

Can Classic Avrami Theory Describe the Isothermal Crystallization Kinetics for Stereocomplex Poly(lactic acid)?*

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Abstract Classic Avrami model and its modifications have found diverse applications in describing the thermal and phase behaviors of inorganic metals and organic polymers. The direct introduction of classic Avrami equation to offer quantitative analyses of crystallization kinetic parameters for enantiomeric poly(lactic acid) (PLA) blends may, however, lead to contradictory conclusions. As revealed by this study, during the characterization of isothermal melt and cold crystallization for stereocomplex PLA containing equal-weight poly(L-lactic acid) and poly(D-lactic acid), the kinetic parameters yielded by Avrami equation are not in line with the classic crystallization hypotheses or the direct morphological observations. The underlying mechanisms, to some extent, lie in the generation of stereocomplex crystals (SCs) during the cooling/heating which affects the subsequent crystallization dynamics. The huge gap between the melting enthalpies of 100% crystalline SCs (142 J/g) and homo-crystals (HCs, 93 J/g) is most likely responsible for the confusing kinetic parameters acquired from the deduction of Avrami equation, which is based on the integration of enthalpies as a function of crystallization time. This prompts for great care that the classic Avrami equation is not applicable to accurately describe the crystallization kinetics of stereocomplex PLA, given the generation of SCs prior to crystallization and the coexistence of HCs and SCs during crystallization.

Keywords Poly(lactic acid); Stereocomplex crystallization; Crystallization kinetics; Classic Avrami theory

INTRODUCTION

The rise of renewable and degradable poly(L-lactic acid) (PLLA) under the biorefinery concept has generated a demand for the enhancement of functional property harnessing, such as sufficient resistance to heat deformation^[1–4]. The formation of highly thermostable stereocomplex crystals (SCs) between the racemic PLLA and poly(D-lactic acid) (PDLA) chains, which are characterized by ~50 °C higher melting temperature than that of the homo-crystals (HCs), affords elucidation of substantially enhanced resistance to heat deformation^[5–8]. This opens up new possibilities to clear away the constraints on PLLA application at high-temperature, marking great potential for substituting the common fossil-fuel plastics, and even for challenging the engineering plastics^[9–13].

Prevailing formation of SCs, coupled with suppressed generation of HCs, is of paramount significance to pursue outstanding thermal resistance^[14, 15]. Quantitative evaluation of the stereocomplex crystallization kinetics and the concentration of SCs represents therefore an important criterion for the development of stereocomplex system^[16–18]. Besides the direct morphological observation such as polarized optical microscopy (POM)^[19], scanning electron microscopy (SEM)^[20] and atomic force microscopy^[21], it is noticed that the classic Avrami

* This work was financially supported by the National Natural Science Foundation of China (No. 21604016) and National Undergraduate Innovation Training Program (No. 201610657004).

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Received October 9, 2016; Revised December 20, 2016; Accepted December 28, 2016

doi: 10.1007/s10118-017-1929-2

equation without modification has been frequently used to quantitatively describe the crystallization kinetics for the system of stereocomplex poly(lactic acid) (PLA)^[22–27]. With addition of a small amount of PDLA (< 10 wt%), seemingly logical conclusions were generally made, as exemplified by the distinct fall of crystallization half-time ($t_{1/2}$, the time necessary for completion of 50% of the crystallization process) during the isothermal melt crystallization ranging from 137 °C to 146 °C^[27]. Moreover, the values of $t_{1/2}$ gradually increased with the increase of crystallization temperature, which was presumably caused by decreased nucleation activity at a higher temperature. In a study on crystallization kinetics of PLA blends containing equal weight of PLLA and PDLA (1:1), an unexpected fall of $t_{1/2}$ during the isothermal melt crystallization at 130, 140 and 160 °C was observed^[24]. Similar discrepant observations were also reported by several other groups^[25, 28, 29], which stimulated us to explore the application feasibility of classic Avrami theory for describing the isothermal crystallization kinetics of stereocomplex PLA. Can we expect quantitative and accurate evaluation of crystallization kinetics for the stereocomplex systems, even when HCs and SCs coexist?

By modeling the isothermal crystallization from the molten and glassy states, here we aim to examine the reliability of employing Avrami equation to evaluate the crystallization kinetics of PLA stereocomplex occurring in the melt and cold crystallization thermoprograms, which have been widely used to define the crystallization ability of PLA^[30, 31].

EXPERIMENTAL

Materials

PLLA comprising 2% D-LA under the trade name of 4032D was procured from NatureWorks (USA), PDLA comprising 1% L-LA was supplied by Polysciences, Inc (USA). PLLA was characterized by a weight-average molecular weight (M_w) of 11.9×10^4 and a number-average molecular weight (M_n) of 6.6×10^4 , while the corresponding values of PDLA were 9.6×10^4 and 6.2×10^4 for M_w and M_n , respectively. Chloroform was obtained from VWR, Germany.

