

## Enhanced Crystallization Kinetics of PLLA by Ethoxycarbonyl Ionic Liquid Modified Graphene

Xu Pei, Cui Zhao-Pei, Ruan Gang, Ding Yun-Sheng

Cite this article as:

Xu Pei, Cui Zhao-Pei, Ruan Gang, Ding Yun-Sheng. Enhanced Crystallization Kinetics of PLLA by Ethoxycarbonyl Ionic Liquid Modified Graphene[J]. *Chinese J. Polym. Sci.*, 2019, 37(3): 243-252. doi: 10.1007/s10118-019-2192-5

View online: <https://doi.org/10.1007/s10118-019-2192-5>

---

### Articles you may be interested in

Crystallization Kinetics and the Fine Morphological Evolution of Poly(ethylene oxide)/Ionic Liquid Mixtures

Chinese J. Polym. Sci. 2017, 35(11): 1402 <https://doi.org/10.1007/s10118-017-1997-3>

CRYSTALLIZATION BEHAVIOR, THERMAL AND MECHANICAL PROPERTIES OF PHBV/GRAPHENE NANOSHEET COMPOSITES

Chinese J. Polym. Sci. 2013, 31(4): 670 <https://doi.org/10.1007/s10118-013-1248-1>

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

Chinese J. Polym. Sci. 2019, 37(3): 258 <https://doi.org/10.1007/s10118-019-2202-7>

P[MMA-IL]修饰石墨烯协同调控PVDF复合物结晶与介电行为

Effect of Graphene Modified by P[MMA-IL] on the Crystallization and Dielectric Behavior of PVDF Composite Film  
高分子学报. 2017(5): 776 <https://doi.org/10.11777/j.issn1000-3304.2017.16231>

纳米压印调控PCL-*b*-PLLA受限结晶取向行为的研究

Studies on the Crystallization Orientation in Micromolded PCL-*b*-PLLA Thin Films  
高分子学报. 2019, 50(1): 82 <https://doi.org/10.11777/j.issn1000-3304.2018.18137>

2-溴丙酰基末端对于PLLA成核行为影响的研究

NUCLEATION EFFECT OF 2-BROMOPROPIONYL END GROUPS ON CRYSTALLIZATION BEHAVIORS OF PLLA  
高分子学报. 2011(6): 666 <https://doi.org/10.3724/SP.J.1105.2011.10166>

# Enhanced Crystallization Kinetics of PLLA by Ethoxycarbonyl Ionic Liquid Modified Graphene

Pei Xu\*, Zhao-Pei Cui, Gang Ruan, and Yun-Sheng Ding\*

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, and Anhui Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei 230009, China

## Electronic Supplementary Information

**Abstract** To investigate the performance of graphene (Gra) modified with ethoxycarbonyl ionic liquid (IL), chain mobility and crystallization kinetics of poly(L-lactic acid) (PLLA), a series of PLLA nanocomposites have been prepared using solution-cast method. IL can improve the dispersion of Gra in PLLA matrix and the samples containing IL have higher growth rate of PLLA spherulite than neat PLLA does. PLLA/IL/Gra and PLLA/2Gra exhibit the same relaxation strength and time of  $\alpha_N$  relaxation that corresponds to the longest normal mode motion at 110–140 °C. PLLA/IL/Gra shows a faster crystallization rate than PLLA/2Gra does, which might be attributed to the Gra-imidazolium cation interaction in IL modified Gra, the significant dispersion effect of IL at Gra surface, and the increase of nuclei density of PLLA/IL/Gra.

**Keywords** Ionic liquid; Graphene; PLLA; Crystallization; Dielectric behavior

**Citation:** Xu, P.; Cui, Z. P.; Ruan, G.; Ding, Y. S. Enhanced crystallization kinetics of PLLA by ethoxycarbonyl ionic liquid modified graphene. *Chinese J. Polym. Sci.* 2019, 37, 243–252.

## INTRODUCTION

Poly(L-lactic acid) (PLLA), as a biodegradable thermoplastic aliphatic polyester, has attracted increasing attention in recent years since it can be completely degraded under the composting conditions in several months.<sup>[1–3]</sup> However, some drawbacks such as low crystallization rate and crystallinity may prevent it from extensive applications.<sup>[4–6]</sup> One of the effective methods for accelerating the crystallization rate is the incorporation of nucleation agents (inorganic or organic nanofillers).<sup>[7–11]</sup> Graphene (Gra) is an allotrope of carbon in the form of two-dimensional, atomic-scale, honey-comb lattice in which each atom forms one vertex. It has many superior properties, such as remarkable thermal, electronic, and mechanical properties.<sup>[12]</sup> The crystallization rate and crystallinity of PLLA gradually increase with increasing concentration of Gra.<sup>[13–15]</sup> Nevertheless, as the concentration of Gra increases further, the poor dispersion of Gra and slow chain mobility of PLLA would inhibit the crystallization ability of PLLA.<sup>[16,17]</sup>

Ionic liquid (IL) is a room temperature molten salt with a bulky organic cation and an inorganic anion, exhibiting good electrical conductivity, high thermal stability, and low vapor pressure.<sup>[18–20]</sup> 3-Methyl-1-(ethoxycarbonyl)imidazolium

tetrafluoroborate could be dispersed homogeneously in PLLA matrix and impose plasticization effect on PLLA.<sup>[21,22]</sup> Dielectric relaxation spectroscopy has been employed to study the effect of IL on chain segment relaxations of PLLA corresponding to the longest normal and the segmental mode motions.<sup>[23–26]</sup> Results show that IL can accelerate the segmental and normal mode motions, and increase the charge carrier movement of IL following the longest motion of chains. More importantly, Zhao *et al.* found that the  $\pi$ -electron-rich Gra can be dispersed in ILs,<sup>[27]</sup> because IL and Gra have strong cation- $\pi$  physical interactions that can improve the dispersion of Gra and maintain the excellent physical properties of Gra.<sup>[28]</sup> This method for dispersing Gra in polymer is simple, environmentally friendly, and has a relatively high efficiency compared with the chemical modification of Gra.<sup>[29,30]</sup> Xu *et al.* proposed a facile strategy to enhance the crystallization kinetics of PLLA with poly(ethylene glycol)-grafted graphene oxide as a heterogeneous nucleation agent and chain mobility promoter simultaneously.<sup>[31]</sup> There are two successive events: the primary nucleation of a new phase from the melt polymer and the three-dimensional growth.<sup>[32–34]</sup>

In this work, 1-((ethoxycarbonyl)methyl)-3-methylimidazolium bromide (IL) and Gra were used to modify the crystal structure and promote the crystallization behavior of PLLA. The dispersion of Gra in PLLA matrix was studied by field emission scanning electron microscopy (FESEM), while the crystallization morphology was characterized with polarized optical microscopy (POM). Differential scanning

\* Corresponding authors: E-mail [chxuper@hfut.edu.cn](mailto:chxuper@hfut.edu.cn) (P.X.)  
E-mail [dingys@hfut.edu.cn](mailto:dingys@hfut.edu.cn) (Y.S.D.)

Received July 4, 2018; Accepted September 25, 2018; Published online November 2, 2018

calorimetry (DSC) and dielectric relaxation spectroscopy (DRS) were utilized to analyze the synergetic effect of Gra and IL on crystallization kinetics and dynamics of relaxations of PLLA.

## EXPERIMENTAL

### Materials

PLLA (4032D) was purchased from Nature works Co., whose weight-average molecular weight and number-average molecular were  $2.0 \times 10^5$  and  $1.2 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ , respectively. The IL, 1-((ethoxycarbonyl)methyl)-3-methylimidazolium bromide, was obtained from Lanzhou Institute of Chemical Physics, China. Gra prepared by physical exfoliation method (0.5–2  $\mu\text{m}$  in diameter, 0.8–1.2 nm in thickness, and 500–1000  $\text{m}^2 \cdot \text{g}^{-1}$  for BET surface area), was obtained from Nanjing XFNANO Materials Tech Co., Ltd.

