

Electronic Supplementary Information

Banded spherulites templated three-dimensional interpenetrated nanoporous materials

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■ EXPERIMENTAL SECTION

1. Materials and Sample Preparation.

The POM (MC 90) samples used in this work were kindly provided by Shenhua Co., Ltd., China. Melt flow index is 9.23 g/10 min. $M_w = 174300$ g/mol and $M_w/M_n = 2.19$. The PLLA sample (included 1.6% of D-lactide content) used was purchased from Nature Works Co. LLC (USA), under the trade name of 3001 D. The M_n and M_w/M_n are reported to be 89300 ± 1000 g/mol and 1.77 ± 0.02 , respectively.¹ Prior to use, PLLA and POM were dried in a vacuum oven at 80 °C for 12 h. The blends with PLLA/POM weight composition varying from 90/10 to 10/90 were prepared using a batch mixer (Haake PolyLab QC) with a twin screw at a rotation speed of 20 rpm at 190 °C for 1 min and then with rotation speed raised to 50 rpm for 5 min.

After blending, all the samples were firstly hot-pressed at 190 °C under a 14 MPa pressure for 3 min to a film with a thickness of 300 μm, and then quickly cooled to 141 °C for the isothermal crystallization of POM, eventually quenched (cool-pressing) rapidly to room temperature. The obtained films were used for the following characterization. The sample films with thickness about 10 μm for SALS and FTIR testing were prepared using the same process.

Extractions were performed in a Soxhlet extraction apparatus. The PLLA components were extracted with chloroform and, therefore, can as well be referred to as the porogen phase. The temperature of the chloroform in the Soxhlet extraction apparatus was about 60 °C. Following the extractions, all the specimens were dried in a vacuum oven at 40 °C. Note that, extractions were repeated until the dried extracted specimens achieved constant weight.

2. Structural Characterization.

The time-resolved small-angle light scattering (SALS) apparatus was the same as that Zheng et al reported in previous paper.² The blend samples were heated from room temperature to 260 °C at a heating rate of 2 °C/min. Phase contrast photographs were obtained by using an Olympus BX51 microscope equipped with a Linkam LTS350 hot stage. The samples were heated from room temperature to 260 °C at a heating rate of 2 °C/min. Infrared spectra of blends were recorded on a Nicolet 6700 time-resolved Fourier transform infrared spectrophotometer (FTIR). The sample was sandwiched between a pair of KBr plates. In all cases spectra were recorded by coadding 32 scans at a 2 cm⁻¹ resolution. Wide-angle X-ray diffraction (WXR) spectra of the films with thickness around 300 μm were collected with a Bruker D8 advance powder diffractometer, using a nickel filtered Cu Kα radiation ($\lambda = 0.1542$ nm).

Morphology of the blends was observed by field-emission scanning electron microscope (FESEM). A Hitachi S-4800 SEM system was used for SEM measurements at an accelerating voltage of 1 kV. All the samples were fractured after immersion in liquid nitrogen for about 15 min. Besides, thin films with the thickness of about 100 nm were prepared by spin-coating 1 wt% hexafluoroisopropanol solution onto a freshly cleaved silicon surface, and were then directly observed under a Nanoscope III MultiMode AFM (Digital Instruments). Both height and phase images were recorded simultaneously with tapping-mode. Typical values for the RMS amplitude and the set-point amplitude ratio (r_{sp} is defined as the ratio of the cantilever's oscillating amplitude to its freely oscillating amplitude) were 2.0 and 0.7 - 0.9V. The amplitude of the freely oscillating cantilever was approximately 40 nm. TESP tips with a resonance frequency of approximately 300 kHz and a spring constant of about 30 N/m were used.

Differential scanning calorimeter (DSC) was carried out under nitrogen flow at a heating rate of 10 °C/min from 10 to 200 °C and then cooled down to 10 °C at the cooling rate of 10 °C/min. It measured with a differential scanning calorimeter (DSC) system (TA Instruments DSC Q2000). The heating and cooling DSC traces were recorded. Before sample scan, the heat flow and temperature of the instrument were calibrated with sapphires and pure indium, respectively.

To further researching, a flowsorb BET instrument was employed to measure the surface area of the extracted samples. And the porosity of the same specimens was as well estimated by mercury intrusion porosimetry, using a Micromeritics Poresizer 9320. The experimental data

treatment is based on the Washburn equation ³

$$P_r = -2\sigma_m \cos \theta$$

Where P is the applied pressure, r is the radius of the pore, σ_m is the surface tension of the mercury, and θ is the contact angle between the polymer and mercury (480 mN/m and 140° were used for all measurements, respectively). This method can provide the number-average diameter (by the volume/surface ratio), the volume-average diameter, and the pore size distribution.

REFERANCES

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- [3] Washburn, E. W. *Phys. Rev.* **1921**, 17, 273.

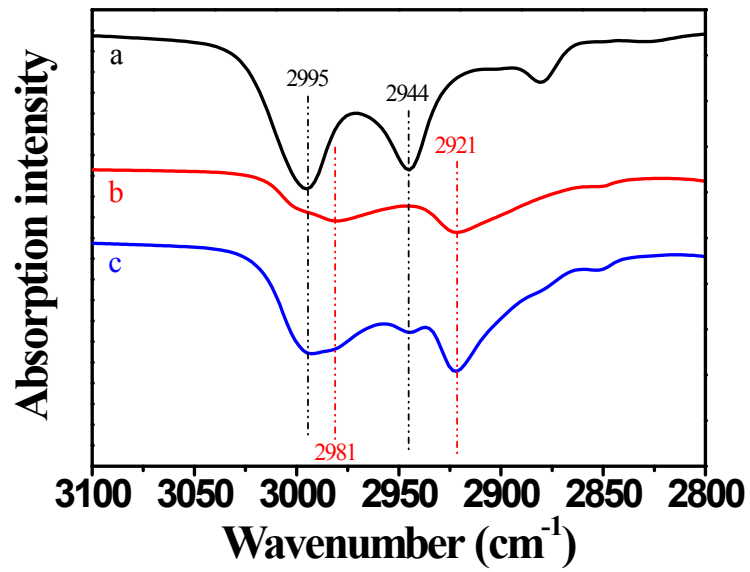


Figure S1. FTIR spectra of (a) cast film from the extraction solution (same spectroscopy to the neat PLLA), (b) remaining materials from PLLA (50/50) after extraction (same spectroscopy to the neat POM), (c) PLLA/POM (50/50) blends.

