Polymorphous Crystallization and Multiple Melting Behavior of Poly(L-lactide): Molecular Weight Dependence

Pengju Pan, Weihua Kai, Bo Zhu, Tungalag Dong, and Yoshio Inoue*

Department of Biomolecular Engineering, Tokyo Institute of Technology, 4259-B-55 Nagatsuta, Midori-ku, Yokohama 226-8501, Japan

Macromolecules 2007, 40, 6898

Introduction

Polymorph PLLA crystals :

α - form crystal : common and stable polymorph

β - form crystal : stretching the α -form(at high drawing and high temperature)

γ - form crystal : epitaxial crystallization

α′ - form crystal : disordered form of α - form crystal

The crystal structure and morphology
associates the mechanical and thermal properties

- crystallization kinetics
- crystalline structure
- melting behavior

⟺ crystallization temperature

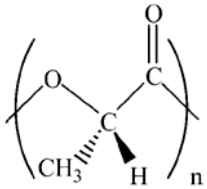
governing of
- the crystallization kinetics
- polymorphism of polymer

⟺ molecular weight (MW)

- polymorphic crystallization
- melting behavior

⟺ molecular weight (MW)

Experimental Section

Materials : 

PLLA , number-average molecular weight (M_n) : 15 KM_n ~ 219 KM_n

Gel Permeation Chromatography (GPC) :

Use to measure Molecular weight of the PLLA samples

Differential Scanning Calorimetry (DSC) :

Use to measure thermal properties of PLLA samples

the isothermal melt-crystallization experiment,
→ melting at 200 °C for 2 min
→Coolling at a rate of 100 °C/min to the desired T_c
→heating to 200 °C at 10 °C/min(or 2 °C/min)

at 90 °C ≤ T_c ≤ 130 °C, the isothermal melt-crystallization time is 60 min.
at T_c > 130 °C and T_c < 90 °C, the isothermal melt-crystallization time is 240 min

Polarized Optical Microscopy (POM) :

The sample place between two glass slides
→heat to 200 °C in a hot stage for 2min
→ the sample quench to the desired T_c

Wide-Angle X-ray Diffraction (WAXD) :

Rigaku RU-200, working at 40 kV and 200 mA,
Scans angles: 5°-50° at a rate of 1°/min.

FTIR Spectroscopy :

FTIR-6100 spectrometer+IMV-4000 multichannel infrared microscope+MCT detector

PLLA sample place between two pieces of BaF_2 slides
→ heat to 200 °C in a hot stage for 2min
→ The sample quench to the desired T_c

study the melting behavior : after the melt-crystallization
the sample heat from T_c to 190 °C at 2 °C/min

the cold-crystallization experiment :
→ melting at 200 °C for 2 min
→ coolling to 0 °C at 100 °C/min
→ reheating to 200 °C at 10 °C/min.

the nonisothermal melt-crystallization experiment :
→ melting at 200 °C for 2 min
→ coolling to 0 °C at 5 °C/min

Table 1. Molecular Weight and Thermal Properties of PLLA Samples

code	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	T_g (°C)	T_{cc} (°C)	T_m (°C)	T_m^0 (°C)
PLLA15	15.4	21.3	1.38	48.0	83.2	160.9	174.2
PLLA41	40.7	64.5	1.58	55.9	104.1	170.2	185.0
PLLA118	118.3	176.6	1.49	59.1	113.9	176.5	192.4
PLLA219	218.6	359.2	1.64	59.7	122.4	173.4	197.6

peak shifts

Difference of ~10 °C between PLLA219 and PLLA15 in T_g, T_m, and T_m^0

M_n: number-average molecular weight
M_w: weight-average molecular weight

T_g : glass transition temperature
T_{cc} : cold crystallization temperature
T_m : melting temperature
T^0_m : equilibrium melting temperature

Results and Discussion

Crystallization Kinetics

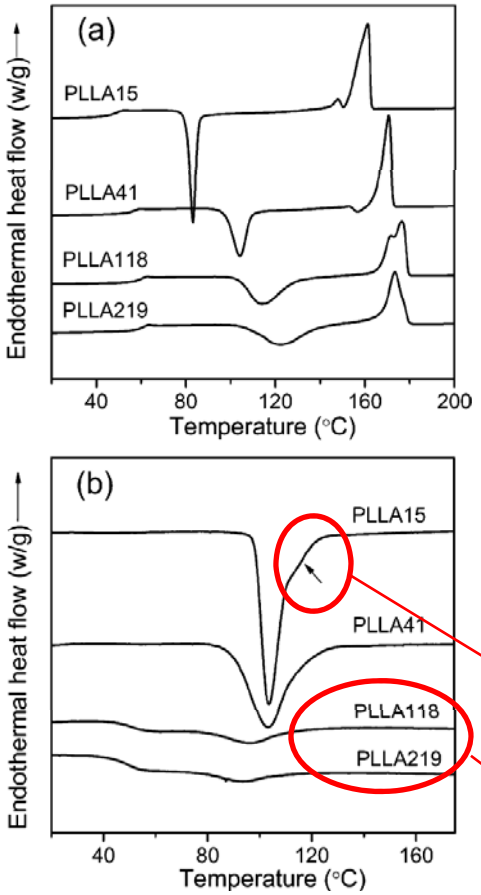


Figure 1. DSC thermograms of (a) cold crystallization at a heating rate of 10 °C/min and
(b) nonisothermal melt-crystallization at a cooling rate of 5 °C/min for PLLA with various MWs.

