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Lamellar Bilayer to Fibril Structure

Transformation of Tough Photonic Hydrogel

under Elongation

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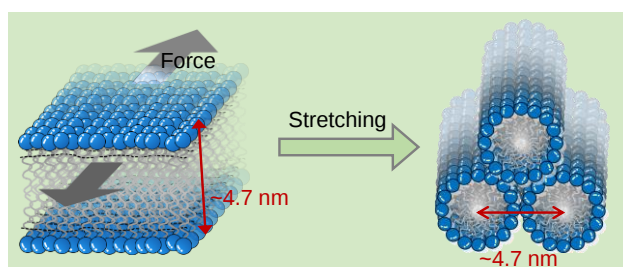
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Table of Contents (TOC) graphic



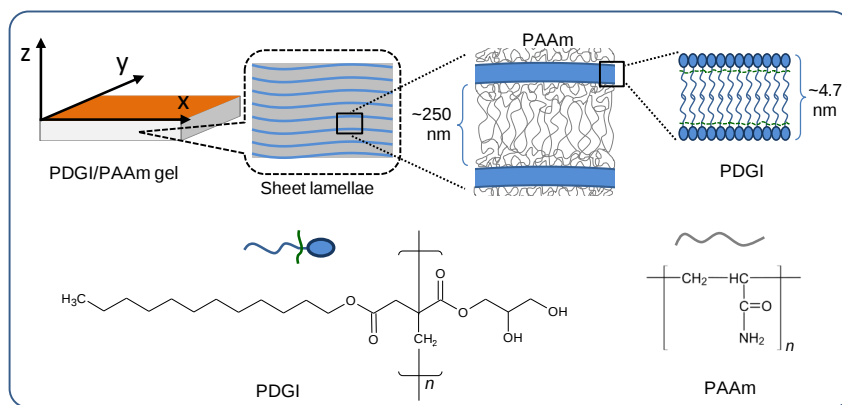
ABSTRACT. Synthetic hydrogels possessing both macroscopic anisotropic structure and toughness, which are analogous to the load-bearing bio-tissues such as muscles and tendons, are rarely available. Studying the molecular mechanism of tough and anisotropic hydrogel under deformation is beneficial to understand the load-deformation functions of soft bio-tissues. In this work, deformation-induced structure transformation of a macroscopically anisotropic and tough hydrogel has been investigated to understand the role of structure evolution for enhanced toughness. At rest, the hydrogel possesses well-defined hierarchical structure in which self-assembled nanometer-thick lamellar bilayers are alternatively stacked in hundred-nanometer-thick hydrogel matrixes. Stretching along the lamellar direction induces structure transformation from lamellar bilayers to hierarchical fibrous structures aligned along the deformation axis. The generated hierarchical structures consist of micrometer-thick fiber bundles made from nanometer-thick fibrils in analogous to tropo-collagen bundles or micro-fibrils of tendon. The fibrous structure formed at large elongation is associated with damage and rupture of the bilayers, which underpins the molecular mechanism of the unique mechanical behaviors of the tough lamellar hydrogel.

KEYWORDS. anisotropy, small angle X-ray scattering, Ruland streak method, string micelle, fiber bundles.

1. INTRODUCTION

Conventional hydrogels are isotropic in structure and weak in mechanical strength. Incorporating energy dissipation during deformation by various molecular mechanisms such as sacrificial bonds endows the dramatic toughening of hydrogels, which greatly expands the potential use of the materials, especially as biomaterials.¹⁻¹² Developing tough hydrogels with anisotropic superstructures of macroscopic scale, as like biological tissues, are still challenging topics. Introducing self-assembling structures into hydrogels is a promising approach. Previously, hydrogel sheets have been synthesized which possess hierarchical structure of self-assembled lamellar bilayers.¹³⁻¹⁶ The hydrogels consist of transversely isotropic (*xy*-plane), lamellar, 1D photonic crystal structures in parallel to the sheet surfaces [**Scheme 1**]. The periodic stacking (along *z*-axis) of water-impermeable bilayers (4.7 nm-thick) are integrated macroscopically and trapped inside polymeric hydrogel matrix (several hundred nm-thick). Specifically, the lamellar bilayers were polymeric surfactant, dodecyl glyceryl itaconate (PDGI) and the hydrogel layers were polyacrylamide (PAAm). The PDGI bilayer membrane has a melting temperature of 43°C.¹⁷ At room temperature, a single bilayer is rigid with a modulus in the order of several MPa, and a PAAm matrix is soft with a modulus of few kPa.^{14,18} The PDGI/PAAm lamellar hydrogels show many unique properties, including one dimensional swelling in thickness direction (*z*-axis), bright structure color, anisotropic diffusion.¹⁴⁻²² Comparing with the pure PAAm hydrogels, PDGI/PAAm lamellar hydrogels show prominently improved mechanical strength and toughness. For example, a PDGI/PAAm lamellar hydrogel, only containing 5 mol% of DGI monomeric molecules in relative to AAm, *i.e.* corresponding to a volume of ~2% of the gel, exhibits tensile fracture strength (~600 kPa), fracture strain (~20), and tearing resistance (~10 kJ/m²) that are ~15 times, ~2 times and ~1000 times of the pure

PAAm hydrogel, respectively.^{9,14,18} The toughness of the PDGI/PAAm gel is in the order of tough DN gels.^{9,18} The remarkable high toughness and extraordinary crack resistance for a high-water content hydrogel, typically 95%, is comparable to conventional elastomers.^{2,23} The exceptional increase in mechanical strength and toughness of the bilayer incorporated hydrogel is attributed to the water-impermeable but lipid-like bilayers, where the reversible and noncovalent hydrophobic associations of polymerized DGI tails serve as reversible sacrificial bonds that allow for energy dissipation and self-recovery capabilities. It is considered that the lipid-like mobile nature of bilayers dramatically enhances the resistance against crack propagation by shielding the crack tip singularity and the gel, thereby, demonstrates unusual crack blunting.¹⁸ However, the molecular mechanism behind the unique mechanical behaviors of the lamellar hydrogels is still unrevealed.



Scheme 1: Schematic illustration of sheet-shape lamellar hydrogel with 1D photonic structure. The hydrogel consists of lamellar bilayers (~ 4.7 nm-thick) of self-assembled poly(dodecyl glyceryl itaconate) (PDGI) and conventional polyacrylamide (PAAm) hydrogel matrix (~250 nm-thick). The PAAm chains are adsorbed on the bilayer surfaces through hydrogen bonding. The gels were prepared by applying shear flow of gel precursor solution between two parallel glass plates *prior to* polymerization.

In this work, we study the structure transformation of the lamellar gels under uniaxial tensile elongation. We first observe the unique macroscopic shape change and microscopic structure change of the gels under tensile elongation by using various optical and microscopic observations in real space. Then, we study the structure change under tensile deformation in reciprocal space by performing *in situ* X-ray scattering. Our study reveals the structure transformation from uniaxially aligned lamellar to multi-scale fiber bundles (1~100 μm in width) consisting of micro-fibril (~ 0.8 μm in length and ~ 4.7 nm in width) above the yield point. Finally, we discuss the mechanism of fibrous structure formation at large elongation and the role of the fibrous structure on the unique mechanical behaviors.

