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Influence of Chain Architectures on Crystallization Behaviors of PLLA Block in PEG/PLLA Block Copolymers

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Electronic Supplementary Information

Abstract The effect of the architecture of poly(ethylene glycol)/poly(L-lactide) (PEG/PLLA) block copolymers on the non-isothermal crystallization behaviors of PLLA blocks was investigated by differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD). 1-Arm MPEG-*b*-PLLA and 4-arm PEG-*b*-PLLA (4PEG-*b*-PLLA) were synthesized by the ring-opening polymerization of L-lactide in the presence of poly(ethylene glycol) methyl ether (MPEG) and 4-arm poly(ethylene glycol) (4PEG). 4-Arm PLLA-*b*-MPEG (4PLLA-*b*-PEG) was synthesized by coupling 4-arm PLLA and MPEG. The WAXD results indicated that the crystalline structure of PLLA blocks did not alter due to the different chain architectures. The average values of Avrami index ($\bar{n}$) were all above 4, which indicated that the nucleation mechanism of PLLA blocks was heterogeneous nucleation, regardless of the architectures. The overall crystallization rates were decreased markedly as following: MPEG-*b*-PLLA > 4PEG-*b*-PLLA > 4PLLA-*b*-PEG, ascribed to the different confinement by PEG blocks and to the steric hindrance of chain architectures. Therefore, the crystallization of PLLA blocks became more difficult and the crystallization activation energy of the PLLA blocks increased due to the confinement of chain architectures.

Keywords Poly(L-lactide); Poly(ethylene glycol)/poly(L-lactide) block copolymer; Non-isothermal crystallization; Chain architecture

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INTRODUCTION

Recently, poly(L-lactide) (PLLA), a renewable and environmentally friendly polymer, has received much attention due to its excellent mechanical properties and good biocompatibility.^[1–4] Therefore, more and more applications in green plastics and biomedicine parts have been developed with PLLA-based materials.^[5–8] However, PLLA exhibits some serious drawbacks of brittleness and stiffness. In order to enlarge the area of application of PLLA, lots of methods were systemically investigated by many researchers to enhance the toughness of PLLA, especially PLLA block copolymers with other different polymer blocks, such as poly(butylene succinate) (PBS),^[9,10] poly(ϵ -caprolactone) (PCL),^[11,12] and poly(ethylene glycol) (PEG).^[13–16] For PEG/PLLA block copolymers, the introduction of PEG could increase the flexibility, hydrophilicity, and degradation resistance of PLLA matrix, and thus could broaden the

applications in drug release and tissue scaffold.^[8,16] On the other hand, PEG and PLLA are thermodynamically miscible, nor are PBS/PLLA and PCL/PLLA block copolymers.^[17–20] As a result, PEG/PLLA block copolymers may have various morphologies, and show different crystallization and melting behaviors as subjected to the specified thermal history.

Crystallization processes could determine the final properties and morphologies of crystalline polymer materials. Therefore, as for crystalline/crystalline PEG/PLLA block copolymers, their crystallization and melting behaviors were concerned by many researchers, despite that the behaviors are more complex than those of crystalline/amorphous and amorphous/amorphous block copolymers.^[20–24] Han *et al.*^[18] reported the confined crystallization in multi-length scales of PLLA-*b*-PEG diblock copolymers. The PEG blocks could crystallize in the inter-fibrillar and inter-lamellar regions of the prior crystallized PLLA. Sun *et al.*^[19] studied the crystalline behaviors of PEG-*b*-PLLA. The PLLA block showed a typical spherulite structure with banded textures while the PEG block showed a single crystal structure with an abundance of screw dislocations. Zhang *et al.*^[21] observed a small endothermic peak and a sharp exothermic peak subsequently in the reheating scan of melt-quenched PLLA-*b*-PEG-*b*-

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PLLA triblock copolymer in DSC thermograms. They confirmed that PLLA did exist as a kind of mesophase through quenching, but not as a normal amorphous phase by FTIR and WAXD. Yang *et al.*^[23] studied the non-isothermal crystallization and melting behaviors of the PEG blocks in the PLLA-*b*-PEG diblock copolymer. They found that the nucleation mechanism of the PEG blocks changed from heterogeneous to homogeneous nucleation with the increase of PLLA block length.

In our previous work, the interaction of PLLA-*b*-PEG diblocks was investigated during a two-step crystallization and the following melting process.^[22,24] PLLA crystallized from 200 °C under different cooling rates could form different microphase separation, inducing the sequentially fractional crystallization of PEG. On the other hand, the different microphase separation could also result in the double-melting behavior of PLLA in the heating process. The effects of molecular weight and architecture on the crystallization of PLLA block and PEG block were investigated for MPEG-PLLA, 2arm-PEG-PLLA, and 4arm-PEG-PLLA block, and one end of PLLA block was restricted in all copolymers. The results showed that the melting temperature of PLLA increased, but the crystallinity of PLLA increased at first and then decreased with the increasing M_n of PLLA block for all block copolymers. Furthermore, the melting temperature and the crystallinity of PLLA blocks decreased when the number of copolymer arms increased from 1 to 4. When M_n of the PLLA block reached a critical value, PEG crystallites disappeared.

In the present work, one confined end of PLLA blocks for MPEG-*b*-PLLA and 4-arm PEG-*b*-PLLA, and two confined ends of PLLA blocks for 4PLLA-*b*-PEG were synthesized, respectively. Through comparison of the non-isothermal behaviors for PLLA blocks with different confinement ends, the effect of the architectures on the crystallization of PLLA blocks was investigated, and the mechanism of PLLA crystallization was discussed.

EXPERIMENTAL

Synthesis and Characterization of the PEG/PLLA Block Copolymers

Poly(ethylene glycol) methyl ether (MPEG, 5.0 kg·mol⁻¹) was purchased from Sigma-Aldrich. 4-Arm PEG (4PEG, 20.0 kg·mol⁻¹) was obtained from Chemical Business Unit Pharmicell Co., Ltd. (South Korea). MPEG and 4PEG as the macroinitiators were processed by azeotropic drying with toluene at *ca.* 140 °C before use. MPEG-*b*-PLLA and 4PEG-*b*-PLLA block copolymers were synthesized by the ring-opening polymerization of L-lactide (L-LA) in the presence of Sn(Oct), initiated by MPEG and 4PEG, respectively.^[24,25] The 4PLLA-*b*-PEG block copolymer was synthesized by coupling of 4-arm PLLA (4PLLA) and MPEG-COOH (5.0 kg·mol⁻¹) under the catalysis of DCC/DMAP.^[26] The synthesis route of 4PLLA-*b*-PEG is shown in Scheme S1 (in electronic supplementary information, ESI). MPEG-COOH was obtained by the reaction of MPEG with succinic anhydride in chloroform.

