ACS Macro Letters

pubs.acs.org/macroletters Letter

Enhanced Nonisothermal Crystallization and Heat Resistance of Poly(L-lactic acid) by D-Sorbitol as a Homogeneous Nucleating Agent

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Cite This: *ACS Macro Lett.* 2021, 10, 154−160 Read Online

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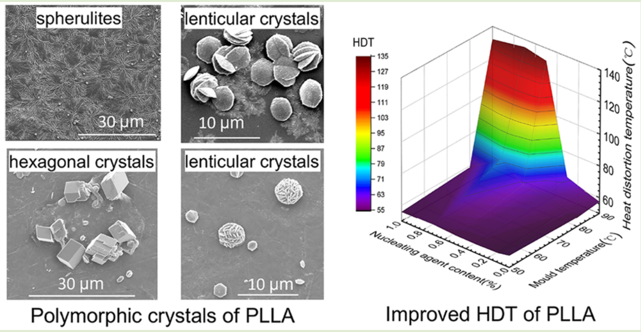

Polymorphic crystals of PLLA

Improved HDT of PLLA

ABSTRACT: We report on enhancing crystallization and heat resistance of poly(L-lactic acid) (PLLA) by D-sorbitol as a small molecule nucleating agent via melt blending. During the reheating process, the cold crystallization disappeared and the crystallinity of nucleated PLLA exceeded 50%. The heat deflection temperature of PLLA was elevated from 56 to 132 °C by simply increasing the mold temperature (90 °C) without an additional annealing treatment. We also observed the polymorphic crystals of PLLA during melt crystallization, i.e., the coexistence of hexagonal and lenticular crystals, along with their various geometrical aggregates in addition to plenty of conventional spherulites. On the basis of the fact that the nonisothermal crystallization temperature of PLLA (110 °C at a cooling rate of 10 °C/min) was higher than the melting point of D-sorbitol (about 93 °C), we speculated that D-sorbitol promoted the crystallization of PLLA through a homogeneous nucleation mechanism.

Over the past two decades, poly(lactic acid) or polylactide (PLA) has become one of the most massive commercially produced and consumed biodegradable polymers,[1] which was extensively applied in many fields, such as disposable products,[2] biomedical materials,[3,4] food packaging,[5] automotive parts,[6] and adhesives.[7] The annual consumption of PLA worldwide exceeds 200 000 t, and production capacity under planning is close to one million tons. The commercial PLA is mainly poly(L-lactic acid) (PLLA), in which the D-lactic acid content is usually less than 6%, otherwise PLA will not crystallize.

PLA has the potential to replace conventional plastics by virtue of its favorable biodegradability, biocompatibility, and mechanical properties. However, its consumption and application are still far behind those of conventional plastics, largely because the slow crystallization rate and low crystallinity make it unsuitable for blow molding. In addition, the brittleness,[8] low elongation at break,[9] and especially the poor heat resistance not only limit its application in the fields requiring high heat resistance, such as engineering plastics and boxes for hot foods, but also trouble the academia and industry for many years. Therefore, improving the crystallization and heat resistance is crucial for expanding the application of PLA.[9−12]

The heat resistance is closely related to the crystallization behavior and crystallinity of polymers. One of the most effective approaches to obtaining high crystallinity for PLA achieves in the formation of stereocomplex crystal (SC) by equimolarly mixing PLLA and poly(D-lactic acid) (PDLA). The melting point of SC is up to 220−230 °C, and the heat resistance is pronouncedly improved. However, the molecular weight beyond a threshold hinders the formation of SC. Examples of other concerns include the high cost of PDLA, especially at a relatively large dosage (isomolar), and the unsuitability of melt processing for the formation of SC. In view of these problems, researchers attempted the use of SC as a nucleating agent and jointly improved the crystallization rate and tensile strength of PLA.[13−15] Nevertheless, once the processing temperature exceeded the melting point of SC, the stereocomplex structure and nucleation would be destroyed and could not be restored.[16−18] Some other approaches have also been explored to improve the heat resistance of PLA; for instance, copolymerization,[19,20] blending,[21,22] nano[23] or fiber filling,[24] and improving crystallinity[25,26] all have been reported. The higher content of introduced components via copolymerization, blending, and filling inevitably deteriorates the degradation tendency and limits the application of PLA in the fields with strict health and biosafety requirements. Moreover, the heat deflection temperature (HDT) of the products is still less than 100 °C, sometimes, the approaches are accompanied by the decline of mechanical properties. Thus, improving the crystallinity by regulating the crystallization behavior of PLA is

