Supplementary Information in Electronic Form

Title: "Distorted Ring-Banded Spherulites in Poly(L-lactic acid)/Poly(ε-caprolactone) Blends"

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Miscibility Characterizations and Crystallization Behaviors of PLLA/PCL blends

The miscibility of the PLLA/PCL blends was investigating using DSC and OM. Samples subjected to DSC measurements were first melted at 190 ^{o}C for 3 min and then quenched to -60 ^{o}C. Curves of following scan with the heating rate as 20 ^{o}C/min are presented in **Fig. S1**. **Fig. S1** shows DSC thermograms of neat PLLA, PCL and PLLA/PCL blends. In the figure, it presents thermal properties and crystallization behaviors as glass transition temperature (T_g), melting temperature (T_m) and cold crystallization temperature ($T_{c,c}$) for neat polymers and the blends of them. According to DSC thermograms in **Fig. S1**, the DSC curve of neat PLLA exhibits a T_g at around 49 ^{o}C, a $T_{c,c}$ at around 82 ^{o}C and a T_m at around 153 ^{o}C. In addition, the neat PCL exhibits a T_m at around 55 ^{o}C. In general, the single-T_g criterion can be adopted to characterize the miscibility of polymer blends. That is, the composition-dependent single T_g can indicate the miscible state for the blends. In **Fig. S1**, it is hardly to find a single T_g for each composition of PLLA/PCL blends. Furthermore, at the temperature around 50 ^{o}C, it shows that the glass transition which might result from the PLLA is significantly overlapped with the melting transition which could arise from the PCL. That is, the glass transition of PLLA could simultaneously occur with the melting transition of PCL by thermal scan of DSC for the blends. Normally in a fully miscible blends with intimate mixing among polymer chains, it should only contain one thermal transition rather than an overlap of several thermal transitions in a specific region of temperature. The phenomenon mentioned above (an overlap of the glass transition of PLLA and the melting transition of PCL) might suggest that the glass transition of PLLA and the melting transition of PCL start from different separated phases as the PLLA-rich phase and the PCL-rich phase, and they can be appeared at the similar region of temperature by DSC thermal scan. Similar thermal behavior as the overlap of multiple thermal transitions around the temperature region close to the T_g of PLLA and the T_m of PCL has been also demonstrated in the literatures.[13,22] Immiscibility of the PLLA/PCL blends has been suggested by those literatures.[13,22] In addition, it also shows that the temperature region of the overlap of multiple thermal transitions does not change with varying blending compositions of the PLLA/PCL blends. Consequently, as shown in **Fig. S1**, the lack of composition-dependent single T_g couple with the overlap of multiple thermal transitions which might start from

different segregated phases as the PLLA-rich phase and the PLC-rich phase in the blends could propose the immiscibility and phase separation behavior in the PLLA/PCL blends. The less composition-dependent T_m of either the PCL-rich phase or the PLLA-rich phase as displayed in **Fig. S1** could also support the immiscibility in the blends. In addition, a decrease of $T_{c,c}$ between the neat PLLA and the PLLA/PCL=90/10 blend is revealed in **Fig. S1**. This result could imply that the presence of PCL might enhance the nucleation of cold crystallization for PLLA in the blends. However, for only the blends with different compositions, no significant shift of the $T_{c,c}$ among different compositions is revealed by **Fig. S1**. The literature has also reported similar phenomenon as the enhancement of the nucleation behavior of PLLA caused by the presence of PCL in the PLLA/PCL blends.[22]