The molecular weight (M_n) and polydispersity index (PDI) of MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG

were determined by ¹H-NMR (Bruker AV 400 MHz) and gel permeation chromatography (GPC, Waters Inc, USA). GPC measurements were performed at 35 °C in chloroform and polystyrene was used as the standard references. The $M_{n, PLLA}$ in the PLLA block copolymers were calculated on the basis of the known M_n of MPEG or 4PEG. Details of the characterization of MPEG-*b*-PLLA and 4PEG-*b*-PLLA have been reported in our previous work.^[24]

For 4PLLA-*b*-PEG, the ¹H-NMR and GPC results are shown in Table 1, and the GPC profiles and ¹H-NMR spectra are presented in Figs. S1 and S2 (in ESI). The PLLA block copolymers were hydrolyzed into lactic acid, and then the L-lactate content (L%) in the PEG/PLLA block copolymers was quantitatively determined by chiral HPLC.^[27] The results are shown in Table 1, and the HPLC chromatograms are presented in Fig. S3 (in ESI).

Table 1 The characteristics of PEG/PLLA block copolymers

Copolymer	$M_{n, PEG}$ (kg·mol ⁻¹)	$M_{n, PLLA}$ (kg·mol ⁻¹)	PDI	L%
MPEG- <i>b</i> -PLLA	5.0	9.0	1.20	100.0
4PEG- <i>b</i> -PLLA	5.0	9.5	1.16	100.0
4PLLA- <i>b</i> -PEG	5.0	9.3	1.63	99.6

$M_{n, PEG}$ and $M_{n, PLLA}$ are the molecular weights of PEG and PLLA for per arm

A differential scanning calorimeter (DSC, Q100, TA instrument) was employed to investigate the non-isothermal crystallization behaviors of MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG block copolymers. The samples were preheated at 200 °C to eliminate the thermal histories and then cooled to -70 °C at different cooling rates (20, 10, 5, and 2 °C·min⁻¹). The cooling and second heating thermograms were recorded.

Wide angle X-ray diffraction measurements (WAXD, Bruker D8) were performed at room temperature using Cu K α radiation (0.154 nm) as the incident X-ray beam. The 2 θ angle ranged from 10° to 30° with a rate of 2 (°)·min⁻¹.

RESULTS AND DISCUSSION

Crystallization Behaviors of PLLA Blocks

The melting temperature of PEG ($T_{m, PEG}$) was *ca.* 50 °C, which was largely below that of PLLA ($T_{m, PLLA}$, ~170 °C). Thus, as the temperature was decreased from 180 °C to 60 °C, the cooling exothermal peaks must be assigned to the crystallization processes of PLLA blocks, as shown in Fig. 1. The crystallization temperature and enthalpy of PLLA blocks ($T_{c, PLLA}$ and $\Delta H_{c, PLLA}$) are displayed in Table 2, which were determined from Fig. 1, and the cooling rates (R_c) were set as 20, 10, 5, and 2 °C·min⁻¹, respectively. For MPEG-*b*-PLLA, with the cooling rate of 20 °C·min⁻¹, $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ were 105.6 °C and 31.1 J·g⁻¹, respectively, which increased monotonically with decreasing cooling rate. The decrease of cooling rate could provide enough time for the ordered arrangement of PLLA block chains, and thus induce the increment of $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$.

For 4PEG-*b*-PLLA and 4PLLA-*b*-PEG, their values of $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ also increased with the decrease of cooling rate, similar that of MPEG-*b*-PLLA. When the cooling rate was at 20 °C·min⁻¹, $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ of

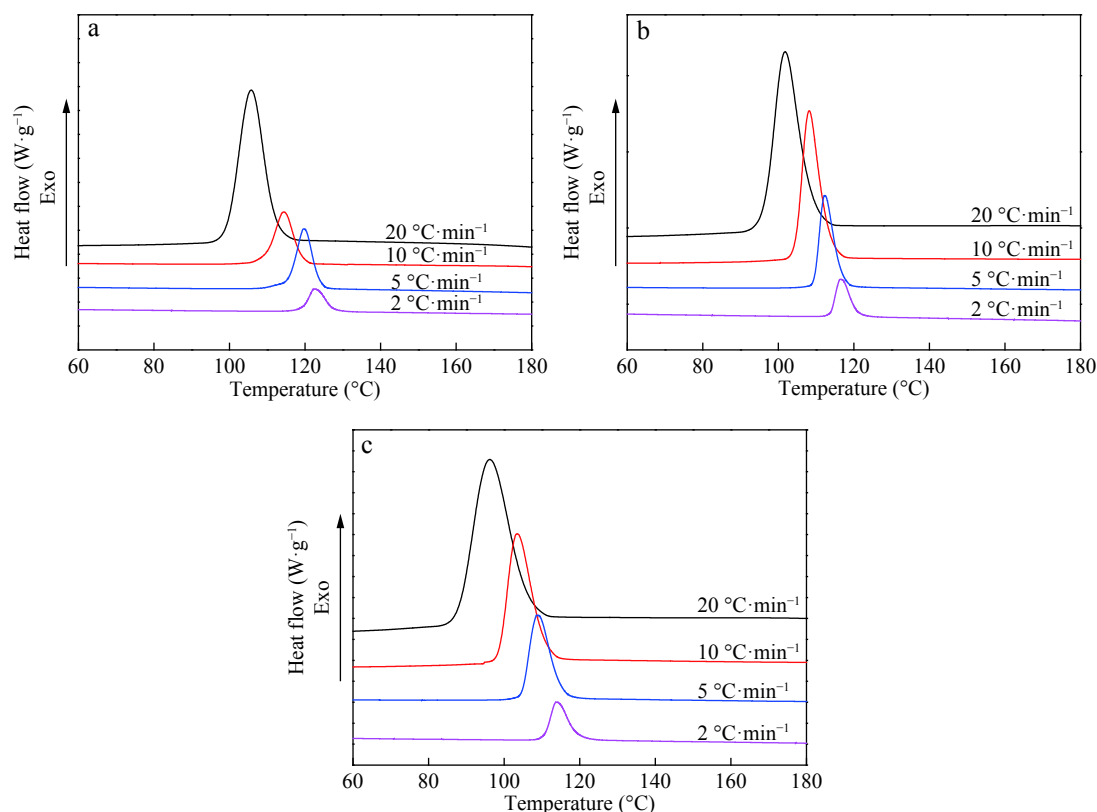


Fig. 1 DSC cooling thermograms of the PLLA blocks from the molten state to 60 °C at different cooling rates: (a) MPEG-*b*-PLLA; (b) 4PEG-*b*-PLLA; (c) 4PLLA-*b*-PEG