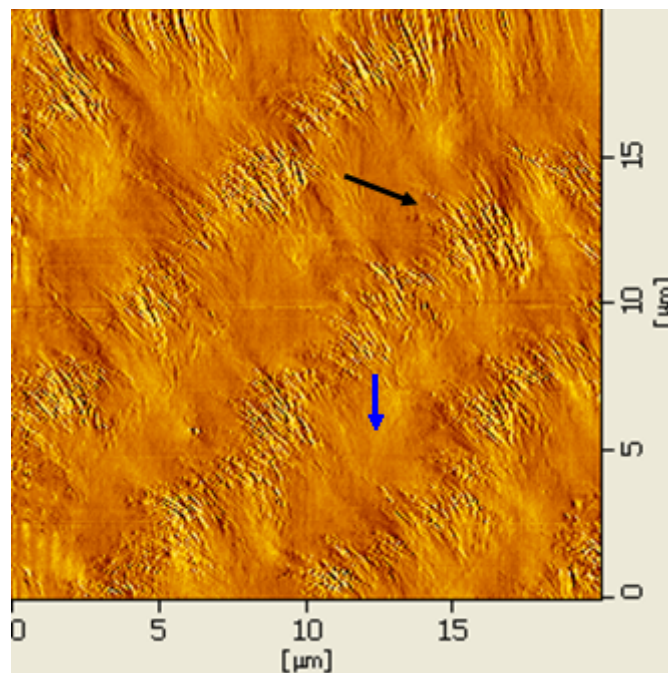


Figure S2. AFM phase image of PLLA/POM (50/50) banded spherulites crystallized at 141 °C.

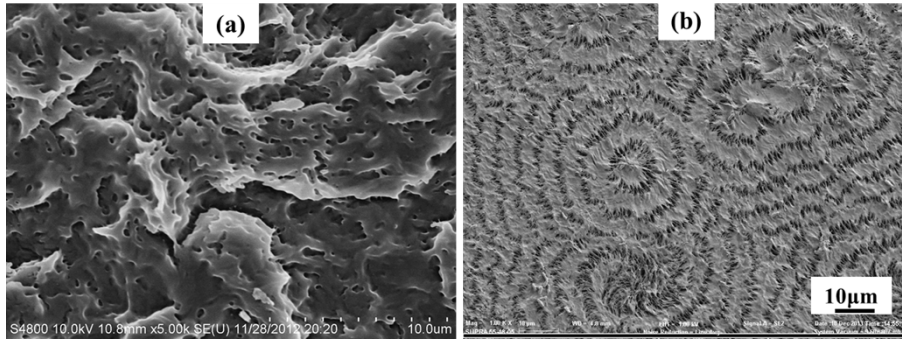


Figure S3. SEM images for the top surface after solvent etching of (a) quenched and (b) high temperature isothermally crystallized PLLA/POM (50/50) sample.

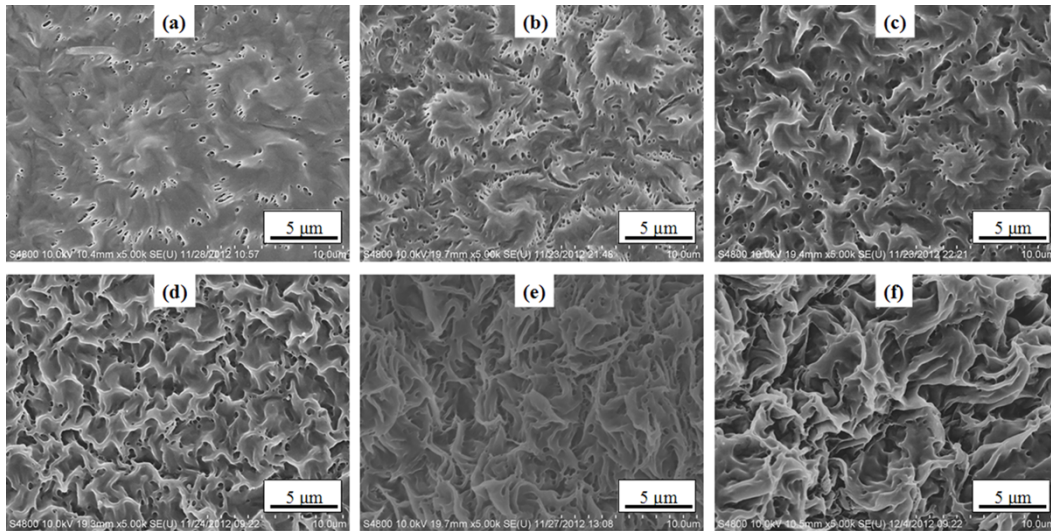


Figure S4. SEM images for the top surface after solvent etching of quenched samples: (a) PLLA/POM (30/70), (b) PLLA/POM (40/60), (c) PLLA/POM (50/50), (d) PLLA/POM (60/40), (e) PLLA/POM (70/30), (f) PLLA/POM (80/20)