Enhancing the Crystallization Performance of Poly(L-lactide) by Intramolecular Hybridizing with Tunable Self-assembly-type Oxalamide Segments

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Abstract In this work, hydroxyl-terminated oxalamide compounds N,N′-bis(2-hydroxyethyl)oxalamide (OXA1) and N,N′-bis(2-hydroxyethyl)oxalamide (OXA2) were synthesized to initiate the ring-opening polymerization of L-lactide for preparation of oxalamide-hybridized poly(L-lactide) (PLA\textsubscript{OXA}), i.e., PLA\textsubscript{OXA1} and PLA\textsubscript{OXA2}. The crystallization properties of PLA were improved by the self-assembly of the oxalamide segments in PLA\textsubscript{OXA}, which served as the initial heterogeneous nuclei. The crystal growth kinetics was studied by Hoffman-Lauritzen theory and it revealed that the nucleation energy barrier of PLA\textsubscript{OXA1} and PLA\textsubscript{OXA2} was lower than that of PLA. Consequently, PLA\textsubscript{OXA} could crystallize much faster than PLA, accompanied with a decrease in spherulite size and half-life crystallization time by 74.8% and 86.5% (T=125 °C), respectively. In addition, the final crystallinity of PLA\textsubscript{OXA1} and PLA\textsubscript{OXA2} was 6 and 8 times higher, respectively, in comparison with that of neat PLA under a controlled cooling rate of 10 °C/min. The results demonstrate that the hybridization of oxalamide segments in PLA backbone will serve as the self-heteronucleation for promoting the crystallization rate. The higher the content of oxalamide segments (PLA\textsubscript{OXA1} compared with PLA\textsubscript{OXA2}), the stronger the promotion effect will be. Therefore, this study may provide a universal approach by hybridizing macromolecular structure to facilitate the crystallization of semi-crystalline polymer materials.

Keywords Poly(L-lactide); Oxalamide compounds; Self-heteronucleation; Crystallization kinetics

INTRODUCTION

With the awareness of environmental protection, an irresistible trend of “plastic limit” and “plastic ban” has gradually formed in recent years. United Nations Environment Programme and World Resources Institute have claimed that at least 127 countries have made regulations to against plastic bags.\cite{1} Apparently, biodegradable polymer materials have been attracting more and more attention. Among them, poly(lactide) (PLA) has been developed rapidly attributed to its outstanding biocompatibility, processability, high tensile strength and elastic modulus. PLA has already been applied in packaging, textiles, and biomedical areas.\cite{2,3} However, the low heat deflection temperature (HDT), melt strength, and crystallinity limit its utilization as a high performance bioplastic.\cite{4,5} Therefore, improving the crystallization performance becomes a crucial point during the processing of PLA.

As is known, heterogeneous nucleating agents are commonly used to enhance both the crystallization rate and the crystallinity in many slowly-crystallizing polymers such as PLA and poly(ethylene terephthalate) (PET). At present, an effective method for improving the crystallization properties of PLA is adding nucleating agents, including inorganic agents such as talc,\cite{6} montmorillonite (MMT) nanocomposite,\cite{7} carbon nanotubes,\cite{8} graphene,\cite{9} and boron nitride nanosheets (BNNSs),\cite{10} organic agents like N,N-ethylene-bis(1,2-hydroxy1,2-ethylaminamine) (EBH),\cite{11} poly(vinylidene fluoride),\cite{12} orotic acid,\cite{13} nucleobases,\cite{14} substituted-aryl phosphate salts (TMP-S),\cite{15} and amide nucleating agents,\cite{16,17,18} and polymeric nucleating agents such as nanocellulose,\cite{19} nanostarch, and PLA stereo-complex. Compared with inorganic nucleating agents, organic additives usually exhibit better compatibility and higher nucleation efficiency because of their controllable shape and size. Amide nucleating agents...
such as $N,N',N''$-tricyclohexyl-1,3,5-benzene-tricarboxylamide (TMC-328)$^{[17]}$ and $N,N'$-bis(benzoyl) hexanedioic acid dihydrazide (TMC-306)$^{[18]}$ seem to have high potential since they facilitate the self-organized superstructure in the PLA melt, which could accelerate the crystallization of PLA.$^{[18,21,22]}$ Recently, our group also revealed that the oxalamide compounds can serve as effective soluble-type nucleating agents for PLA.$^{[18,21,22]}$ The oxalamide compounds were capable of self-assembling via hydrogen bonding into needle-like superstructures that facilitate the nucleation effect and accelerate the crystallization of PLA.