Table 2 The summary of $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ of PLLA blocks in MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG

R_c	MPEG- <i>b</i> -PLLA		4PEG- <i>b</i> -PLLA		4PLLA- <i>b</i> -PEG	
	$T_{c, PLLA}$ (°C)	$\Delta H_{c, PLLA}$ (J·g ⁻¹)	$T_{c, PLLA}$ (°C)	$\Delta H_{c, PLLA}$ (J·g ⁻¹)	$T_{c, PLLA}$ (°C)	$\Delta H_{c, PLLA}$ (J·g ⁻¹)
20 °C·min ⁻¹	105.6	31.1	101.8	30.3	96.2	26.4
10 °C·min ⁻¹	114.5	35.5	108.3	32.9	103.5	30.3
5 °C·min ⁻¹	119.8	37.6	112.4	34.9	108.8	31.3
2 °C·min ⁻¹	122.6	38.5	116.4	36.1	113.4	32.5

4PEG-*b*-PLLA were 101.8 °C and 30.3 J·g⁻¹, respectively, and those of 4PLLA-*b*-PEG were 96.2 °C and 26.4 J·g⁻¹.

The crystallization of PLA polymers is mainly affected by molecular architectures, such as molecular weight, optical purity, and branching architecture.^[28,29] As shown in Table 1, the optical purity of PLLA blocks in the PEG/PLLA block copolymers was nearly 100%, the molecular weights of PLLA block and PEG block were about 9.0 and 5.0 kg·mol⁻¹, respectively. As a result, the different crystallization behaviors of PLLA block in MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG were influenced by the cooling rates and the branching structures. At a given cooling rate, $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ of 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG were lower than those of MPEG-*b*-PLLA, which may be ascribed to the branch structures. Compared with MPEG-*b*-PLLA, the branch structure of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG increased the steric hindrance and viscosity, and hindered their PLLA block chains to form ordered crystals. In the 4PLLA-*b*-PEG copolymer, one end of PLLA block was fixed with initiator by covalent bond, and another end of PLLA block was connected to PEG block. As a result, the

steric hindrance of the branch structure and PEG block connected to the PLLA block could decrease the motion ability of PLLA block during the crystallization process; two confinement ends of PLLA blocks resulted in the further decrease of $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ for 4PLLA-*b*-PEG. Thus, $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ of 4PLLA-*b*-PEG were the lowest, as compared with those of MPEG-*b*-PLLA and 4PEG-*b*-PLLA. The crystallization and melting behaviors of PEG block are presented in Figs. S4 and S5 (in ESI), and the temperature ranged from 60 °C to -70 °C. In the cooling process from the melt state, PLLA crystallized at first and induced the micro-phase separation of PEG in PEG-*b*-PLLA block copolymers.^[18] The effect of the micro-phase separation on the sequential crystallization of PEG was also reported in our previous work.^[22] These results proved that the crystallization behaviors of PEG blocks were influenced by not only chain architectures, but also the different micro-phase structures derived from the crystallization of PLLA blocks. Compared with PEG crystallization, the crystallization kinetics of PLLA blocks was not discussed detailedly under different confinement environments. As a result, this work was pro-

posed to investigate the effect of chain architectures on the non-isothermal kinetics of PLLA block in PEG/PLLA block copolymers.

Melting Behaviors and Crystal Structures of PLLA Blocks

Fig. 2 shows the melting behaviors of PLLA blocks in MPEG-*b*-PLLA (Fig. 2a), 4PEG-*b*-PLLA (Fig. 2b), and 4PLLA-*b*-PEG (Fig. 2c) through cooling at different R_c s.

The melting behaviors of MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG showed some differences in multiple melting peaks. Nevertheless, the melting temperature and enthalpy ($T_{m, PLLA}$ and $\Delta H_{m, PLLA}$) were calculated according to Fig. 2 and shown in Table 3. With the decreasing cooling rate, $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ increased obviously for each block copolymer, but the values of $T_{m, PLLA}$ and $\Delta H_{m, PLLA}$ were very close for all the block copolymers at different cooling rates. The slight differences between $\Delta H_{m, PLLA}$ and $\Delta H_{c, PLLA}$ for each copolymer could be ascribed to the melt-recrystallization of the PLLA blocks in the second heating. However, Tsuji *et al.*^[28] reported that the crystallization of

PLLA blocks as the shell in four-armed diblock PDLLA-*b*-PLLA (4-DL-L) and as the core in four-armed diblock PLLA-*b*-PDLLA (4-L-DL) did not occur, ascribed to the disturbance effect of incorporated amorphous PDLLA blocks. Compared with the PDLLA blocks, the PEG blocks were flexible, and thus promoted the crystallization of the PLLA blocks in 4PEG-*b*-PLLA and 4PLLA-*b*-PEG. Therefore, the crystallization of PLLA blocks was weakly confirmed by the PEG blocks in the PEG/PLLA block copolymers.

For MPEG-*b*-PLLA, the multiple melting behaviors of PLLA were observed at different cooling rates, at a temperature range from 150 °C to 160 °C. As the cooling rates decreased, the position of lower PLLA melting peaks moved gradually to higher temperature. It was ascribed to the different acceleration effects of PEG on the melting of PLLA crystals induced by micro-phase separation, which has been reported in our previous work.^[22] These multiple melting behaviors were absent for 4PEG-*b*-PLLA and 4PLLA-*b*-PEG. However, a small exothermal peak of PLLA was observed before the main melting peaks of PLLA in the 4-arm block