Received: November 30, 2020
Accepted: January 4, 2021

https://dx.doi.org/10.1021/acsmacrolett.0c00830

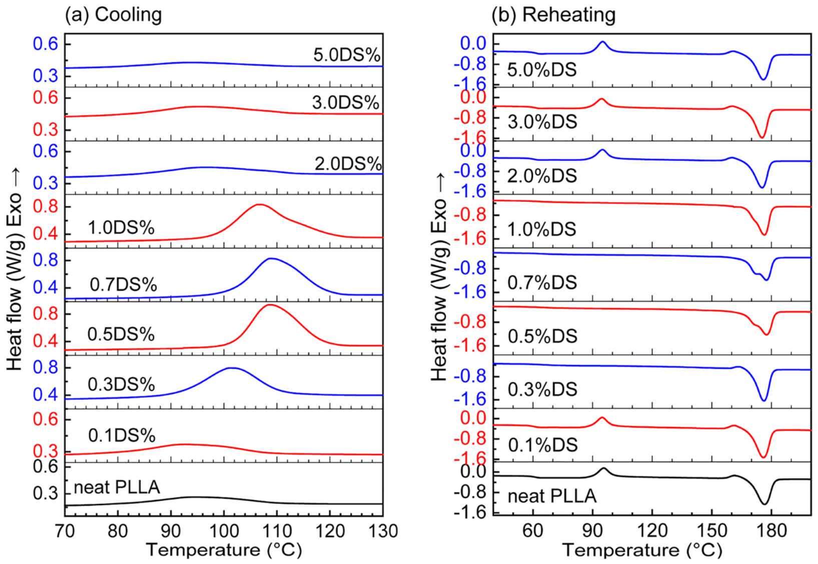

Figure 1. DSC curves of PLLA/DS for cooling (a) and reheating (b) processes under the same rate of 10 °C/min.

Table 1. Nonisothermal Crystallization Parameters of PLLA

	cooling process				reheating process					
samples	T_c (°C)	ΔH_c (J/g)	X_c (%)	$T_{onset} - T_c$(°C)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)	X_c* (%)
neat PLLA	94.6	7.8	8.3	16.4	60.6	176.6	42.2	95.6	18.5	25.3
PLLA/0.1%DS	94.7	10.7	11.4	16.0	60.8	176.1	44.7	94.8	18.1	28.5
PLLA/0.3%DS	101.2	34.8	37.3	10.0	63.8	176.2	44.5			47.7
PLLA/0.5%DS	108.5	42.2	45.3	10.3	63.3	177.5	46.2			49.5
PLLA/0.7%DS	110.2	45.8	49.2	10.2	63.8	177.5	47.8			51.4
PLLA/1.0%DS	106.7	36.2	39.0	10.3	63.7	176.4	45.9			49.5
PLLA/2.0%DS	95.2	8.0	8.8	17.6	61.8	175.4	36.5	95.0	17.9	20.3
PLLA/3.0%DS	94.0	8.5	9.3	17.0	60.9	175.4	38.8	94.5	15.7	25.4
PLLA/5.0%DS	92.7	4.0	4.5	17.0	61.5	176.0	37.2	95.0	19.2	20.2

considered as the promising method to solve the heat resistance defect.

In this regard, extensive efforts have been made in recent years focusing on regulating the crystallization behavior of PLA by adding a nucleating agent. The inorganic nucleating agents used for PLA include nanoparticles and nanolayered materials, such as talc,[27] sepiolite,[28] modified montmorillonite,[29] carbon nanotubes,[30] halloysite nanotube,[31] hydroxyapatite,[32] and carbon black.[33,34] These nucleating agents have shown a remarkable nucleation effect but hardly help with increasing the crystallinity. The reported organic nucleating agents for PLA mainly cover amides,[35−37] hydrazine/hydrazide,[38−45] phenylmalonate,[46] aromatic sulfonate derivatives,[47] phenyl phosphate,[48−50] biuret,[51] phthalimide,[52] zinc lactate,[53] zinc citrate complex,[54] PDLA,[55] branched PLA,[56] amino acids, and poly(amino acids).[57] Some biobased materials and their derivatives such as orotic acid,[58] biobased carbon,[59] cyclodextrin,[60] xylanate,[61] ramie fiber,[62] wood powder,[63] cyclohexanol,[64] cellulose nanocrystalline,[65] and chemically modified thermoplastic starch,[66] were also investigated. Although these nucleating agents were found to improve the crystallization rate and nonisothermal crystallization temperature of PLA to some extent, the achieved crystallinity hardly exceeded 40%, and cold crystallization would occur in the reheating process. The limited improvement in HDT, i.e., from about 55 °C to 60−70 °C, has little significance for practical application.[67] Hence, it is necessary to supplement the nucleating agents with further annealing treatment to increase the crystallinity of PLA.[45,68−71] Studies found that the annealing treatment could raise the HDT over 120 °C.[72,73] However, the additional annealing treatment complicated the production process and dramatically reduced production efficiency. It is imperative to find a nucleating agent that can adapt to the conventional melt processing and significantly improve the heat resistance of PLA without annealing treatment.

