Supporting Information

Surface-directed self-epitaxial crystallization of poly(εcaprolactone) from isotropic to highly orientated Lamellae

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Figure S1. The surface of the unstretched substrate after immersing in the mixed solvent (acetic acid/distilled water, v/v = 77/23).

*Calculation of the Average Crystallite Size (L*_{hkl}). The amorphous diffraction (pink curve) and crystalline diffractions ((110) crystallographic plane – blue curve; (200) crystallographic plane – green curve; (111) crystallographic plane – yellow curve) were assumed to fit a Lorentzian distribution. The R² fit value of all the samples is ~0.998, indicating a quite strong fit with the actual data. The full width at half maximum (B_{hkl}) is obtained from the 1D WAXD fit profile (**Table S1**). The average crystallite size (L_{hkl}) was calculated according to the Scherrer equation.

	S0	S150	S300	S400	S450
B ₁₁₀	0.235	0.307	0.306	0.347	0.367
B ₂₀₀	0.321	0.431	0.431	0.472	0.497
B ₁₁₁	0.271	0.286	0.285	0.302	0.311

Table S1. The full width at half maximum (B_{hkl}) of individual *hkl* plane.



Figure S2. (a) Selected 1D WAXD fitted profile of S300. (b) The change of average crystallite size of the (110), (200) and (111) of the uniaxial substrate with the stain.

Derivation of the Equation to Calculate Orientation Degree of PCL. The lamellar orientation can be calculated by the Herman's orientation function ($f_{\rm H}$), as defined in Eq S1,

$$f_{H} = \frac{3\left\langle\cos^{2}\theta\right\rangle_{c} - 1}{2} \tag{S1}$$

where $\langle \cos^2 \theta \rangle_c$ is the squared average cosine of orientation angle (θ), which is determined by the angle between the *c*-axis and the stretching direction.¹ However, the orientation of *c*-axis in the polymer crystals can be reflected directly by X-ray diffraction measurements if there is a set of symmetric planes to reveal the c-axis orientation. Wilchinsky suggested it was possible to describe the average orientation by measuring diffraction of two sets of planes, which contain the c-axis, and LaShanda extended this transformation to PCL unit cell.²⁻³ Then the $\langle \cos^2 \theta \rangle_c$ in PCL unit cell can be quantified by Eq S2,

$$\left\langle \cos^2 \theta \right\rangle_c = 1 - 1.441 \left\langle \cos^2 \theta \right\rangle_{110} - 0.559 \left\langle \cos^2 \theta \right\rangle_{200}$$
 (S2)

where $\langle cos^2 \theta \rangle_{hk0}$ is the squared average cosine of each hk0 reflection, described as Eq S3,

$$\left\langle \cos^2 \theta \right\rangle_{hk0} = \frac{\int_0^{\pi/2} I(\theta_{hk0}) \sin \theta_{hk0} \cos^2 \theta_{hk0} d\theta_{hk0}}{\int_0^{\pi/2} I(\theta_{hk0}) \sin \theta_{hk0} d\theta_{hk0}}$$
(S3)

Differential Scanning Calorimetry (DSC) Measurement. DSC measurement was carried out on a differential scanning calorimeter (Q2000, TA Instrument, USA), which was calibrated using indium as a standard. The specimen (~ 5 mg) was heated at a rate of 10 °C min⁻¹ from 20 to 80 °C in nitrogen atmosphere (50 mL min⁻¹).



Figure S3. DSC scans of various PCL substrates.

Thermal behavior of PCL substrate can be reflected by DSC scans. The melting points are defined as the temperature of the endothermic peak from DSC curves, and the crystallinity (X_c) was evaluated by the ratio of ΔH value of the PCL substrate to the melting enthalpies of perfect PCL crystal (136 J g⁻¹).⁴



Figure S4. SEM images of oriented lamellae before and after ultrasonic treatment for 30 min; and (b) before and after compressing by a 1000 g weight for 5 min.



Figure S5. AFM height images and cross profiles of S150, S400, S450, ES150, ES400, and ES450.



Figure S6. SEM images of (a_1, a_2) isotropic 3D PCL porous scaffolds, (b_1, b_2) oriented 3D PCL porous scaffolds, (c_1, c_2) 3D-printed PCL scaffolds, and (d_1, d_2) electrospun PCL fibers decorated by surface-directed self-epitaxial crystallization.

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