### Sample Preparation

Prior to the preparation of the nanocomposites, PLLA was dried at 60 °C in vacuum overnight. Then, PLLA was dissolved in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) with magnetic stirring at room temperature for 4 h. Simultaneously, IL was dissolved in  $\text{CH}_2\text{Cl}_2$  and Gra was dispersed in the IL solution under sonication for 4 h. The suspension of Gra or modified Gra was added to the PLLA solution, and the mixture was subjected to ultrasonic treatment for 2 h to form uniform slurries. Afterwards, the mixture was heated at 50 °C for 8 h to remove solvent and dried in a vacuum oven at 60 °C for 24 h. Finally, the nanocomposites were compressed into films (around 200  $\mu\text{m}$  thickness) by hot pressing (190 °C under 1.2 MPa for 7 min) for DSC and dielectric measurements. The composite formulations are shown in Table 1. In addition, IL-modified graphene (The mass fraction ratio of graphene to ionic liquid is 1:1) was prepared for TEM measurement.

**Table 1** Composite formulations

| Sample        | PLA (wt%) | Gra (wt%) | IL (wt%) |
|---------------|-----------|-----------|----------|
| PLLA          | 100       | 0         | 0        |
| PLLA/2IL      | 99.98     | 0         | 0.02     |
| PLLA/2Gra     | 99.98     | 0.02      | 0        |
| PLLA/IL/Gra   | 99.98     | 0.01      | 0.01     |
| PLLA/2IL/2Gra | 99.94     | 0.02      | 0.02     |

### Characterization

The morphologies of Gra and modified Gra were examined by field emission transmission electron microscopy (FETEM, JEM-2100F, JEOL). Before observation, Gra was dispersed in dichloromethane to make a  $0.5 \text{ mg} \cdot \text{mL}^{-1}$  dispersion with the aid of sonication. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB250Xi spectrometer (Thermo, America) with the measurement range of 0–800 eV.

FESEM (Hitachi, SU8020) was used to investigate the dispersion of Gra in PLLA matrix. The acceleration voltage is 3 kV. Before observation, the samples were fractured cryogenically in liquid nitrogen and a thin layer of gold was sprayed on the surface. To investigate the nucleation and growth of spherulites for PLLA composites under isotherm-

al crystallization, an Olympus BX51 microscope (Olympus Co., Japan) equipped with a Micro Publisher 3.3 RTV CCD was utilized. The nucleation density and growth rate of spherulites were measured by Image J software. The nonisothermal and isothermal crystallization behavior was investigated by DSC (METTLER TOLEDO, DSC 1). For the nonisothermal crystallization, samples were heated from 25 °C to 200 °C and held for 5 min to eliminate the thermal history. Then they were cooled to 0 °C at predetermined cooling rates (2.5 and 10 °C·min<sup>-1</sup>, respectively). In the second heating stage, the samples were heated to 200 °C at a rate of 10 °C·min<sup>-1</sup>. For the isothermal crystallization, thermal history of samples was also erased initially. Then they were cooled at a rate of 50 °C·min<sup>-1</sup> to the predetermined crystallization temperature ( $T_c$ ) and held for enough long time until the isothermal crystallization was completed. All these experiments were carried out under nitrogen atmosphere. The films were coated with silver electrodes of 1 cm in diameter for AC dielectric measurement. The dielectric permittivity was measured with Agilent E4980A LCR meter in the temperature range from 110 °C to 140 °C. The measurement frequency range of the instrument was 20 Hz–2 MHz.

## RESULTS AND DISCUSSION

### Characterization of Ionic Liquid-modified Gra

According to the TEM image of pristine Gra displayed in Fig. 1(a), the Gra sheets show an obviously wrinkled structure and entangle with each other due to the thermodynamic stability of the two dimensional membrane. After being non-covalently modified with ethoxycarbonyl ILs, the Gra sheets maintain nanosheet morphology, while the number of wrinkles decreases and the transparency of Gra nanosheets declines (Fig. 1b). This indicates that numerous ILs were adhered homogeneously to the surface of Gra nanosheets, owing to the strong cation- $\pi$  physical interactions between ILs and Gra nanosheets.<sup>[27]</sup>

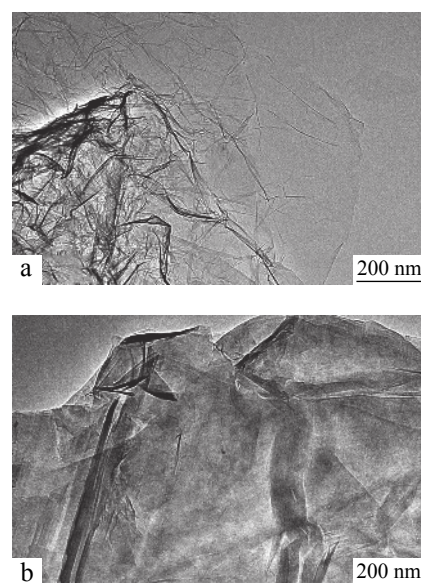


**Fig. 1** TEM images of (a) Gra and (b) modified Gra (IL/Gra)

Fig. 2(a) is XPS full scan spectra of Gra and IL-Gra. The C/O ratio of Gra was 6.10, while the C/O ratio of IL-Gra decreased to 5.41, indicating a significant increase in oxygen-containing groups. At the same time, the binding energy peak of N1s and Br3d appeared at 401.7 and 68 eV, respectively, in the full XPS spectrum of IL-Gra. To further confirm the existence of N in Gra, the XPS N1s spectra of Gra and IL-Gra were measured as shown in Fig. 2(b). It was found that the N1s spectrum of Gra was only a baseline with no intensity signal for N1s. In contrast, a strong signal appeared at 401.7 eV in the spectrum of IL-Gra, which corresponded to N–C and –N=C bonds on imidazole ring of IL. Figs. 2(c) and 2(d) are the C1s spectra of Gra and IL-Gra, respectively. The C1s binding energies at different binding states in Gra were C–C (284.8 eV), C–O (286.4 eV), and C=O (287.3 eV). The new binding states of C atoms in the IL-Gra spectrum can be found such as O=C=O (289.0 eV), C–N (285.9 eV), and C=N (287.0 eV), which mainly derived from IL. These observations prove that IL can be strongly adsorbed on the Gra sheet by cation- $\pi$  interactions.<sup>[28]</sup>

### Dispersion of Gra in PLLA Matrix

Fig. 3 displays the FESEM micrographs of cryogenically fractured surfaces for PLLA/2Gra and PLLA/2IL/2Gra. First, no pores or voids can be observed in cryogenically fractured surfaces of the composites, manifesting that the solvent used to prepare the samples and air were fully removed from the samples. Second, the numerous bright region in Fig. 3(a) represents the aggregation of Gra that is coated by PLLA matrix. It indicates the poor dispersion of Gra in PLLA

matrix. On the contrary, the layer structure of Gra dispersed uniformly in matrix is found in Fig. 3(b). These observations suggest that IL containing ethoxycarbonyl group can improve the compatibility between Gra and PLLA matrix, resulting in a uniform dispersion of Gra in PLLA matrix. The cation- $\pi$  interaction between IL and Gra can hinder Gra aggregation because Gra is an excellent electron-donating  $\pi$  system and the imidazolium cation of IL is an electron-deficient  $\pi$  system.<sup>[35]</sup>

### Morphology of Isothermal Crystallization for Nanocomposites

The morphology evolutions of nanocomposites isothermally crystallized at 130 °C are displayed in Fig. 4. Several nuclei appear in the supercooled melt of neat PLLA after 10 min crystallization (Fig. 4a), while the PLLA composites containing Gra show more nuclei (Figs. 4b, 4d, and 4e). It can be attributed to the heterogeneous nucleation ability of Gra for PLLA crystallization. The nuclei density, namely the number of nuclei per unit volume, is  $5.86 \times 10^5 \text{ cm}^{-3}$  in PLLA/2Gra,  $5.32 \times 10^4 \text{ cm}^{-3}$  in PLLA/IL,  $3.37 \times 10^5 \text{ cm}^{-3}$  in PLLA/IL/Gra, and  $3.99 \times 10^5 \text{ cm}^{-3}$  in PLLA/2IL/2Gra. Though the content of Gra of PLLA/2Gra is twice as that of PLLA/IL/Gra, the nucleation density of PLLA/2Gra is not twice as that of PLLA/IL/Gra. IL can improve the dispersibility of Gra in PLLA matrix and PLLA/IL/Gra must undergo surface-induced nucleation of the modified Gra.<sup>[14]</sup>