Beside the incorporation of a nucleating agent, many studies were trying to improve the crystallization performance of PLA by tailoring its molecular structures using the active end groups (—OH and —COOH). For example, Pan et al.$^{[24]}$ prepared 2-ureido-4(1H)-pyrimidone (UPy)-bonded supramolecular PLLA (SM-PLLA) by using UPy-terminated low-molecular-weight (LMW) PLLA, and its crystallization kinetics and polymorphic crystalline structure were compared with the conventional PLLA. Although the crystallization rate and crystallinity of the SM-PLLA were depressed, it provided an alternative for the investigation of PLA crystals. Kodal et al.$^{[25]}$ investigated the effects of epoxy functionalized poly(hedral oligomeric silsesquioxane) (G-POSS) nanoparticles, which was then grafted onto the ends of PLA chain, on the crystallization performance of PLA. The results indicated that the epoxy group of G-POSS can accelerate the crystallization rate during cooling, which is supposed to be responsible for the inter-/intramolecular physical (H-bonding) or chemical (covalent) interactions among the end groups of PLA. Meanwhile, some researchers have also prepared the PLA hybrids, such as PEGylated PLA-phospholipon$^{[26]}$ and silica groups$^{[27]}$ at the end of PLA chain. The results showed that both the crystallinity and the toughness of PLA were improved. Therefore, the intermolecular interaction is conducive to the crystallization of PLA, and the crystallization performance of PLA was improved by the molecular design and synthesis.

In consideration of the advantages of amide nucleating agent mentioned above, we designed the oxalamide segments (OXA) as self-heteronucleation site in the PLA backbone to provide a new approach to enhance the crystallization of PLA. The OXA-functionalized PLA was then designed, synthesized, and characterized, and the effect of OXA segments on the crystallization kinetics of PLA was investigated as well.

**EXPERIMENTAL**

**Materials**

L-lactide with a purity of 99% was provided by Jiangsu Jiuding Biotechnology Co., Ltd., China. Tin(II) bis(2-ethylhexanoate) (Sn(Oct)$_2$) was supplied by Aladdin Chemical Reagent, China. Chloroform, toluene, tetrahydrofuran, ethanol, hydrochloric acid, ethyl acetate, methanol, ethylenediamine, diethyl oxalate, and 2-aminoethanol with the purity of 99% were purchased from Sinopharm Group Chemical Reagent China.

**Sample Preparation**

**Preparation of OXA1 initiator**

The $N,N'$-bis(2-hydroxyethyl) oxalamide, shorted as OXA1, was synthesized according to the method reported previously.$^{[28]}$

Briefly, diethyl oxalate (6.8 mL, 0.05 mol) was dissolved in 70 mL of ethanol solution in a 250 mL round-bottom flask. Then 2-methylaminoethanol (15 mL, 0.25 mol, 5-fold excess) was added dropwise in this solution and the mixture was mechanically stirred at 400 r/min for 24 h to get the precipitates. The precipitates were then filtered using a Büchner funnel, and washed with ethanol and dried in the vacuum oven at 60 °C to yield a white-powder (5.56 g, 53.6%). The reaction is shown in Fig. 1(a) schematically.

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**Fig. 1** Schematic of synthesis of (a) OXA1, (b) PLA$_{OXA1}$, (c) DEO, (d) OXA2, and (e) PLA$_{OXA2}$.  
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Preparation of PLA_{OXA1}
OXA1 and the purified L-lactide were dried in a vacuum oven for 12 h at 60 °C before use. The preparation of PLA_{OXA1} was carried out as following: the purified L-lactide (10 g, 0.07 mol), OXA1 (0.5 g, 0.0028 mol), and SnOct (0.05 g, 0.5%) were mixed at 135 °C for 24 h. The product was named as PLA_{OXA1} (8.06 g, 76.8%). The reaction is schematically shown in Fig. 1(b).