Herein, we report a seminal approach for dramatically improving the crystallization of PLLA with a unique mechanism by incorporating D-sorbitol (DS) via melt blending, which is capable of significantly increasing both the crystallinity and heat resistance of PLLA.

The nonisothermal crystallization behavior of PLLA was investigated by differential scanning calorimetry (DSC), and the thermograms of neat and nucleated PLLA during programmed cooling and reheating processes are shown in Figure 1. The crystallization parameters derived from DSC data are listed in Table 1, including the peak temperature of (cold) crystallization, T_c (T_{cc}), the exothermic enthalpy of crystallization (ΔH_c), the difference between the onset crystallization temperature (T_{onset}) and T_c, the glass transition temperature (T_g), and the melting temperature of crystals (T_m). The crystallinities during the cooling process (X_c) and reheating process (X_c^*) are calculated according to eqs 1 and 2:

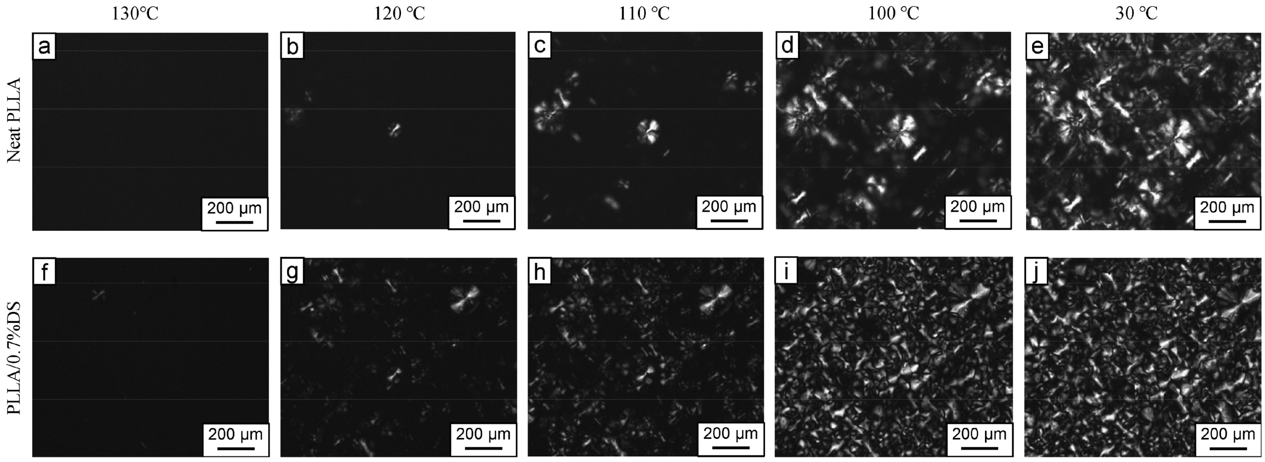

Figure 2. Evolution of crystal morphology of Neat PLLA and PLLA/0.7%DS with a cooling rate of 10 °C/min at 130, 120, 110, 100, and 30 °C, respectively.