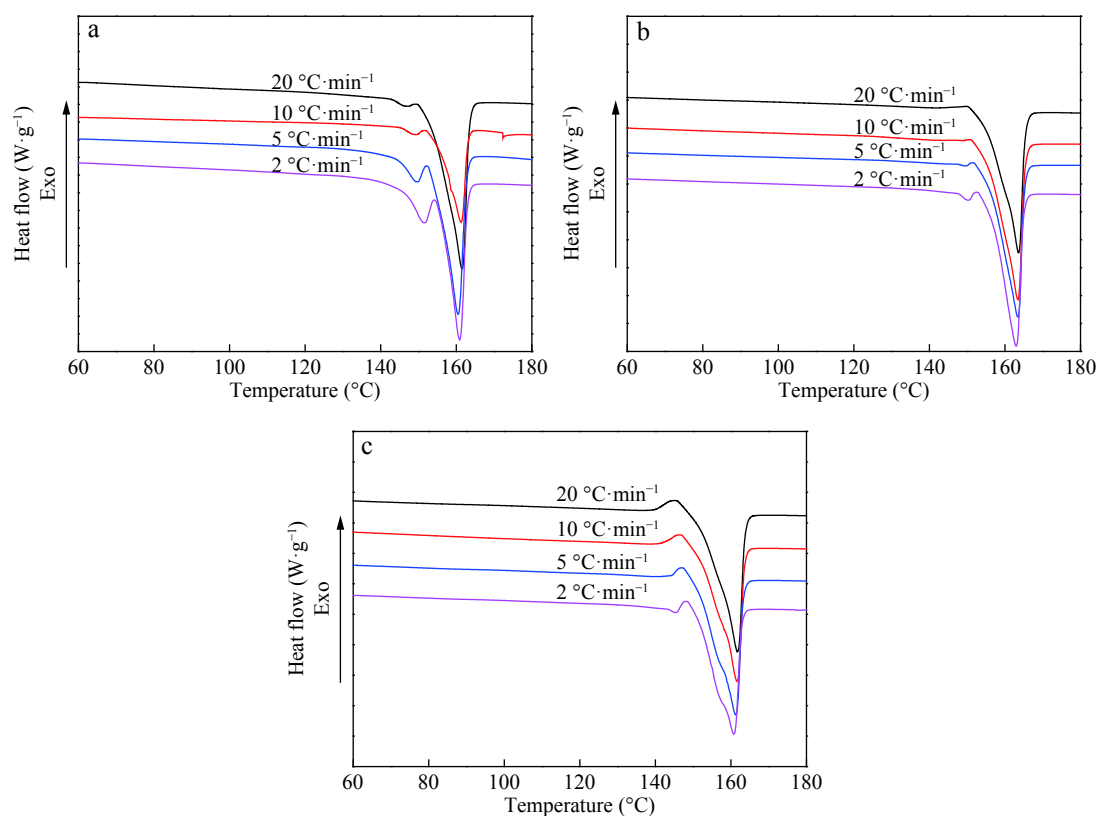


Fig. 2 The second DSC heating profiles at 10 °C·min^{−1} after cooling from the molten state at different cooling rates: (a) MPEG-*b*-PLLA; (b) 4PEG-*b*-PLLA; (c) 4PLLA-*b*-PEG

Table 3 The summary of $T_{m, PLLA}$ and $\Delta H_{m, PLLA}$ of PLLA blocks of MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG

R_c	MPEG- <i>b</i> -PLLA		4PEG- <i>b</i> -PLLA		4PLLA- <i>b</i> -PEG	
	$T_{m, PLLA}$ (°C)	$\Delta H_{m, PLLA}$ (J·g ^{−1})	$T_{m, PLLA}$ (°C)	$\Delta H_{m, PLLA}$ (J·g ^{−1})	$T_{m, PLLA}$ (°C)	$\Delta H_{m, PLLA}$ (J·g ^{−1})
20 °C·min ^{−1}	161.5	37.4	163.6	36.8	161.7	32.4
10 °C·min ^{−1}	161.2	38.6	163.4	37.5	161.6	34.6
5 °C·min ^{−1}	160.5	40.1	163.4	38.0	161.3	34.9
2 °C·min ^{−1}	160.9	39.8	163.0	39.5	160.8	34.8

copolymers, which might correspond to the δ -to- α phase transition.^[29,30] This exothermal peak indicated the formation of PLLA δ -form crystal during the cooling processes. For 4PEG-*b*-PLLA, the area of phase transition peak decreased with the decreasing cooling rates and was hardly detected as the cooling rate was 5 °C·min⁻¹, while for 4PLLA-*b*-PEG, the phase transition of PLLA blocks could always be seen, regardless of the cooling rates. At the same cooling rate, the PLLA blocks of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG preferred to crystallize as δ -form, which may result from the steric hindrance caused by the branch structures.

The crystal structures of PLLA blocks were investigated by WAXD, as shown in Fig. 3. Before WAXD measurements, the samples were first heated to 200 °C to eliminate the thermal histories and then cooled to -70 °C at different cooling rates. In previous work,^[22] the characteristic diffraction peaks of MPEG appeared at 19.3° and 23.5°. For PLLA, the diffraction peaks of PLLA α -form crystal were observed at 15°, 16.9°, 19.1°, 21°, 22.5°, and 27.4° (X-ray wavelength was 0.154 nm), corresponding to (010), (110/200), (203), (204), (210), and (207) planes, respectively, while for PLLA δ -form crystal, the diffraction peaks shifted to 16.7° and 18.9°, and the peaks at 15° and 22.5° disappeared.^[31,32] As shown in Fig. 3(a), for MPEG-*b*-PLLA block copolymer cooled at 20 °C·min⁻¹, the typical diffraction peaks were all observed at 15.0°, 16.9°, 19.1°, 22.5°, and 23.5°. The peak at 23.5° was ascribed to PEG crystals, and the peaks at 15.0°, 16.9°, 19.1°, and 22.5° could be ascribed to PLLA α -form crystals. The appearance of peaks at 15° and 22.5° indicated

the formation of PLLA α -form crystal. WAXD patterns of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG are shown in Figs. 3(b) and 3(c), and similar peaks were observed at 15°, 16.9°, 19.1°, 21°, and 22.5°. Combining with the melting behaviors of PLLA, it was indicated that the α - and δ -form crystallites coexisted during the crystallization of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG. In addition, the location of diffraction peaks did not change for different copolymers and the cooling rates, which implied that the crystal structures of PLLA and PEG from the molten state were not influenced by the chain architectures and the cooling rates.