Characterization

Stereocomplex PLA (named Complex) films with a thickness of $\sim 20 \mu\text{m}$ were prepared by casting the chloroform solution containing equal-weight PLLA and PDLA. Figure 1 illustrates the temperature protocols for differential scanning calorimetry (DSC) programs carried out on a Mettler Toledo DSC 820 of (a) melt crystallization and (b) cold crystallization, both of which were followed by a heating program to determine the melting behaviors of the crystalline entities during the isothermal crystallization.

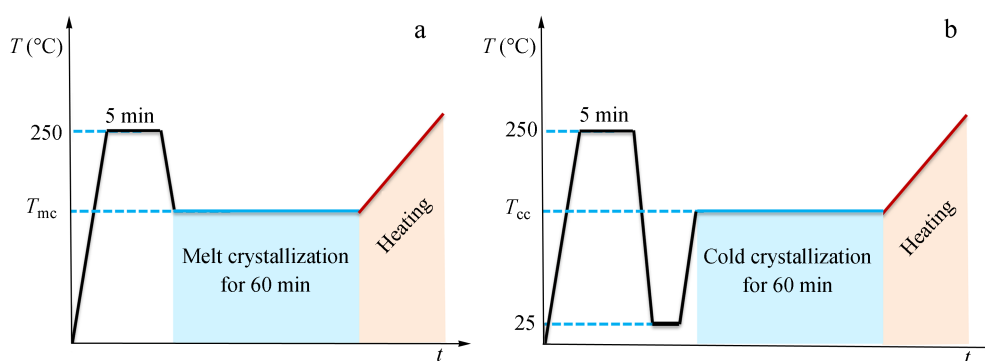


Fig. 1 Temperature profile of the isothermal (a) melt and (b) cold crystallization of Complex in the nitrogen atmosphere. The samples (5–6 mg) were melted at 250 °C for 5 min to erase the thermal history, and then: (a) quenched at a rate of 100 K/min to the crystallization temperatures (T_{mc} , 150, 165 and 180 °C) for 60 min, followed by a steady heating to 250 °C (10 K/min); (b) quenched at a rate of 100 K/min to room temperature, staying there for 2 min, and rapidly heated (100 K/min) to the crystallization temperatures (T_{cc} , 150, 165 and 180 °C) for 60 min and finally heated to 250 °C (10 K/min).

Two-dimensional wide-angle X-ray diffraction (2D-WAXD) was performed using a home-made laboratory instrument (Bruker NanoStar, Cu K α radiation) in Crystallography Lab of University of Sheffield. The X-ray beam with a wavelength of 0.154 nm was focused on an area of 4 $\mu\text{m} \times 4 \mu\text{m}$, and the distance from the sample to the detector was 350 mm. An X-ray CCD detector with a resolution of 2300 $\times$ 2300 pixels (Model Mar 345, Rayonix Co., Ltd., USA) was used to collect the 2D patterns. An Optiphot 2 microscope equipped with a Leica digital camera was used for polarized optical microscopy (POM) observation of the crystalline morphology. Scanning electron microscopy (SEM) was performed on an S-4800 SEM (Hitachi, Japan), operated at a low accelerating voltage of 0.5 kV, prior to which the crystallized Complex was etched in alkaline solution. Size exclusive chromatography (SEC) was performed on a Verotech PL-GPC 50 Plus system equipped with a PL-RI Detector and two PolarGel-M Organic (300 $\times$ 7.5 mm) columns from Varian. The samples dissolved in chloroform were injected with a PL-AS RT autosampler, with chloroform as the mobile phase (1 mL/min, 35 $^{\circ}\text{C}$). A Perkin-Elmer 2000 spectrometer was used to record FTIR spectra with 16 scans at a resolution of 4 cm^{-1} . 2D-FTIR absorbance patterns were imaged using a PerkinElmer Spotlight 400 system equipped with an optical microscope (Bucks, UK).

RESULTS AND DISCUSSION

Figures 2(A) and 2(B) show the isothermal curves of melt and cold crystallization, respectively. The curves yielded from the two crystallization modes shared some important features. First, multiple exothermic peaks were observed during melt and cold crystallization at 150 $^{\circ}\text{C}$, resulting primarily from the preferable stereocomplex crystallization at higher temperatures and successive homo-crystallization assisted by the existing SCs. Second, the number and intensity of the exothermic crystallization peaks evidently decayed as the temperature increased, especially the peaks assigned to homo-crystallization. On the other hand, samples crystallized from the glassy state were characterized by a higher crystallization ability compared to those submitted to melt crystallization. A narrow and strong exothermic peak was observed for the cold crystallization at 180 $^{\circ}\text{C}$, while a broad and weak peak was presented in the case of the melt crystallization.

The application of classic Avrami equation (Eq. 1) in describing the melt and cold crystallization kinetics yielded the plots of relative crystallinity as a function of crystallization time, as summarized in Figs. 2(A1) and 2(B1).