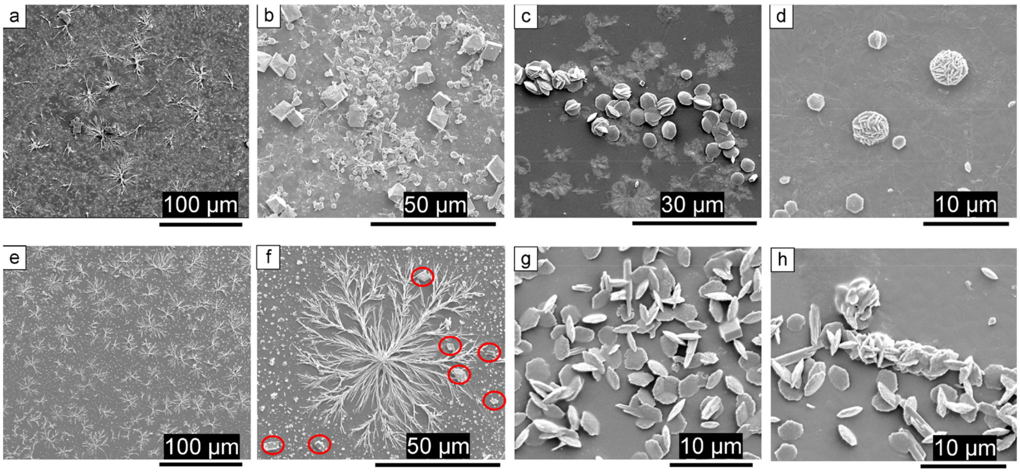

Figure 3. SEM photomicrographs of nonisothermal crystalline samples of neat PLLA (a)−(d) and PLLA/0.7%DS (e)−(h) etched by the solution of sodium hydroxide at 25 °C for 12 h.

$$X_c\ (\%) = \frac{\Delta H_c}{\Delta H_m^0 \times (1 - \varphi)} \times 100\% \tag{1}$$

$$X_c^*\ (\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times (1 - \varphi)} \times 100\% \tag{2}$$

where ΔH_m^0 is the melting enthalpy of 100% crystallized PLLA (93.7 J/g),[74] φ is the mass fraction of the nucleating agent, ΔH_m is the melting enthalpy, ΔH_c is the enthalpy of crystallization, and ΔH_{cc} is the exothermic enthalpy of cold crystallization. The absolute values of enthalpies are used.

The neat PLLA and PLLA/0.1%DS show similar flat curves. The exothermic peak of crystallization appears only as a slight bulge between 80 and 110 °C during the programmed cooling process, implying the low crystallization capacity (Figure 1a). The cold crystallization peaks around 95 °C are observed for both in the reheating process (Figure 1b), meaning that the low quality of DS (0.1%) does not alter the crystallization behavior of PLLA.

A further increase in the DS content brings up the distinct emergence of the crystallization peaks and the rapid shift of T_c to a high temperature in the cooling process with a maximum of 110 °C at 0.7% DS addition, corresponding to an increase of 16 °C compared with that of neat PLLA. This change suggests that DS, as a nucleating agent, significantly promotes the crystallization of PLLA. With further raising the DS dosage to 1%, the increase in T_c begins to decline, and the crystallization peaks disappear at higher DS dosage (2% to 5%), which can be ascribed to the decreased nucleation effect of DS caused by uneven dispersion. As a weathervane for the overall rate of crystallization, the smaller the value of $T_{onset} - T_c$ is, the faster the crystallization completes. This value is about 10 °C when the DS dosage ranged from 0.3% to 1%, which is lower than that of neat PLLA and PLLA/0.1%DS (16 °C). This effect further proves that the crystallization of PLLA is effectively improved.

Nucleating agents are mainly used to increase the crystallization rate, but not necessarily helpful to the crystallinity at the same time. For the samples with DS dosage from 0.3% to 1%, the cold crystallization is found to be absent and the crystallinities are significantly higher than those of other samples. The presence of bimodal melting peaks at DS dosage of 0.5% to 1.0% indicates the coexistence of less-ordered α' and ordered α crystal forms. The endothermic peaks at the low-temperature side correspond to the α' to α phase transition, while the peaks at the high-temperature side ascribe to the melting of α crystal form.[75] Both of the crystallinities of the cooling and reheating processes (Table 1) show a similar trend as the crystallization temperature and the values of X_c^* are always higher than X_c. The maximum of crystallinity appears at the DS dosage of 0.7%; meanwhile, the difference between X_c* (51%) and X_c (49%) is minimal, indicating a more perfect crystallization. Thus, there is no doubt that DS plays a significant role in nucleating and dramatically raises the crystallinity without a further annealing treatment, which is conducive to improve the heat resistance of PLLA.

