Supporting Information [Scheme 1, experimental section, S1, S2, S3]

A Novel Hexagonal Crystal with a Hexagonal Star-Shaped Central Core in Poly(L-lactide) (PLLA) Induced by an Ionic Liquid

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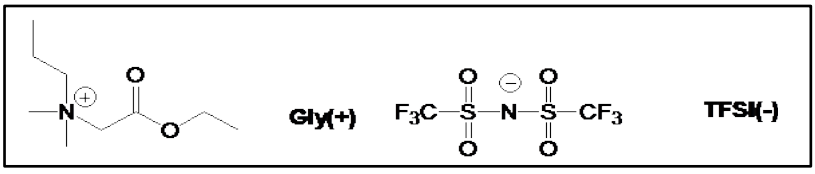

Scheme 1. Chemical structure of [Gly][TFSI] ionic liquid

Experimental section

Materials and preparation

Poly(L-lactide) (PLLA) with a weight-average molecular weight of 11,000 g.mol^{-1} and PDI of 1.10 was purchased from Polysciences, Inc. (USA). The PLLA was used as received. For this grade of PLLA, T_g = 45.3 ^oC and T_m = 155 ^oC. N-alkyl-substituted glycine ester $[Gly]^+$ and bis(trifluoromethanesulfonyl)imide $[TFSI]^-$ ionic liquid was prepared in Prof. Sun, I-Wen lab. (Chemistry Department, NCKU).

PLLA and ionic liquid were dissolved in chloroform at concentration of 2 wt.-% to form solution to be cast into blend sample of PLLA/IL (95/5). A drop of solution of the polymer blend was deposited and uniformly spread onto a micro glass slide at 45 ^oC. The PLLA/IL solution as cast films was then dried in an atmosphere to fully evaporate the solvent. Neat PLLA film samples (without IL) were also prepared for the comparation observation. Prior to the characterization, the dried film samples were heated to T_{max} = 190 ^oC for 2 min to erase the thermal history then rapidly transferred to the T_c = 110 ^oC for crystallization.

Apparatus and procedures

A polarized optical microscopy (POM, Nikon Optiphot-2), equipped with a digital camera charge-coupled device (CCD) and a microscopic hot stage (Linkam THMS-600) with TP-92 temperature programmer was carried out to observe the crystalline morphology and crystal growth of the polymer.

The detailed lamellar arrangement was investigated by atomic-force microscopy (AFM, diCaliber, Veeco Corp., Santa Barbara, USA), which were made in the intermittent tapping mode with an installed

silicon-tip (f_o = 70 kHz, r = 10 nm). The largest scan range was 150 μm × 150 μm and the scan was kept at 0.5 Hz for the overview scan and zoom-regions (5 μm × 5 μm). Thin films were deposited on substrates of glass slides, with an open face for AFM characterization. Samples before and after water etching were characterized to measure the roughness of the crystal surface. AFM measurements were also carried out to determine the height difference between the center and surrounding part.

Supporting figures (S1-S3)