Optical microscopy (OM) was also performed for evaluating the miscibility between PLLA and PCL. **Fig. S2** shows the OM results of PLLA/PCL blends with various compositions recorded at different temperatures. As OM results shown in **Fig. S2**, phase separation domains are exhibited in all images, inferring that the PLLA/PCL blends are with heterogeneous phase behavior. Similar result showing heterogeneous phase behavior for the PLLA/PCL blends has been also demonstrated in the literature.[27] The results of OM can also support the immiscibility of PLLA/PCL blends found by 1DSC characterization. Furthermore, non-isothermal crystallization was also investigated for the blends of PLLA/PCL by DSC. For non-isothermal crystallization, specimens were first melted at 190 ^oC to remove thermal history and then cooled at 10 ^oC/min to enable non-isothermal crystallization. **Fig. S3** reveals DSC results of non-isothermal crystallization of neat PLLA, PCL and PLLA/PCL blends. As DSC thermograms shown in **Fig. S3**, besides those results of neat polymers, the DSC curve of each blending composition displays two isolated peaks. That is, under non-isothermal crystallization, each blending composition presents two non-isothermal crystallization peaks isolated with each other. The peak at higher temperature and that at lower temperature could be caused by the non-isothermal crystallization of PLLA-rich phase and that of PCL-rich phase, respectively, in the blends. Two non-isothermal crystallization peaks resulting from different phases of components might infer that the molten state of PLLA/PCL blends is heterogeneous. Under cooling treatment for the blends of PLLA and PCL, polymer chains of different components could start their non-isothermal crystallization from different segregated phases such as the PLLA-rich phase and the PCL-rich phase in heterogeneous molten state. Therefore, two isolated peaks of non-isothermal crystallization are revealed in DSC curves of the PLLA/PCL blends. The results obtained from non-isothermal crystallization measurements could also fit with the characterizations of DSC and OM as shown in **Figs. S1** and **S2**, which proposing the immiscibility for the blends of

PLLA and PCL.