the effect of various MWs *on* the isothermal crystallization

With decreasing MW,
the crystallization peak shifts to higher temperature and becomes much sharper,

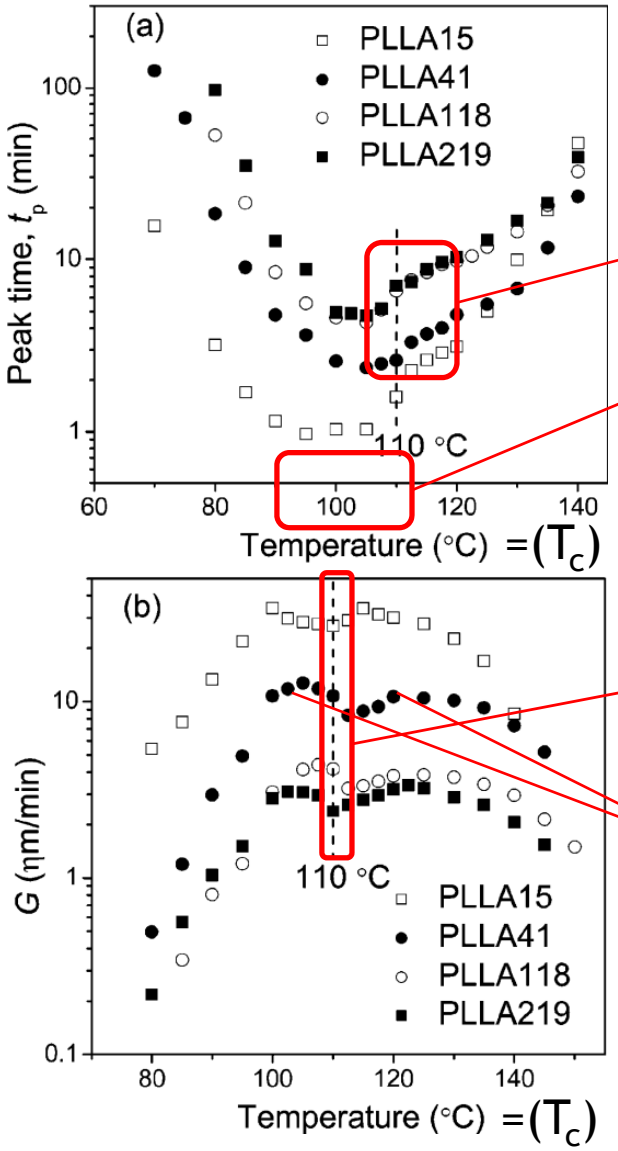
⇓

the crystallization rate increases

the crystallization mechanism changes

the crystallization cannot be finished

the effect of T_c *on the crystallization* behavior



critical temperature (110°C) is almost not affected by MW.

t_p value increases suddenly

crystallization is fastest

almost not influenced by MW

multipeaked spherulite growth kinetics

the difficulty in nucleation at low undercooling
and the poor diffusivity at high undercooling

bell-shaped growth

Figure 2. (a) Peak time (t_p) and (b) spherulite radius growth rate (G) of PLLA with various MWs as a function of Tc.

- the lower MW samples show much faster crystallization rate than those of the higher MW ones.

the mobility of polymer chains improve
the much easier diffusion of polymer chains

- the crystallization kinetics are strongly dependent on the MW of PLLA.