2. RESULTS AND DISCUSSION

2.1 Macroscopic shape change of the gel during elongation

The xyz coordinate with respect to a sheet-shape PDGI/PAAm lamellar hydrogel is defined in **Scheme 1**. The PDGI/PAAm gel sample was fixed in a tensile stage and stretched along the x-axis such that force/elongation was applied parallel to PDGI lamellae (xy-plane). The photographs of the gel taken at various elongation ratios (λ_x) are shown in **Figure 1a**. The PDGI lamellae are parallel to the plane of the paper in the photographs. Local λ_x was calculated based on the two marking lines made on the gel *prior to* deformation. The photographs show a weak blueshift of color with elongation. Stress-strain behavior of the gel is shown in **Figure 1b**. A clear yielding was observed at $\lambda_x \sim 1.6$, indicating a large structure change of PDGI lamellae under deformation. Reflection spectrum of the gel quantitatively shows weak blueshift of peak maximum, λ_{max} , (inset) and peak broadening with increase in λ_x (**Figure 1c**). As shown in **Figure 1d**, the inter-lamellar spacing (d) estimated from Bragg's law shows a small decrease

with increase in λ_x while the full width at half maximum ($\Delta\lambda_{1/2}$) of the reflection peak shows significant increase at $\lambda_x > 1.5$ that indicates the distortion of periodic lamellar structure in agreement with the yielding.

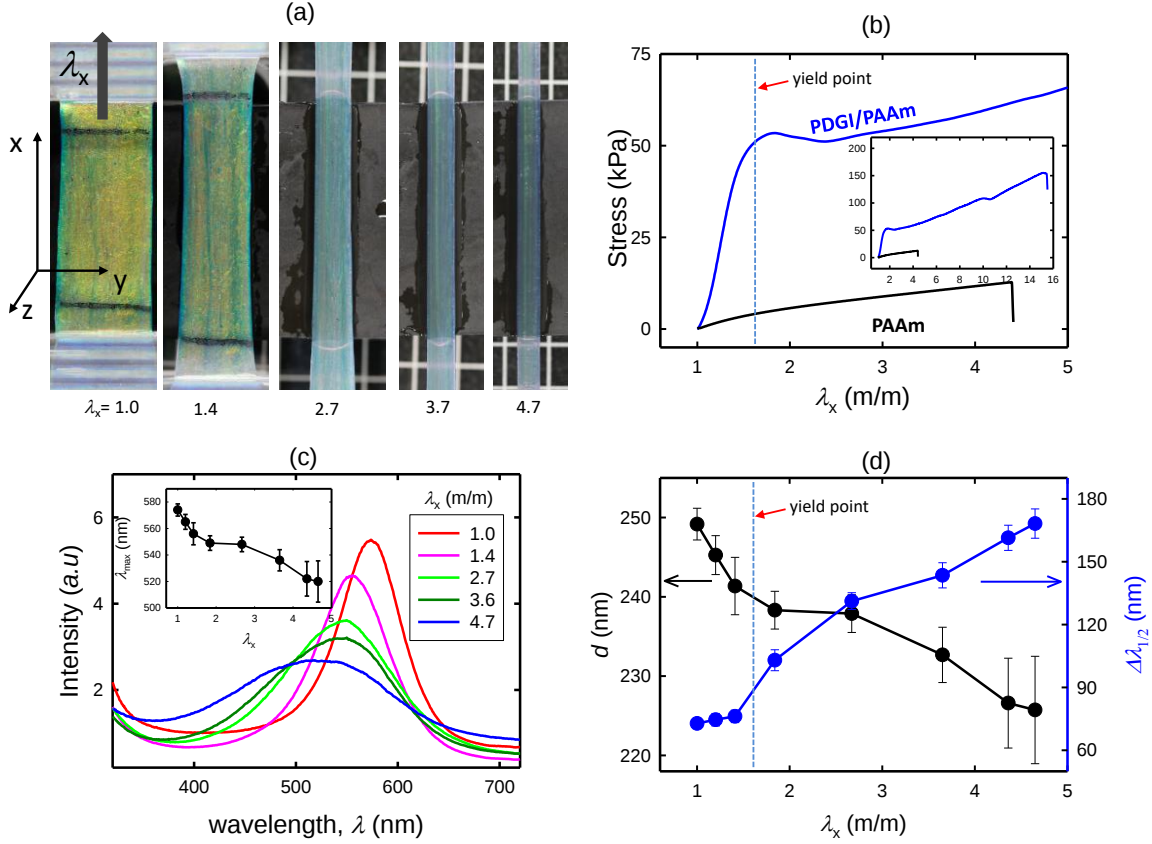


Figure 1. Photographic, mechanical and reflection properties of a PDGI/PAAm hydrogel under tensile deformation. (a) Photographs of the gel taken at various tensile elongation ratios (λ_x) shows weak blue shift of color; (b) Stress-elongation ratio curves of the PDGI/PAAm gel and PAAm gel as a reference at a deformation rate of 60 mm/min; (c) Light reflection spectra taken at 60° incident and reflection angles, and peak wavelength (λ_{max}) (inset), at various λ_x ; (d) Inter-lamellar spacing, d estimated from the peak of the reflection spectra and full width at half maximum ($\Delta\lambda_{1/2}$) of the peak for various λ_x .

Figure 2a shows the relative changes of sample size in the transverse directions, parallel (λ_y) and perpendicular (λ_z) to the lamellae, during elongation along the longitudinal direction (λ_x). The deformation of the anisotropic lamellar hydrogels under elongation is very different from the isotropic material.²² When the lamellar gel is deformed along λ_x direction, change in width direction (λ_y) is much significant than the change in thickness direction (λ_z). This behavior is very different with that of an unconfined isotropic gel. For example, the PAAm gel shows identical changes in λ_y and λ_z , in good agreement with the theoretical curve for isotropic, non-compressive materials, $\lambda_y = \lambda_z = \lambda_x^{-1/2}$. By comparing with the results for isotropic PAAm, λ_y is greater than, and λ_z is smaller than the isotropic deformation for the PDGI/PAAm gel. That is, the PDGI/PAAm gel exhibits significant lateral contraction but little thickness contraction in accordance with the longitudinal elongation. The volume ratio before and after the elongation, corresponding to $\lambda_x \lambda_y \lambda_z$, remains almost constant upon stretching for the PDGI/PAAm as like as the PAAm gel, confirms the non-compressibility of the materials at the observation time scale (**Figure S1**). The unique deformation of the PDGI/PAAm hydrogels is attributed to the water-impermeable property and rigidity of the PDGI bilayers that intend to maintain their area under deformation. **Figure 2b** demonstrates the sample area ($\lambda_x \lambda_y$) change for PDGI/PAAm gel under deformation. The $\lambda_x \lambda_y$ for bilayer gel slightly increases with elongation at large λ_x , which is in sharp contrast to the unconfined isotropic PAAm gel that largely increases with elongation and follows the theoretical curve for isotropic, non-compressive materials, $\lambda_x \lambda_y = \lambda_x^{1/2}$.

