Asymmetric Growth of Co-Crystallized Nano- and Micrometer-Sized Lamellae to Janus-Faced Spherulites in Poly(L-lactic acid) with Amorphous Poly(methyl methacrylate)

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Supporting Information

Experimental Section

Molecular weight (M_w), polydispersity index (PDI), glass transition temperature (T_g), as well as melting peak temperature (T_m) of each material used in this study are listed in **Table 1**. Different compositions of PLLA/PMMA blend solutions were prepared by solvent blending at 50 °C using chloroform as the solvent. The solutions were then cast on glass substrates (on 50 °C preset hotplate) to make thin-film or bulkier thick samples. Different thicknesses of film samples (vary from 5 to 30 μm) were obtained by controlling the concentration of solution casting on the substrate. Degassing process was performed at 40 °C in a vacuum oven for more than 4 hours to get rid all the solvent properly. Samples were melt-crystallized at crystallization temperature (T_c) ranging from 90 to 120 °C. A more comprehensive study was performed on PLLA/PMMA (80/20) samples crystallized at 115 °C. Blending 20 wt% amorphous PMMA into PLLA and crystallization at specific T_c's induce unique "Janus-face" spherulitic morphologies with half-and-half birefringence patterns on spherulites, whose interior crystal assembly was the main subject of this study.

After designated crystallization at specific T_c's, the film/bulk PLLA/PMMA samples were randomly fractured so that the interior lamellae could be observed from all possible perspective angles of collective viewpoint to construct 3D profiles of spherulites. The fractured samples were then exposed to acetone vapor on a 50 °C preset hotplate for 20 minutes then washed by immersing the samples in acetone liquid for 2 seconds to disclose the detail lamellar crystal structure in the spherulites. Degassing was performed after etching in a 40 °C vacuum oven for a couple of hours.

A light-polarized optical microscope (POM) (Nikon Optiphot-2) with first order tint plate, equipped with a Nikon Digital camera system for microscopy Digital Sight (DS-U1) and a microscope hot stage (Linkam THMS-600 with T95 temperature programmer) was used to observe the spherulitic development and morphology of PLLA/PMMA blend samples during crystallization, prior, and after etching treatment. A Shimadzu XRD-6000 X-ray diffractometer with copper Kα radiation (at 30 kV and 40 mA) and chromatized wavelength of 1.542 Å (0.154 nm) was used to characterize the crystal structure of PLLA at different conditions (scanning rate = 2° min^{-1}). An atomic-force microscopy (AFM) (diCaliber, Bruker-Veeco Co., Santa Barbara, CA) was used in intermittent tapping mode with a silicon tip (f = 300 kHz, r = 10) installed to scan the

surface topography of spherulites. A scanning electron microscopy (SEM) (FEI Quanta-400F) was used to characterize the detail lamellar arrangement of fractured surfaces of samples in correlation to their top free surfaces before and after the etching process. The samples were coated with gold vapor deposition using vacuum sputtering before the SEM characterization.

Table 1. Materials and Properties

Materials	**M_w (g mol^{-1})**	**PDI**	**T_g (°C)**	**T_m (°C)**
PLLA 5.6*k*[a]	5 600	1.19	13.2	140
PLLA 11*k*[a]	11 000	1.1	45.3	155
PLLA 51.6*k*[b]	51 600	1.43	54.2	171
PMMA 13*k*[b]	13 000	1.4	79	
PMMA 100*k*[c]	100 000	1.58	97	
PMMA 240*k*[b]	240 000	1.49	99	

[a)] Polysciences, Inc.; [b)] Sigma Aldrich Inc.; [c)] Chimei, Inc.