The variation of spherulite radius as a function of time for PLLA and its composites during isothermal crystallization at 130 °C is shown in Fig. 5. Generally speaking, the plot of spherulite radius versus crystallization time provides a

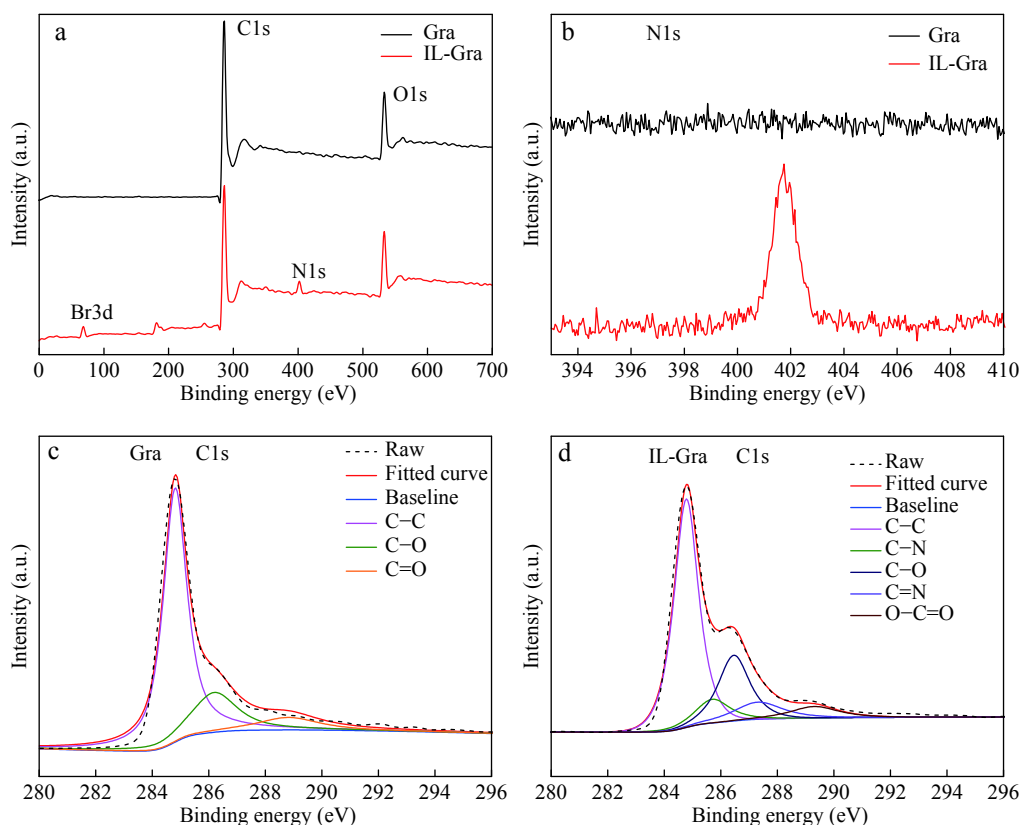


Fig. 2 (a) XPS surveys; High resolution XPS spectra of (b) N1s, (c, d) C1s of Gra and IL-Gra, respectively

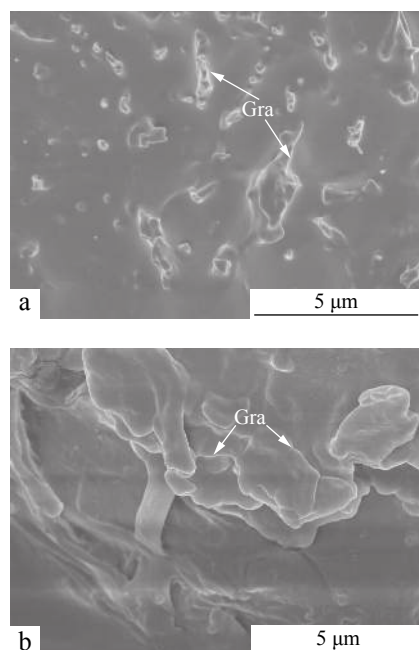


**Fig. 3** FESEM images of dispersions of different PLLA nanocomposites: (a) PLLA/2Gra, (b) PLLA/2IL/2Gra

straight line. Thus, the crystal growth rate ( $G$ ) of different samples can be deduced from the slope of lines. The growth rate of PLLA and PLLA/2Gra is  $2.44$  and  $2.39 \mu\text{m}\cdot\text{min}^{-1}$ , respectively. This demonstrates that  $G$  of PLLA declines slightly with the incorporation of Gra because the increase of system viscosity limits the mobility of PLLA chains during the crystallization process. It is noticeable that the crystal growth rate rises to  $2.86$ ,  $2.80$ , and  $2.90 \mu\text{m}\cdot\text{min}^{-1}$  for PLLA/2IL, PLLA/IL/Gra, and PLLA/2IL/2Gra, respectively, which can be attributed to the interaction between ethoxycarbonyl of IL and ester group of PLLA.<sup>[36]</sup>  $G$  is connected to the ability of chain movement and ordered arrangement. The mobility of PLLA chain segment is facilitated because the ethoxycarbonyl group IL contained has great compatibility with PLLA matrix and weakens the interaction between PLLA chain segments. Although the presence of Gra increases the nucleation density of PLLA, the spherulite growth rate of PLLA/2Gra decreases slightly possibly due to the prevented diffusion of PLLA chain segment and restrained growth of spherulite by Gra. Compared with PLLA/2IL, the spherulite growth rate of PLLA/2IL/2Gra has a slight increase. IL can improve the dispersibility of Gra in PLLA matrix, and more dispersive ILs wrapped on Gra sur-

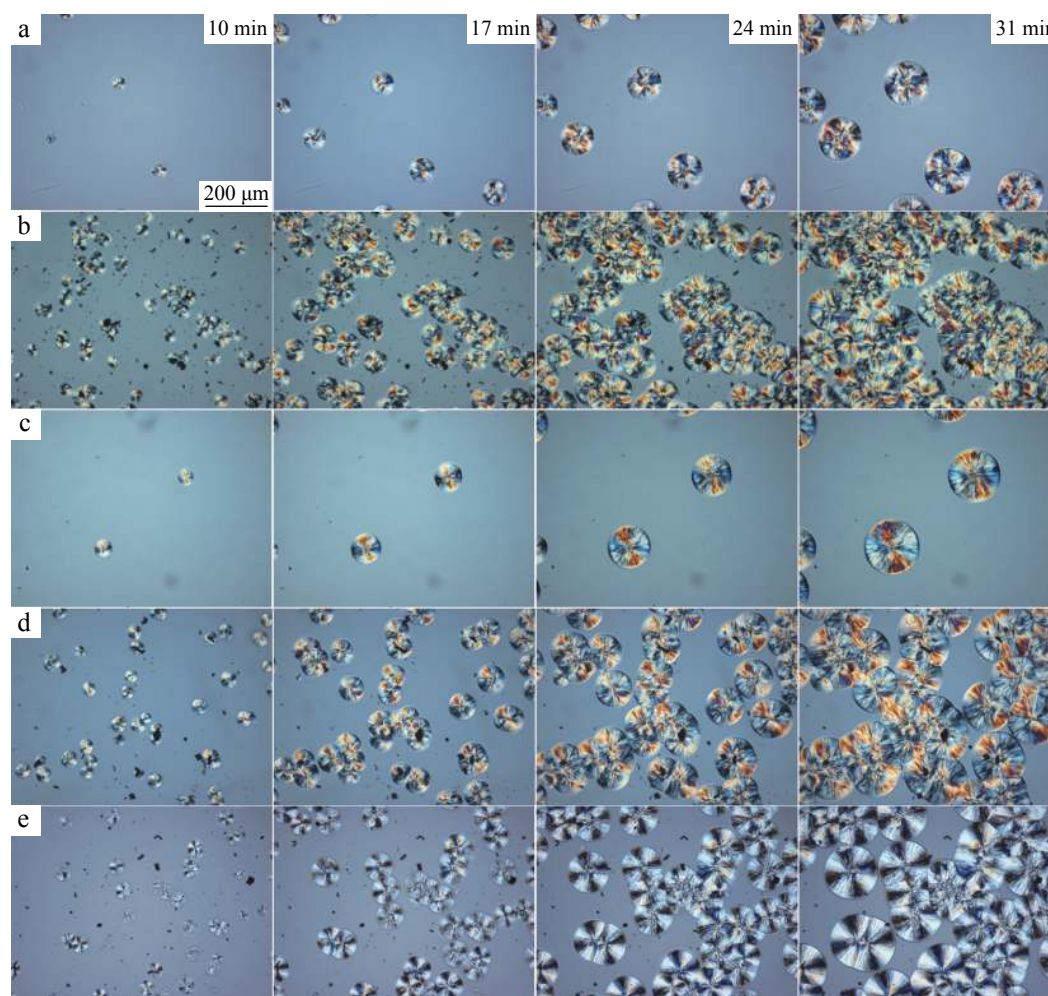


**Fig. 4** The POM micrographs of isothermal crystallization at  $130\text{ }^{\circ}\text{C}$  for neat PLLA and its nanocomposites: (a) Neat PLLA; (b) PLLA/2Gra; (c) PLLA/2IL; (d) PLLA/IL/Gra; (e) PLLA/2IL/2Gra