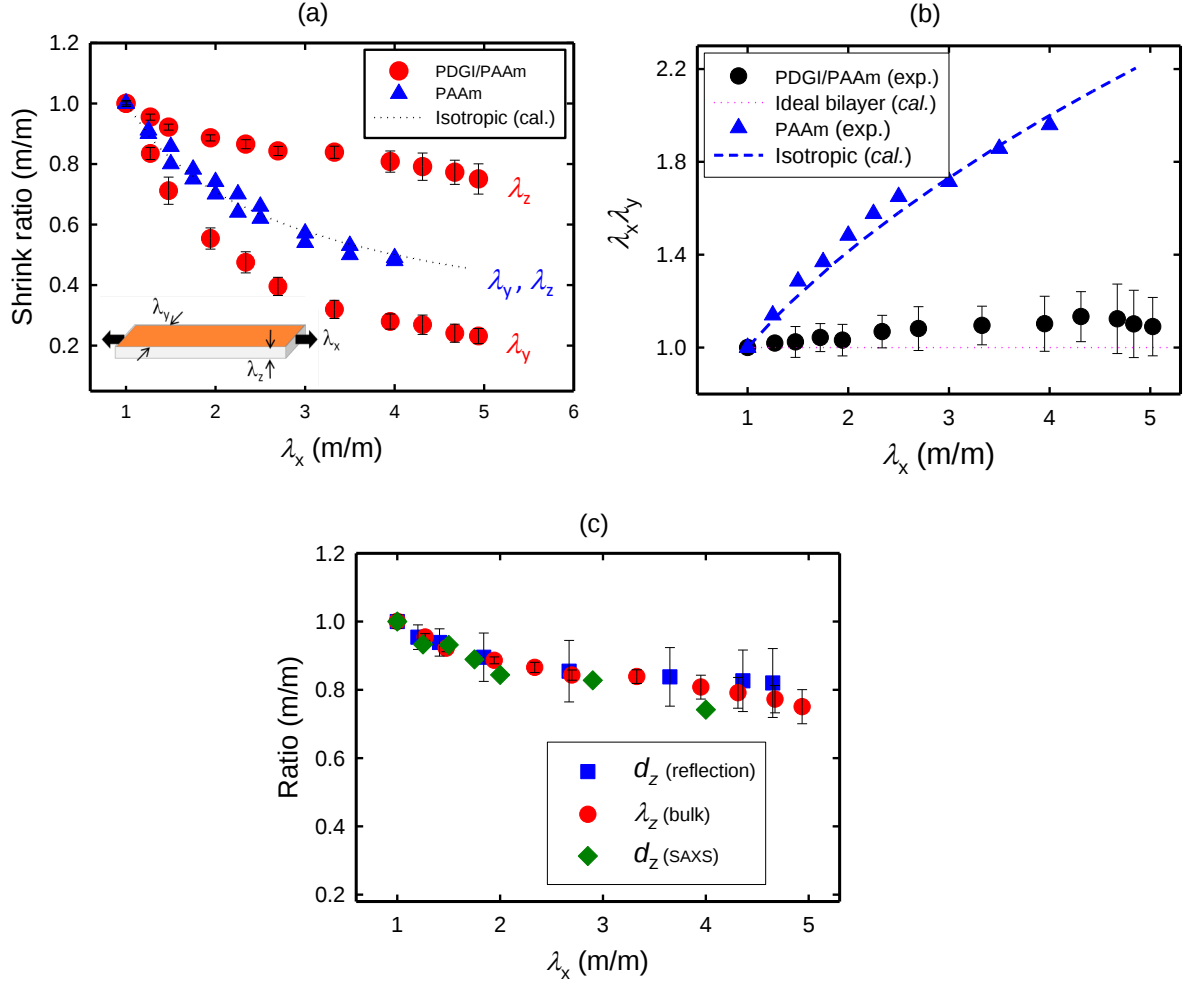


Figure 2. Shape changes of anisotropic PDGI/PAAm gel and isotropic PAAm gel during elongation. (a) Deformation ratio in transverse directions (λ_y , λ_z) of gels during elongation in longitudinal direction (λ_x). The black dotted curve represents the theoretical curve, $\lambda_y = \lambda_z = \lambda_x^{-1/2}$ for isotropic and non-compressive materials. (b) The sample surface area $\lambda_x \lambda_y$ change in response to the elongation λ_x . The dotted blue curve represents the theoretical curve $\lambda_x \lambda_y = \lambda_x^{1/2}$ for isotropic and non-compressive materials. The pink dotted line represents for a constant surface area $\lambda_x \lambda_y = 1$. (c) Comparison of the changes in sample thickness, λ_z (bulk measurement) and the changes in the inter-bilayer distance ($d_z = d/d_0$) for reflection spectra measurement (d_z , reflection) and small angle X-ray measurement, (d_z , SAXS) with elongation λ_x . For reflection

spectra, d and d_0 are obtained from peak maximum ($\lambda_{\max}$) of optical reflection spectra at λ_x and $\lambda_x=1$, respectively. For SAXS measurement, d and d_0 at λ_x and $\lambda_x=1$, respectively, are obtained from q ($d=2\pi/q$) for 1st order peak maximum of intensity vs. q plot.

The unique deformation of the lamellar gel could be explained by its hybrid structure. In the macroscopic gel of centimeter scale, the macroscale lamellar membranes and hydrogel layers are in extremely high confinement state. To keep a constant area, a bilayer undergoes large shrink laterally along the y-axis in response to elongation along x-axis, while the PAAm layers confined between the lamellar membranes intend to shrink isotropically in the two transverse directions. As the modulus of a bilayer is ~1000 times (stiffness 20 times) higher than that of PAAm layer, the deformation is governed by the bilayers that shrink more along y-axis to keep the same membrane area. As a result, the soft PAAm gel layers are suffered compression by the more stiff bilayers along the y-axis and also deform more along z-axis. Therefore, the net result is the weaker thickness reduction of the PAAm gel layers in z-direction.

To clarify if the weak blueshift of the reflection spectrum is related to the above anisotropic deformation mechanism, the deformation ratio in sample thickness direction (λ_z) is compared to the inter-bilayer spacing ratio ($d_z=d/d_0$) at various elongations, where d and d_0 are inter-bilayer distances at λ_x and $\lambda_x=1$, respectively. The d and d_0 are obtained from peak maximum ($\lambda_{\max}$) of optical reflection spectra. λ_z and d_z are in good agreement except at very large λ_x (>4), as shown in **Figure 2c**. Since the deformation up to a large elongation ($\lambda_x \sim 5$) is reversible,¹⁸ the bilayers do not flow while maintaining the constant area upon large deformation. These results show that the interfacial bonding between the bilayer and the PAAm gel layer is strong enough to pin the bilayers from flow during large elongation. The molecular mechanism of inter-layers bonding is

still not clear. Previous study has shown that PDGI and PAAm are independently polymerized, although the gels were obtained by one-pot polymerization.²⁴ Topological entanglement between PDGI and PAAm chains, and the physical adsorption of the PAAm chains on the bilayer surfaces are possible mechanisms.²⁵

2.2 Microscopic structure change with elongation

To get insight into the structure change upon deformation, we observed the surface morphology of the gels under deformation using optical microscope (**Figure 3**).

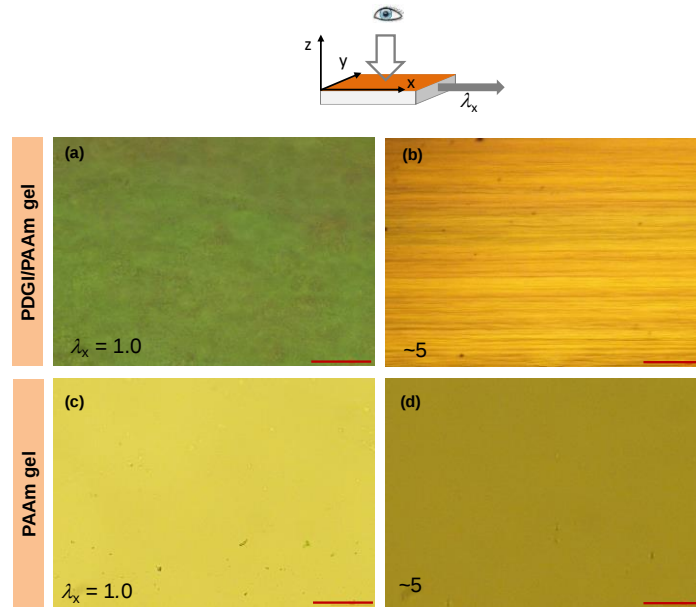


Figure 3. Microscopic observation of the PDGI/PAAm and PAAm gels at various deformation ratios (λ_x) to reveal the change in surface topography. Transmission optical microscopic images of the PDGI/PAAm gel at deformation ratio (λ_x) of 1 (a) and 5 (b). The rod-like fibrous domains are evident at elongation of 5 along the stretching direction. In contrast, PAAm gel at λ_x of 1 (c) and 5 (d) does not show any noticeable change in structure or the formation of fibrous domain. The scale bar is 100 μm and identical for all images.