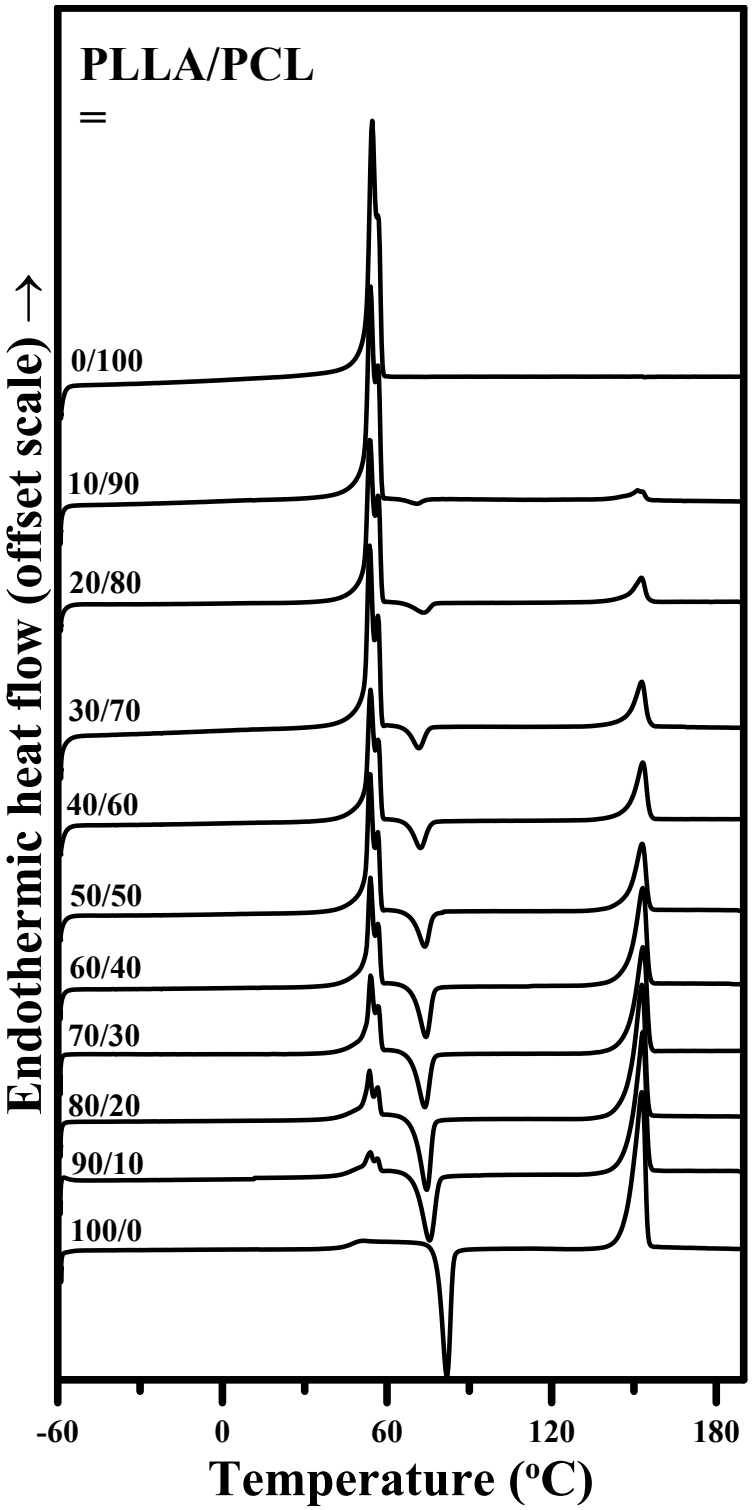

Fig. S1 DSC thermograms for the PLLA/PCL blends of different compositions (wt. ratio).

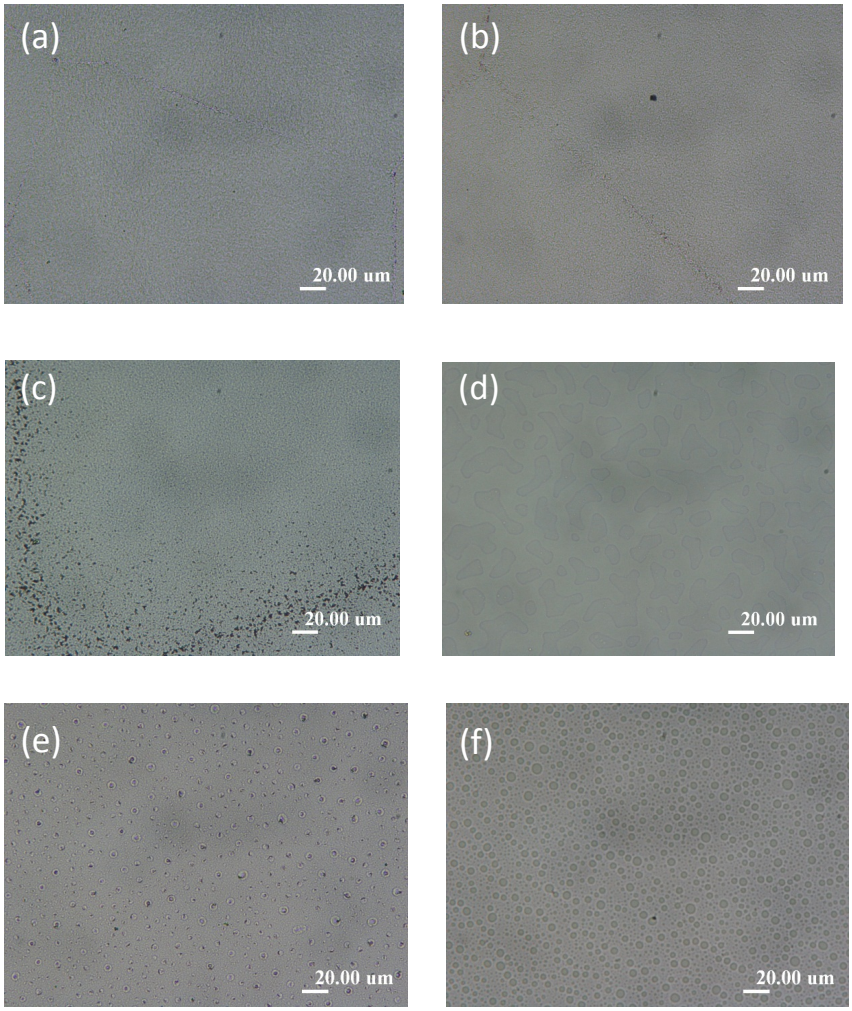

Fig. S2 OM images of PLLA/PCL blends with various compositions recorded at different temperatures: (a) 80/20 at r.t., (b) 80/20 at 190 ^{o}C, (c) 50/50 at r.t., (d) 50/50 at 190 ^{o}C, (e) 20/80 at r.t., and (f) 20/80 at 190 ^{o}C.

