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Supporting Information

Lamellar Bilayer to Fibril Structure Transformation of Tough Photonic Hydrogel under Elongation

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I. Analysis of experimental data

I-1: The change of volume of the gels with elongation

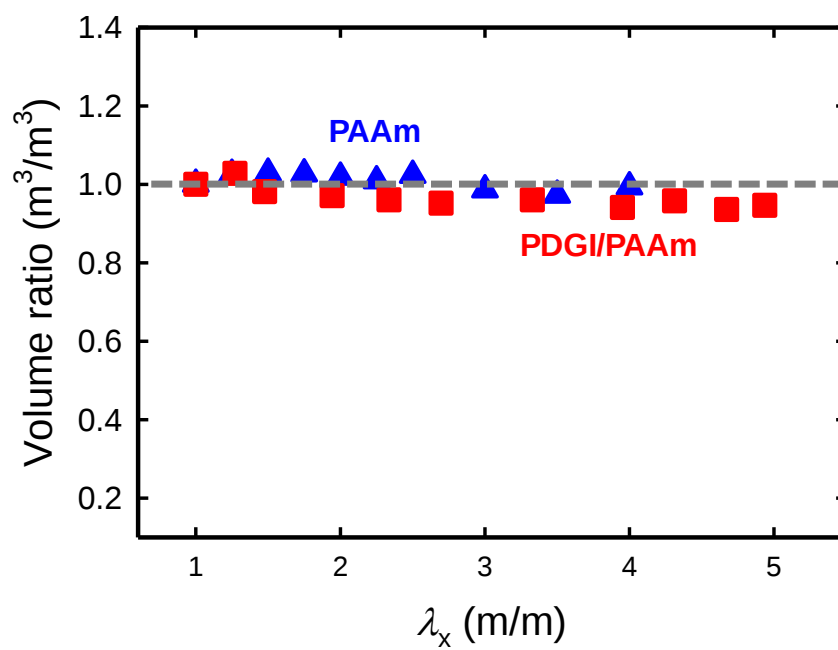


Figure S1: The variation of sample volume ratio $\lambda_x\lambda_y\lambda_z$ during elongation.

I-2: In situ small-angle X-ray scattering (SAXS) in low q -range ($0.02 \sim 1.3 \text{ nm}^{-1}$) to observe any bending/wrinkling of lamellar bilayer.

