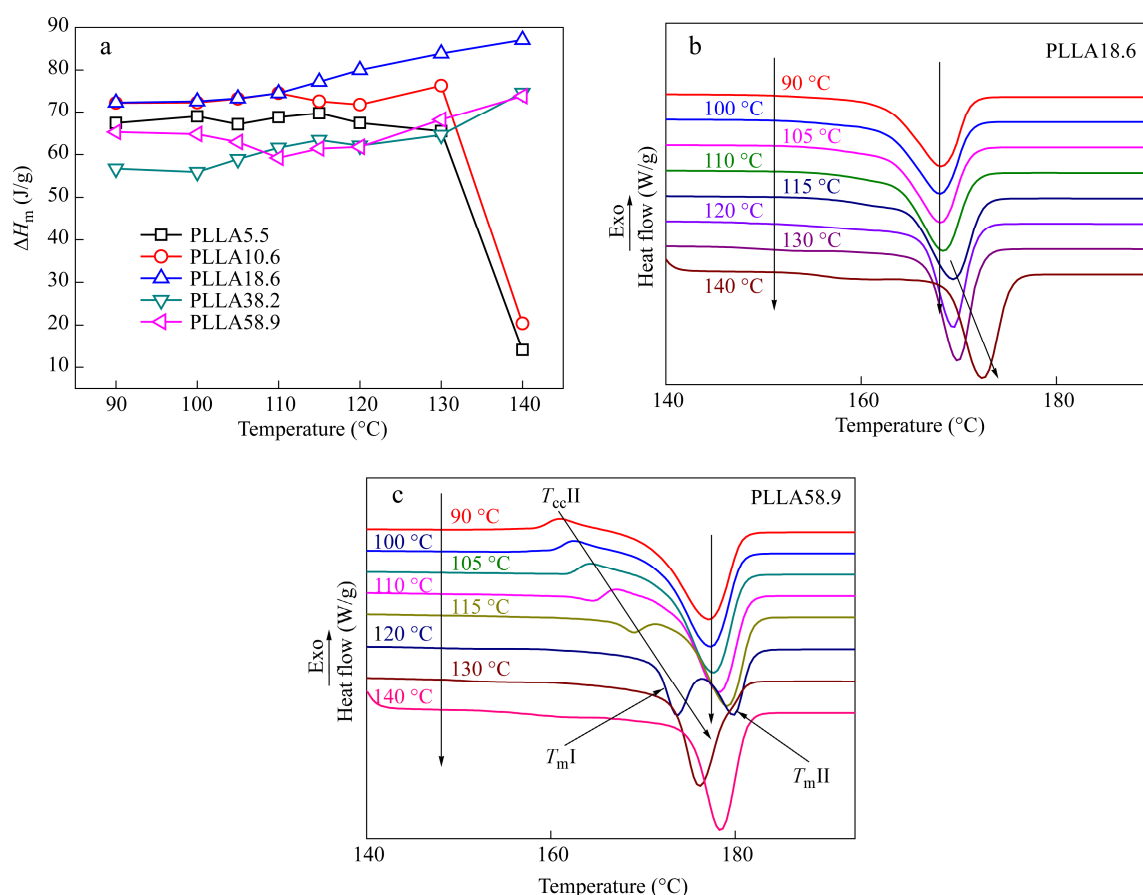


Fig. 6 (a) The melting enthalpy against M_n from DSC heating curves, (b) DSC heating scans of PLLA18.6 after isothermal crystallization and (c) DSC heating scans of PLLA58.9 after isothermal crystallization

CONCLUSIONS

In our work, the effects of molecular weight on the crystallization and melting behaviors were investigated for PLLA with M_n ranged from 5.5 kg/mol to 58.9 kg/mol by DSC and WAXD. With the increase of M_n , the crystallization rate and melting enthalpy firstly reached the highest values for PLLA of 18.6 kg/mol, and then dropped. The bell-shaped curve was observed for the dependence of the crystallization rate against M_n . The melting enthalpy of PLLA18.6 reached 87.1 J/g, which was the highest value reported in the literature. With M_n increasing, the critical temperature for the formation of δ - and α -form increased. For the low- M_n PLLA, T_{ccII} was not observed in the DSC curves, because the δ -form crystals could quickly transform into α -form crystals since relatively high chain mobility in the reheating process. With the increase of M_n , intensity of T_{ccII} enhanced generally, because the lower chain mobility might slow the δ - to α -form crystals transition and the enthalpy of crystal transition could be detected by DSC.

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