Crystalline Structure

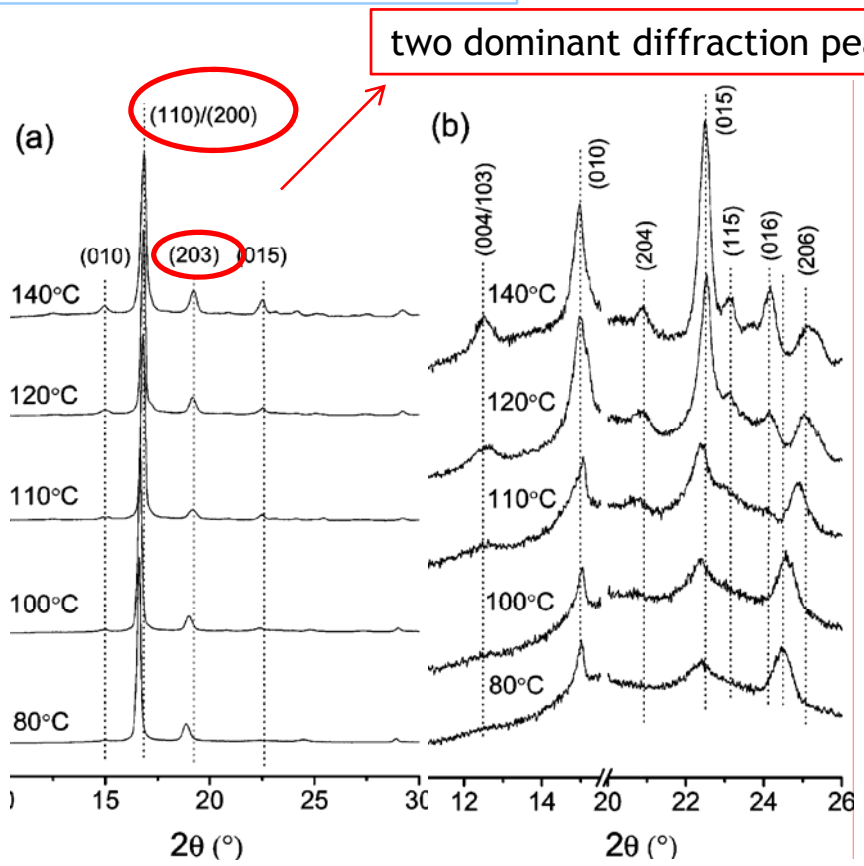


Figure 3. (a) WAXD patterns and (b) enlarged WAXD patterns of PLLA15 isothermally melt-crystallized at T_c = 80-140 °C.

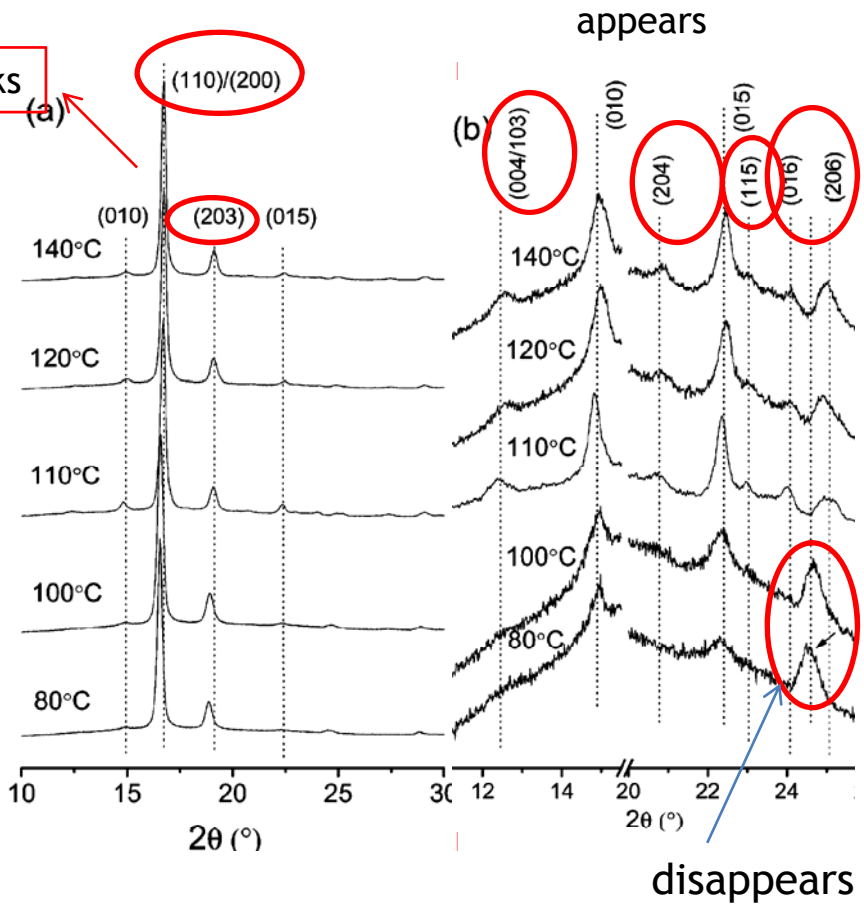
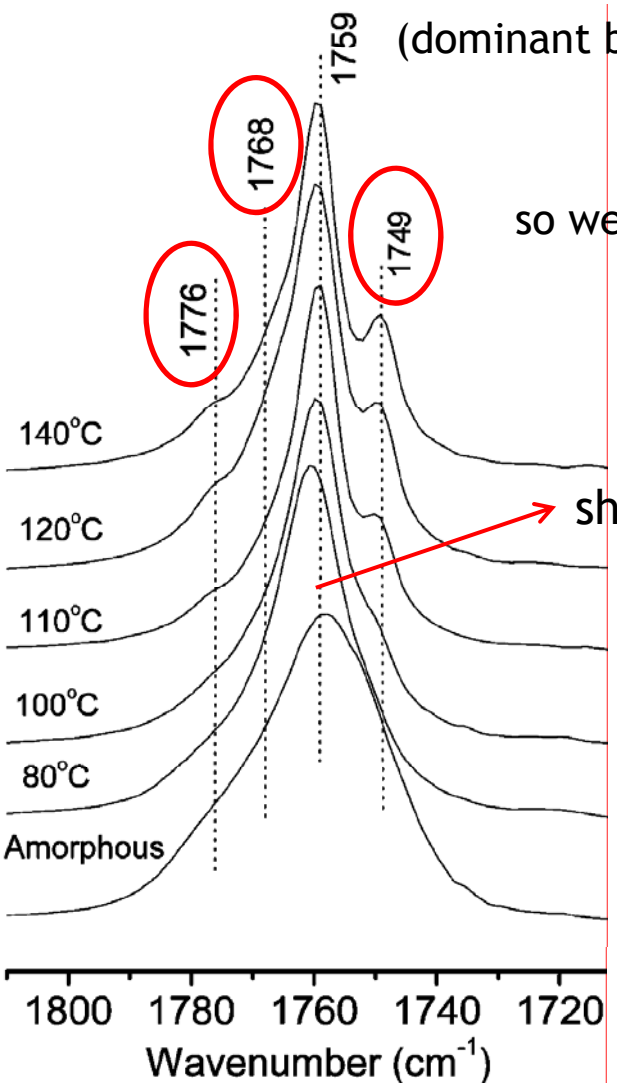