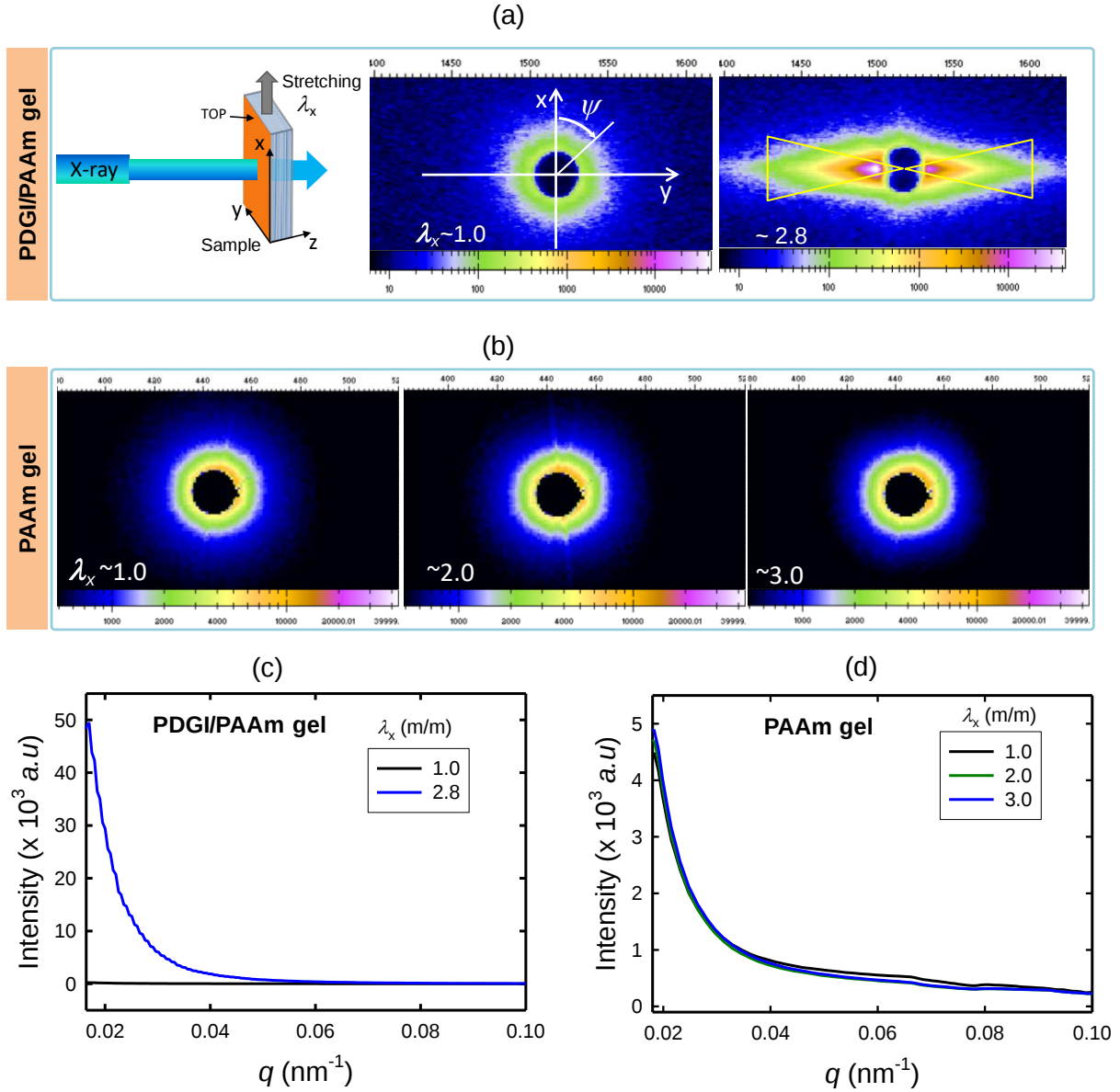


Figure S2: In situ small-angle X-ray scattering (SAXS) experiments performed during tensile deformation in a low q -range ($0.02 \sim 1.3 \text{ nm}^{-1}$). Set-up of the gel deformation and X-ray scattering are shown. Tensile deformation was applied vertically, in parallel to the PDGI lamellae, and the X-ray was imposed perpendicular to lamellar plane. 2D SAXS image was collected behind the sample. (a,b) 2D SAXS images of the PDGI/PAAm gel and PAAm gel as reference are shown for various elongation ratios. At $\lambda_x \sim 1$, SAXS patterns for both gels show a very weak and diffuse scattering, indicating the in-plane isotropic structure as expected for PDGI/PAAm gel when the X-ray beam was imposed perpendicular to the lamellar plane and isotropic PAAm gel. At $\lambda_x \sim 2.8$, two scattering streaks in the direction (y-axis) perpendicular to deformation direction (x-axis) were clearly observed for the

PDGI/PAAm gel. On the other hand, the isotropic PAAm gel does not show any significant change in the SAXS scattering pattern upon deformation at all, and no noticeable scattering streaks was observed even at higher deformation ($\lambda_x \sim 3$). (c,d) 1D SAXS intensity vs. scattering vector, q obtained from 2D SAXS images for both gels. The intensity is an integration of azimuth angle, ψ , over a narrow range ($\psi = \pm 5^\circ$) in the equatorial direction. No correlation peaks were observed which is in contrast for the X-ray scattering performed parallel to lamellar layer.

I-3: Analysis of SAXS data for estimation of structure size.