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

where X_t represents the relative crystallinity, n represents the Avrami exponent that is normally an integer between 1 and 4 associated with the nature of nucleation and growth geometry of the crystals, K is the overall crystallization rate constant, and t is the crystallization time. Figure 2(A1) presents normal S-shaped curves for all the samples during melt crystallization, regardless of the crystallization temperature. By contrast, irregular T-shaped plots were exhibited for the cold-crystallized Complex (Fig. 2B1), as a result of the multiple exothermic peaks during the crystallization starting from the glassy state. Next, employing logarithmic properties to both sides of Eq. (1), the following Eq. (2) can be obtained:

$$\lg[-\ln(1 - X_t)] = n \lg t + \lg K \quad (2)$$

The values of K and n were produced from the linear fitting of $\lg[-\ln(1 - X_t)]$ versus $\lg t$ (Figs. 2A2 and 2B2). The linear portion of about 5%–15% of relative crystallinity, a range normally adopted to discuss the Avrami parameters, was applied to obtain the parameters n and K . One may note that convex fitting curves were observed for Complex after cold crystallization, particularly at 165 and 180 $^{\circ}\text{C}$ (Fig. 2B2), in contrast to the nearly linear curves fitted for melt crystallization. Moreover, Figs. 2(C) and 2(D) illustrate the melting behavior of the crystalline entities developed during the isothermal crystallization, leading to the direct identification of the coexistence of SCs and HCs after crystallization below the T_m of HCs (150 $^{\circ}\text{C}$), and the exclusive formation of SCs due to melting of SCs at a higher temperature (180 $^{\circ}\text{C}$).

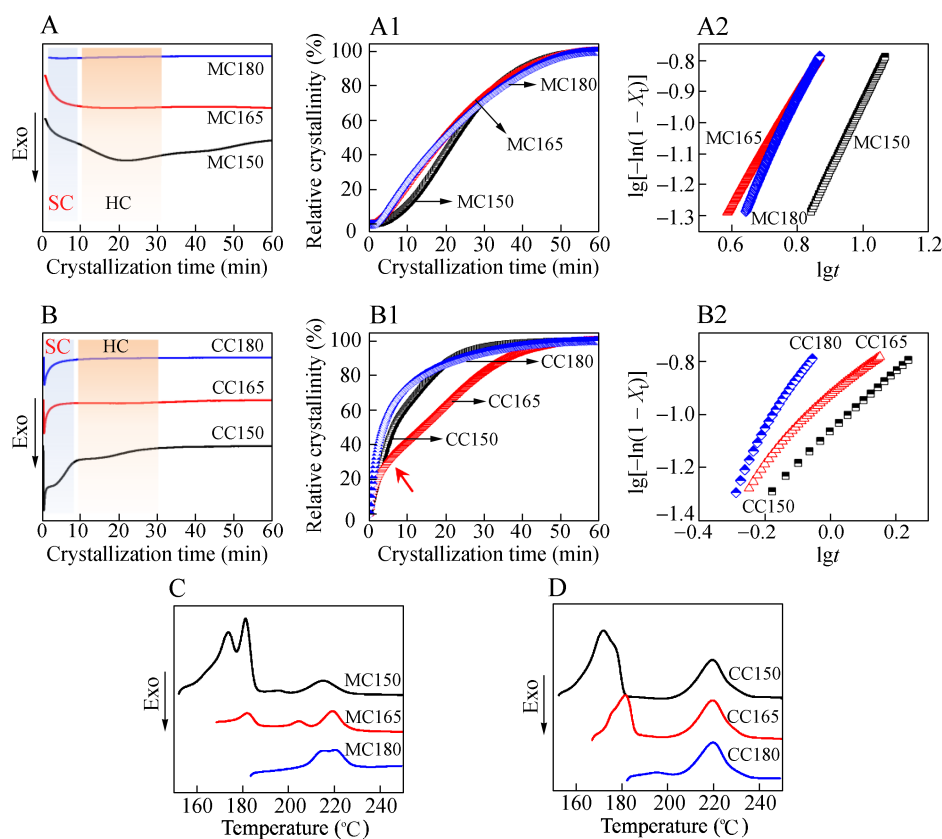


Fig. 2 Isothermal crystallization kinetics determined by DSC

Isothermal curves during (A) melt and (B) cold crystallization, the integrated enthalpies of which yield (A1, B1) the relative crystallinity as a function of crystallization time. The fitting of relative crystallinity based on the early-stage crystallization produces (A2, B2) Avrami plots. The successive heating traces after isothermal melt and cold crystallization are shown in (C) and (D), respectively.