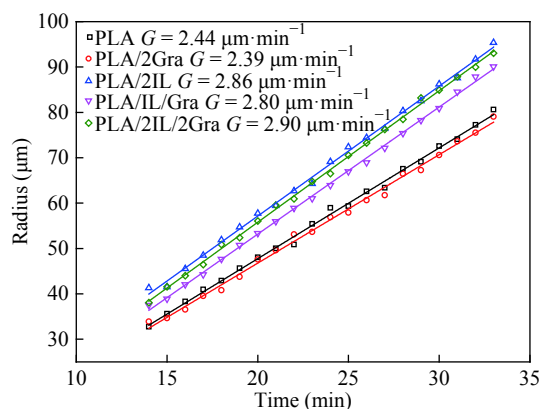


**Fig. 5** Spherulite radius versus crystallization time of neat PLLA and its nanocomposites during isothermal crystallization at 130 °C.  $G$  represents the spherulite growth rate.

face promote the spherulite growth greatly due to the enhanced segmental mobility of PLLA. Thus, the synergistic effects of IL and Gra on crystallization of PLLA can be described as follows. Gra increases the nucleation density and IL promotes the spherulite growth during the crystallization process.

### Behavior of Nonisothermal Crystallization

Fig. 6 displays the second heating curves obtained by DSC, and the corresponding crystallization parameters are shown in Tables 2 and 3. As can be seen from Fig. 6(a), all the samples exhibit two obvious transitions, including the exothermic peak attributed to cold crystallization behavior ( $T_{cc}$ ), and the endothermic peak attributed to the melting of the PLLA crystallites. After cooling down at a rate of 2.5 °C/min,  $T_{cc}$ s of PLLA/2Gra and PLLA/IL/Gra are 121.3 and 125.4 °C, respectively. Compared with  $T_{cc}$ s of PLLA,  $T_{cc}$ s of PLLA/2Gra and PLLA/IL/Gra decrease 10 and 5.9 °C, respectively. The variation of  $T_{cc}$  is related to chain movement of PLLA. Furthermore, with the incorporation of Gra, the degree of crystallinity,  $X_c$ , increases significantly.  $X_c$  of PLLA/IL/Gra is 16.5%, which is the same as that of PLLA/2Gra. It can be seen that 2Gra of PLLA/2Gra has the same effect on nucleation and chain movement of PLLA as IL/Gra of PLLA/IL/Gra does. However,  $X_c$  of PLLA/2IL is

lower than that of neat PLLA because IL can inhibit nucleation of PLLA.<sup>[37]</sup>  $X_c$  of PLLA/2IL/2Gra reduces because of the inhibition effect on chain movement of PLLA with more Gra.

### Isothermal Crystallization Kinetics

The isothermal DSC thermograms of PLLA and its composites at different temperatures are displayed in Fig. 7. Some features can be found from the plots. The PLLA and PLLA/2IL exhibit the lower crystallization rate, and the exothermic peaks are inconspicuous and broad. However, with the incorporation of Gra, the exothermic peaks of samples become narrow and sharp, which means the faster crystallization rate and higher degree of crystallinity of the composites. The nucleating effect of Gra causes more nuclei and enhancements of crystallization rate. Fig. 8 shows the relative crystallinity ( $X_t$ ) versus crystallization time of PLLA and composites.  $X_t$  at a certain crystallization time ( $t$ ) can be calculated according to the equation as follows:

$$X_t = \frac{Q_t}{Q_\infty} = \frac{\int_0^t (dH/dt)dt}{\int_0^\infty (dH/dt)dt} \quad (1)$$

where  $Q_t$  and  $Q_\infty$  are the heats generated at time  $t$  and at infinite time, respectively, and  $dH/dt$  is the rate of heat evolution. Obviously, all plots exhibit a sigmoid dependence with time. In addition, with the incorporation of Gra, the crystallization time of samples is shortened largely. It is worth noting that PLLA/IL/Gra shows a higher crystallization rate at 130 °C. It is well known that the Avrami equation (Eq. 2) can be used to further describe isothermal crystallization kinetics of neat PLLA and composites.

$$X_t = 1 - \exp(-kt^n) \quad (2)$$

where  $X_t$  is related to the relative crystallinity at time  $t$ ,  $n$  is the Avrami exponent which depends on the type of nucleation and the growth mechanism,  $k$  is the Avrami rate constant related to the nucleation and the growth rate parameters, and  $t$  is the isothermal crystallization time. Eq. (2) can be rearranged by taking logarithms on both sides:

$$\lg[-\ln(1 - X_t)] = n \lg t + \lg k \quad (3)$$

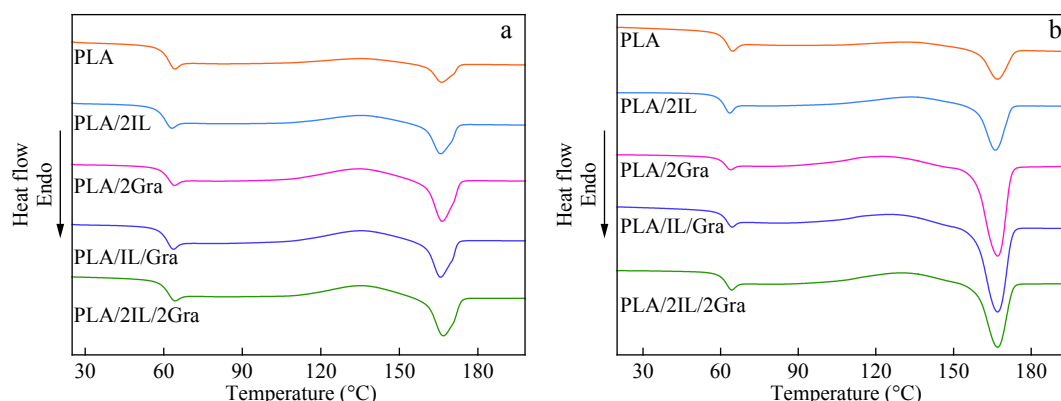


**Fig. 6** Melting behaviors of nonisothermal crystallization processes for neat PLLA and its nanocomposites when first cooling down at (a) 10 °C·min<sup>-1</sup> and (b) 2.5 °C·min<sup>-1</sup>, respectively

**Table 2** Thermal properties of the second heating curves for PLLA and its nanocomposites after cooling at 10 °C·min<sup>-1</sup>

| Sample        | $T_{cc}$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) |
|---------------|---------------|------------|--------------------|
| PLLA          | 134.3         | 166.5      | 3.3                |
| PLLA/2IL      | 135.4         | 166.2      | 5.5                |
| PLLA/2Gra     | 134.1         | 166.5      | 7.2                |
| PLLA/IL/Gra   | 134.6         | 165.9      | 6.4                |
| PLLA/2IL/2Gra | 136.2         | 166.8      | 7.6                |

**Table 3** Thermal properties of the second heating curves for PLLA and its nanocomposites after cooling at 2.5 °C·min<sup>-1</sup>

| Sample        | $T_{cc}$ (°C) | $T_m$ (°C) | $\Delta H_{cc}$ (J/g) | $\Delta H_m$ (J/g) | $X_c$ (%) |
|---------------|---------------|------------|-----------------------|--------------------|-----------|
| PLLA          | 131.3         | 167.2      | 6.9                   | 9.7                | 3.0       |
| PLLA/2IL      | 133.2         | 166.3      | 12.1                  | 13.4               | 1.4       |
| PLLA/2Gra     | 121.3         | 167.3      | 15.3                  | 30.6               | 16.5      |
| PLLA/IL/Gra   | 125.4         | 167.2      | 13.9                  | 29.2               | 16.5      |
| PLLA/2IL/2Gra | 129.4         | 167.0      | 14.0                  | 21.7               | 8.3       |

The reported enthalpy value for PLLA with 100% crystallinity is 93 J·g<sup>-1</sup>

According to Eq. (3),  $n$  and  $k$  can be obtained from the slope and intercept of the straight line by plotting  $\lg[-\ln(1 - X_t)]$  versus  $\lg t$ . The significant parameter to describe the isothermal crystallization kinetics is the half-time of crystallization ( $t_{1/2}$ ), defined as the time needed to reach 50% crystallinity.<sup>[38]</sup> As the Avrami plots shown in Fig. 9, all the curves have good linear relationships.