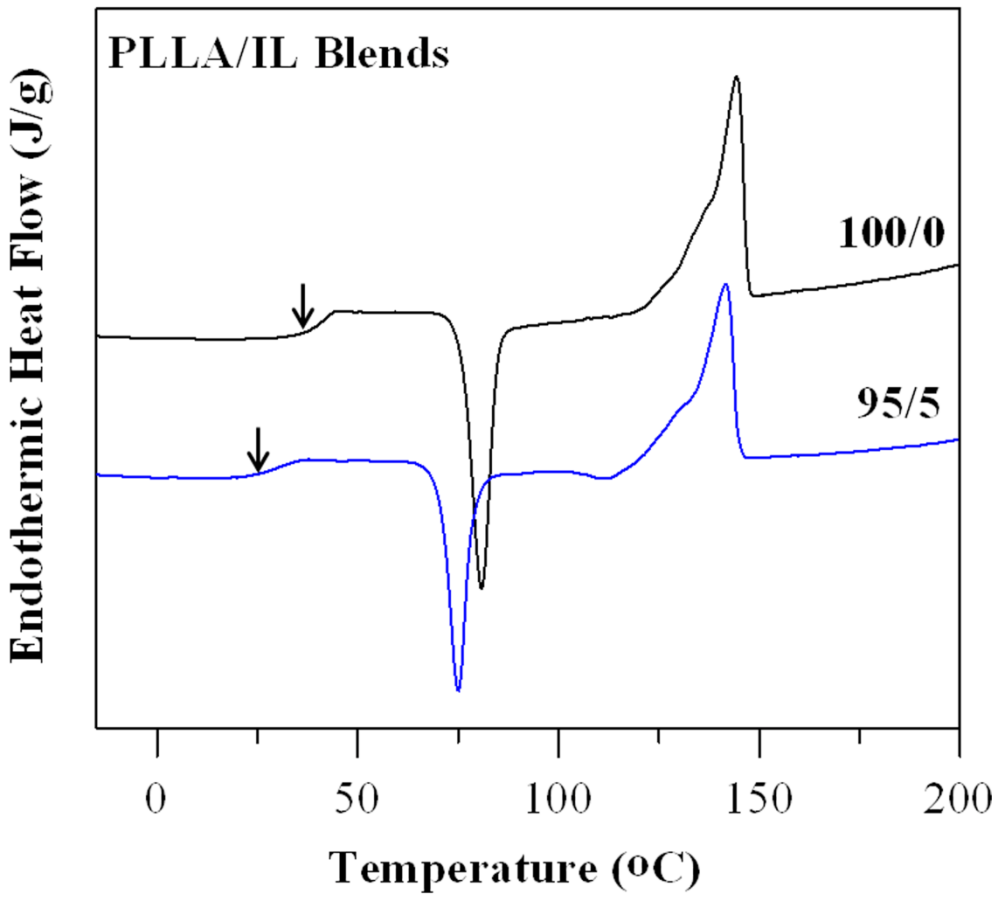

Figure S1. DSC thermograph of neat PLLA and PLLA/IL (95/5), showing the decrease of T_g.

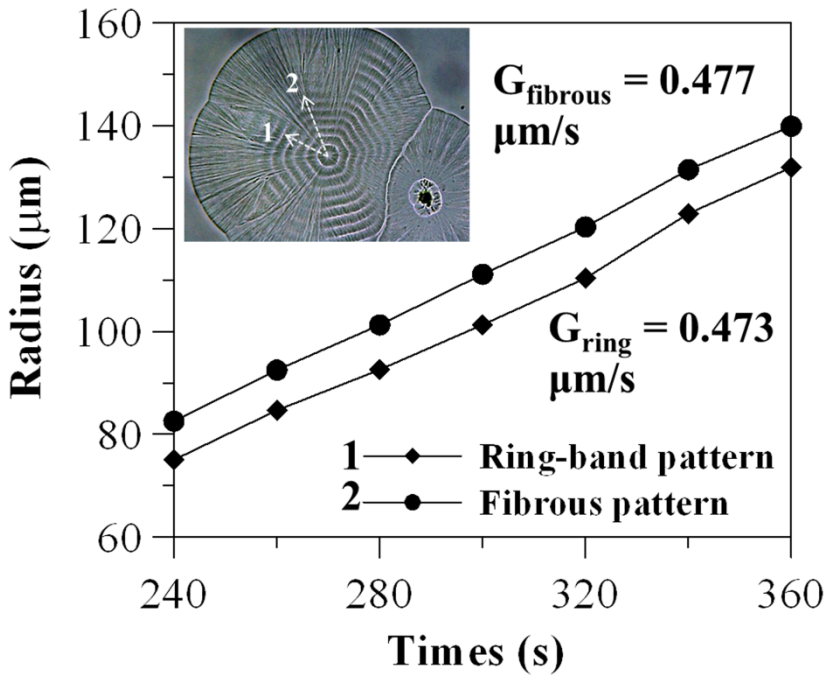

Figure S2. Graph of crystal radius vs. crystallization time of neat LM_w-PLLA, melt-crystallized at T_c = 110 °C.