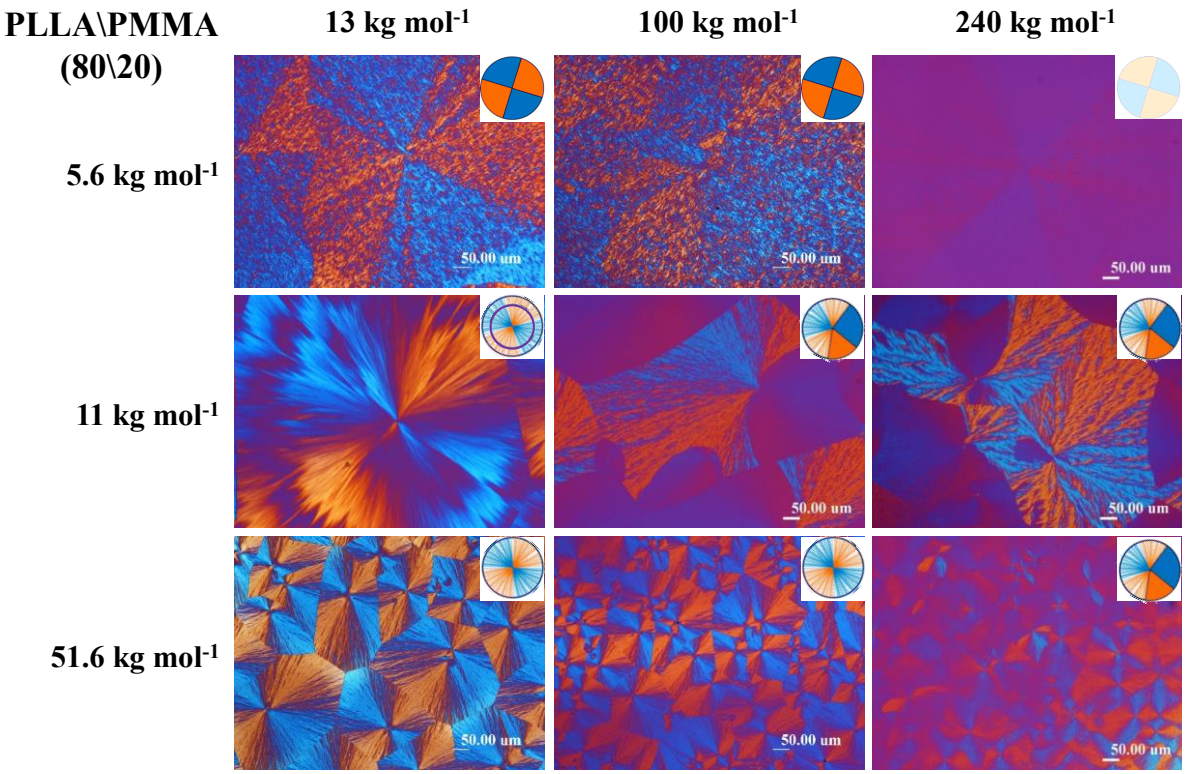

Figure S1. POM images of PLLA/PMMA (80/20) blends of different molecular weights melt-crystallized at 115 °C.

