Electronic Supplementary Material (ESI) for RSC Advances.


# Stereocomplexation kinetics of enantiomeric poly(L-lactide)/ poly(D-lactide) blends seeded by nanocrystalline cellulose

Long Jiang, Pei Lv, Piming Ma*, Huiyu Bai , Weifu Dong, Minqing Chen*

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu, China

* Corresponding author:
E-mail address: p.ma@jiangnan.edu.cn, mq-chen@jiangnan.edu.cn
Fax: +86-510-85917763;
Tel: +86 510-85917090;

**Experimental section**

**Materials:** Neat PLLA (PDLA, $M_n$ = 86 kDa, PDI = 1.8) and neat PDLA (PLLA, $M_n$ = 51 kDa, PDI = 1.4) in the form of granules were provided by Purac, the Netherlands. The optical purity of the PLLA and the PDLA is around 99%. The nanocrystalline cellulose (NCC) was made from acid hydrolysis of microcrystalline cellulose as reported in literature.[1, 2] Chloroform (purity = 99.5%) is purchased from Sinopharm Group Chemical Reagent Co., Ltd. China. All materials were used as received.

**Sample Preparation:** Briefly, the PDLA and PLLA were first dissolved in chloroform at 40 °C with continuous stirring and then the NCC was added forming a homogeneous mixture. Finally the mixture was casted, evaporated and dried completely under vacuum condition at 45℃ to obtain PLLA/PDLA/NCC blends. A PLLA/PDLA blend was prepared via the same procedure as reference. The weight ratio of PLLA to PDLA was fixed at 1:1 while the NCC content of 1 wt% and 25 wt% was chosen to check the effect of both low and high NCC loadings on the stereocomplexation of PLA.

**Differential Scanning Calorimetry (DSC):** The crystallization behavior of the PLLA/PDLA/NCC samples was studied by using DSC (DSC 8000, Perkin Elmer). The samples were heated to 250 ℃ at 20℃/min and kept for 2 min to erase the thermal history and then cooled to room temperature (RT) at 10℃/min. The cooling DSC curves were recorded to study nonisothermal crystallization. For isothermal crystallization, fresh samples were quenched (50℃/min) to desired temperatures directly after melting at 250 ℃ for 2 min and kept at the desired temperatures until the crystallization was complete. The subsequent melting behavior was also monitored by heating the isothermally crystallized samples to 250 ℃ again at 10℃/min.

**Wide angle X-ray diffraction (WAXD):** Wide angle X-ray diffraction of the PLLA/PDLA/NCC samples were carried out by using an X-ray diffractometer (Bruker AXS D8, Germany) with a Ni-filtered Cu Kα radiation source with a

wavelength of 1.542 Å. The measurements were operated at 40 kV and 40 mA with scan angles from 5° to 35°at a scan rate of 3°/min. The samples were treated by Linkam hot-stage unit (cool from melt 250 °C to RT at 10℃/min) before the WAXD measurement.

**Polarized optical microscopy (POM):** POM Axio Scope 1 (Carl Zeiss MicroImaging GmbH, Germany) equipped with a hot-stage unit (Linkam THMS600, UK) was used to investigate the morphology and growth of stereocomplex PLA. The samples were first melted at 250℃ for 2 min and then cooled down rapidly (50℃/min) to the required isothermal crystallization temperature. The radii of SC spherulites were recorded as a function of time to measure the crystal growth rate, i.e., $G = dr/dt$, where $r$ is the radius and $t$ is the time.

## Results and discussion

Although 160 °C is lower than the $T_m$ of PLLA and PDLA but it is already too high for PLLA or PDLA to crystallize upon cooling from the melt, notably at a high cooling speed of 10 °C/min. Taking the PDLA as an example, the DSC heating and subsequent cooling curves are shown in Figure S1.

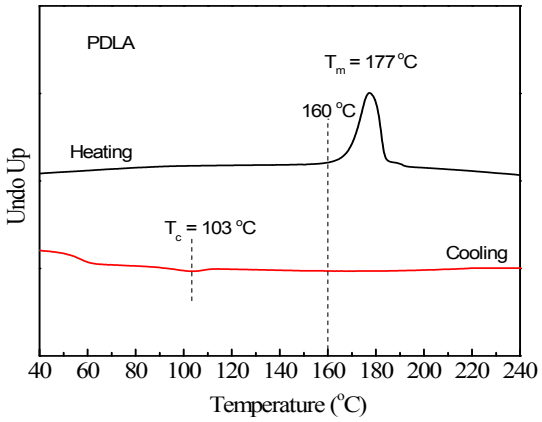


Figure S1: DSC heating and subsequent cooling curves of neat PDLA showing the $T_m$ and $T_c$ at 177 and 103 °C, respectively.

The POM results of neat PDLA, cooling from the melt to room temperature, are shown in Figure S2. Apparently, no crystals were detected at 160 °C upon cooling at 10 °C/min. Only few spherulites appeared when the temperature was reduced to ~110 °C.