Figure 4. (a) WAXD patterns and (b) enlarged WAXD patterns of PLLA219 isothermally melt-crystallized at T_c = 80-140 °C.

IR spectra of the C=O stretching band (1810-1710 cm-1)



(dominant band)

so weak three new bands

shifts toward lower wavenumber side by about 1 cm-1

Figure 5. IR spectra in the 1810-1710 cm-1 region of amorphous and crystalline PLLA15 isothermally melt-crystallized at T_c = 80-140 °C.

WAXD patterns and IR spectra ➡ α -form crystal is produced at high T_c
α′ -form crystal is produced at low T_c

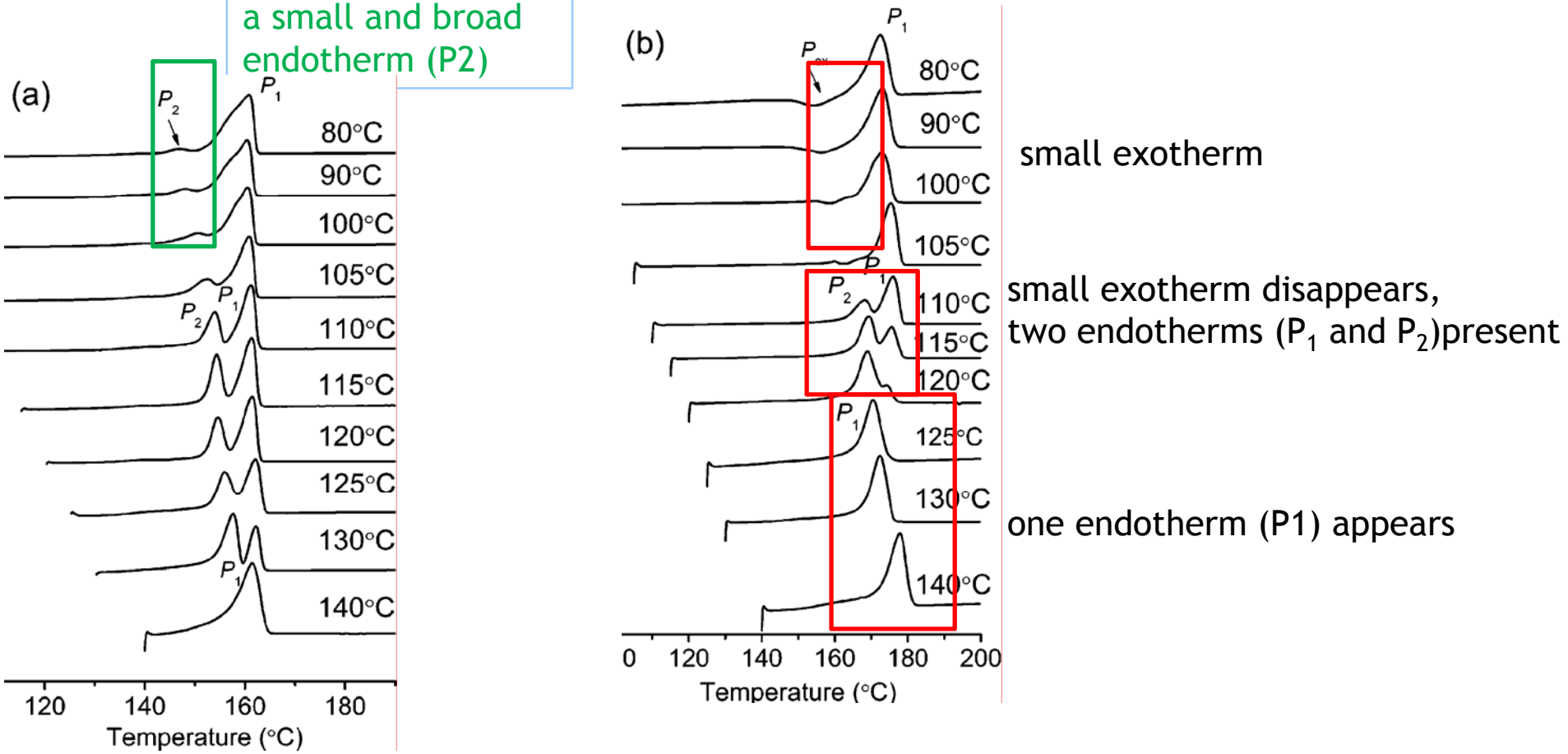
100-120 ℃ : the mixture of α′- and α-form crystals
the crystallization kinetics change discontinuously (Figure 2)