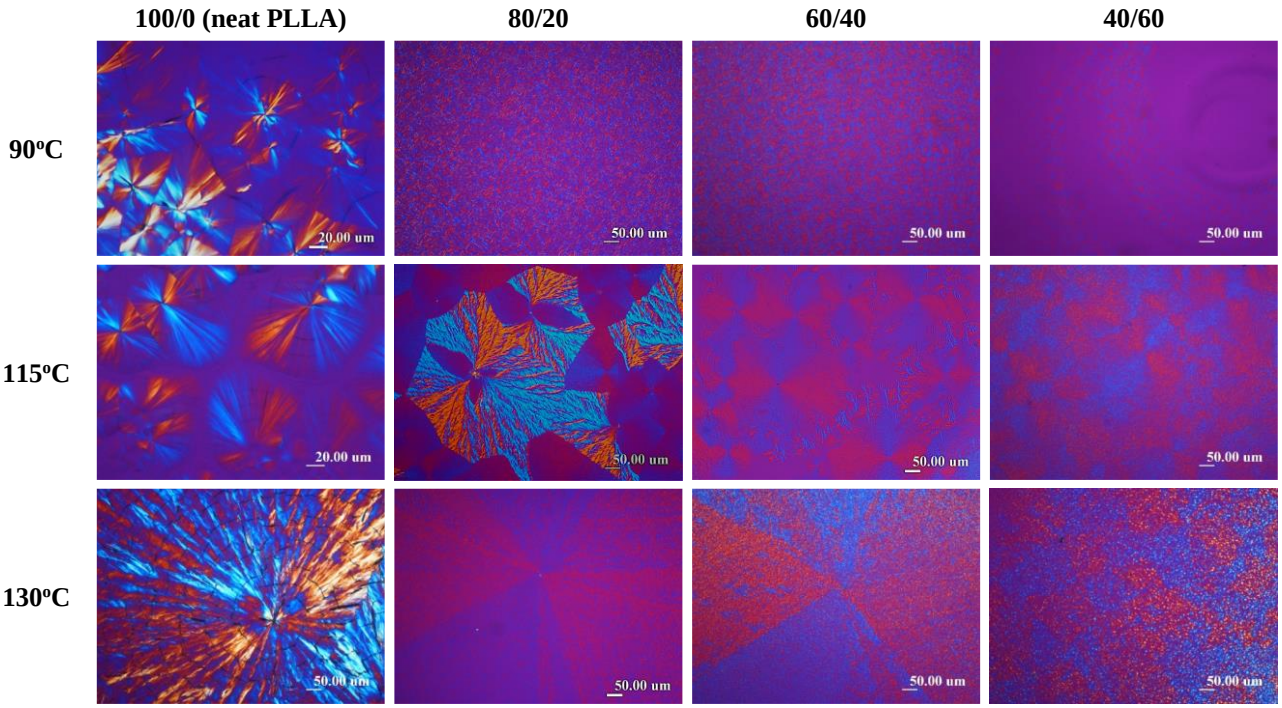

Figure S2. POM images of various compositions of 11k_PLLA/240k_PMMA blends melt-crystallized at different T_c's as indicated on graphs.