Preparation of OXA2 initiator
The diethyl 2,2'-[ethane-1,2-diylbis(azanediyl)]bis(2-oxoacetate), named as DEO, was synthesized by ethylenediamine (3.0 mL, 0.05 mol) and diethyl oxalate (73.0 mL, 0.5 mol, 10-fold excess). A solution of ethylenediamine in tetrahydrofuran was added dropwise into the solution of diethyl oxalate. The mixture was mechanically stirred at 400 r/min for 24 h at 30 °C to obtain the precipitates. The reaction route is shown in Fig 1(c).

The N,N'-[ethane-1,2-diyl]bis(N-[2-hydroxyethyl] oxalamide), shorted as OXA2, was synthesized using DEO (13 g, 0.05 mol) and ethanalamine (30.5 mL, 0.5 mol, 10-fold excess). The solution of DEO/chloroform was added dropwise into an ethanalamine/tetrahydrofuran, and the mixture was mechanically stirred under reflux for 24 h to obtain the precipitates. The reaction route is shown in Fig. 1(d).

Synthesis of PLA_{OXA2}
OXA2 and the purified L-lactide were dried in a vacuum oven for 12 h at 60 °C before use. The preparation of PLA_{OXA2} was carried out as following: the purified L-lactide (10 g, 0.07 mol) in toluene, OXA2 (0.5 g, 0.0017 mol), and SnOct (0.05 g, 0.5 wt%) were mixed and at 135 °C for 24 h. The product was named as PLA_{OXA2} (7.92 g, 75.4%). The reaction is schematically shown in Fig. 1(e). For comparison, PLA (6.88 g, 65.5%) was also synthesized via ring-opening polymerization initiated by the trace amount of water.

Characterizations
Nuclear magnetic resonance (NMR)
The structures of the synthesized OXA1, DEO, OXA2, PLA, PLA_{OXA1}, and PLA_{OXA2} were analyzed by ¹H-NMR spectroscopy in DMSO (δ 2.51) via a 400 MHz nuclear magnetic resonance apparatus (BRUKER AVANCE III 400 MHz, Germany). Each sample (5–6 mg) was sufficiently dissolved in a suitable deuterated reagent.

Fourier transformed infrared (FTIR)
The infrared absorption spectra of the synthesized OXA1, DEO, OXA2, PLA, PLA_{OXA1}, and PLA_{OXA2} were analyzed using a total reflection Fourier transform infrared spectrometer (Nicolet 6700, USA Thermo Fisher Scientific). The final spectrum of each sample was obtained at a resolution of 4 cm⁻¹ in the wavenumber range of 500–4000 cm⁻¹ with an average of 32 scans.

 Gel permeation chromatography (GPC)
The molecular weights and molecular weight distributions of the synthesized PLA, PLA_{OXA1}, and PLA_{OXA2} were measured by gel permeation chromatography (Waterside, USA) in tetrahydrofuran (THF) by using polystyrene as a standard. The THF solutions of each sample were diluted to a concentration of 1.0 mg/mL for all GPC experiments. Then the diluted solutions were filtered through a 0.22 μm needle-type organic filter membrane, and 20 μL of each filtered solution was injected into the system through a sampler.

Differential scanning calorimetry (DSC)
The crystallization behavior was studied by differential scanning calorimetry (DSC 8000, Perkin Elmer). For non-isothermal crystallization experiments, the samples were heated to 180 °C at 30 °C/min and held for 3 min to remove thermal history. Subsequently, the samples were cooled to 0 °C at a cooling rate of 10 °C/min and then heated up to 180 °C at 10 °C/min. For isothermal crystallization experiments, after melting at 180 °C for 3 min, the samples were cooled to 125 °C at 100 °C/min and then held at this temperature for crystallization. The process diagrams of non-isothermal crystallization and isothermal crystallization are shown in Fig. S1 (in the electronic supplementary information, ESI). All tests were carried out in a nitrogen atmosphere.

Wide angle X-ray diffractometry (WAXD)
The samples were evaluated by an X-ray diffractometer (Bruker AXS D8, Germany) equipped with a Ni-filtered Cu Kα X-ray source at a wavelength of 0.154 nm. The measurements were conducted at 40 kV and 40 mA with scan angles (2θ) from 3° to 35° at a scan rate of 3°/min.