Some important crystallization kinetic parameters acquired during the isothermal crystallization, including $t_{1/2}$, K and n , are summarized in Table 1. It is, however, notable to find the illogical fall in $t_{1/2}$ (from 22.5 min to 19.4 and 19.0 min) and rise of K (from $0.7 \times 10^{-3} \text{ min}^{-n}$ to 4.8×10^{-3} and $3.3 \times 10^{-3} \text{ min}^{-n}$) for melt crystallization as the temperature increased from 150 °C to 165 and 180 °C, indicating the enhanced crystallization kinetics and nucleation activity. This is contrasted with the general knowledge that the nucleation activity is normally suppressed with the increase in temperature, as mainly indicated by the increased $t_{1/2}$ and decreased K ^[32, 33]. Moreover, the comparison of melting enthalpies of the crystalline entities provides the contradictory results, displaying largely declined concentration of HCs and slightly varied SC concentrations as increasing temperature. The distinct enhancement of crystallization kinetics recorded for cold crystallization, in comparison to melt crystallization, is in line with the popular hypothesis that polymer chains starting from the glassy state are characterized by higher nucleation activity compared to those from the molten state^[30]. Three notable variations were observed as the temperature increased, which could lead to confusion in understanding the crystallization kinetics: (1) dramatic rise of $t_{1/2}$ from 6.5 min (at 150 °C) to 14.0 min (at 165 °C), followed by a sharp decline to 3.8 min (at 180 °C); (2) two jumps of K up to $220.9 \times 10^{-3} \text{ min}^{-n}$ from the lowest point of $45.3 \times 10^{-3} \text{ min}^{-n}$; (3) the extremely low n value approaching 1 for cold crystallization performed at 150 and 165 °C, an indication of two-dimensional crystallization, instead of the normal spherulitic development in three dimensions. The comparison of melting enthalpies of the cold-crystallized Complex, again, goes against the isothermal kinetics, judging from the drastic fall in HC concentrations (from 42.0 J/g to 17.6 and 0 J/g) and

moderately fluctuated concentration of SCs (from 27.6 J/g to 25.9 and 34.3 J/g) with increasing temperature. The evaluation of crystallization kinetics based on classic Avrami equation for both cold and melt crystallization, thus, yielded contradictory results even concerning the variations of crystal concentrations determined by the melting enthalpies.

Table 1 Crystallization kinetic parameters of Complex recorded during the isothermal crystallization and melting behaviors evaluated by successive heating

T_c (°C)	Melt crystallization			Cold crystallization		
	150	165	180	150	165	180
$t_{1/2}$ (min)	22.5	19.4	19.0	6.5	14.0	3.8
K ($\times 10^{-3} \text{ min}^{-n}$)	0.7	4.8	3.3	45.3	114.6	220.9
n	2.2	1.8	2.0	1.2	1.2	2.0
T_{m1} (°C)	173.0/179.8	179.7	— ^a	172.0/176.2	176.1/181.6	— ^a
ΔH_{m1} (J/g)	44.1	4.1	0	42.0	17.6	0
T_{m2} (°C)	216.4	204.7/219.2	217.6/223.7	219.4	219.6	194.9/219.8
ΔH_{m2} (J/g)	13.1	10.1	15.9	27.6	25.9	34.3

^a Not applicable

2D-WAXD measurements featuring high sensitivity in detecting the crystalline morphology such as crystal form and crystallinity were performed to provide complementary information for DSC evaluation^[34]. The experiment was carried out according to our recent work^[15], and the results are presented in Figs. 3(A)–3(C). The 2D-WAXD patterns of Complex crystallized at varied temperatures are compared in Fig. 3(A), producing

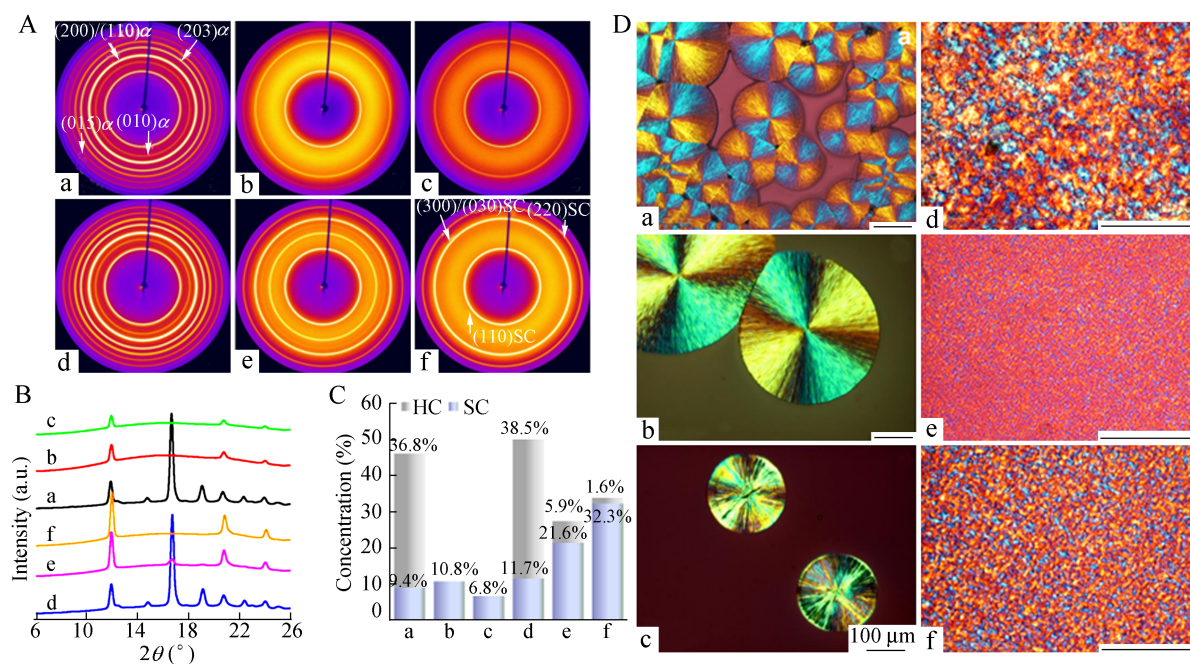


Fig. 3 Crystalline morphology of isothermally crystallized stereocomplex PLA: (A) 2D-WAXD patterns, (B) 1D-WAXD intensity profiles, (C) concentrations of HCs and SCs and (D) POM observation for the PLA blends submitted to melt crystallization at (a) 150 °C, (b) 165 °C and (c) 180 °C, and cold crystallization at (d) 150 °C, (e) 165 °C and (f) 180 °C for 60 min, respectively