Non-isothermal Crystallization Kinetics

The Avrami equation modified by Jeziorny

It is well known that Ozawa theory has been successfully used to interpret non-isothermal crystallization processes for many polymers. However, Yang *et al.*^[23] demonstrated that an Avrami equation modified by Jeziorny was able to agree with PEG-*b*-PLLA block copolymers, rather than the Ozawa model. The Avrami equation modified by Jeziorny is:^[33]

$$\lg[-\ln(1-X)] = \lg Z + n \lg t \quad (1)$$

where n is Avrami index, and Z is the growth rate constant. X is the relative crystallinity as a function of time (t) and defined as following:

$$X = \frac{\int_t^{t_0} (dH_c/dt) dt}{\int_{t_1}^{t_0} (dH_c/dt) dt} \quad (2)$$

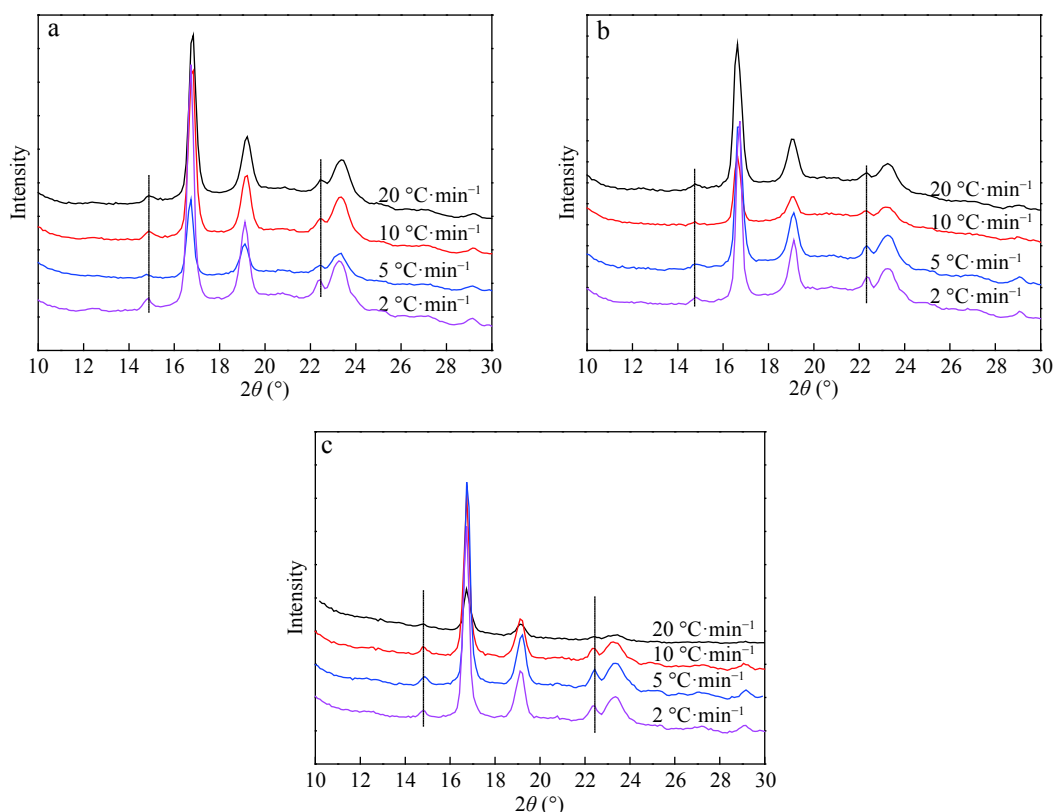


Fig. 3 WAXD patterns of the copolymers cooled from the molten state at different cooling rates: (a) MPEG-*b*-PLLA; (b) 4PEG-*b*-PLLA; (c) 4PLLA-*b*-PEG

where t_0 and t_1 are time at which the crystallization process started and ended, respectively. So, $\lg[-\ln(1-X)]$ versus $\lg t$ should follow a straight line at every cooling rate, from which n and Z could be obtained.

To avoid deviation from the theoretical curves, as suggested by Tsuji *et al.*,^[28] X in the range of 5%–30% was used for estimating n and $\lg Z$. In Fig. 4, $\lg[-\ln(1-X)]$ was plotted as a function of $\lg t$ for MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG at different cooling rates. It was obvious that the linear relationships between $\lg[-\ln(1-X)]$ and $\lg t$ were relatively decent, of which the slope and intercept are corresponded to n and $\lg Z$, respectively. The results are shown in Table 4. For MPEG-*b*-PLLA diblock copolymer, when the cooling rate was 20 °C·min⁻¹, the value of the Avrami index n was 10.17; while the cooling rates decreased, the values of n were 13.41, 13.35, and 10.13, respectively. Yang^[23] pointed out that n was an adjustable parameter in the non-isothermal process, and had different physical significance as in isothermal crystallization because of the change of temperature under nonisothermal conditions. Similar regularities were presented for 4PEG-*b*-PLLA and 4PLLA-*b*-

PEG. Above all, the average values of Avrami index ($\bar{n}$) in the non-isothermal crystallization processes were 11.8, 10.9, and 8.2 for MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG block copolymers, respectively. It was demonstrated that all PLLA blocks were nucleated by heterogeneous nuclei and grew as three-dimensional. Besides, $\bar{n}$ had a trend to be smaller with $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ of the PLLA block decreasing for block copolymers. As Jeziorny^[33] pointed out, Z should be corrected by Eq. (3) (the corrected growth rate constant was labeled as Z_c).

$$\lg Z_c = \lg Z / R_c \quad (3)$$

The obtained results are also shown in Table 4. It could be seen that Z_c also decreased with the decreasing cooling rate, which may suggest the Avrami equation modified by Jeziorny could not completely interpret the overall crystallization rates of PLLA blocks in block copolymers with different structures.

Mo method

For comparison, another model by Mo was also tested, which was first reported in the reference.^[34] It combined the