Polarized optical microscopy (POM)
The evolutions in crystal morphology during non-isothermal and isothermal crystallization were monitored with a POM (Axio Imager A2POL polarizing microscope, Zeiss, Germany) in combination with a Linkam THMS600 hot stage. The samples of PLA, PLA_{OXA1}, and PLA_{OXA2} were sandwiched between two clean glass slides, and then melted at 180 °C for 3 min, followed by cooling down to 125 °C at 40 °C/min for isothermal crystallization. The detailed conditions of the non-isothermal crystallization test are the same as that of DSC. The morphological changes during the heating and the cooling cycle were monitored by a digital camera to record the process of crystal growth and morphology.

Rheological behavior
Rheological experiments were implemented by a DHR-2 rheometer (TA Instruments, USA) in a plate-plate configuration to study the effects of self-assembly of OXA segments on the crystallization of PLA, PLA_{OXA1}, and PLA_{OXA2}. The details of non-isothermal crystallization are shown in Fig. 1(a) and 1(b).

RESULTS AND DISCUSSION
Characterization on the Molecular Structures of OXA and PLA_{OXA}
The ¹H-NMR spectra of OXA1 and PLA_{OXA} are shown in Figs. 2(A) and 2(B), respectively. The specific data are as follows: ¹H-NMR (400 MHz, DMSO, δ, ppm): 8.5 (t, 2H), 4.75 (t, 2H), 3.45 (q, 4H), 3.21 (q, 4H), wherein the triplet at δ=8.58 is the proton at the hydroxyl group (−OH) at both ends of the monomer OXA1, and the quartet at δ=3.45 is assigned to the methylene group adjacent to the terminal hydroxyl group (−OH). Meanwhile, the quartet at δ=3.21 is associated with the protons of the methylene group (−CH₂−) adjacent to the amide group, and the triplet at δ=8.58 is the...
signal of the amide (−NH−) of the hydrogen proton resonance. 1H-NMR (400 MHz, DMSO, δ ppm): 8.87 (t, 2H), 5.47 (d, 2H), 5.28–5.14 (q, 60H), 3.91 (q, 4H), 3.79 (q, 4H), 1.53–1.32 (d, 180H), wherein the bimodal at δ=5.47 is the signal of the proton at the terminal hydroxyl group (−OH) of PLA_{OXA2}, and the triplet at δ=4.23–4.07 is that of the methylene group (−CH₂−) adjacent to the terminal hydroxyl group. In the meantime, the ternary signal at δ=3.38 is the proton resonance signal of the methylene group (−CH₂−) adjacent to the amide group, while the quadruple signals at δ=5.28–5.14 and δ=1.53–1.32 are assigned to the hydrogen proton resonance signals on the methine (−CH−) and methyl (−CH₃−) on the PLA chain. The triplet at δ=8.87 is the signal of the amide (−NH−) of the hydrogen proton resonance. These results indicate the successful synthesis of PLA_{OXA2}. The 1H-NMR spectra of OXA2 and PLA_{OXA2} are shown in Figs. 2(C) and 2(D), and the specific data are as follows: 1H-NMR (400 MHz, TFA, δ ppm): 4.66 (t, 4H), 3.91 (q, 4H), 3.79 (q, 4H) and 1H-NMR (400 MHz, DMSO, δ ppm): 8.65 (t, 4H), 5.21 (t, 32H), 3.97 (d, 2H), 3.66 (q, 4H), 3.40–3.30 (q, 4H), 1.47 (t, 96H). It is worth noting that the amide (−NH−) of PLA_{OXA1} shows signal at δ=8.87, whereas that of the amide (−NH−) of PLA_{OXA2} shifts to lower chemical shifts (δ=8.65), which might be due to the stronger hydrogen bonding interactions. Besides, the insets in Figs. 2(B) and 2(D) show that the intensity of oxalamide segments of PLA_{OXA2} is approximately twice higher than that of PLA_{OXA1}. All these results clearly indicate that OXA2 and PLA_{OXA2} have been successfully synthesized and the structure is clear. (The 1H-NMR spectra of DEO and PLA are shown in Fig. S2 in ESI).