According to Zhang et al.,
- both the α′- and α -form crystals have the same 10_3 helix chain conformation and orthorhombic unit cell
- the packing of the side groups in the helical chains of the α′-form crystal is less ordered and looser than that of the R-form crystal.

Because the different crystal modifications usually have the different crystallization kinetics(the different nucleation or growth mechanisms) , it is reasonable to consider that the discontinuousness of crystallization kinetics is due to the polymorphism of PLLA.

DSC Measurements on the Melting Processes

a small and broad endotherm (P2)



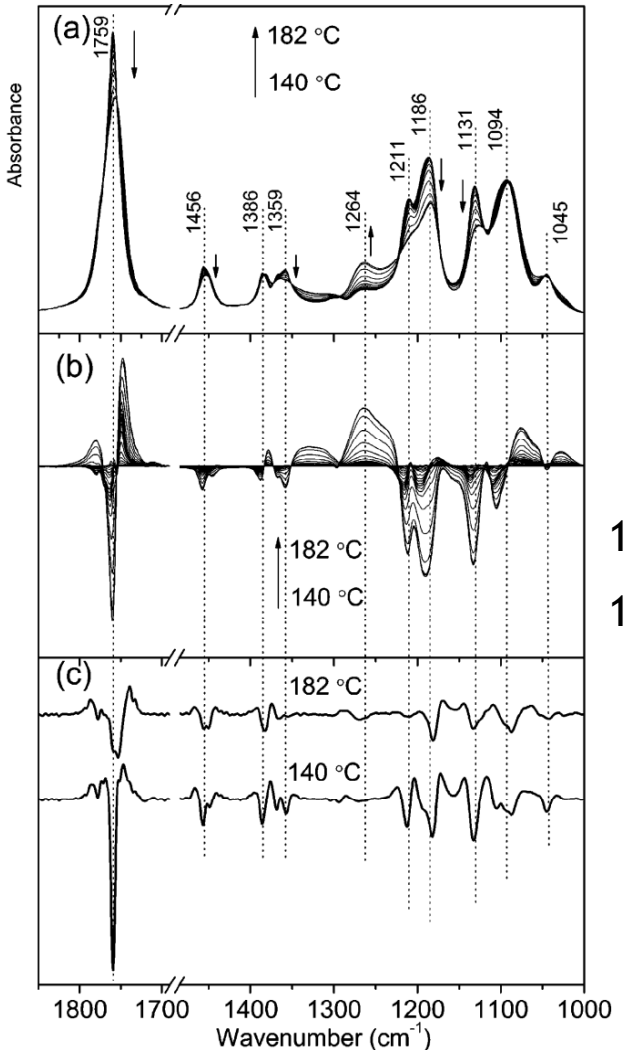
small exotherm

small exotherm disappears, two endotherms (P_1 and P_2)present

one endotherm (P1) appears

Figure 6. DSC heating curves of (a) PLLA15 and (b) PLLA118 isothermally melt-crystallized at various T_cs.

In Situ Observation on Polymorphic Melting of High-MW PLLA



The C=O bands are greatly sensitive to the crystalline structure of PLLA(in Figure 5).

The C=O bands are mainly evaluated here.

1850-1700 cm-1 : C=O stretching band group

1300-1000 cm-1 : C-O-C, CH_3, C-CH_3, and their coupling Vibration

Figure 7. (a) Temperature-dependent IR spectra, (b) difference spectra calculated by subtracting the initial crystalline spectra (at 140°C), in the 1850-1000 cm-1 range for **PLLA118** isothermally melt-crystallized at T_c = 80 °C registered in the heating process at a rate of 2 °C/min from 140 to 182 °C. (c) Second derivatives of the spectra collected before (at 140 °C) and after (at 182 °C) melting.