For undeformed samples, random surface morphology is observed on the PDGI/PAAm gel while no surface feature is observed on the PAAm gel (**Fig. 3 a, c**). At $\lambda_x \sim 5$, a clear surface texture aligned along the stretching direction is observed for PDGI/PAAm gel (**Fig. 3b**) in contrast to PAAm gel that shows no structural features at the similar elongation (**Fig. 3d**). Polarizing optical microscopic (POM) observation further justified the change in internal microstructure of the PDGI/PAAm gel upon deformation along x-axis, as shown in **Figure 4**.

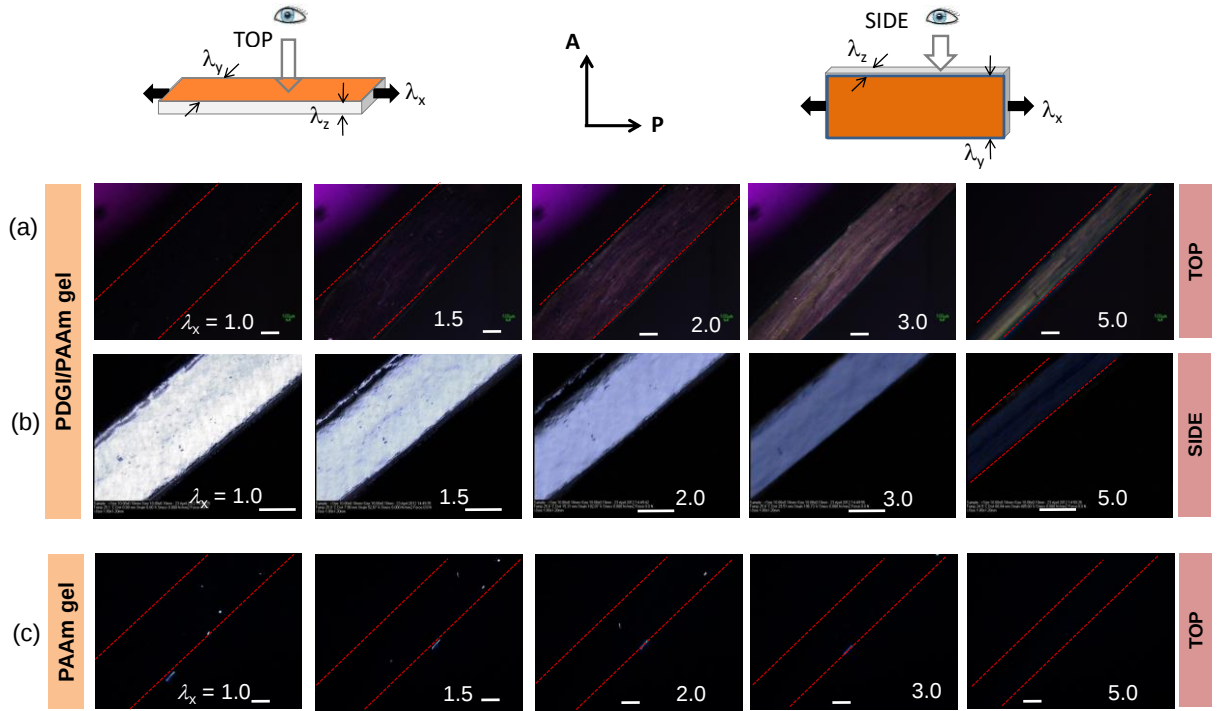


Figure 4. Monitoring of PDGI/PAAm and PAAm gel upon tensile deformation (velocity ~ 60 mm/min) under cross nicol using polarizing optical microscope (POM) to reveal the change in internal structure. Photographs were taken for both top (a) and side (b) views at various deformation ratios. The arrangement of sample's orientation and polarizers for both top and side views are also shown above. (c) POM images of PAAm gel from top views at various elongation ratios. Due to isotropic nature of PAAm, side view is expected to be identical with the top view. The scale bars are 500 μm . Red dotted lines indicate the sample's edges.

At relaxed state ($\lambda_x \sim 1$), gel exhibits negligible birefringence in the top view (xy-plane) (**Figure 4a**), as expected from the isotropic in-plane structure, but strong birefringence in the side view (xz-plane) (**Figure 4b**) which attributes to the uniaxially aligned PDGI lamellar stacking. Upon stretching, the opposite scenario is observed; the birefringence starts to appear in the top view but diminishes in the side view above $\lambda_x=2$. Decrease of birefringence in the side view indicates disordering or rupturing of PDGI lamellae upon deformation. On the other hand, the increase in birefringence in top view indicates the formation of oriented structure under large elongation. Absence of noticeable birefringence for PAAm gel up to a deformation of $\lambda_x \sim 5$ (**Figure 4c**) indicates that the birefringence in the top view of PDGI/PAAm gel at large elongation comes from new structure of PDGI.

To reveal the oriented structure aligned along the elongation direction, scanning electron microscope (SEM) observation was further performed. The PDGI/PAAm gel was pre-stretched to an elongation ratio, $\lambda_x \sim 5$, and then was freeze-dried. SEM images taken on as-prepared surfaces from the top are shown in **Figure 5a**. The gel with no pre-stretching ($\lambda_x \sim 1$) exhibits a quite smooth surface (**Figure 5a-i**), whereas multiscale fiber-like bundles aligned along the stretching direction are observed (**Figure 5a ii-v**). The bundles have hierarchal structure, and the finest bundles are $\sim 1\mu\text{m}$ in diameter. In contrast, the pre-stretched PAAm gel ($\lambda_x \sim 5$) shows irregular texture (**Figure 5b**). Accordingly, the bundle structure evolves from the PDGI bilayers.

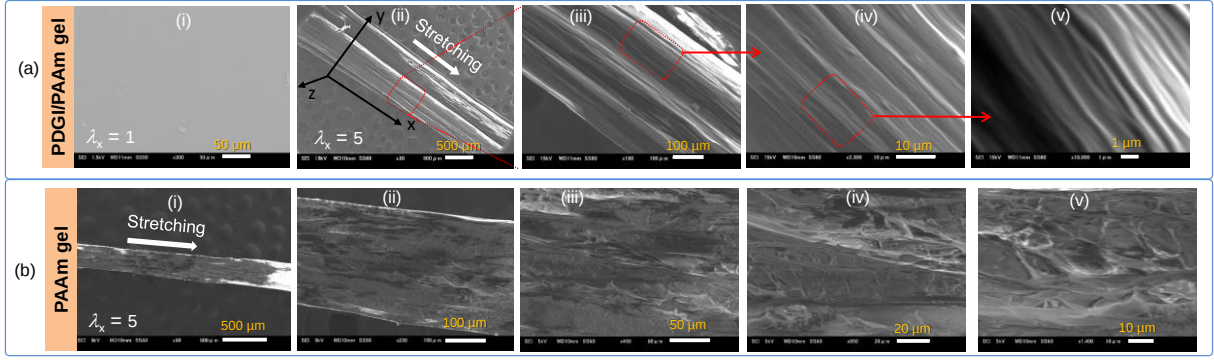


Figure 5. Scanning electron microscope (SEM) images of the freeze-dried PDGI/PAAm (a) and PAAm gels (b) pre-stretched at $\lambda_x \sim 5$ [except a(i)]. Figure a(i) is for the freeze-dried PDGI/PAAm gel without any pre-stretching $\lambda_x \sim 1$ as reference. The observations were performed on as-prepared (freeze dried) surface from the top view.