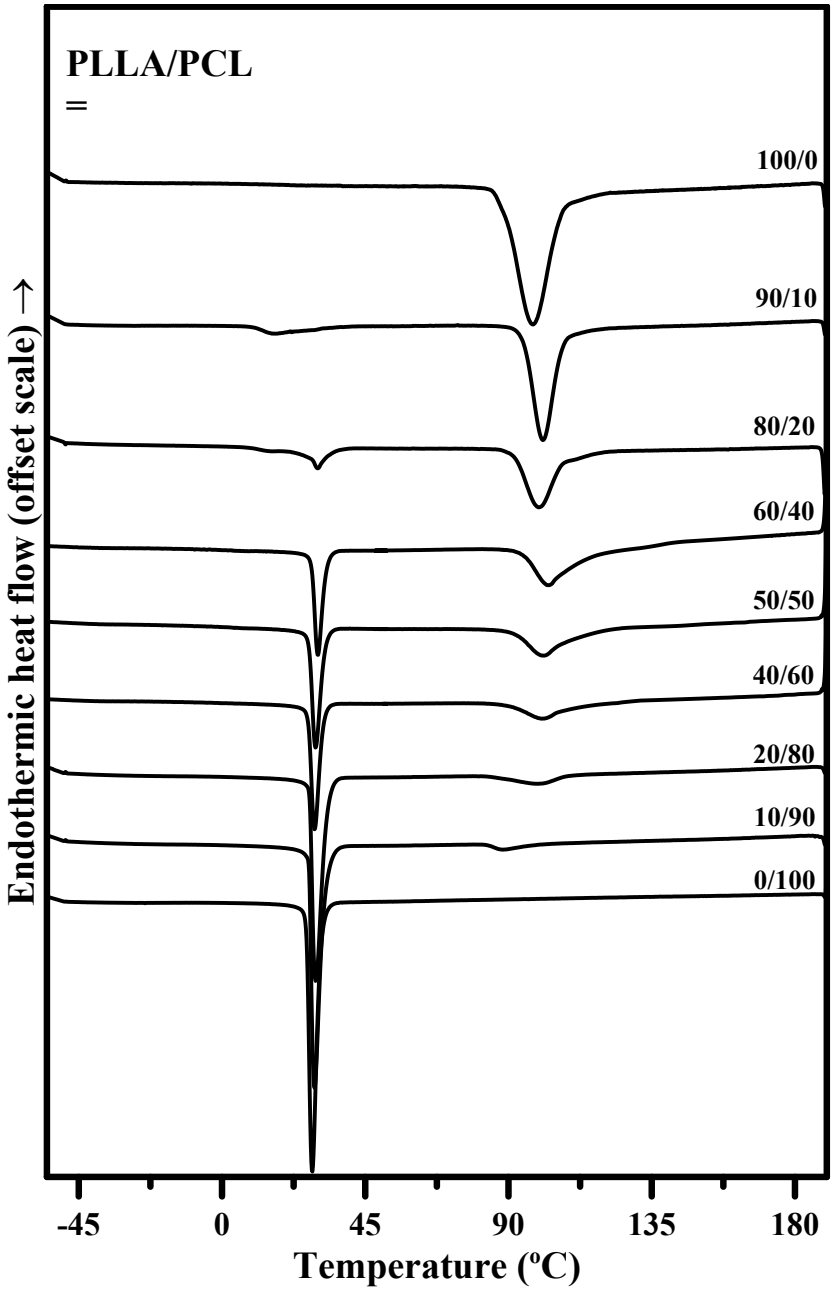

Fig. S3 DSC non-isothermal crystallization results for the PLLA/PCL blends with different compositions.