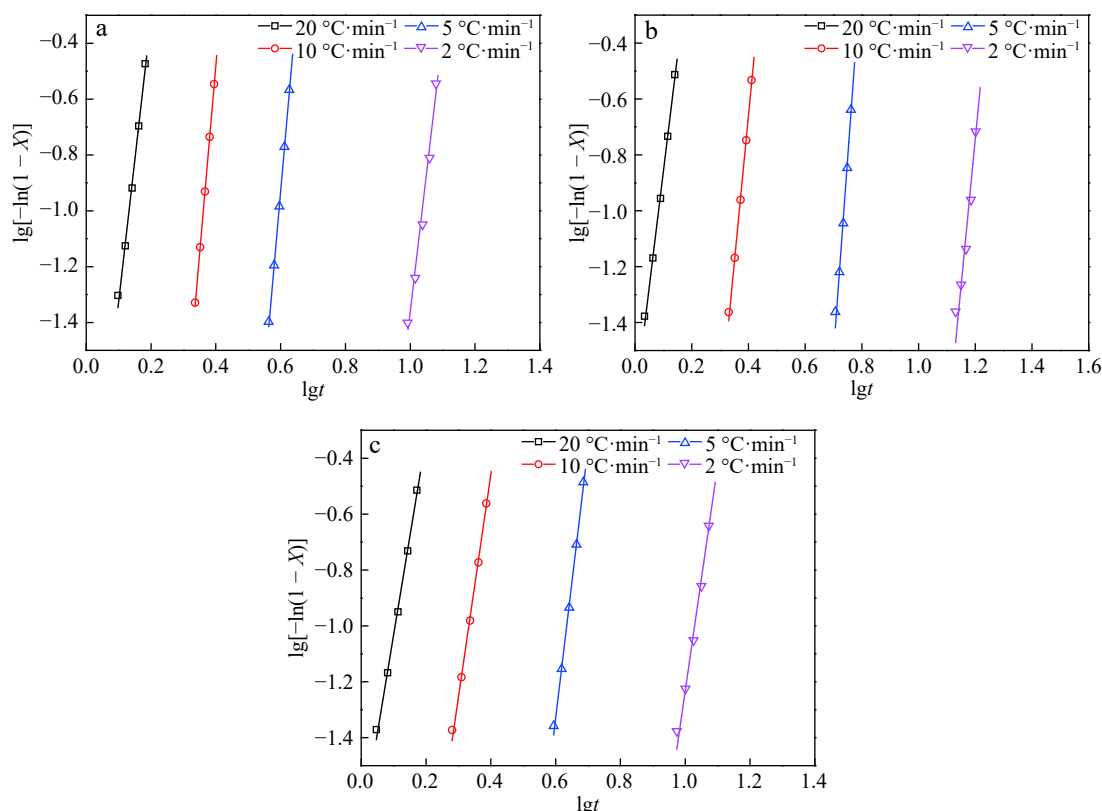


Fig. 4 $\lg[-\ln(1-X)]$ as a function of $\lg t$ of PLLA block: (a) MPEG-*b*-PLLA; (b) 4PEG-*b*-PLLA; (c) 4PLLA-*b*-PEG

Table 4 The summary of Avrami n and $\lg Z$ of PLLA block of PEG/PLLA block copolymers with different structures

R_c	MPEG- <i>b</i> -PLLA			4PEG- <i>b</i> -PLLA			4PLLA- <i>b</i> -PEG		
	n	$\lg Z$	$\lg Z_c^a$	n	$\lg Z$	$\lg Z_c^a$	n	$\lg Z$	$\lg Z_c^a$
20 °C·min ⁻¹	10.17	-2.34	-0.12	8.36	-1.68	-0.084	7.09	-1.73	-0.087
10 °C·min ⁻¹	13.41	-5.85	-0.59	10.68	-4.87	-0.49	7.91	-3.65	-0.37
5 °C·min ⁻¹	13.35	-8.94	-1.79	13.91	-11.29	-2.26	9.74	-7.15	-1.43
2 °C·min ⁻¹	10.13	-12.13	-6.07	10.52	-13.34	-6.67	8.07	-9.27	-4.64

^a $\lg Z_c$ was obtained by the Eq. (3)

Avrami and Ozawa equations, shown as Eq. (4):

$$\lg R_c = \lg F(T) - (n/m) \lg t \quad (4)$$

where n and m are Avrami and Ozawa index, respectively. $F(T)$ is defined as the value of the cooling rate, at which polymers reach a given crystallinity during unit crystallization time.^[31] So there was a negative correlation between $F(T)$ and the overall crystallization rate. With a certain crystallization, the plots of $\lg R_c$ versus $\lg t$ will show a straight line. The slope is the negative ratio of the Avrami and Ozawa index ($-n/m$), and the intercept refers to $\lg F(T)$. Different from the growth rate constants Z and Z_c by Jeziorny, $F(T)$ claims a clear physical significance, which is expected to exhibit the effect of architectures of block copolymers on the overall crystallization rates.

The relative crystallinities (X) here were set as 0.2, 0.4, 0.6, and 0.8. For MPEG-*b*-PLLA, plots of $\lg R_c$ as a function of $\lg t$ displayed straight and parallel lines in Fig. 5(a). It indicated that n/m were similar for MPEG-*b*-PLLA at different relative crystallinities. $\lg F(T)$ was also obtained from the intercepts, according to Eq. (4). When X was 0.2, $\lg F(T)$ was 1.34. With X increasing to 0.4, 0.6, and 0.8, $\lg F(T)$ became 1.38, 1.42, and 1.46, respectively. The overall crystallization constant $F(T)$ increased obviously with the increase of X . Mo plots of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG are also shown in Figs. 5(b) and 5(c). n/m and $\lg F(T)$ of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG could also be calculated from the intercepts in Figs. 5(b) and 5(c). Similar to MPEG-*b*-PLLA, n/m of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG did not change obvi-

ously with the variable X , but $\lg F(T)$ for 4PEG-*b*-PLLA and 4PLLA-*b*-PEG also increased monotonically as X increasing.

In order to investigate the effect of chain architectures on the overall crystallization rate of PLLA block, $\lg F(T)$ is plotted as a function of X for MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG in Fig. 6. As mentioned above, $\lg F(T)$ of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG both increased monotonically as X increased from 0.2 to 0.8. However, $\lg F(T)$ changed with the chain architectures of PEG/PLLA block copolymers with the same X . When X was 0.4, $\lg F(T)$ were 1.47 and 1.44 for 4PLLA-*b*-PEG and 4PEG-*b*-PLLA, respectively. $\lg F(T)$ of MPEG-*b*-PLLA was 1.38, which was smaller than those of 4PEG-*b*-PLLA and 4PLLA-*b*-PEG. The physical meaning of $F(T)$ was given by Mo as following: once the crystallinity of polymer reached a certain degree during unit time, the corresponding value of cooling rate had been determined. In other words, the smaller $F(T)$ of polymer indicated a faster overall crystallization rate. Therefore, it was confirmed that the overall crystallization rates of PLLA blocks were greatly influenced by the chain architectures as the following: MPEG-*b*-PLLA > 4PEG-*b*-PLLA > 4PLLA-*b*-PEG. $T_{c, PLLA}$ and $\Delta H_{c, PLLA}$ also decreased as the same order with the same R_c , as shown in Table 2.