2.3 Molecular level structure change with elongation by small-angle X-ray scattering

To elucidate the structure change in small scales that could not be observed by SEM, *in situ* small-angle X-ray scattering (SAXS) experiments were performed during the elongation of the gel at the same tensile velocity as discussed in **Figure 1**. First, we study the change of bilayer structure by performing SAXS in a low q -range ($0.02 \sim 1.3 \text{ nm}^{-1}$) to the cross-section of the PDGI/PAAm gel. In this configuration, the X-ray beam was imposed parallel to the PDGI lamellar plane (xy -plane) along the y -axis while the gel was elongated along lamellar plane in x -axis (**Figure 6a**: top-left). A series of 2D SAXS patterns of PDGI/PAAm gel at different stretching were achieved and some selected patterns are shown in **Figure 6a**. Anisotropic scattering patterns, with two sets of peak up to the 4th order, were observed. Such symmetric peaks are originated for the highly periodic 1D lamellar structure. Specifically, at rest ($\lambda_x \sim 1$), the SAXS peaks show broad distribution in the azimuth direction that indicates undulation of the lamellar layers. This is in consistent with the rough surface morphology observed in **Figure 3a**.

The appearance of peak patterns on an axis tilting to the equatorial axis at $\lambda_x = 1$ is due to the misalignment of the sample to the vertical direction during SAXS measurement. At λ_x of 1.5, the SAXS peak patterns become sharp in the azimuth direction, which indicates that the lamellar layers under stretching become flat. Above $\lambda_x \sim 1.5$, the peak broadens with respect to scattering vector q and the intensity decreases, while the distribution in azimuth direction keeps narrow. At $\lambda_x \sim 4.0$, the peak become very weak and broad so that the 1st order scattering spots are merged with the subsequent spots.

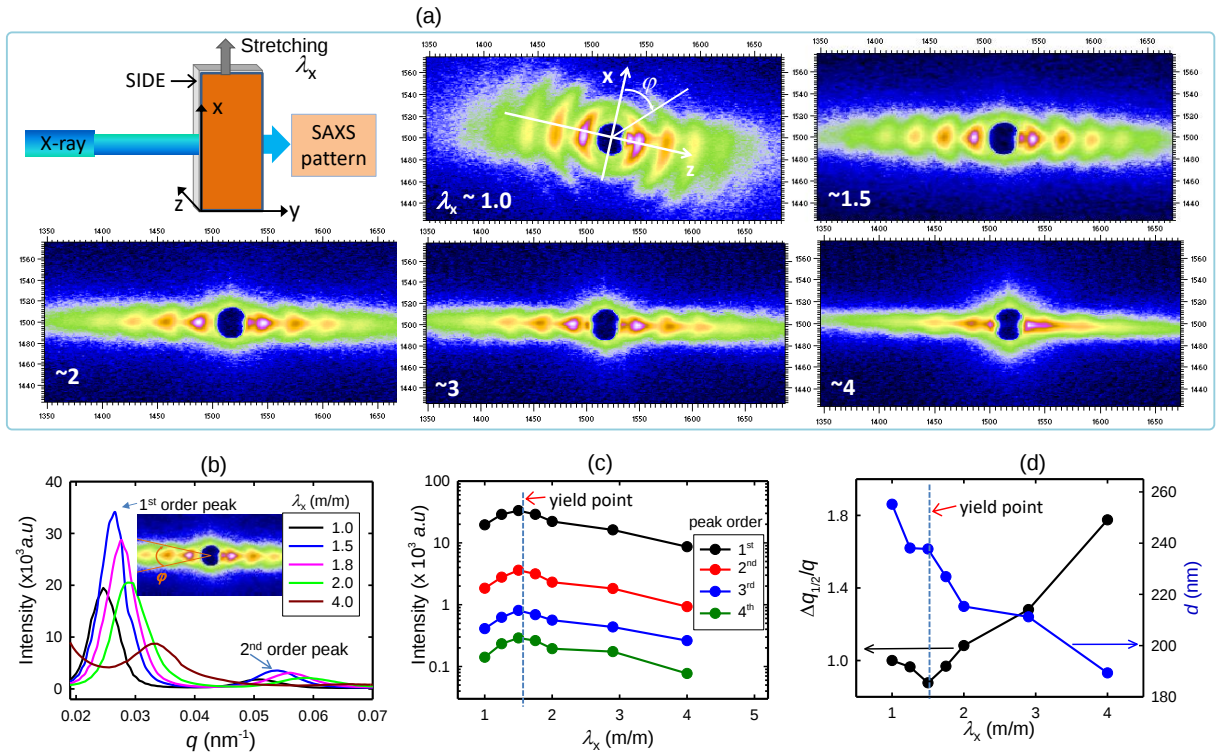


Figure 6. *In situ* small-angle X-ray scattering (SAXS) experiments performed for PDGI/PAAm gel under tensile deformation in a low q -range ($0.02 \sim 1.3 \text{ nm}^{-1}$). (a) Set-up of the measurement is shown in the top-left. Gel was deformed vertically parallel to PDGI lamellae and X-ray beam was also imposed parallel to lamellar plane. 2D SAXS images taken at various

elongations from 1 to 4 are also shown. (b) 1D SAXS intensity vs. scattering vector, q obtained from 2D SAXS images where 1D intensities were integrated from the azimuth angles, ϕ of 180° . The intensity vs. q profile shows clear scattering peak up to 4th order (q range for the 1st and 2nd order peaks are only shown here). (c) Intensity of the peaks (1st to 4th order) is plotted against deformation ratio. (d) Plots of the relative full width at half maximum ($\Delta q_{1/2}/q$) and inter lamellar distance (d) of the 1st order peak against deformation ratio, λ_x .

2D SAXS patterns at various elongations are integrated into 1D SAXS intensity vs. q curves. **Figure 6b** shows the intensity vs. q curves in a q -range of $0.02\sim 0.07\text{ nm}^{-1}$ for the 1st and 2nd order peaks. The intensities of the 1st to 4th order peaks as a function of λ_x are shown in **Figure 6c**. The relative full width at half maximum ($\Delta q_{1/2}/q$) and interlayer spacing (d) estimated from the 1st order scattering peak (q_1), are plotted against λ_x (**Figure 6d**). Initial increase of peak intensity and decrease of peak width up to $\lambda_x \sim 1.5$ further justify that the initial bilayer undulation disappears at moderate stretching. Above $\lambda_x \sim 1.5$, the peak intensity decreases and the peak width increases that indicate the large distortion or rupture of the lamellar structure. However, as shown in **Figure 2c**, the interlayer spacing ratio, $d_z(\text{SAXS}) = d/d_0$ obtained from SAXS shows a good coincidence with the deformation ratio of sample thickness λ_z , except at very large elongation, $\lambda_x \sim 4$. The coincidence of macroscopic deformation and microscopic structure indicates that the layered structure of bilayers is preserved up to very large λ_x (~ 4).