The diffraction rings attributed to the lattice planes (010), (200)/(110), (203) and (015) of α -form HCs are identified in (A), as well as those assigned to the lattice planes (110), (300)/(030) and (220) of SCs. Based on the sum of HC and SC concentrations, the crystallinity can be produced. The increase in crystallization temperature caused the substantially decayed nucleation activity for melt-crystallized samples, while extremely dense crystalline entities were formed during cold crystallization, showing weak relation to the temperature (D). The scale bars represent 100 μm .

the corresponding intensity profiles (Fig. 3B). During the crystallization at 150 °C, independent of the initial state, both HCs and SCs were generated, which aroused the diffraction peaks located at $2\theta = 15.0^\circ$, 16.7° , 19.1° and 22.5° , and $2\theta = 11.9^\circ$, 20.7° and 23.9° , respectively^[35]. As the temperature increased to 165 and 180 °C, exclusive formation of SCs was traced during melt crystallization, while weak diffraction peaks assigned to HC formation were found during cold crystallization. Figure 3(C) reveals that the crystallinity of the cold-crystallized samples was basically higher than the crystallinity of the melt-crystallized samples, primarily arising from the metastable or imperfect crystalline entities existing in the former ones that were allowed to crystallize preferentially^[36]. In particular, the crystallinity after melt crystallization gradually dropped from the highest value of 46.2% for the crystallization at 150 °C to 6.8% when crystallized at 180 °C. This, however, yielded inconsistent results with the isothermal kinetic parameters, *i.e.*, enhanced crystallization based on the declined $t_{1/2}$ and increased K . Although enhanced generation of SCs was observed during cold crystallization at a higher temperature, the crystallinity suffered a profound decay from 50.2% at 150 °C to 27.5% and 33.9% at 165 and 180 °C, respectively. This evidently gives rise to the conflict of apparently increased crystallization kinetics as evaluated from the constant K .

Given the increased K and decayed $t_{1/2}$ during melt crystallization at higher temperatures, one may expect decreased size for the spherulites. However, it falls into the incorrect assertion as inspected by POM observation. Figures 3(D)(a)–3(D)(c) show that the spherulites for the Complex melt-crystallized at 150 °C were characterized by an average radius of $(126 \pm 15) \mu\text{m}$, surprisingly climbing to $(206 \pm 43) \mu\text{m}$ when the Complex melt-crystallized at 165 °C and back to the comparable level of $(115 \pm 22) \mu\text{m}$ when this crystallization done at 180 °C. It was accompanied by a substantial decrease in the nucleation density. The incredibly high nucleation density made it difficult to distinguish the spherulites formed during cold crystallization (Figs. 3D(d)–3D(f)).

The crystalline morphology was observed under SEM, as shown in Fig. 4^[37]. The crystalline structure for the spherulites formed during melt crystallization at 150 °C shows that extremely compact nano-sized SC spheres were assembled during the lamellar development (Figs. 4a and 4a1). This is consistent with the demonstration of the coexistence of SCs and HCs after crystallization below the melting points of HCs, as evidenced by DSC melting curves and WAXD data (Figs. 2 and 3). Regular spherulitic texture was generated during the melt crystallization at 180 °C, originated from the central nuclei (Figs. 4b and 4b1). During the cold crystallization at 180 °C, Figs. 4(c) and 4(c1) demonstrate that extremely tiny crystalline entities were developed probably due to the high nucleation activity from the glassy state.