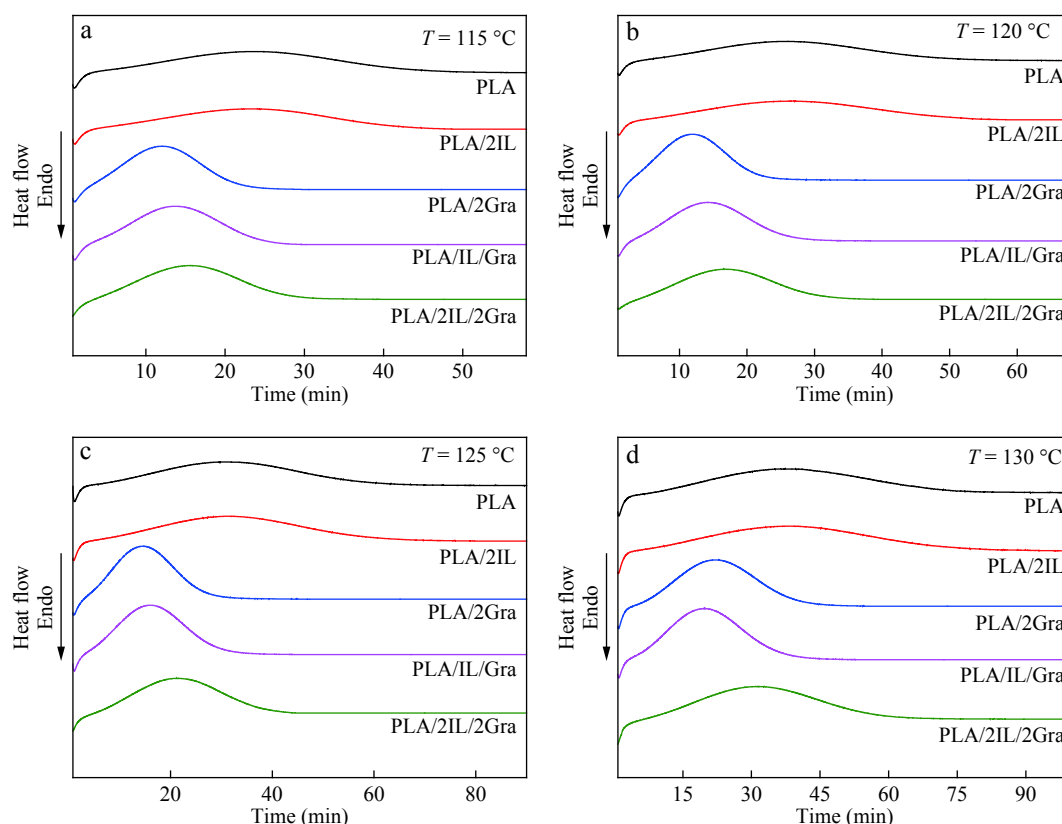
Kinetic parameters directly evaluated from the sigmoid curves are listed in Table S1 (in electronic supplementary information, ESI). The range of  $n$  values is 2.2–2.4 for PLLA at the different crystallization temperatures, which is similar to the values reported in literatures.<sup>[39]</sup> For PLLA without

any heterogeneous nucleus, its nucleation type should predominantly be homogeneous nucleating and its growth dimensions should predominantly be a three-dimensional growth.<sup>[40]</sup> The  $n$  values of PLLA/IL have the same range as those of neat PLLA. With the incorporation of Gra, the  $n$  values increase slightly to 2.4–2.6, indicating the crystallization mechanism of PLLA may not change significantly. The values of  $k$  for PLLA decrease with the increasing crystallization temperature, implying that the crystallization process is controlled by nucleating rate because of the low degree supercooling.<sup>[41]</sup> Other composites also have the same tendency with neat PLLA. In addition, the values of  $k$  for PLLA/2Gra are greater than those of neat PLLA and other composites at 115–125 °C, which can be attributed to the good nucleation ability of Gra in PLLA matrix. It is noteworthy that PLLA/IL/Gra has faster crystallization rate than PLLA/2Gra does at 130 °C. IL modification can prevent the aggregation of Gra and improve the rate of nucleation and regular arrangement of PLLA chains. With the increase of temperature, PLLA/2IL/2Gra can decrease the crystallization rate by inhibiting chain movement of PLLA.

The isothermal crystallization is thermally activated, and the crystallization rate  $k$  can be approximately written as:<sup>[42]</sup>

$$\frac{1}{n} (\ln k) = \ln k_0 - \frac{\Delta E}{RT_c} \quad (4)$$

where  $k_0$  is a temperature-independent pre-exponential factor,  $\Delta E$  is total activation energy,<sup>[43]</sup>  $T_c$  is the temperature of isothermal crystallization, and  $R$  is the gas constant.

**Fig. 7** DSC curves of isothermal crystallization for neat PLLA and its nanocomposites at various temperatures of (a) 115 °C, (b) 120 °C, (c) 125 °C, and (d) 130 °C

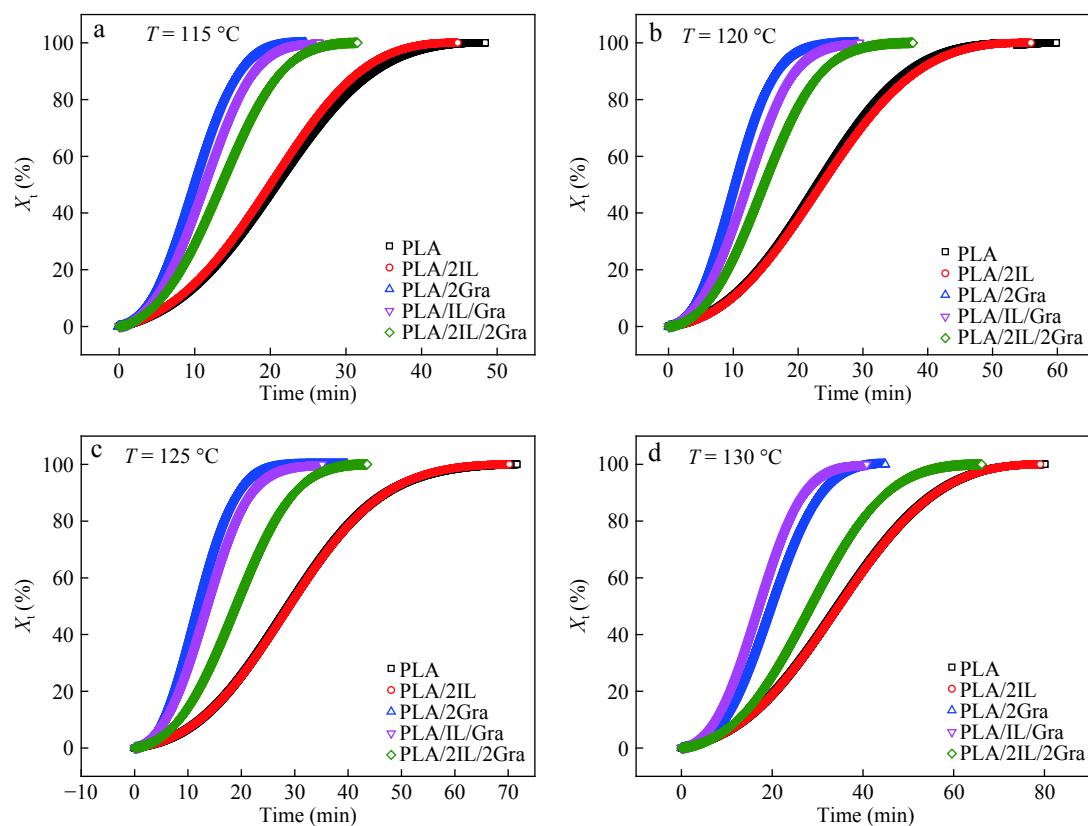


**Fig. 8** Plots of relative crystallinity ( $X_t$ ) as a function of crystallization time for neat PLLA and its nanocomposites at (a) 115 °C, (b) 120 °C, (c) 125 °C, (d) 130 °C