To reveal if the elongation induces any bending or wrinkle of the lamellar layers as observed for the deformation of thin sheet,²⁶ next, we study the in-plane structure change with elongation of the PDGI/PAAm gel in the same low q -range ($\sim 0.02\text{-}1.3\text{ nm}^{-1}$) as shown in **Figure S2**. The X-ray beam was imposed perpendicularly (along z -axis) to the lamellae (xy -plane). A series of

2D SAXS patterns of PDGI/PAAm gel at different elongations were achieved and patterns at $\lambda_x \sim 1$ and $\lambda_x = 2.8$ are shown in **Figure S2a**. At $\lambda_x \sim 1$, SAXS pattern shows a very weak and diffuse isotropic scattering that confirms the in-plane isotropic structure of bilayers. At $\lambda_x = 2.8$, the patterns become strongly anisotropic with prominently enhanced scattering intensity in the equatorial direction. 1D SAXS intensity vs. q curves by integrating 2D images at narrow azimuthal angle ($\psi = 90 \pm 5^\circ$) along the equatorial axis are shown in **Figure S2c**. No scattering peak appears in the curve. This indicates the absence of any periodic lamellar structure vertical to the sample surface by elongation in the q -range investigated. So, the weakening of the scattering signal in cross-section view (**Figure 6c**) is not due to bending of bilayers, but due to structure rupture under large elongation. On the other hand, the isotropic PAAm gel does not show any significant change in the SAXS scattering pattern upon elongation, and no noticeable scattering streaks is observed even at higher deformation ($\lambda_x \sim 3$) (**Figure S2b,d**).

To reveal if any smaller in-plane structure is induced by elongation, we further performed the SAXS up to a higher q -range (~ 0.05 - 5.0 nm^{-1}) than that shown earlier in **Figure 6** and **Figure S2**. The X-ray beam was imposed perpendicularly (along z -axis) to the lamellae (xy -plane) and 2D images are shown in **Figure 7**. For deformation below $\lambda_x \sim 2.0$, the scattering pattern is almost isotropic and amorphous. At λ_x above 2.0, strong anisotropic scattering appears. Two scattering streaks in the equatorial axis (y -axis) are clearly observed perpendicular to deformation direction (x -axis) and the streaks become sharper at higher elongations. Such streaks are characteristic for rod-like structures,²⁷ which might be related to the fiber-like morphology along the elongation direction (x -axis) observed earlier by SEM (**Figure 5**). At and above $\lambda_x \sim 2.4$, beside the SAXS streak pattern at low q -range, two broad scattering spots are noticed at high

q -range along the equatorial axis ($\psi = 90^\circ$). This suggests the correlation between the rod-like structures along the y -axis.

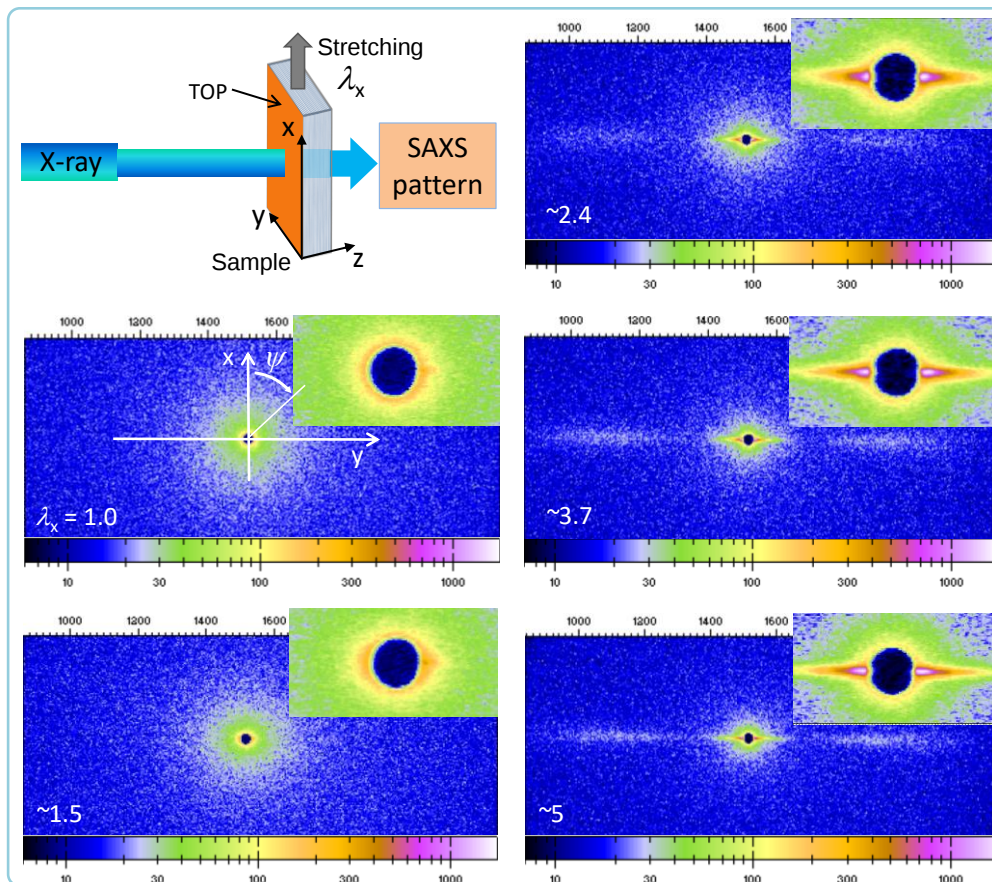


Figure 7. In situ small-angle X-ray scattering (SAXS) experiments of the lamellar gel performed during tensile deformation in a high q -range (0.05 - 5.0 nm^{-1}). Set-up of the gel deformation and X-ray scattering are shown. Tensile deformation was applied vertically, in parallel to the lamellae, and the X-ray was imposed perpendicular to the lamellar plane. 2D SAXS image was collected behind the sample. Some selected 2D SAXS images of PDGI/PAAm gel at different elongation ratios, λ_x . Inset images are the magnified view of low q -range.

To analyze the rod-like structures, the scattering intensity, I in the equatorial direction is analyzed for various deformations. **Figure 8a** shows the plots of intensity vs. q for various λ_x , where the intensity is integrated over an azimuth angular range ($\psi = 90 \pm 5^\circ$) on the equatorial axis. The intensity decreases rapidly in low q -range, which is characteristic for the streak pattern. Interestingly, a broad peak was clearly visualized at a q -value of $\sim 1.34 \text{ nm}^{-1}$, corresponding to a d -spacing of $\sim 4.7 \text{ nm}$ for elongation at and above $\lambda_x = 2.4$. The scattering intensity at small q ($< 0.5 \text{ nm}^{-1}$) also increases at and above $\lambda_x = 2.4$. The normalized intensities, $(I - I_0)/I_0$, for $q = 0.07 \text{ nm}^{-1}$ and 1.34 nm^{-1} at various λ_x are shown in **Figure 8b**. A sudden jump at $\lambda_x = 2.1$ are clearly observed, indicating the rod-like structure formation above this elongation. This critical elongation is slightly above the yielding point (**Figure 1b**).

2.4 Determination of the domain size formed during elongation

Ruland streak method is employed to analyze the streak in SAXS patterns for estimating the size of structure formed during elongation of the gel.^{27–29} According to the Ruland method, the scattering from rod-like objects follows the Lorentzian distribution. The apparent azimuthal width, B , is a function of rod length (L), and the azimuthal width (B_ϕ) due to mis-orientation,

$$B = \frac{2\pi}{Lq} + B_\phi$$

Here, B represents the integral half peak width of the azimuthal profile from the SAXS streak. According to the above equation, L can be estimated from the slope of the linear plot $B \sim 1/q$.