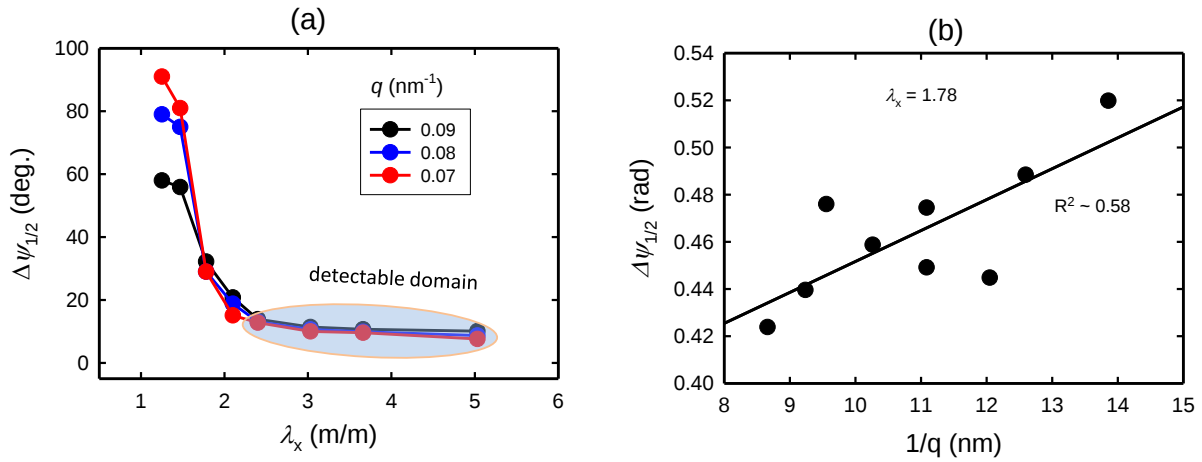


Figure S3: Analysis of structure change for PDGI/PAAm gel during tensile deformation from SAXS data. (a) Deformation dependence of azimuthal width ($\Delta\psi_{1/2}$) for several scattering vector, q . The values of $\Delta\psi_{1/2}$ were obtained from Lorentz fitting of the observations. (b) The Ruland plot, azimuthal width ($\Delta\psi_{1/2}$) vs. $1/q$, for $\lambda_x = 1.78$, as a typical example to shows no linear correlation below $\lambda_x = 2.4$. Therefore, no rod-like structure is formed below $\lambda_x = 2.4$.

II. Experimental details

II-1: *Reflection spectrum*

The reflection spectrum of various gel samples was measured by a combined set up of light source, variable angle measurement device, and an analyzer. A Xe lamp was used as a light source to obtain the reflection spectrum. Reflection measurement optics with variable angles (Hamamatsu Photonics KK, C10027A10687) were used to detect the reflected light. A photonic multichannel analyzer (Hamamatsu Photonics KK, C10027) was used for analyzing the detected signal. The entire reflection spectrum was obtained by keeping both the incident (Bragg's angle) and reflection angles at 60° , and the wavelength at maximum, $\lambda_{\max}$, was obtained from the reflection spectrum. The distance between two lamellar layers, d , was determined using Bragg's law of diffraction, $\lambda = 2nd \sin \theta$, where $n = 1.33$ (refractive index of water), θ is Bragg's angle or incident angle, and λ is the wavelength at the maximum of the reflection spectrum.

II-2: *Measurement of transverse sample size at longitudinal elongation*

The gel sample was cut into rectangular sheets of various sizes, $\sim 50 \times (1-8) \times 1.2 \text{ mm}^3$ for determining the width ratio (λ_y) and $\sim 30 \times 1 \times 1.2 \text{ mm}^3$ for determining the thickness ratio (λ_z). Then the rectangular sheet was fixed at the jaws of a manually controlled deformation stage equipped with length scale. The deformation stage was placed in the sample stage of a polarizing optical microscope (POM). The gel was deformed to a pre-defined length and both the optical microscopic images and the conventional camera photographs were captured. The longitudinal deformation ratio (λ_x) was achieved from the distance between the marking spots on the sample using the photographic images. Changes in transverse dimensions (λ_y) were precisely measured from both the POM and photographic images using conventional image processing software. The thickness change (λ_z) for the sample of sizes of $\sim 50 \times \sim 1 \times 1.2 \text{ mm}^3$ was measured using rheometer at various elongations. λ_z for the sample of sizes of $\sim 50 \times$

$(2-8) \times 1.2 \text{ mm}^3$ was measured using rheometer at various elongations since it is difficult to get microscopic images for the cross-section of large width ($>2 \text{ mm}$) sample.

II-3: Optical observation

The anisotropic structure of the gel sample was observed by the polarized optical microscope (POM, Nikon Eclipse LV100POL) under crossed nicol at room temperature. The observation was performed from the top surface (top view) and the cross section (side view) of the sheet-shape gels by placing on a glass plate. *Prior to* observation, the gel sample was cut into a rectangular sheet ($\sim 50 \times 2 \times 1.2 \text{ mm}^3$ for top view and $\sim 30 \times 1 \times 1.2 \text{ mm}^3$ for side view) and fixed at the jaws of a computer controlled tensile deformation stage [Linkam, Model-10073A]. The sample setup was placed at the sample stage of POM and deformed at a velocity of $\sim 60 \text{ mm/min}$. POM images were recorded by a camera at various elongations during the deformation.

II-4: Scanning Electron Microscope (SEM) observation

Water swollen PDGI/PAAm and PAAm gels were clumped in a tensile deformation stage and stretched up to an elongation ratio, $\lambda_x \sim 5$. The clumped sample was kept in deep freezer (-18°C) for 3 h. The solidified gel was then placed in the freeze-dryer at -60°C and allowed to dry using a temperature-time programming for 24 h. As prepared gel sample was put in an ion sputter for 180 s prior to SEM measurement for the surface morphology.