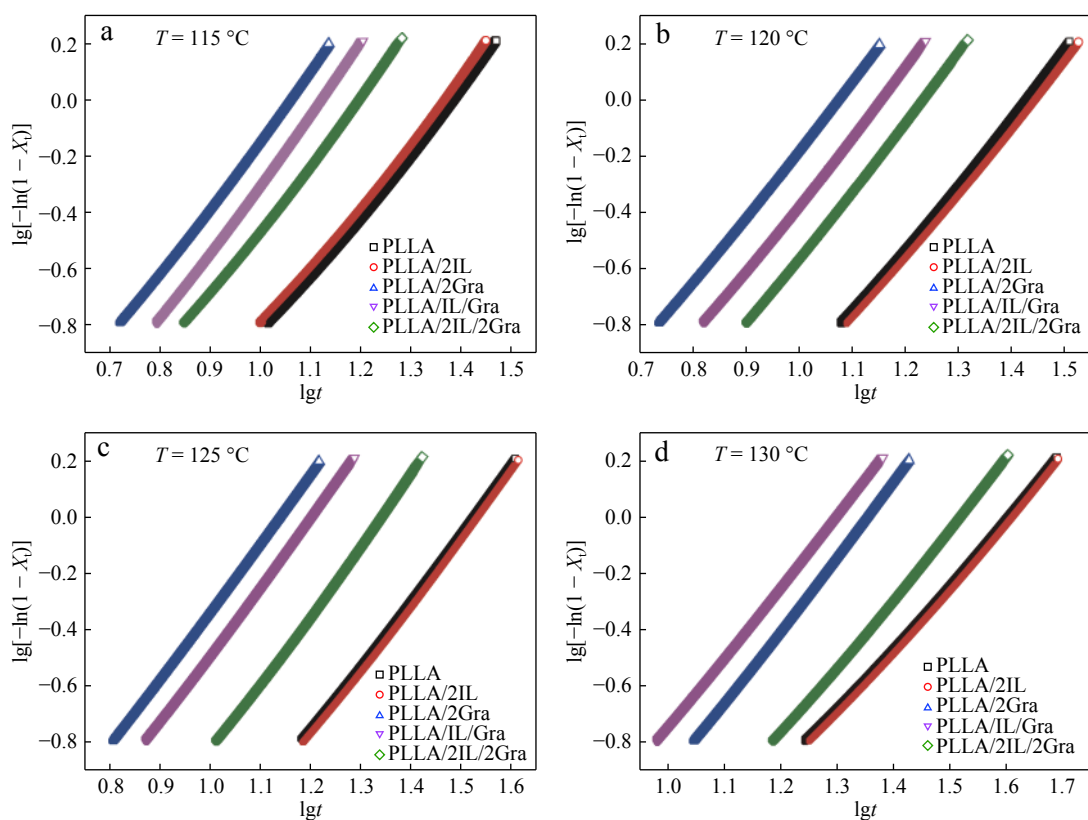


**Fig. 9** Plot of  $\lg[-\ln(1 - X_t)]$  versus  $\lg t$  for isothermal crystallization of samples under various temperatures: (a) 115 °C, (b) 120 °C, (c) 125 °C, and (d) 130 °C

Fig. 10 shows the Arrhenius plots of  $(1/n)\ln k$  versus  $1/T_c$ . The  $\Delta E$  values are  $-31.0$ ,  $-36.6$ ,  $-14.6$ ,  $-20.7$ , and  $-71.7$   $\text{kJ}\cdot\text{mol}^{-1}$  for PLLA, PLLA/2IL, PLLA/2Gra, PLLA/IL/Gra, and PLLA/2IL/2Gra, respectively. The value of  $\Delta E$  is negative because the melting crystallization is an exothermic process. It can be found that with the incorporation of Gra, the  $\Delta E$  value of composites is smaller than that of neat PLLA due to the nucleation effect of Gra in PLLA matrix. The  $\Delta E$  value of PLLA/2IL increases compared with that of neat PLLA because IL can inhibit the nucleation of PLLA slightly.

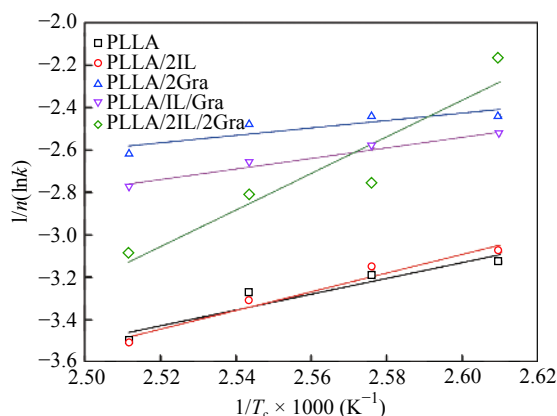


**Fig. 10** Determination of the activation energy by plotting  $1/n(\ln k)$  versus  $1/T_c$  based on the Arrhenius equation. The Avrami parameter  $k$  can be deduced from isothermal crystallization.

## Dielectric Relaxation Behavior

Dielectric relaxation spectroscopy (DRS) is performed with neat PLLA and composites. Fig. 11 shows the frequency dependence of the imaginary part ( $\epsilon''$ ) of the dielectric permittivity for PLLA and composites at 110–140 °C. Normal mode ( $\alpha_N$ ) process in the neat PLLA is visible clearly at low frequency.<sup>[41–43]</sup> Molecular motion in PLLA is controlled by largely different length scales ranging from the local segmental motion ( $\alpha$ ), responsible for the glass transition, to the cooperative motions and the normal-mode relaxation, responsible for fluctuation of the end-to-end vector of chains prevailing in the viscoelastic terminal relaxation.<sup>[44,45]</sup> The incorporation of IL has a slight effect on the relaxation frequency and intensity of dielectric loss because of the significant dispersion effect of IL on Gra surface. The increase of relaxation frequency and intensity for  $\alpha_N$  relaxation may be attributed to the chain movement of PLLA by 2Gra, IL/Gra or 2IL/2Gra following the end-to-end vector in the direction parallel to the chain contour. The change of  $\alpha_N$  relaxation of PLLA/IL/Gra and PLLA/2Gra is basically the same trend. It is concluded that 2Gra of PLLA/2Gra has the same effect on chain movement as IL/Gra of PLLA/IL/Gra does, and is different from that of PLLA/2IL/2Gra.