The FTIR spectra of the synthesized PLA, OXA1, and PLA_{OXA1} are shown in Fig. 3(a). The characteristic bands of OXA1 are found at 3300 cm⁻¹ (ν_{C−N}, 1650 cm⁻¹ (amide I, ν_{C=O}), 1550–1450 cm⁻¹ (amide II, ν_{C−N}+δ_{N−H}), and 1320–1250 cm⁻¹ (amide III, ν_{C−N}+δ_{N−H}). In the PLA_{OXA1} spectrum, the band at 1750 cm⁻¹ is attributed to the C=O vibration of PLA, while the band at 1650 cm⁻¹ (associated with the C=O stretching vibration on the amide I band of OXA1) shifts to 1678 cm⁻¹. This can be explained as that the hydrogen-bonding interaction formed between the OXA1 segments in the PLA_{OXA1} backbone was weakened when compared with OXA1 compound. These results indicate that OXA1 and PLA_{OXA1} are successfully prepared. Fig. 3(b) shows FTIR spectra of PLA, DEO, OXA2, and PLA_{OXA2}. The characteristic bands of DEO are found at 3300 cm⁻¹ (ν_{C−N−H}), 3000 cm⁻¹ (ν_{C−H}), 1750 cm⁻¹ (ν_{C−O}), 1650 cm⁻¹ (amide I, ν_{C−O}), 1570–1510 cm⁻¹ (amide II, ν_{C−N}+δ_{N−H}), and 1335–1200 cm⁻¹ (amide III, ν_{C−N}+δ_{N−H}). The infrared absorption band of C=O of the ester group at 1750 cm⁻¹ (OXA2) disappears, while the C=O stretching vibration band at 1650 cm⁻¹ and the NH stretching vibration band at 3300 cm⁻¹ are significantly enhanced. A broad hydroxyl absorption band appearing at 3500 cm⁻¹ is consistent with the structure of OXA2. The characteristic band of PLA_{OXA2} is found at 1750 cm⁻¹ (ν_{C−O}). The NH stretching vibration band and amide I band absorption band at 1650 cm⁻¹ significantly de-
crease, indicating that the amide group has been introduced into the PLA chain. Figs. 3(c) and 3(d) show the FTIR spectra of PLA, PLA\textsubscript{OXA1}, PLA\textsubscript{OXA2}, and the proposed hydrogen-bonded N\textendash H\textendash C\textendash =O groups in oxalamide groups. The absorption band at 1681 cm\textsuperscript{-1} could be an indicator of hydrogen-bonded carbonyl groups of PLA\textsubscript{OXA1} in the ordered state, whereas that of the hydrogen-bonded groups of PLA\textsubscript{OXA2} shifts to lower wavenumber of 1640 cm\textsuperscript{-1}, attributed to the stronger H bonding interactions. A similar phenomenon was also observed in poly(ether amide) system.\textsuperscript{[29]} Thus, FTIR spectra evidenced that a more extensive hydrogen bonding could be formed in the order of hard segments consisting of multiple oxalamide groups, in respect to that comprising of single oxalamide unit.

The molecular weights (\(M_\text{w}\) and \(M_\text{n}\)) and polydispersity indexes (PDI) of PLA, PLA\textsubscript{OXA1}, and PLA\textsubscript{OXA2} were characterized by gel permeation chromatography (polystyrene standard), and the results are shown in Table 1.

### Table 1

| Sample | \(M_\text{w}\) (kg/mol) | \(M_\text{n}\) (kg/mol) | Polydispersity Index (PDI) |
|--------|-----------------|-----------------|-----------------|
| PLA    | 12.6            | 14.5            | 1.15            |
| PLA\textsubscript{OXA1} | 11.6            | 18.4            | 1.59            |
| PLA\textsubscript{OXA2} | 12.3            | 15.7            | 1.28            |

Note: \(M_\text{n}\) is obtained by GPC.

Non-isothermal Crystallization and Crystal Morphology Analysis

Figs. 4(a) and 4(b) show the cooling and second heating scan curves of PLA and PLA\textsubscript{OXA} detected by DSC. It can be seen that the crystallization of PLA is slow and no discernible crystallization peak was visible in the cooling process. For PLA\textsubscript{OXA1} and PLA\textsubscript{OXA2}, the crystallization peaks appeared at around 105 and 108 °C, respectively. Moreover, during the subsequent heating scans, the cold crystallization enthalpy of PLA\textsubscript{OXA} was significantly decreased. Compared with PLA, PLA\textsubscript{OXA1} had two amide groups next to each other in reverse, which allowed the formation of two hydrogen bonds per oxalamide motif, resulting in an increased tendency to crystallize into sheet-like structures.\textsuperscript{[30]} With a higher content of amide groups in molecule, the cold crystallization enthalpy of PLA\textsubscript{OXA2} was further decreased. The crystallinity \(X_c\) of PLA, PLA\textsubscript{OXA1}, and PLA\textsubscript{OXA2} can be calculated by Eq. (1):