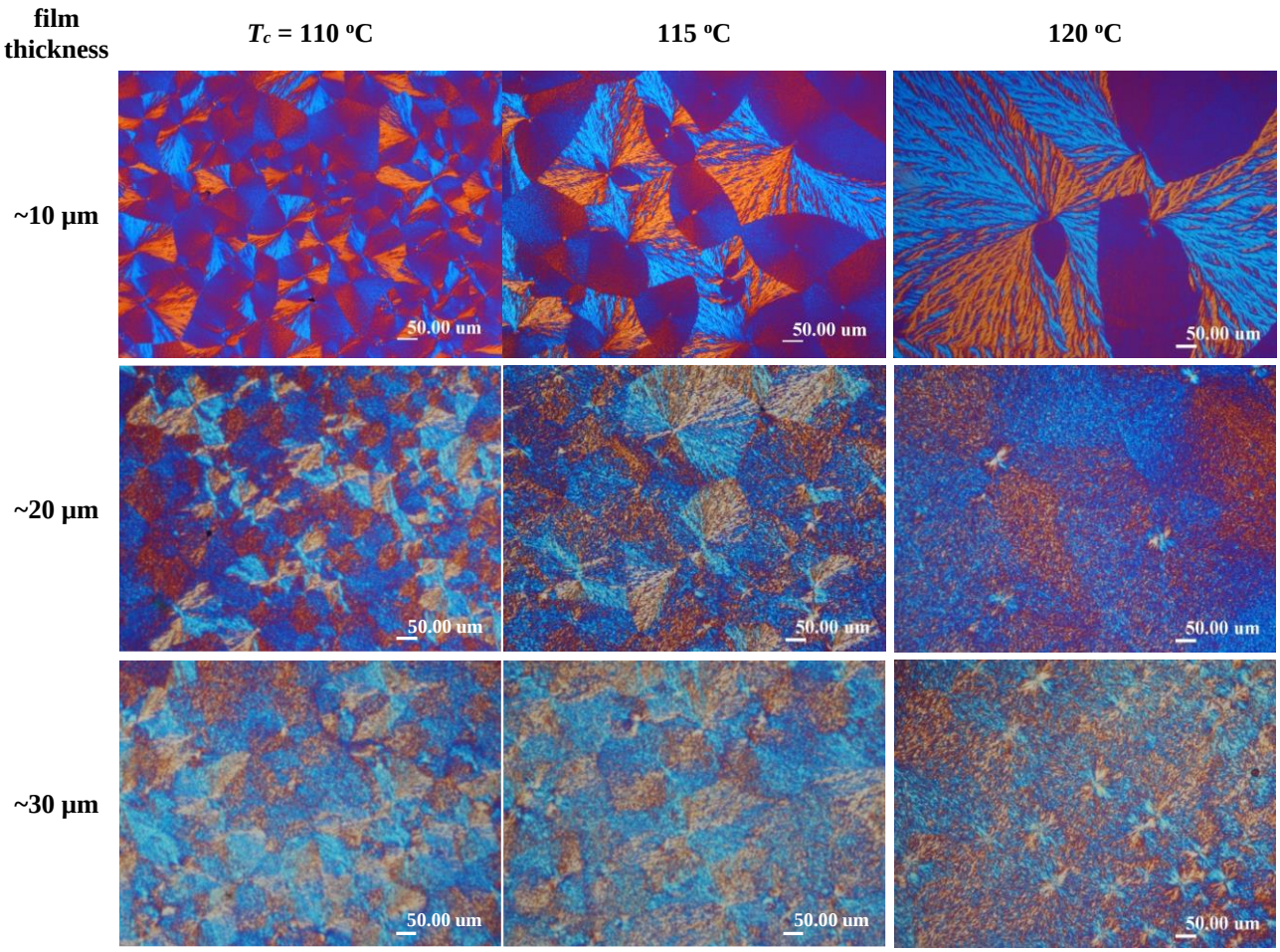

Figure S3. POM images of PLLA/PMMA (80/20) samples of different thicknesses melt-crystallized at various T_c's as labeled on the graph.

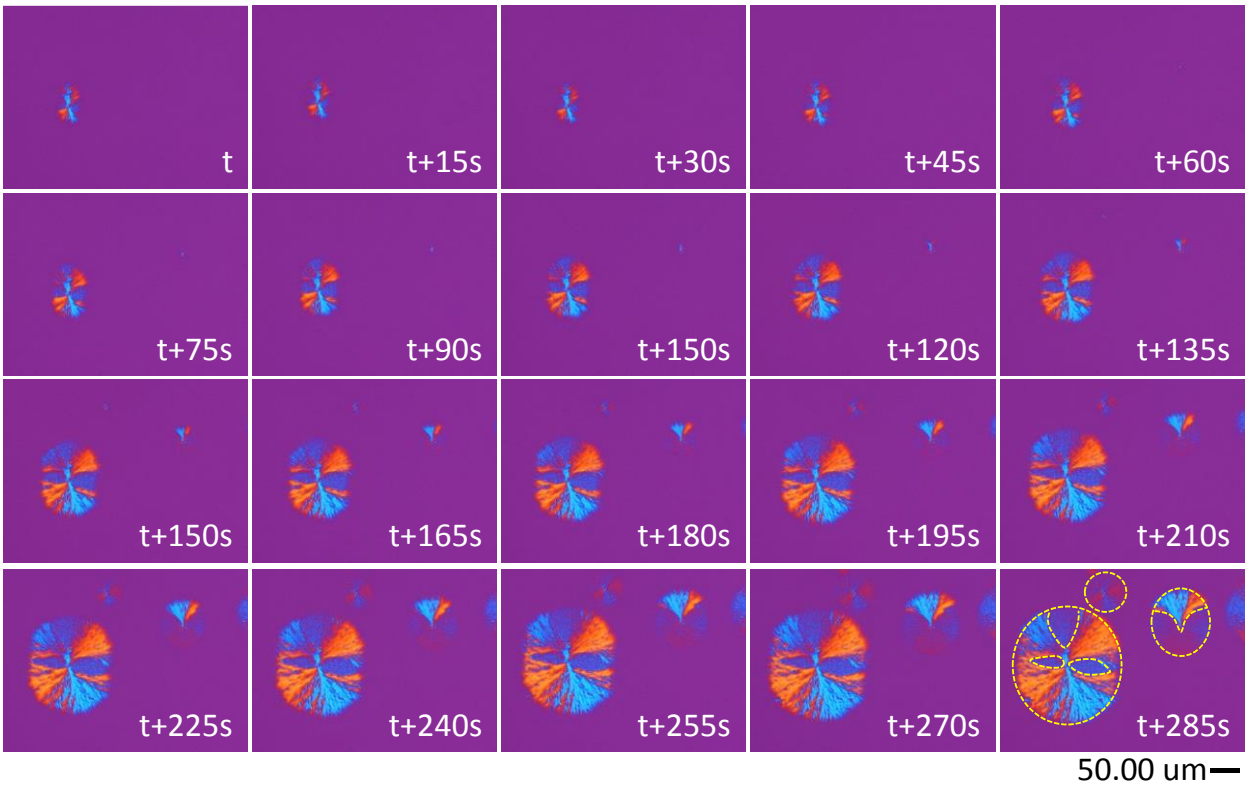

Figure S4. POM in situ crystallization observation of PLLA/PMMA (80/20) blends at 115 ºC.