The overall rate of crystallization depends on two factors: nucleation rate and crystal growth rate. Gra acts as heterogeneous nucleating agent to increase the nucleation rate, leading to an increase of the overall crystallization rate. On

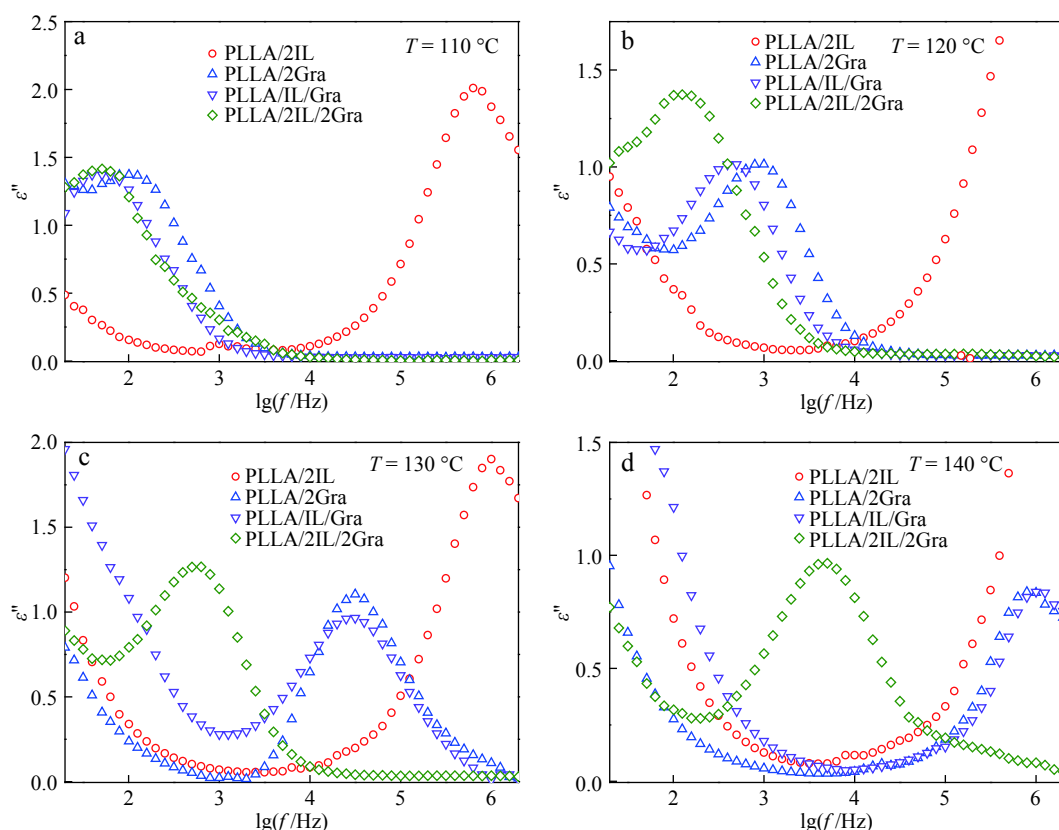


**Fig. 11** The frequency dependence of  $\epsilon''$  for PLLA and PLLA nanocomposites under different temperatures: (a) 110 °C, (b) 120 °C, (c) 130 °C, and (d) 140 °C

the other hand, the formation of Gra aggregation decreases the nucleating efficiency of individual Gra, also contributing to the reduction of crystallization kinetics, which can be confirmed by the number of active heterogeneities from POM graphs. In addition, the increase of Gra could induce topological confinement effect which eventually results in a reduction in chain mobility of PLLA. The results suggest that the IL-modified Gra enhances the crystallization rate of PLLA when the mass fraction ratio of Gra to IL is optimized. In PLLA/IL/Gra, the Gra-imidazolium cation interaction in IL-modified Gra can improve the dispersion of Gra, and increase the nuclei density of PLLA/IL/Gra compared with PLLA/2Gra. 2Gra of PLLA/2Gra has the same effect on chain movement as IL/Gra of PLLA/IL/Gra does because IL enhances the mobility of PLLA chain segments, while Gra restrains the mobility of PLLA chain segments. When the optimized mass fraction ratio of Gra to IL is 1:1, Gra as a good nucleating agent and IL as the significant dispersion agent at Gra surface can promote the crystallization of PLLA.

## CONCLUSIONS

PLLA-based nanocomposites filled with IL and Gra were prepared by a solution-blending method. The samples containing IL can accelerate the growth rate of spherulites for PLLA, indicating that IL may improve the rate of regular arrangement of PLLA chains. The change of  $\alpha_N$  relaxation of PLLA/IL/Gra and PLLA/2Gra basically has the same trend and 2Gra of PLLA/2Gra has the same effect on chain movement as IL/Gra of PLLA/IL/Gra does. PLLA/IL/Gra has the faster crystallization rate than that of PLLA/2Gra, which might be attributed to the Gra-imidazolium cation interaction in IL-modified Gra, the significant dispersion effect of IL at Gra surface, and the increase of nuclei density of PLLA/IL/Gra. When the optimized mass fraction ratio of Gra to IL is 1:1, Gra as a good nucleating agent and IL as the significant dispersion agent at Gra surface can promote the crystallization of PLLA.

## 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/s10118-019-2192-5>.

## ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51603060) and the Fundamental Research Funds for the Central Universities (No. JZ2017YYPY0250).

## REFERENCES

- Gupta, B.; Revagade, N.; Hilborn, J. Poly(lactic acid) fiber: An overview. *Prog. Polym. Sci.* **2007**, *32*, 455–482.
- Drumright, R. E.; Gruber, P. R.; Henton, D. E. Polylactic acid technology. *Adv. Mater.* **2000**, *23*, 1841–1846.
- Proikakis, C. S.; Mamouzelos, N. J.; Tarantili, P. A.; Andreopoulos, A. G. Swelling and hydrolytic degradation of poly(D, L-lactic acid) in aqueous solutions. *Polym. Degrad. Stab.* **2006**, *91*, 614–619.
- Hiljanen-Vainio, M.; Varpomaa, P.; Seppälä, J.; Törmälä, P. Modification of poly(L-lactides) by blending: Mechanical and hydrolytic behavior. *Macromol. Chem. Phys.* **1996**, *197*, 1503–1523.
- Aou, K.; Hsu, S. L.; Kleiner, L. W.; Tang, F. W. Roles of Conformational and configurational defects on the physical aging of amorphous poly(lactic acid). *J. Phys. Chem. B* **2007**, *111*, 12322–12327.
- Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. B. Poly(lactic acid) crystallization. *Prog. Polym. Sci.* **2012**, *37*, 1657–1677.
- Xing, Q.; Li, R. B.; Dong, X.; Zhang, X. Q.; Zhang, L. Y.; Wang, D. J. Phase morphology, crystallization behavior and mechanical properties of poly(L-lactide) toughened with biodegradable polyurethane: Effect of composition and hard segment ratio. *Chinese J. Polym. Sci.* **2015**, *33*, 1294–1304.
- Yang, G.; Gao, Q.; Ouyang, C. F.; Zheng, K. S.; Guo, Y. Influence of nucleating agent on PLLA crystalline and mechanical properties. *Adv. Mater. Res.* **2013**, *624*, 269–273.
- Xing, Q.; Li, R. B.; Dong, X.; Luo, F. L.; Kuang, X.; Wang, D. J.; Zhang, L. Y. Enhanced crystallization rate of poly(L-lactide) mediated by a hydrazide compound: Nucleating mechanism study. *Macromol. Chem. Phys.* **2015**, *10*, 1134–1145.
- Shi, H.; Chen, X.; Chen, W. K.; Pang, S. J.; Pan, L. S.; Xu, N.; Li, T. Crystallization behavior, heat resistance, and mechanical performances of PLLA/myo-inositol blends. *J. Appl. Polym. Sci.* **2017**, *134*, 44732.
- Xing, Q.; Li, R. B.; Zhang, X. Q.; Dong, X.; Wang, D. J.; Zhang, L. Y. Tailoring crystallization behavior of poly(L-lactide) with a low molecular weight aliphatic amide. *Colloid Polym. Sci.* **2015**, *293*, 3573–3583.
- Chen, L.; Hou, X.; Song, N.; Shi, L.; Ding, P. Cellulose/graphene bioplastic for thermal management: Enhanced isotropic thermally conductive property by three-dimensional interconnected graphene aerogel. *Compos. Part A: Appl. S.* **2018**, *107*, 189–196.
- Xu, J. Z.; Chen, T.; Yang, C. L.; Li, Z. M.; Mao, Y. M.; Zeng, B. Q.; Hsiao, B. S. Isothermal crystallization of poly(L-lactide) induced by graphene nanosheets and carbon nanotubes: A comparative study. *Macromolecules* **2010**, *43*, 5000–5008.
- Liang, Y. Y.; Yang, S.; Jiang, X.; Zhong, G. J.; Xu, J. Z.; Li, Z. M. Nucleation ability of thermally reduced graphene oxide for polylactide: Role of size and structural integrity. *J. Phys. Chem. B* **2015**, *119*, 4777–4787.
- Papageorgiou, G. Z.; Terzopoulou, Z.; Bikiaris, D.; Triantafyllidis, K. S.; Diamanti, E.; Gournis, D.; Pissis, P. Evaluation of the formed interface in biodegradable poly(L-lactic acid)/graphene oxide nanocomposites and the effect of nanofillers on mechanical and thermal properties. *Thermochim. Acta* **2014**, *597*, 48–57.
- Manafi, P.; Ghasemi, I.; Karrabi, M.; Azizi, H.; Ehsaninamin, P. Effect of graphene nanoplatelets on crystallization kinetics of poly(lactic acid). *Soft Mater.* **2014**, *12*, 433–444.
- Huang, H. D.; Xu, J. Z.; Fan, Y.; Xu, L.; Li, Z. M. Poly(L-lactic acid) crystallization in a confined space containing graphene oxide nanosheets. *J. Phys. Chem. B* **2013**, *117*, 10641–10651.
- Plechova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.
- Armand, M.; Endres, F.; Macfarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.* **2009**, *8*, 621–629.
- Rogers, R. D.; Seddon, K. R. Ionic liquids—solvents of the future? *Science* **2003**, *5646*, 792–793.