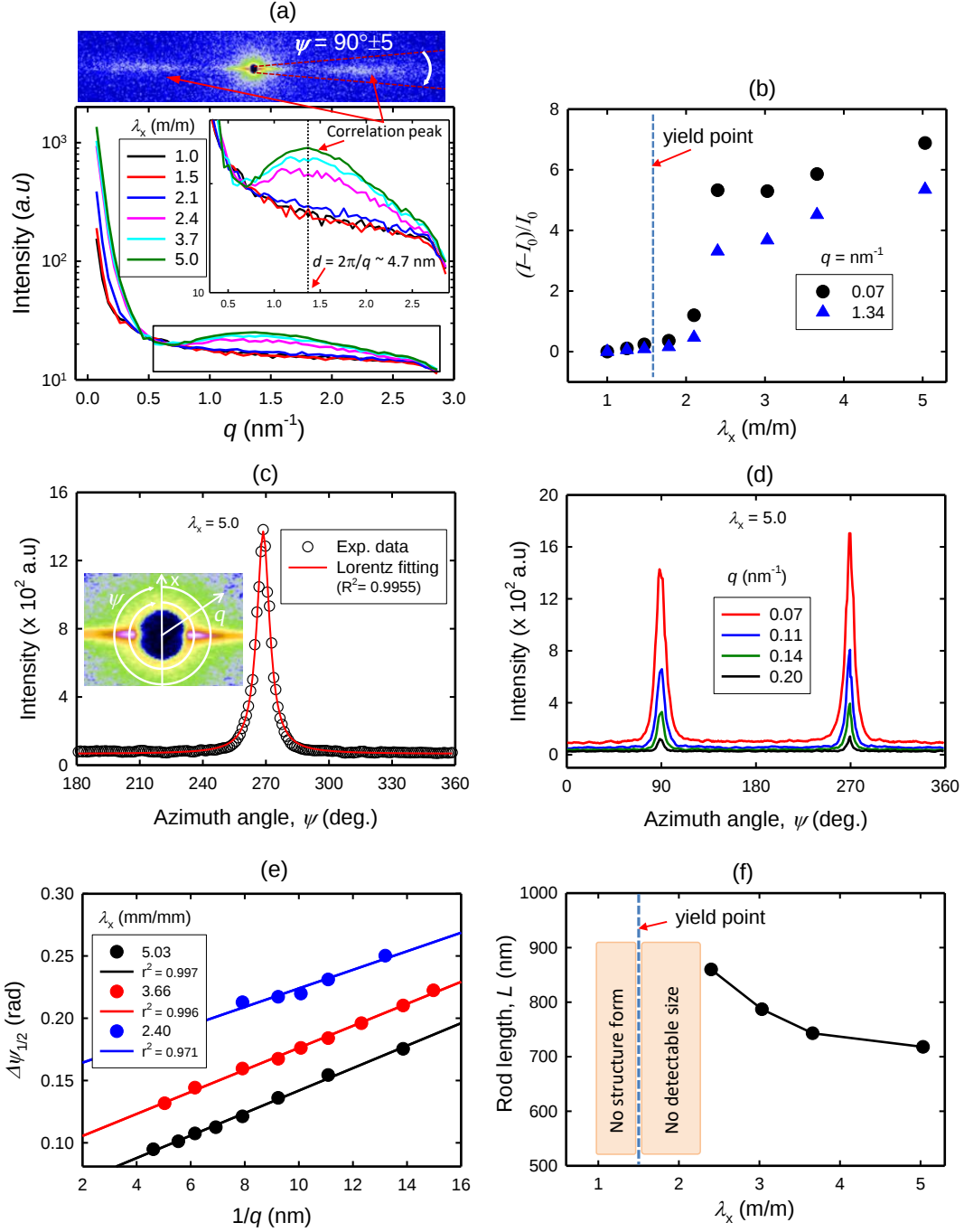


Figure 8. Analysis of structure transformation and Ruland streak method for size estimation of tensile-induced rod-like structure. (a) 1D SAXS intensity vs. scattering vector, q obtained from 2D SAXS images (**Figure 7**). The intensity is an integration of azimuth angle, ψ , over a narrow range ($\psi = \pm 5^\circ$) in the equatorial direction. (b) Intensity ratio $[(I-I_0)/I_0]$ at $q = 0.07$

and 1.34 nm^{-1} are shown at various deformations (λ_x). Here, I and I_0 are intensity for λ_x 's and $\lambda_x = 1$, respectively. Intensity ratio for $q = 1.34 \text{ nm}^{-1}$ are multiplied by a factor of 10 to fit in the plot scale. (c) Lorentz profile fitting of the 1D SAXS intensity vs. azimuth angle (ψ) plot. The plot was obtained by integrating the 2D SAXS image of the gel ($\lambda_x = 5.0$) at a scattering vector, $q = 0.05 \text{ nm}^{-1}$. (d) Intensity vs. ψ profiles at various q at a fixed elongation ($\lambda_x = 5.0$). Azimuthal widths at various q are obtained from fitting curve of Lorentz functions. (e) The Ruland plots, azimuthal width ($\Delta\psi_{1/2}$) vs. $1/q$, for various λ_x above 2.4 show linear correlation. (f) Average length of rod-like structure at various deformations estimated from the Ruland streak method. The rod length (L) is obtained from the slope of straight line of azimuthal widths, $\Delta\psi_{1/2}$ vs. $1/q$ plots for various λ_x . No detectable rod-like structure is formed at $\lambda_x < 2.4$.

The plot of intensity vs. azimuthal angle (ψ) (**Figure 8c**) shows the azimuthal distributions of intensity profile at $q = 0.05 \text{ nm}^{-1}$ of $\lambda_x = 5$ which is well fitted by the Lorentzian distribution. The Lorentzian fitting of intensity vs. azimuth angle (ψ) profiles for various q ranges at the fixed elongation ($\lambda_x = 5$) are shown in **Figure 8d**. Azimuthal width, $\Delta\psi_{1/2}$, was calculated from the fitted Lorentzian profiles for various q ranges of different λ_x . $\Delta\psi_{1/2}$ vs. λ_x for various q ranges are shown in **Figure S3a**. It is worth to mention here that initial sharp decreasing of $\Delta\psi_{1/2}$ with λ_x and saturation above $\lambda_x = 2.1$ indicates the detectable structure formation at large deformation. **Figure 8e** shows the Ruland plot, $B(=\Delta\psi_{1/2})$ vs. $1/q$, for various λ_x . The azimuthal width shows good linearity at and above λ_x of 2.4. Below $\lambda_x = 2.4$, plot of $\Delta\psi_{1/2}$ vs. $1/q$ shows poor linear correlation, as observed in **Figure S3b** for $\lambda_x = 1.78$, as an example. These results indicate that the rod-like structure starts to appear at $\lambda_x = 2.4$. The length of rod, L , decreases modestly from 860 to 720 nm, with the increase of λ_x from 2.4 to 5, as shown in **Figure 8f**.

2.5 Mechanism of the overall structure transformation

From the above structure analysis, we summarize the structure evolution of the lamellar gel during elongation by illustration shown in **Figure 9**. At rest ($\lambda_x = 1$), the lamellar bilayer possesses slight undulation (**Figure 9a**). With small elongation along the x-axis, the undulation disappears (**Figure 9b**) as revealed by the peak sharpening of SAXS (**Figure 6d**). At $\lambda_x \sim 1.6$, the bilayer assembly starts to yield by reassembling into an elongated shape while maintaining nearly the constant area. Above yielding ($\lambda_x > 1.6$, **Figure 1b**), the bilayer starts to have micro-cracks (**Figure 9c**), which are revealed by sudden peak broadening of optical (**Figure 1d**) and SAXS (**Figure 6d**) spectra, as well as slight increase in sample surface area (**Figure 2b**). At $\lambda_x > 2.4$, the ruptured bilayer transforms to fibrils of 720–860 nm in length aligned along the elongation direction (x-axis) and the average side-to-side correlation of fibrils is ~ 4.7 nm along the y-axis (**Figure 9d**), as noticed in **Figure 8f** and **Figure 8a**, respectively. The average side-to-side spacing of fibrils is equal to the diameter of single wall string micelle of PDGI molecules. The formation of string micelle destroys the inter-lamellar correlation along the z-axis, as revealed by the decrease in birefringence (**Figure 4b**) and the SAXS peak broadening (**Figure 6b**) observed from the cross-section of the gel at large elongation. The distinct increase in the sample surface area at large elongation (**Figure 2b**) is due to the bilayer ruptures and string micelle formation.