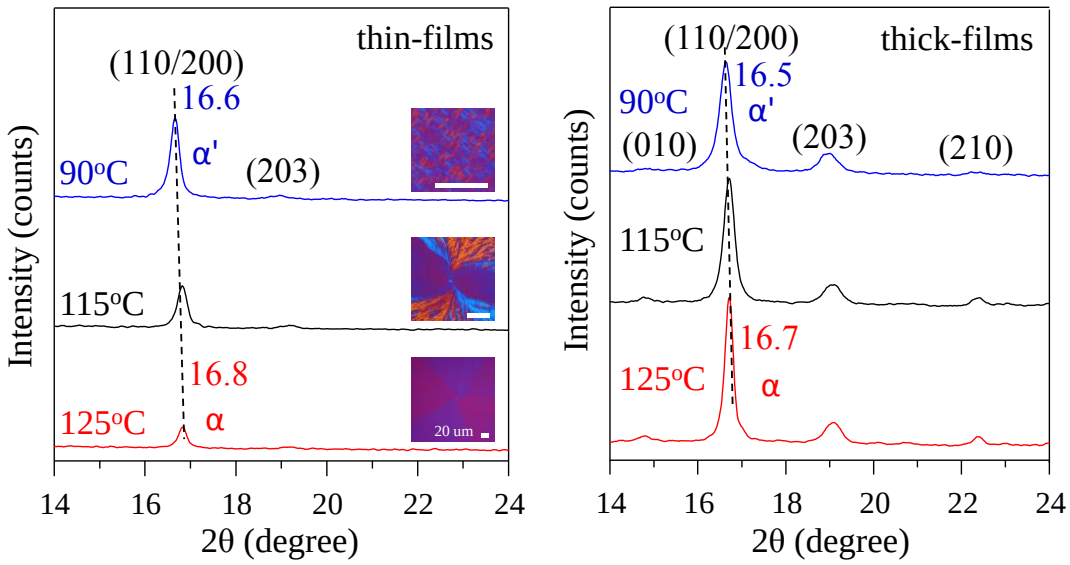

Figure S5. WAXD profiles of thin-films vs. thick-films of PLLA/PMMA (80/20) blend crystallized at different T_c as listed on each graph, showing the shifted diffraction (110/200) peak from α' to α-form as the T_c increases.

The α-form PLLA has two chains with 10_3 helical conformations packed into an orthorhombic unit cell with a = 10.7 Å, b = 6.45 Å, c = 27.8 Å.[1] The α'-form PLLA has a distorted 10_3 helical conformation packed into a slightly larger pseudo-hexagonal crystal lattice.[1-2]

References:

[1] Kawai, T.; Rahman, N.; Matsuba, G.; Nishida, K.; Kanaya, T.; Nakano, M.; Okamoto, H.; Kawada, J.; Usuki, A.; Honma, N.; Nakajima, K.; Matsuda, M. *Macromolecules* **2007**, *40*, 9463-9469.

[2] Kalish, J. P.; Aou, K.; Yang, X.; Hsu, S. L. *Polymer* **2011**, *52*, 814-821.

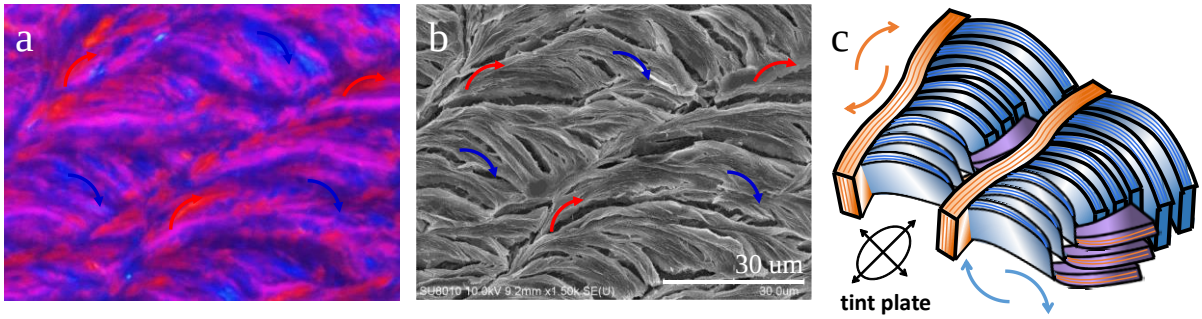

Figure S6. POM graph (a) and SEM counterpart (b) as well as a scheme (c) demonstrating the correlation between lamellae orientations and interference colors in the dendritic face after acetone etching.