- 21 Scott, M. P.; Brazel, C. S.; Benton, M. G.; Mays, J. W.; Holbrey, J. D.; Rogers, R. D. Application of ionic liquids as plasticizers for poly(methyl methacrylate). *Chem. Commun.* **2002**, 13, 1370–1371.
- 22 Gui, H.; Li, Y.; Chen, S.; Xu, P.; Zheng, B.; Ding, Y. Effects of biodegradable imidazolium-based ionic liquid with ester group on the structure and properties of PLLA. *Macromol. Res.* **2014**, 22, 583–591.
- 23 Leng, J.; Purohit, P. J.; Kang, N.; Wang, D. Y.; Falkenhagen, J.; Emmerling, F. Structure-property relationships of nanocomposites based on polylactide and MgAl layered double hydroxides. *Eur. Polym. J.* **2015**, 68, 338–354.
- 24 Saiter, A.; Delpouve, N.; Dargent, E.; Oberhauser, W.; Conzatti, L.; Cicogna, F.; Passaglia, E. Probing the chain segment mobility at the interface of semi-crystalline polylactide/clay nanocomposites. *Eur. Polym. J.* **2016**, 78, 274–289.
- 25 Klonos, P.; Terzopoulou, Z.; Koutsoumpis, S.; Zidropoulos, S.; Kripotou, S.; Papageorgiou, G. Z.; Pissis, P. Rigid amorphous fraction and segmental dynamics in nanocomposites based on poly(L-lactic acid) and nano-inclusions of 1-3D geometry studied by thermal and dielectric techniques. *Eur. Polym. J.* **2016**, 82, 16–34.
- 26 Xu, P.; Gui, H. G.; Yang, S. Z.; Ding, Y. S.; Hao, Q. Dielectric and conductivity properties of poly(L-lactide) and poly(L-lactide)/ionic liquid blends. *Macromol. Res.* **2014**, 22, 304–309.
- 27 Zhao, Y.; Hu, Z. Graphene in ionic liquids: Collective van der Waals interaction and hindrance of self-assembly pathway. *J. Phys. Chem. B* **2013**, 36, 10540–10547.
- 28 Saxena, A. P.; Deepa, M.; Joshi, A. G.; Bhandari, S.; Srivastava, A. K. Poly(3,4-ethylenedioxythiophene)-ionic liquid functionalized graphene/reduced graphene oxide nanostructures: Improved conduction and electrochromism. *ACS Appl. Mater. Interface* **2011**, 4, 1115–1126.
- 29 Lu, J.; Yang, J. X.; Wang, J.; Lim, A.; Wang, S.; Loh, K. P. One-pot synthesis of fluorescent carbon nanoribbons, nanoparticles, and graphene by the exfoliation of graphite in ionic liquids. *ACS Nano* **2009**, 8, 2367.
- 30 Li, Y.; Wang, Y.; Liu, L.; Han, L.; Xiang, F.; Zhou, Z. Crystallization improvement of poly(L-lactide) induced by functionalized multiwalled carbon nanotubes. *J. Polym. Sci., Part B: Polym. Phys.* **2009**, 47, 326–339.
- 31 Xu, J. Z.; Zhang, Z. J.; Xu, H.; Chen, J. B.; Ran, R.; Li, Z. M. Highly enhanced crystallization kinetics of poly(L-lactic acid) by poly(ethylene glycol) grafted graphene oxide simultaneously as heterogeneous nucleation agent and chain mobility promoter. *Macromolecules* **2015**, 48, 4891–4900.
- 32 Li, Y.; Wu, H.; Wang, Y.; Liu, L.; Han, L.; Wu, J.; Xiang, F. Synergistic effects of PEG and MWCNTs on crystallization behavior of PLLA. *J. Polym. Sci., Part B: Polym. Phys.* **2010**, 48, 520–528.
- 33 Androsch, R.; Iqbal, H. N.; Schick, C. Non-isothermal crystal nucleation of poly (L-lactic acid). *Polymer* **2015**, 81, 151–158.
- 34 Brüster, B.; Montesinos, A.; Reumaux, P.; Pérez-Camargo, R. A.; Mugica, A.; Zubitur, M.; Addiego, F. Crystallization kinetics of polylactide: Reactive plasticization and reprocessing effects. *Polym. Degrad. Stab.* **2018**, 148, 56–66.
- 35 Hu, Y.; Xu, P.; Gui, H.; Yang, S.; Ding, Y. Effect of graphene modified by a long alkyl chain ionic liquid on crystallization kinetics behavior of poly(vinylidene fluoride). *RSC Adv.* **2015**, 112, 92418–92427.
- 36 Chen, H. M.; Du, X. C.; Yang, A. S.; Yang, J. H.; Huang, T.; Zhang, N.; Zhang, C. L. Effect of graphene oxides on thermal degradation and crystallization behavior of poly(L-lactide). *RSC Adv.* **2014**, 7, 3443–3456.
- 37 Wei, T.; Pang, S.; Xu, N.; Pan, L.; Zhang, Z.; Xu, R.; Lin, Q. Crystallization behavior and isothermal crystallization kinetics of PLLA blended with ionic liquid, 1-butyl-3-methylimidazolium dibutylphosphate. *J. Appl. Polym. Sci.* **2015**, 132, 41308.
- 38 Schick, C. Differential scanning calorimetry (DSC) of semicrystalline polymers. *Anal. Bioanal. Chem.* **2009**, 395, 1589–1611.
- 39 Wu, D.; Cheng, Y.; Feng, S.; Yao, Z.; Zhang, M. Crystallization behavior of polylactide/graphene composites. *Ind. Eng. Chem. Res.* **2013**, 52, 6731–6739.
- 40 Xiao, H.; Lu, W.; Yeh, J. T. Effect of plasticizer on the crystallization behavior of poly(lactic acid). *J. Appl. Polym. Sci.* **2009**, 113, 112–121.
- 41 Zhao, Y.; Qiu, Z.; Yang, W. Effect of functionalization of multiwalled nanotubes on the crystallization and hydrolytic degradation of biodegradable poly(L-lactide). *J. Phys. Chem. B* **2008**, 112, 16461–16468.
- 42 Mijović, J.; Sy, J. W. Molecular dynamics during crystallization of poly(L-lactic acid) as studied by broad-band dielectric relaxation spectroscopy. *Macromolecules* **2002**, 35, 6370–6376.
- 43 Jeszka, J. K.; Pietrzak, L.; Pluta, M.; Boiteux, G. Dielectric properties of polylactides and their nanocomposites with montmorillonite. *J. Non-Cryst. Solids* **2010**, 356, 818–821.
- 44 Brás, A. R.; Viciosa, M. T.; Wang, Y.; Dionísio, M.; Mano, J. F. Crystallization of poly(L-lactic acid) probed with dielectric relaxation spectroscopy. *Macromolecules* **2006**, 39, 6513–6520.
- 45 Klonos, P.; Kripotou, S.; Kyritsis, A.; Papageorgiou, G. Z.; Bikiaris, D.; Gournis, D.; Pissis, P. Glass transition and segmental dynamics in poly(L-lactic acid)/graphene oxide nanocomposites. *Thermochim. Acta* **2015**, 617, 44–53.