\[
X_c = \frac{(\Delta H_m - \Delta H_{cc})(\omega \times \Delta H^0_m)}{100}
\]  

where \(\Delta H_m\) and \(\Delta H_{cc}\) are melt and cold crystallization enthalpies of PLA, respectively, \(\omega\) is the weight proportion of PLA in PLA\textsubscript{OXA}, while \(\Delta H^0_m = 93.6\ \text{J/g}\) is the melting enthalpy of PLA with a crystallinity of 100%.\textsuperscript{[28,31]}

\(X_c\) of PLA\textsubscript{OXA1} and PLA\textsubscript{OXA2} was 23.6% and 57.6%, respectively, while it is only 11.8% for PLA (Table 2). The amide groups in polymers may form original nucleus due to the
N—H—O═C hydrogen bonding, which makes the PLA chains easier to pile up and crystallize. Besides, a higher content of oxalamide segments has stronger promotion effect on the PLA crystallization rate and crystallinity. The formation of PLA, PLA_{OXA1}, and PLA_{OXA2} crystallites was also evidenced by WAXD analysis and the results are presented in Fig. 4(c). The diffraction peak intensity of PLA_{OXA} is significantly larger than that of PLA, indicating a higher crystallinity, which is consistent with the DSC results. 2θ = 13.7°, 16.8° and 19.2° are assigned to the (010), (200)/(110), and (203) planes of PLA crystal[32], respectively, which indicated that the amide groups of PLA_{OXA} did not change its crystal form.[33]

The crystal morphology evolution of PLA, PLA_{OXA1}, and PLA_{OXA2} in non-isothermal crystallization is observed by POM and the results are shown in Fig. 5. Only sparse spherulites could be observed for PLA when it was cooled from 110 °C to 30 °C. In contrast, in the cases of PLA_{OXA1} and PLA_{OXA2}, lots of small spherulites appeared at 110 °C, and more spherulites were visible when the temperature decreased to 30 °C. The POM results indicated that the density of PLA_{OXA2} spherulites was higher than that of PLA_{OXA1}, whereas the size was not obviously varied. According to the Gutzow and Dobrera models,[34] PLA_{OXA} had higher nucleation efficiency than that of PLA (Fig. S3 and Table S1 in ESI).

**Isothermal Crystallization and Crystal Morphology Analysis**

Figs. 6(a) and 6(b) exhibit the DSC isothermal heat flow and relative crystallinity curves of PLA, PLA_{OXA1}, and PLA_{OXA2} crystallized at 125 °C as a function of time. The crystallization of PLA was not completed until 35 min, while PLA_{OXA1} and PLA_{OXA2} showed obvious isothermal crystallization peaks and could crystallize completely within 8 and 4 min, respectively. These results prove again that the amide groups in polymers could accelerate the crystallization of PLA segments.

Avrami equation[35] (Eq. 2) was used to describe the isothermal crystallization kinetics of PLA and PLA_{OXA1} samples at 125 °C:

$$\log(1 - X_t) = n \log(t) + \log k$$

where $X_t$ is the relative crystallinity, $n$ is the Avrami exponent, $k$ is the crystallization rate constant, and $t$ is the crystallization time.

The linear fitting of $\log(1 - X_t)$ versus $\log(t)$ is shown in Fig. 6(c). A linear portion of relative crystallinity was used to calculate $n$ and $k$, as shown in Table 3. For the ideal isothermal crystallization process, $n$ should be an integer, which depends on the nucleation mechanism and the growth mode. The value of the samples in this study is non-integer, between 2.7–3.5, suggesting that the polymer crystallizes may be a combination of flaky crystal and three-dimensional spherulites.[36] The half-life crystallization time ($t_{1/2}$) of PLA, PLA_{OXA1}, and PLA_{OXA2} at 125 °C can be calculated by Eq. (3).