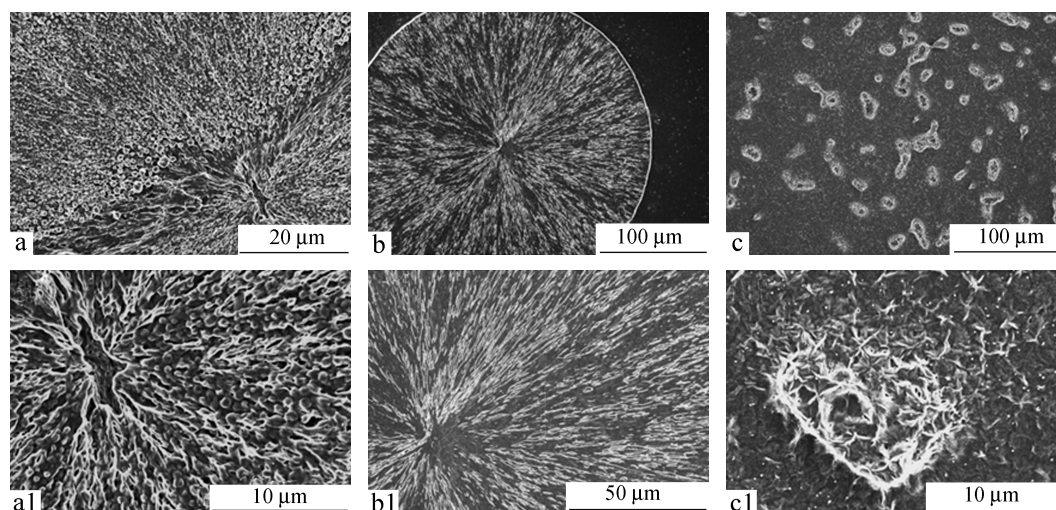


Fig. 4 Typical SEM micrographs showing the crystalline structure for the Complex after melt crystallization and cold crystallization: (a) melt crystallization at 150 °C, (b) melt crystallization at 180 °C and (c) cold crystallization at 180 °C

Overlapping the classic Avrami fitting analyses and an assortment of crystalline morphology characterization, the classic Avrami theory appears not applicable to describe the isothermal crystallization kinetic parameters for stereocomplex PLA. In an endeavor to probe the underlying mechanisms for the unavailability, we first examined the possibility of chain degradation and oxidation during the high-temperature melting, taking advantage of SEC determination (Fig. 5a) and FTIR measurements (Fig. 5b). Figure 5(a) suggests that molecular weights were not altered by high-temperature melting at 250 °C for 5 min, because of the high thermal stability of stereocomplex PLA and the protection from oxidation in the nitrogen atmosphere^[15]. This assumption is supported by the FTIR spectra showing that no oxidation was triggered during the melting (Fig. 5b), except for the disappearance of the broad peak around 3300 cm⁻¹ (H-bond generation) after melting at 250 °C for 5 min.

Next, the initial states prior to the melt and cold crystallization were characterized using 2D-FTIR imaging, which features a combination of high spatial resolution and high sensitivity to crystal identification at molecular level^[38–40]. We mainly focused on examining the generation of SCs during the heating/cooling, taking into consideration of the facts that: (1) stereocomplex crystallization was preferentially elicited due to the higher nucleation activity, (2) SCs could generate pronounced effects on the overall crystallization kinetics. Figures 5(c) and 5(d) show the 2D-FTIR patterns for the characteristic band of 910 cm⁻¹ to spatially map the distribution of SCs^[41], demonstrating a strong dependence on the supercooling degree and cooling rate. The application of higher cooling rate obviously reduced the concentration of SCs, regardless of the temperature program. It is instructive to use high heating/cooling rate to the preset isothermal crystallization temperature. It is notable that, for common DSC apparatus, the overshoot of heat flow is generally caused by using too high rate. Moreover, the higher supercooling degree used in Fig. 5(d), *i.e.*, cooling to 25 °C followed by heating to 150 °C, created a higher concentration of SCs in comparison to the monotonous cooling (Fig. 5c). The gap of SC