The activation energy barrier (ΔE) for the nonisothermal crystallization of PLLA melt is calculated by the Kissinger equation.[76] The ΔE dramatically decreases from 30.8 kJ/mol for neat PLLA to 11.3 kJ/mol for the nucleated PLLA, indicating that the nucleated PLLA is easier to crystallize (Figure S1).

The real-time polarized optical microscopy (POM) observation was adopted to monitor the evolution of nonisothermal crystallization (Figure 2). The spherulites of neat PLLA began to emerge at 120 °C, whereas the initial crystallization of nucleated PLLA occurred at 130 °C. It is noteworthy that PLLA/0.7%DS presents a much higher nucleation density at the same temperature (i.e., 110 °C), and thus the spherulite size decreases from 100 to 200 μm for neat PLLA to approximately 50−100 μm for nucleated PLLA (Figure 2e,j).

We also observed the polymorphic crystals of PLLA, which differed from the reported simplex spherulite. To obtain the fine structure of PLLA crystals, programmedly cooled samples were etched using a water/methanol solution of sodium hydroxide for scanning electron microscopy (SEM) observation. The SEM images of the PLLA crystal morphology are shown in Figure 3. A large number of spherulite skeletons with central radiating shape are found on the surface of both neat and nucleated PLLA samples (Figure 3a,e,f). Besides, some hexagonal crystals of 5−10 μm (Figure 3b,f) and piles of orthohexagonal lenticular crystals of 3−7 μm are also observed. Except for the solitary existence of lenticular crystal, there are also complex geometric shapes that are composed of three or more lenticular crystals, such as spherical (Figure 3c,d) or shish-kebab conglomerates (Figure 3h). This phenomenon is found in both neat and nucleated samples, indicating that DS does not change the fundamental mechanism of PLLA crystal growth. The lenticular crystal has the precisely same Raman spectrum as that of PLLA, and the only difference of hexagonal-like crystals is that the original peak at 300 cm^{-1} shifts to a lower wavenumber (280 cm^{-1}), as shown in Figure S2. It is probably due to the more orderly and compacted molecular stack in the hexagonal-like crystals, which offers crystals good chemical stability, and also explains why their surface remains smooth and regular shapes similar to that of single crystals. Raman spectroscopy confirms that both the lenticular and hexagonal-like crystals are PLLA, ruling out the possibility that these crystals with particular morphology are DS or impurity. It is found for the first time that the nonisothermal melt-grown crystals of PLLA have other crystal morphologies besides spherulites, and this polymorphous phenomenon can only be observed in the isothermal solution-grown process.[77,78]

Different from the programmed cooling in DSC analysis, the molding conditions of PLLA, such as mold temperature and pressure holding time, directly determine the cooling rate and further affect the crystallinity and heat resistance of the products. To reveal the influence of molding conditions on the heat resistance of the products, two strategies were used. One is to ensure a short molding cycle (maintaining the pressure for 20 s), and the other is to adjust the cooling rate by reducing the temperature difference between the melt and the mold, i.e., increasing the mold temperature. In actual massive production, once the mold temperature is higher than 90 °C, the sample is not easy to solidify in a timely fashion, which affects the mold release and production efficiency. Thus, the highest mold temperature was set as 90 °C. The DSC curves, X-ray diffraction patterns, HDT, and crystallinity of injection molding samples under different mold temperatures are shown in Figures S3 and S4 and Table 2. The DSC curves of the injected samples show a single melting peak belonging to the α-form crystal, which means that only one crystal form exists in the injected samples. Among those with the DS dosage of 0.3%−1%, only three samples molded at 90 °C show an HDT exceeding 132 °C, indicating that the mold temperature of 90 °C and DS dosage higher than 0.3% are the optimal conditions for good heat resistance. It should be noted that the HDT of several samples was not improved even though their crystallinity exceeded 50% at the mold temperatures of 80 and 90 °C, implying that the difference of the cooling rate results in quite different crystalline properties. This phenomenon involves a complex, synergistic promoting effect of the nucleating agent, cooling rate, and the melt shear on PLLA chains during processing. Moreover, the increase of molecular weights and the strengthened entanglement definitely hinder the crystallization, while the melt shear should facilitate the disentanglement for crystallization. Therefore, the evolution of crystal morphology and crystallinity under different molecular weights and melt shear conditions, as well as their further influence on HDT are of growing concern.