$$t_{1/2} = (\ln 2)/k^{1/n}$$

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**Table 2**

| Sample   | $T_s$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $X'_{c}$ (%) | $X'_{cc}$ (%) |
|----------|------------|------------|--------------------|------------|--------------------|-------------|--------------|
| PLA      | 60.2       | 112.5      | 20.6               | 167.8/161.8| 31.6               | 89.7        | 3.6          | 11.8 | 3.9 | 2.5 |
| PLA_{OXA1} | 52.2       | 98.0       | 11.2               | 157.9      | 33.3               | 105.2       | 24.6         | 23.6 | 26.3 | 25.2 |
| PLA_{OXA2} | 58.6       | 94.8       | 4.1                | 163.7      | 58.0               | 108.6       | 34.1         | 57.6 | 36.4 | 36.0 |

Note: $T_s$ is the crystallization temperature, $\Delta H_c$ is the temperature drop crystallization enthalpy, $T_m$ is the cold crystallization temperature, $\Delta H_m$ is the cold crystallization enthalpy, $T_c$ is the melting point, $\Delta H_c$ is the melting enthalpy. $X_t$ is calculated from the DSC data by Eq. (1), while $X'_{c}$ is calculated from $X_c = \Delta H_c/(\Delta H_c + \Delta H_m) \times 100\%$ and $X'_{cc}$ is calculated from the WAXD data.
Eq. (4):  
\[
G = G_0 \exp \left[ - \frac{U^*}{R(T_c - T_\infty)} \right] \exp \left[ - \frac{K_g}{T_c(\Delta T)^f} \right]
\]

where $G$ is the crystal growth rate (shown in Fig. 8a), $T_c$ is the isostructural crystallization temperature (125 °C), $R$ is the gas constant, $G_0$ is the pre-exponential factor, $T_\infty = T_g - 30$ K. $U^*$ represents the activation energy required for crystallization, $\Delta T = T_m - T_c$, $T_m$ is the equilibrium melting point of the samples, $f = 2T_c/T_m + T_c$, and $K_g$ is the nucleation constant, as shown in the following Eq. (5):

\[
K_g = \frac{mb_0a_0(\Delta H_f)}{\Delta n_k}
\]

where $a$ and $a_0$ are the lateral and end-surface free energies, respectively, $b_0$ is a monatomic (or monomolecular) layer of fixed thickness, and $k$ is the Boltzmann constant. The values of $m$, which is dependent on the regime of crystallization, are determined as 4, 2, and 4 for regimes I, II, and III, respectively. 

The crystal growth kinetics of PLA, PLA$_{OXA1}$, and PLA$_{OXA2}$ were shown in Fig. 8(b). It was found that PLA, PLA$_{OXA1}$, and PLA$_{OXA2}$ had two linear regions, which represent the crystallization mechanism II at higher temperatures and the crystallization mechanism III at lower temperatures, respectively. $K_g^{II}$ of PLA, PLA$_{OXA1}$ and PLA$_{OXA2}$ was $8.1\times10^8$ K$^2$, $6.0\times10^8$ K$^2$ and $3.1\times10^8$ K$^2$, respectively, while $K_g^{III}$ of PLA, PLA$_{OXA1}$ and PLA$_{OXA2}$ was $3.2\times10^6$ K$^2$, $2.0\times10^6$ K$^2$ and $1.4\times10^6$ K$^2$, respectively.
The smaller the $K_g^I$ or $K_g^II$ value is, the smaller the nucleation energy barrier of PLA$_{OXA1}$ and PLA$_{OXA2}$ is needed to surmount.\[40]

### Table 3

| Sample  | n   | $k$ (min$^{-1}$) | $t_{1/2}$ (min) |
|---------|-----|-----------------|-----------------|
| PLA     | 2.7 | $2.9 \times 10^{-4}$ | 16.3            |
| PLA$_{OXA1}$ | 3.3 | $6.4 \times 10^{-1}$ | 4.1             |
| PLA$_{OXA2}$ | 3.5 | $4.0 \times 10^{-2}$ | 2.2             |

Fig. 6 (a) DSC isothermal heat flow, (b) relative crystallinity curves, and (c) Avrami plots of PLA, PLA$_{OXA1}$, and PLA$_{OXA2}$ isothermally crystallized at 125 °C.

Fig. 7 POM images (scale bar=200 µm, the same magnification) of PLA (top), PLA$_{OXA1}$ (middle) and PLA$_{OXA2}$ (bottom) isothermally crystallized at 125 °C.