Activation energy of the non-isothermal crystallization (E)

In this work, the activation energy was obtained by KAS method.^[35,36] The method is a linear integral isoconversional method, shown as the following equation:

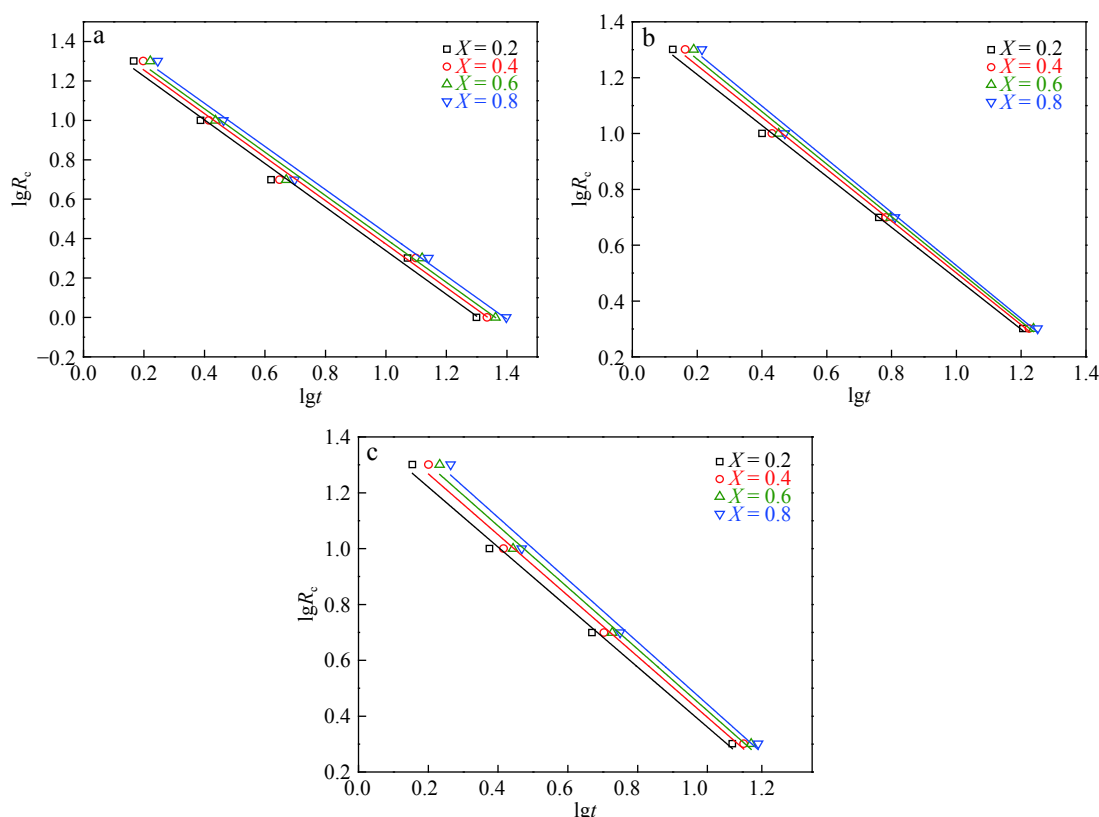


Fig. 5 $\lg R_c$ versus $\lg t$ of PLLA block at different relative crystallinities: (a) MPEG-*b*-PLLA; (b) 4PEG-*b*-PLLA; (c) 4PLLA-*b*-PEG

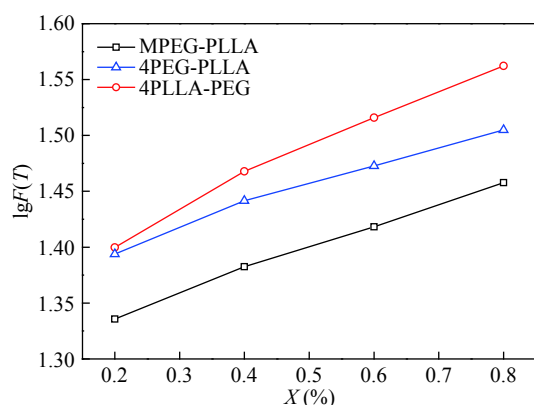


Fig. 6 $\lg F(T)$ versus the relative crystallinity (X) of MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \ln\left(\frac{AR}{E_\alpha}\right) - \frac{E_\alpha}{RT_{\alpha,i}} \quad (5)$$

where R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), A is the pre-exponential factor, E_α is the activation energy. Herein, α and β_i denotes the degree of relative crystallinity X and the cooling rate R_c , respectively. $T_{\alpha,i}$ represents the temperature at which X reached a constant value α as the cooling rate set as β_i . The subscript i is the ordinal number representing experiments performed at different cooling rates. The values of A and E_α are obtained from the slope ($\frac{E_\alpha}{R}$) and the intercept ($\ln(\frac{AR}{E_\alpha})$) of this straight line.

The relative crystallinity X is shown in Fig. 7 as a function of the crystallization temperature $T_{\alpha,i}$. For isoconversional computation (shown as Eq. 5), the values of α were selected as 0.1–0.9, and the related $T_{\alpha,i}$ were obtained from Figs. 7(a)–7(c). Then the obtained $\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$ were plotted as

a function of $1/T_{\alpha,i}$. As shown in Fig. S6 (in ESI), a series of straight lines were obtained, and the slope was defined as $(-E_\alpha/R)$. As shown in Fig. 8, the obtained E_α is plotted as a function of α . It was obvious that the activation energy of PLLA block increased gradually with the increasing degree of crystallinity. For each α , the values of E_α increased as the following order: MPEG-*b*-PLLA < 4PEG-*b*-PLLA < 4PLLA-*b*-PEG, which suggested that the crystallization of PLLA block became more difficult.