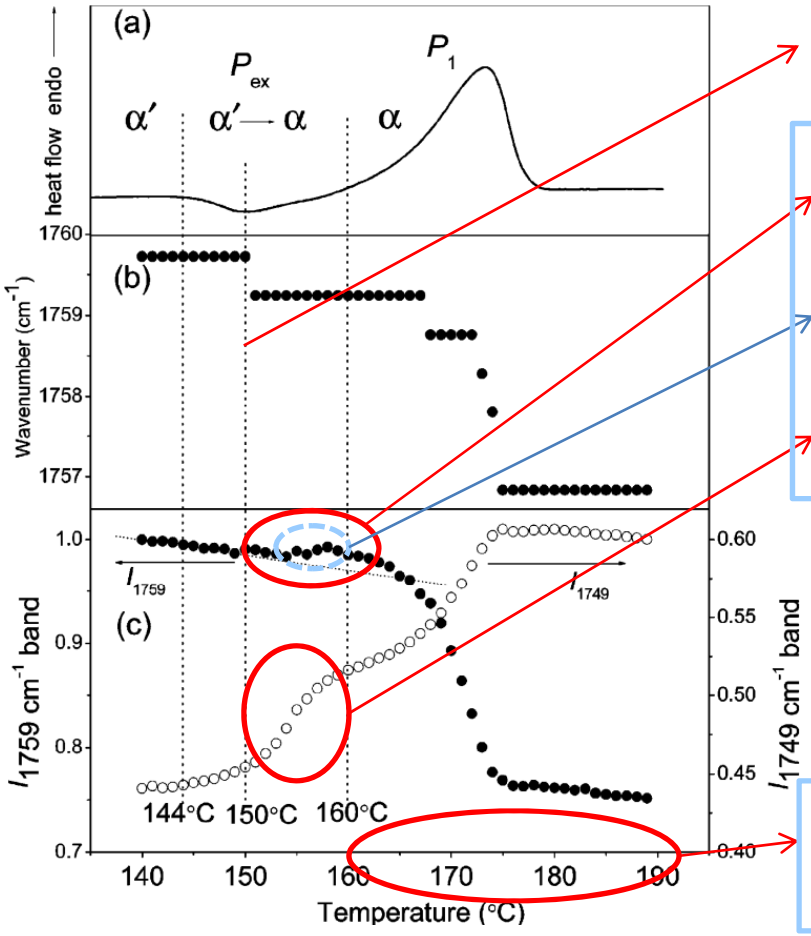


Figure 8. (a) DSC heating curve, temperature-dependent (b) wavenumber of the C=O stretching band, and (c) normalized intensity of the 1759 and 1749 cm-1 bands for **PLLA118** isothermally meltcrystallized at T_c = 80°C during the heating process at a rate of 2 °C/min.

the peak shift to lower wavenumber of C=O banc

linear change

I_{1759} increase

drastic increase of I_{1749}

↔ Figure 9a

increase of the content of the amorphous phase

C=O band shifts toward lower wavenumber

↕ Figure 9b

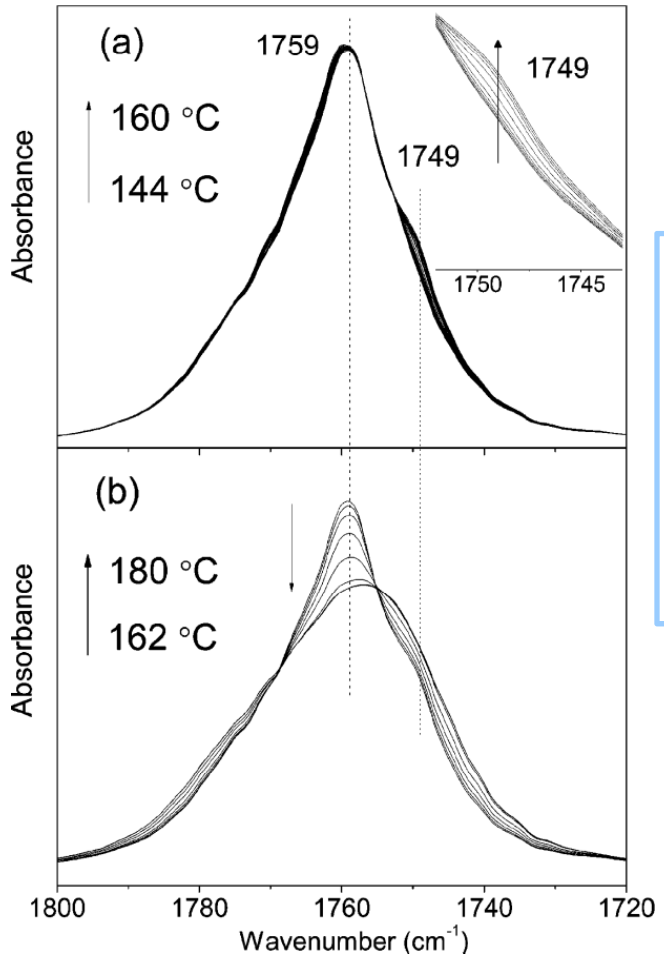


Figure 9. Temperature-dependent IR spectra in the 1800-1720 cm-1 range for **PLLA118** isothermally melt-crystallized at T_c = 80°C registered in the heating process at 2 °C/min from (a) 144 to 160°C and (b) 162 to 180°C.

Figure 8, Figure 9

- α′- to α-crystalline phase transition occurs prior to the major melting

- C=O band of the α′-form crystal locates at higher wavenumber than that of the α-form crystal.