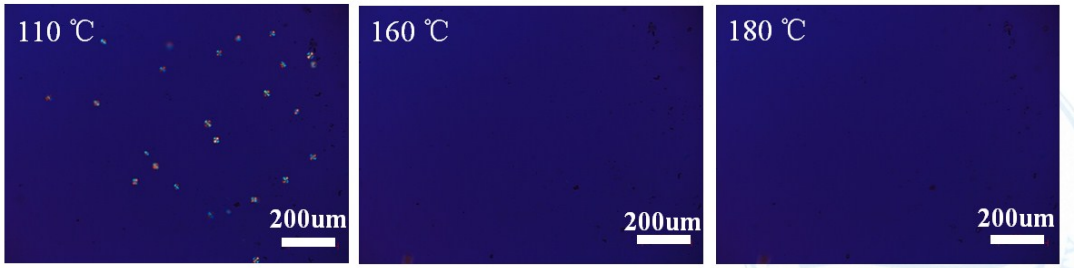


Figure S2: POM images of PDLA taken at different temperatures during cooling at 10 °C/min.

Moreover, it can be concluded from the XRD patterns (NCC 0 wt% and 1 wt%) that no obvious HC was detected after cooling from the melt (Figure 1B in the manuscript). Based on the above results and discussion, it can be concluded that the crystals formed at 160 °C should be only stereocomplex PLA.

The half-crystallization time ($t_{0.5}$) of the PDLA/PLLA/NCC blends were shown in Fig. S3 as a function of temperature and NCC content. Obviously, the $t_{0.5}$ of the PDLA/PLLA blends is remarkably decreased after the incorporation of NCC. It can be seen that PDLA/PLLA, in the presence of NCC, the $t_{0.5}$ finished within several minutes. In contrast, the $t_{0.5}$ of neat PDLA/PLLA blends took around 90 minutes at the same temperature (e.g., 190 ℃).

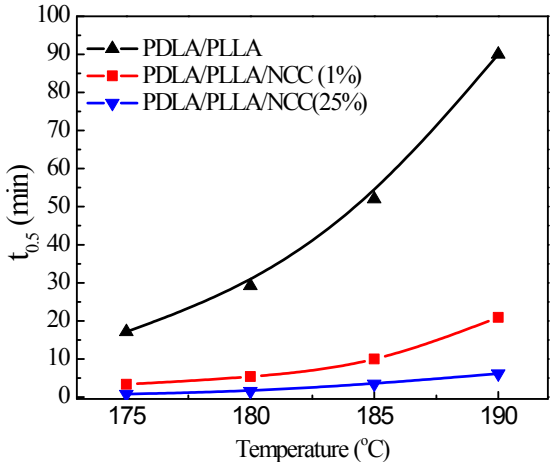


Fig. S3 The half-crystallization time ($t_{0.5}$) of PDLA/PLLA/NCC blends

The spherulitic morphology of PDLA/PLLA, PDLA/PLLA/NCC (1%) and PDLA/PLLA/NCC (25%) samples at 190 ℃ are shown in Fig. S4. It can be found from Fig. S4 that, at the same temperature, the nucleation density of the samples increases with increasing the NCC content. On the other hand, the POM images demonstrate that the growth of spherulites became very slow and even nearly stopped in the late stage of the isothermal crystallization.

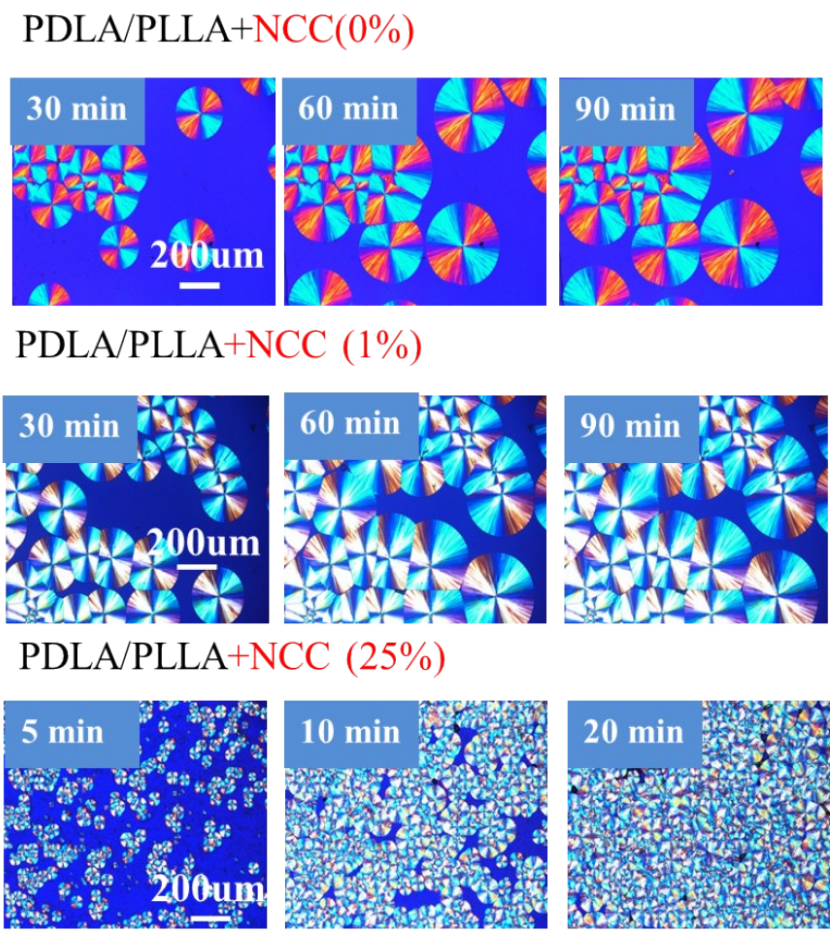


Fig. S4 POM images of the PDLA/PLLA/NCC (0, 1, 25 wt%) samples as a function of isothermal crystallization time. The experiment was performed at 190℃.

**References**

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