As mentioned above, the effect of chain architectures of PEG/PLLA block copolymers on the non-isothermal behaviors of PLLA was investigated by the Avrami equation modified by Jeziorny and Mo method. The E_α value was calculated by the isoconversional method. The results indicated the nucleation manners of PLLA blocks were all heterogeneous nucleation, which had no change with the different chain architectures of MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG block copolymers. However, the overall crystallization rates and E_α of PLLA block were greatly influenced by the chain architectures of the block copolymers. For the branched copolymers (4PLLA-*b*-PEG and 4PEG-*b*-PLLA), the overall crystallization rates of PLLA block were

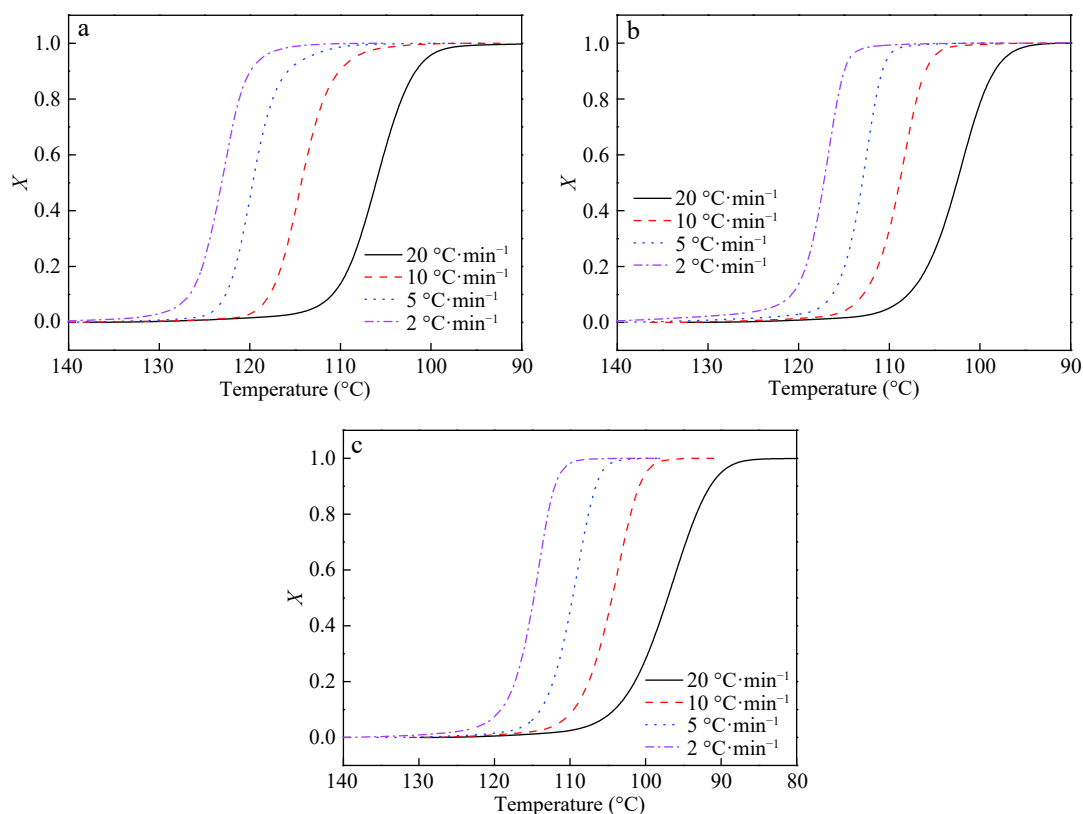


Fig. 7 Plots of the relative crystallinity X as a function of the crystallization temperature T of PLLA blocks of (a) MPEG-*b*-PLLA, (b) 4PEG-*b*-PLLA, and (c) 4PLLA-*b*-PEG block copolymers

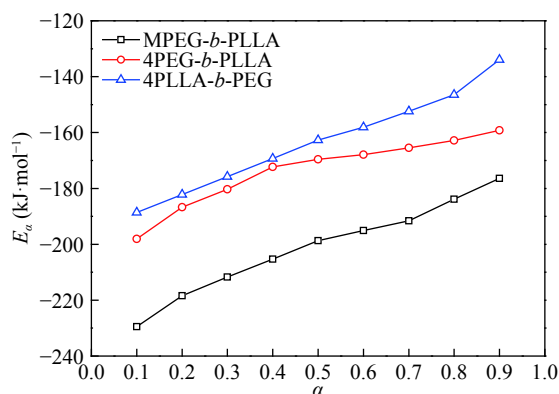


Fig. 8 Plots of E_a as a function of $\alpha(X)$ of PLLA blocks in MPEG-*b*-PLLA, 4PEG-*b*-PLLA, and 4PLLA-*b*-PEG block copolymers

lower than that of linear MPEG-*b*-PLLA, while the value of E_a increased gradually. This could be ascribed to the branched structures, which may enhance the steric hindrance and obstruct the crystallization of PLLA. On the other hand, though 4PEG-*b*-PLLA and 4PLLA-*b*-PEG possessed similar branched structures, the overall crystallization rates and E_a of PLLA block were also a bit different. For 4PEG-PLLA, its PLLA block located at the PEG arm end of branch structure and another end of PLLA could be in free motion, while for 4PLLA-*b*-PEG, the two ends of PLLA block were confined by PEG block and the branched structure, respectively. As a result, the overall crystallization rate for 4PLLA-*b*-PEG was the lowest among three type block copolymers, while its E_a showed the maximum value.

CONCLUSIONS

In this work, MPEG-*b*-PLLA and 4-arm PEG-*b*-PLLA block copolymers were synthesized by ring-opening polymerization initiated by MPEG and 4-armed PEG, respectively, while 4-arm PLLA-*b*-MPEG was synthesized by coupling of 4-armed PLLA and MPEG-COOH. The crystalline structure and non-isothermal crystallization behavior of PLLA block were investigated by DSC and WAXD. The Avrami equations modified by Jeziorny and Mo method were both used to investigate the crystallization behaviors of PLLA. The values of activation energy (E_a) of PLLA block were investigated by the isoconversional method. The results were concluded as follows:

1. The crystalline structure of PLLA block was not altered by the different chain architectures.
2. As the cooling rate was the same, the crystallization temperature ($T_{c, PLLA}$) and crystallization enthalpy ($\Delta H_{c, PLLA}$) changed with variable chain architectures: MPEG-*b*-PLLA > 4PEG-*b*-PLLA > 4PLLA-*b*-PEG.
3. The Avrami index n were all above 4, which indicated the nucleation mechanism of the PLLA block was heterogeneous nucleation for all the block copolymers, regardless of the copolymer architectures and cooling rates.
4. The overall crystallization rates of PLLA block were markedly decreased with chain architectures as following: MPEG-*b*-PLLA > 4PEG-*b*-PLLA > 4PLLA-*b*-PEG, which could be ascribed to the different confinement by PEG and

steric hindrance.

5. E_a of PLLA block increased gradually as the following order: MPEG-*b*-PLLA < 4PEG-*b*-PLLA < 4PLLA-*b*-PEG, indicating the crystallization of PLLA block became more difficult with the increasing confinement.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2202-7>.

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