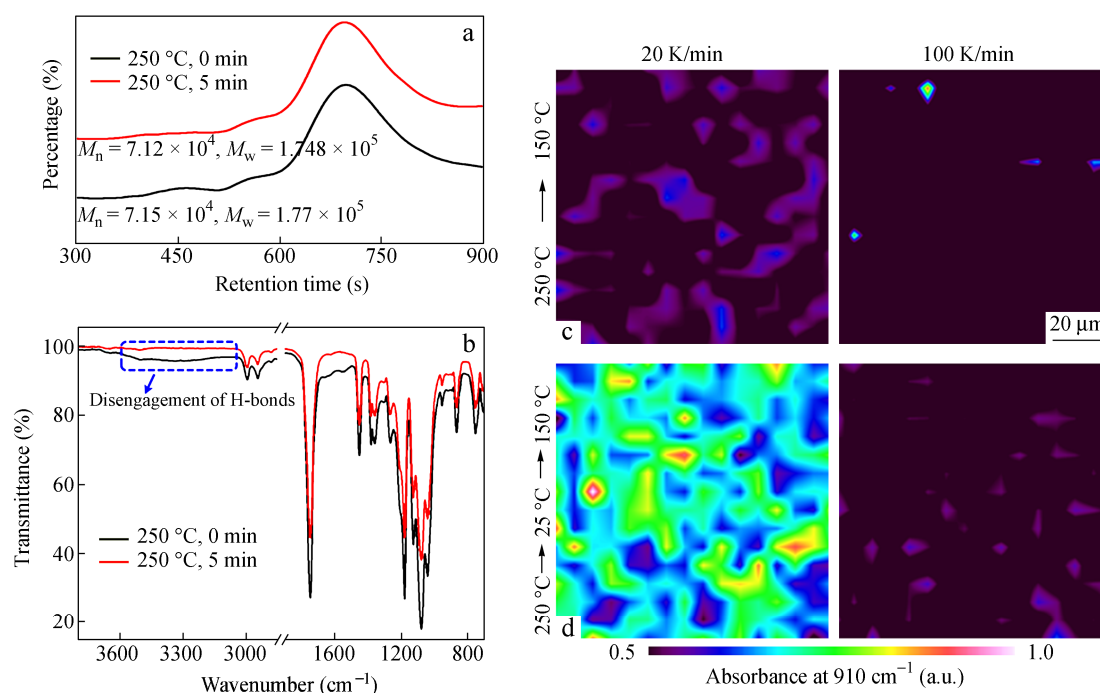


Fig. 5 Examination of thermo-induced chain degradation during melting and generation of SCs after quenching: (a) SEC curves demonstrating that the 5 min melting at 250 °C did not cause chain degradation; (b) FTIR spectra indicating that the major change at the molecular level triggered by the 5 min melting at 250 °C was the disengagement of H-bonds; (c, d) 2D-FTIR absorbance patterns of the characteristic band 910 cm⁻¹, which was elicited by the generation of SCs, for the samples quenched at the rates of 20 and 100 K/min prior to the (c) melt and (d) cold crystallization (Clearly the application of higher supercooling degree and lower cooling rate led to the generation of more SCs.)

concentration was further enlarged by a lower cooling/heating rate, as exemplified by the highest absorbance intensity observed in the glassy sample cooled and heated at a rate of 20 K/min. This indicates that, during the normal DSC program (100 K/min), an uncertain amount of SCs has been developed prior to the isothermal crystallization, especially for the cold crystallization program starting from the glassy state.

CONCLUSIONS

This study examines the validity of Avrami theory to describe the crystallization kinetics of stereocomplex PLA. In addition to the formation of SCs arising from the prominent nucleation ability of SCs, the pronounced gap between the enthalpies of melting for 100% crystalline SCs (142 J/g) and that for HCs (93 J/g) is primarily responsible for the contradictory kinetic parameters obtained from Avrami equation^[42, 43]. The main kinetic parameters are produced from the linear fitting of the plots of $\lg[-\ln(1 - X_t)]$ versus $\lg t$, based on the curves of relative crystallinity at the early stage (5%–15%). The relative crystallinity is, however, calculated by integrating the dynamic enthalpy variations as a function of crystallization time. With simultaneous development of SCs and HCs, the integrated area cannot reflect the exact crystallinity at the specific point, resulting in kinetic parameters contradictory with the general knowledge and other characterization results.

It is reasonable to assume that the classic Avrami equation can be applied to describe the crystallization kinetics as long as (1) SCs are exclusively formed during the high-temperature melt crystallization, and (2) no or few SCs are generated in the initial states prior to the crystallization. It is worth noting that the initial states should be precisely controlled, and the applicable temperature window may be extremely narrow to make reliable conclusions, far above the melting points of HCs as the melt crystallization at 165 °C cannot produce pure SCs. For the cold crystallization, the coexistence of HCs and SCs is observed even with the crystallization at 180 °C, making it almost impossible to accurately evaluate the crystallization kinetics based on classic Avrami equation. Ongoing efforts to the modification of Avrami equation may lead to quantitative, accurate analyses of crystallization kinetics, which can be applicable in the temperature zones above and below the melting points of HCs.

ACKNOWLEDGMENTS The authors are deeply indebted to Dr. Patrick Baker from the Department of Molecular Biology and Biotechnology, University of Sheffield for his kind help during the X-ray measurements.

REFERENCES

- 1 Xu, H., Liu, C.Y., Chen, C., Hsiao, B.S., Zhong, G.J. and Li, Z.M., *Biopolymers*, 2012, 97: 825
- 2 Xie, L., Xu, H., Niu, B., Ji, X., Chen, J., Li, Z.M., Hsiao, B.S. and Zhong, G.J., *Biomacromolecules*, 2014, 15: 4054
- 3 Xu, H., Xie, L., Chen, J.B., Jiang, X., Hsiao, B.S., Zhong, G.J., Fu, Q. and Li, Z.M., *Mater. Horiz.*, 2014, 1: 546
- 4 Sun, X., Tokuda, A., Oji, Y., Nakatani, T., Tsuji, H., Ozaki, Y., Yan, S. and Takahashi, I., *Macromolecules*, 2012, 45: 2485
- 5 Ikada, Y., Jamshidi, K., Tsuji, H. and Hyon, S.H., *Macromolecules*, 1987, 20: 904
- 6 Zhang, J., Duan, Y., Sato, H., Tsuji, H., Noda, I., Yan, S. and Ozaki, Y., *Macromolecules*, 2005, 38: 8012
- 7 Tsuji, H., Hosokawa, M. and Sakamoto, Y., *ACS Macro Lett.*, 2012, 1: 687
- 8 Sveinbjörnsson, B.R., Miyake, G.M., El-Batta, A. and Grubbs, R.H., *ACS Macro Lett.*, 2014, 3: 26
- 9 Sun, Y. and He, C., *ACS Macro Lett.*, 2012, 1: 709
- 10 Andersson, S.R., Hakkarainen, M. and Albertsson, A.C., *Polymer*, 2013, 54: 4105
- 11 Andersson, S.R., Hakkarainen, M., Inkinen, S., Södergård, A. and Albertsson, A.C., *Biomacromolecules*, 2010, 11: 1067
- 12 Andersson, S.R., Hakkarainen, M., Inkinen, S., Södergård, A. and Albertsson, A.C., *Biomacromolecules*, 2012, 13: 1212
- 13 Inkinen, S., Hakkarainen, M., Albertsson, A.C. and Södergård, A., *Biomacromolecules*, 2011, 12: 523
- 14 Sugai, N., Yamamoto, T. and Tezuka, Y., *ACS Macro Lett.*, 2012, 1: 902
- 15 Xu, H., Wu, D., Yang, X., Xie, L. and Hakkarainen, M., *Macromolecules*, 2015, 48: 2127