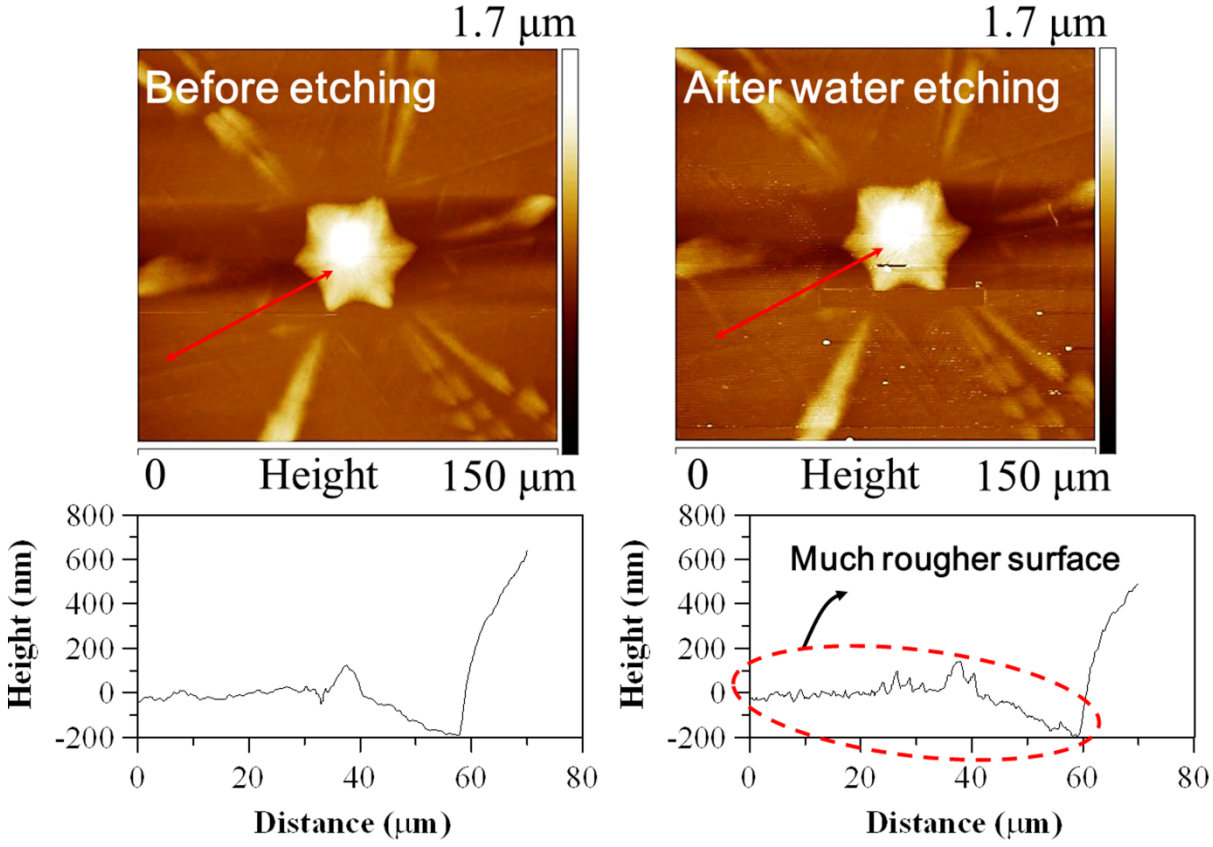

Figure S3. AFM height images and height profiles of novel crystal before and after water etching process.