To study the effect of T_c on the melting process, using time- resolved FTIR spectroscopy.

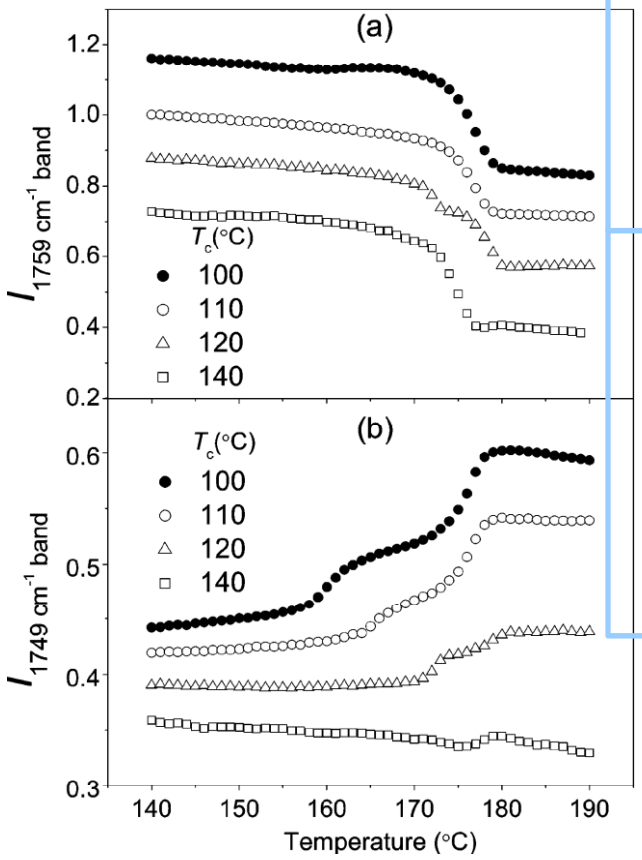


Figure 10. Temperature-dependent normalized intensity of the (a) 1759 and (b) 1749 cm-1 bands for **PLLA118** isothermally melt-crystallized at T_c = 100, 110, 120, and 140°C during the heating process at a rate of 2°C/min.

at T_c = 100 °C,
the I_{1759} and I_{1749} values have the very similar tendency of variation as those of PLLA118 crystallized at T_c = 80°C

indicating that the α´- to α-crystalline phase transition occurs before melting.

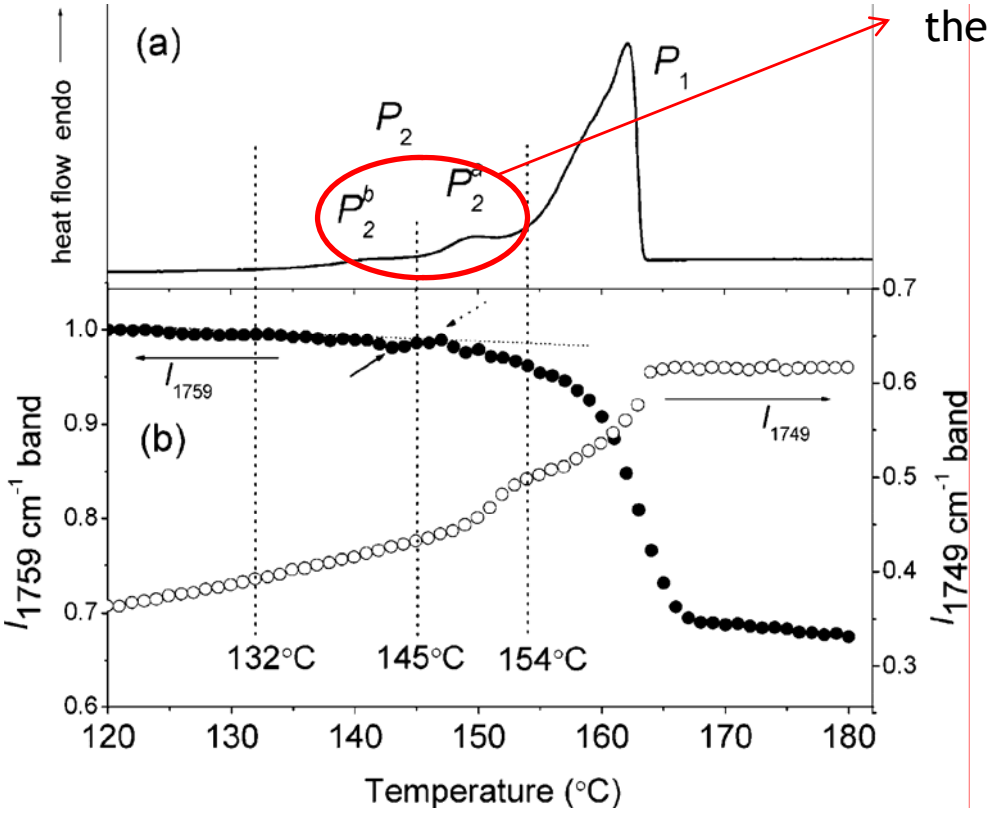
at T_c = 110 and 120 °C,
the increase of I_{1759} disappears, but the increase of I_{1749} is much weaker before the dominant melting.

the α´- to α-crystalline phase transition and the melting of the original α -form crystal.

at T_c = 140 °C,
no increase of the I_{1749} value before the melting is observed, and also the I_{1749} value decreases monotonously in the heating process

direct melting of the α-form crystal.