Table 2. Crystallization Parameters and HDT of the Injection Molded PLLA

mold temp (°C)	D-sorbitol content (%)	T_g (°C)	T_m (°C)	X_c* (%)	HDT (°C)
50	0	64.9	177.0	23.4	57
	0.1	66.2	177.1	22. 6	56
	0.3	65.5	177.1	19.8	56
	0.5	65.8	176.3	19.2	56
	0.7	65.3	176.3	23.5	56
	1.0	65.3	176.1	19.4	56
80	0	65.7	176.2	29.9	56
	0.1	63.3	176.5	47.4	56
	0.3	67.4	176.2	49.7	61
	0.5	64.7	176.6	53.1	62
	0.7	66.9	176.2	53.7	73
	1.0	67.2	176.4	52.4	59
90	0	60.6	176.4	19.4	57
	0.1	66.5	177.6	44.8	60
	0.3	67.6	177.1	54.6	64
	0.5	67.4	176.9	51.1	132
	0.7	66.9	176.7	54.7	135
	1.0	67.0	176.7	55.6	132

The nucleating agents used for biodegradable polyesters are largely based on heterogeneous nucleation. During the cooling process, the nucleating agents either remain in the solid form (their melting points are higher than the processing temperature, such as talc,[79] cyclodextrin,[80] phthalimide,[81] and oriotic acid[58]) or solidify earlier than the polymer melts (the melting point or the glass transition temperature of the nucleating agents are between the crystallization temperature of the polymer and the processing temperature[46,82]).

Herein, D-sorbitol with a melting point around 93 °C was used as the nucleating agent to promote the crystallization of PLLA, and the nonisothermal crystallization temperature of nucleated PLLA is found to be 110 °C; thus, D-sorbitol and PLLA are both in the molten state during crystallization and D-sorbitol easily disperses at the molecular level in the PLLA matrix. This molten condition indicates that D-sorbitol nucleation is realized via a novel approach, i.e., homogeneous nucleation. A hypothetical nucleating mechanism of D-sorbitol is shown in Figure 4.

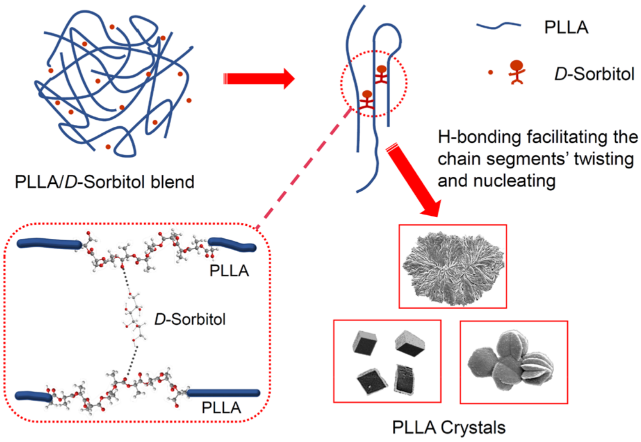

Figure 4. A proposed mechanism for D-sorbitol facilitating the nucleation of PLLA

The H-bonding interaction between the hydroxyl group of D-sorbitol and the carbonyl group of PLLA may effectively induce the twisting and folding of PLLA chain segments, to promote the orderly stacking of PLLA chains, which favors overall nucleation and crystal growth.

In summary, molten D-sorbitol, as a small molecule nucleating agent, effectively facilitated the homogeneous nucleation of PLLA, which was quite different from the conventional heterogeneous nucleation. The overall crystallization rate and the crystallinity of PLLA were significantly improved. Under conventional processing conditions, the HDT of PLLA could exceed 132 °C by simply increasing the mold temperature without an additional annealing treatment. To our knowledge, this is the first report on the polymorphous phenomenon of PLLA, i.e., the coexistence of three crystal morphologies, and is expected to provide a new internal clue to improving the crystallization ability of polylactic acid.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00830.

> Materials, experimental section, activation energy for nonisothermal crystallization, $\ln(\Phi/T_c^2)$ vs $1/T_c$ for nonisothermal crystallization, Raman spectra of polymorphic crystals, DSC curves, and XRD patterns for the injection molded and programmedly cooled samples (PDF)

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Funding

National Natural Science Foundation of China (51473007).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors specially acknowledge the support from the National Natural Science Foundation of China (51473007)

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