- 16 Rahman, N., Kawai, T., Matsuba, G., Nishida, K., Kanaya, T., Watanabe, H., Okamoto, H., Kato, M., Usuki, A., Matsuda, M., Nakajima, K. and Honma, N., *Macromolecules*, 2009, 42: 4739
- 17 Lotz, B.A., *ACS Macro Lett.*, 2015, 4: 602
- 18 Zhang, P., Tian, R., Na, B., Lv, R. and Liu, Q., *Polymer*, 2015, 60: 221
- 19 Bouapao, L. and Tsuji, H., *Macromol. Chem. Phys.*, 2009, 210: 993
- 20 He, Y., Xu, Y., Wei, J., Fan, Z. and Li, S., *Polymer*, 2008, 49: 5670
- 21 Marubayashi, H., Nobuoka, T., Iwamoto, S., Takemura, A. and Iwata, T., *ACS Macro Lett.*, 2013, 2: 355
- 22 Schmidt, S.C. and Hillmyer, M.A., *J. Polym. Sci., Part B: Polym. Phys.*, 2001, 39: 300
- 23 Anderson, K.S. and Hillmyer, M.A., *Polymer*, 2006, 47: 2030
- 24 Bao, R.Y., Yang, W., Jiang, W.R., Liu, Z.Y., Xie, B.H. and Yang, M.B., *J. Phys. Chem. B*, 2013, 117: 3667
- 25 Saeidlou, S., Huneault, M.A., Li, H. and Park, C.B., *Polymer*, 2013, 54: 5762
- 26 Wei, X.F., Bao, R.Y., Cao, Z.Q., Zhang, L.Q., Liu, Z.Y., Yang, W., Xie, B.H. and Yang, M.B., *Colloid Polym. Sci.*, 2014, 292: 163
- 27 Wei, X.F., Bao, R.Y., Cao, Z.Q., Yang, W., Xie, B.H. and Yang, M.B., *Macromolecules*, 2014, 47: 1439
- 28 Na, B., Zhu, J., Lv, R., Ju, Y., Tian, R. and Chen, B., *Macromolecules*, 2014, 47: 347
- 29 Saeidlou, S., Huneault, M.A., Li, H., Sammut, P. and Park, C.B., *Polymer*, 2012, 53: 5816
- 30 Xu, H., Feng, Z.X., Xie, L. and Hakkarainen, M., *ACS Sustainable Chem. Eng.*, 2016, 4: 334
- 31 Xu, H., Hua, G., Odelius, K. and Hakkarainen, M., *Macromol. Chem. Phys.*, 2016, 217: 2567
- 32 Pradell, T., Crespo, D., Clavaguera, N. and Clavaguera-Mora, M., *J. Phys.: Condens. Matter*, 1998, 10: 3833
- 33 Cheng, S.Z. and Wunderlich, B., *Macromolecules*, 1988, 21: 3327
- 34 Xu, H., Xie, L., Jiang, X., Li, X.J., Li, Y., Zhang, Z.J., Zhong, G.J. and Li, Z.M., *J. Phys. Chem. B*, 2014, 118: 812
- 35 Xu, H., Xie, L., Jiang, X., Hakkarainen, M., Chen, J.B., Zhong, G.J. and Li, Z.M., *Biomacromolecules*, 2014, 15: 1676
- 36 Mano, J.F., Wang, Y., Viana, J.C., Denchev, Z. and Oliveira, M.J., *Macromol. Mater. Eng.*, 2004, 289: 910
- 37 Xu, H., Zhong, G.J., Fu, Q., Lei, J., Jiang, W., Hsiao, B.S. and Li, Z.M., *ACS Appl. Mater. Interfaces*, 2012, 4: 6774
- 38 Xu, H., Xie, L. and Hakkarainen, M., *ACS Sustainable Chem. Eng.*, 2015, 3: 1443
- 39 Xu, H., Yang, X., Xie, L. and Hakkarainen, M., *Biomacromolecules*, 2016, 17: 985
- 40 Xu, H., Xie, L., Wu, D. and Hakkarainen, M., *ACS Sustainable Chem. Eng.*, 2016, 4: 2211
- 41 Zhang, J., Sato, H., Tsuji, H., Noda, I. and Ozaki, Y., *Macromolecules*, 2005, 38: 1822
- 42 Pan, P., Yang, J., Shan, G., Bao, Y., Weng, Z., Cao, A., Yazawa, K. and Inoue, Y., *Macromolecules*, 2012, 45: 189
- 43 Fischer, E., Sterzel, H.J. and Wegner, G., *Colloid Polym. Sci.*, 1973, 251: 980