In Situ Observation on Polymorphic Melting of Low-MW PLLA



the broad endothermic peak consists of two parts

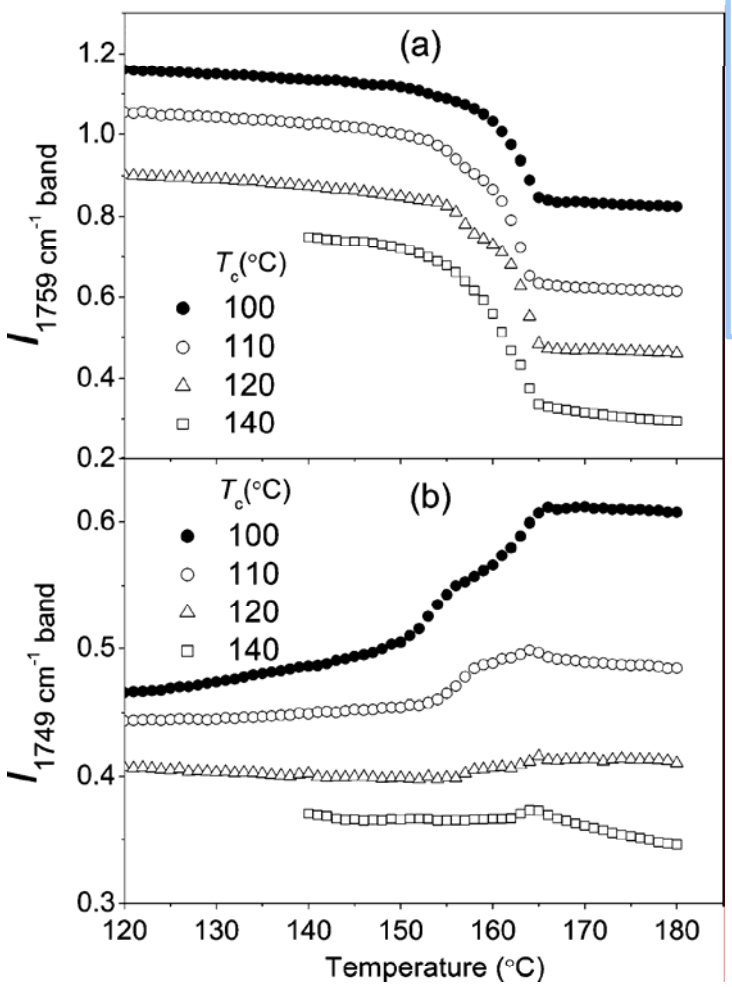
- at T < 140 °C,
  I_{1759} value first decreases

- nearby 145 °C,
  I_{1759} increases

- at T < 145 °C,
  I_{1749} value increases gradually

- at 145-154 °C,
  the sharper increase of the I_{1749}

Figure 11. (a) DSC heating curve and (b) temperature-dependent normalized intensity of the 1759 and 1749 cm-1 bands for **PLLA15** isothermally melt-crystallized at T_c = 80 °C during the heating process at a rate of 2 °C/min.



at Tc = 100 °C,
the I_{1759} and I_{1749} values have the very similar tendency of variation as those of PLLA15crystallized at T_c = 80°C

the melting of the α′-form crystal and α -form crystal from occur simultaneously

at T_c = 120 and 140 °C, the I_{1749} value does almost not change during the heating process

the α -form crystal is developed

At *Tc > 130 ℃,*
the as-produced α -form crystal is perfect enough and it melts directly without the melt-recrystallization process,

Figure 12. Temperature-dependent normalized intensity of the (a) 1759 and (b) 1749 cm-1 bands for **PLLA15** isothermally melt-crystallized at T_c = 100, 110, 120, and 140 °C during the heating process at a rate of 2 °C/min.

Conclusions

the melting of PLLA is found to be also greatly influenced by T_c and MW

In the PLLA crystallized at low T_c, the transition from disordered α′- form crystal to ordered α-form crystal prior to the dominant melting was confirmed

In the high- MW PLLA crystallized at low T_c,
almost all the α′-form crystals transform into the α -one in the heating scan

In the low-MW PLLA crystallized at low T_c,
the α′-form crystals only partially transform into the α-one, and some amounts of α′-form crystals melt directly without transition during the heating process

With the increase of T_c, the melting of PLLA with various MWs changes from the phase transition + melting mechanism to the usual melt-recrystallization mechanism.

the effects of T_c and MW on the polymorphism are quite important to interpret the peculiar thermal behavior of PLLA as well as for controlling the physical properties of PLLA by optimizing the crystallization process.