Fig. 8 (a) The temperature-dependence of crystal growth rates ($G$) of PLA, PLA$_{OXA1}$, and PLA$_{OXA2}$ and (b) plots of $\ln G + U^* / (R(T_c - T_\infty))$ versus $10^5/T_c (\Delta T)^f$ for PLA, PLA$_{OXA1}$, and PLA$_{OXA2}$.

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Proposed Nucleation and Crystallization Mechanism of PLAOXA

There have been numerous studies in the nucleation mechanism of organic and inorganic agents in promoting PLA crystallization, but self-assembly mechanism of the intramolecular nucleating agents is rarely investigated. Fig. 9 shows the variation of storage modulus with temperature for the PLA, PLAOXA1, and PLAOXA2 melts during cooling. When the temperature of PLA decreased from 180 °C to 100 °C, the storage modulus rose sharply around 115 °C. Only one transition point of storage modulus appeared for pure PLA, whereas two transition points for PLAOXA1 and PLAOXA2 samples could be observed at 130/119 and 145/123 °C, respectively. The former one at the higher temperature was mainly attributed to the self-assembly of OXA segments via the hydrogen bonds, which was confirmed by the 1H-NMR spectra (Figs. 2b and 2d) and the FTIR spectrum (Fig. 3c), causing the melt modulus to rise rapidly in the cooling process. The latter one at the lower temperature was mainly associated with the rapid crystallization of the PLA chains.

Recent studies show that polymer crystallization accelerated by nucleating agents involved several mechanisms including the epitaxial growth on nucleator surface, chemical reaction, and hydrogen bonding interactions between nucleator and polymer. Xing et al. proposed that the hydrogen bonding between $\sim$NH groups of hydrazide-type nucleator and $-\text{C}==\text{O}$ groups of PLA can promote nucleation and folding crystallization of the PLA chains. In this work, the amide groups are embedded in the PLA chain to form the hydrogen bonds, thereby promoting crystallization. On the basis of the aforementioned results, a schematic illustration is proposed for the mechanism discussion, i.e., the hydrogen bonds between the OXA segments inducing the nucleation and crystallization of PLAOXA, as shown in Fig. 10. In the melt state, the PLA chains are in random coil state and OXA segments are in the middle of the PLA backbone, which is illustrated in Fig. 10(a). In the cooling process, hydrogen bonds are formed between amide groups to accelerate the generation and growth of original nuclei, and PLA chains close to the amide groups could be quickly accumulated and crystallized forming microcrystalline. The presence of original nuclei will reduce the activation energy and provide a large number of nucleation sites for crystallization of PLAOXA chains, as illustrated in Figs. 10(b) and 10(c). The original nuclei have high nucleation activity, which can improve the crystallization rate and crystallinity of PLAOXA.

CONCLUSIONS

In this study, novel hydroxyl-terminated oxalamide nucleating agents were synthesized and used to initiate the ring-opening polymerization of L-lactide for preparing PLAOXA1 and PLAOXA2. Non-isothermal crystallization behavior showed that PLAOXA crystallized faster than neat PLA, and the crystallinity increased from 11.8% (PLA) up to 23.6% (PLAOXA1) and 57.6% (PLAOXA2), respectively. The isothermal crystallization showed that the half-life crystallization time at 125 °C was shortened from 16.3 min (PLA) to 4.1 (PLAOXA1) and 2.2 min (PLAOXA2). In the meanwhile, the crystal growth kinetics of PLAOXA was studied based on Hoffman-Lauritzen theory and it revealed that both $K_g^+$ and $K_g^-$ values of PLAOXA were lower than those of PLA, indicating that the nucleation energy barrier for PLAOXA is lower. Therefore, the hybridization of oxalamde segments in backbone of PLA facilitated the self-assembling between amide groups in different PLA chains, and then served as self-heteronucleation for accelerating the crystallization rate and increasing the crystallinity of PLA. In addition, PLAOXA2 had

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greater enhancement effects on the crystallization kinetics than PLA\_DRAT, which was ascribed to the higher content of oxalamide segments. Thus, this study may provide a universal approach of hybridizing molecular chain to enhance the crystallization performance for versatile polymer materials.

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/s10118-020-2461-3.

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