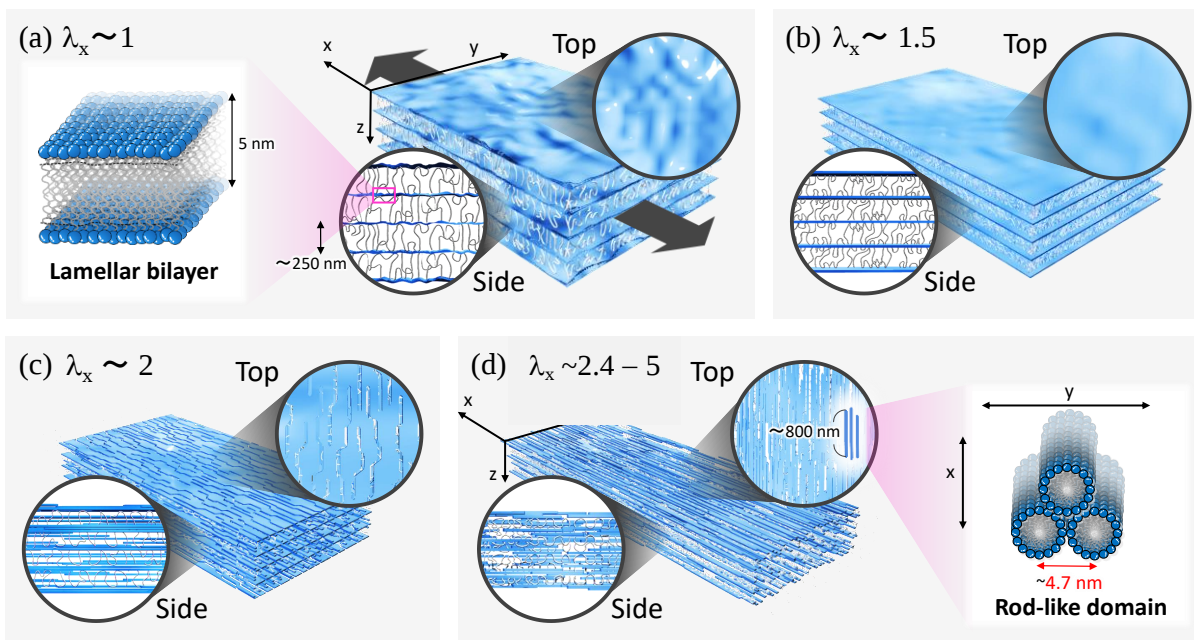


Figure 9. Schematic illustration of structure changes during tensile deformation of the lamellar gels. (a) At rest ($\lambda_x = 1$), lamellar sheets are in 1D crystalline structure with slight undulation of the bilayers. (b) With small tensile deformation ($\lambda_x \sim 1.5$), the undulation disappears and the lamellar bilayer becomes flat. Above the yielding point ($\lambda_x \sim 2.0$), the rigid bilayer assembly starts to yield, generating micro-cracks. (d) At large strain ($\lambda_x = 2.4 \sim 5.0$), rod-like PDGI bundles are formed that align along the deformation (x-axis). The rod-like domains possess side-to-side correlation with wide distribution of spacing (an average of ~ 4.7 nm) along the y-axis. The distortion of lamellar bilayers causes poor correlation between the layers along the z-axis. Therefore, perfect 1D lamellar structure of PDGI/PAAm gel disappears.

The uniaxially aligned surface textures of the PDGI/PAAm gel along the elongation direction observed in microscope (**Figure 3b**) are in excellent agreement with fiber bundle alignment in SEM images (**Figure 5a**) and the string micelle formation determined from SAXS pattern (**Figure 7 and 8**). It should be noted that, the size of hierarchical fiber bundles (width of 1 ~100

μm) in SEM images (**Figure 5a**) are significantly larger than the size of string micelles (4.7 nm width and $\sim 0.8 \mu\text{m}$ length). The large size bundles (diameter of $1 \sim 100 \mu\text{m}$) are beyond the observation scale of SAXS measurement.³⁰ The hierarchical micro-to-nano structure elucidated in this study is in analogous to the hierarchical structure found in tendon/ligament³¹ in which primary, secondary and tertiary fiber bundles (1 to several $100 \mu\text{m}$) are formed from tropo-collagen/fibrils (several nm to $1 \mu\text{m}$).

The above structure analysis shows that the transformation of the lamellar bilayer structure in to fibrous structure is initiated by the rupture of the lamellar bilayers during tensile deformation. However, the rupture occurs in the direction of elongation, which is different from simple expectation.²⁵ It is associated with the different deformation modes between hydrophobic lamellar bilayers and isotropic PAAm hydrogel layers. The bilayers intend to maintain a constant area during deformation while the PAAm layers intend to deform isotropically and therefore their surface area increases with deformation. Since the lamellar layers of several nanometer-thick are imbedded in the soft and elastic PAAm matrix of several hundred nm thick, large internal stress mismatch is generated between bilayers and PAAm gel layers. As a result, the PAAm gel layers exert a tension on PDGI bilayers in the transverse direction (y-axis) during elongation along the x-axis. This tension breaks the bilayers into pieces along the x-axis and to stabilize the structure, the bilayers form rod-like domain along the elongation direction. We note that such structure change of the rigid and thin bilayers imbedded in soft hydrogel layers is very different from the deformation of a free-standing thin sheet. For a free thin sheet with large aspect ratio, elongation usually induces wrinkle formation in thickness direction since the bending requires much lower energy than the stretching deformation.²⁶ As PDGI thin sheet are imbedded into thick PAAm layers in this gel system, the wrinkle formation is suppressed.

The deformation-induced breaking of the lipid-like bilayers inside the isotropic hydrogel matrix accounts for the large and reversible hysteresis observed during cyclic tensile deformation.¹⁸ The large energy dissipation due to rupture of the hydrophobic association of the bilayers explains the high toughening of the PDGI/PAAm gel.¹⁸ Furthermore, the fiber structure along the tensile direction imbedded in the soft PAAm matrix should suppress the crack growth along the direction vertical to the fiber orientation, and therefore enhances the crack resistance dramatically.¹⁸ The role of fiber structure for the enhancement of toughness has common features with the soft collagenous tissues found in tendon or ligament.^{32,33}

3. CONCLUSIONS

In this paper, anisotropic hydrogel sheets that consist of several thousands of alternating layers of PDGI lamellae and PAAm matrix have been vigorously investigated during uni-axial tensile elongation. The unique mechanical behaviors such as sharp tensile yielding, large extensibility, and extremely high crack resistance are associated with the structure transformation of the PDGI/PAAm gel. Macroscopic geometry and microscopic structure change of lamellar bilayers under elongation are correlated with *in situ* X-ray scattering under tensile elongation in reciprocal space. The study reveals the generation of fiber bundle structures (~ 100 to $1\ \mu\text{m}$ in width) and fibril-like string micelles ($\sim 0.8\ \mu\text{m}$ in length and $\sim 4.7\ \text{nm}$ in diameter) under elongation above the yield point, which are aligned along the deformation axis. Formation of multi-scale fiber bundles made of string-like micelles explains the energy dissipation mechanism together with high toughness. At large elongation, the alternating arrangement (along x-axis) of PDGI lamellae and PAAm matrix transforms into a new structural arrangement in which PDGI

fiber bundles are aligned alternately with the soft PAAm matrixes (along the y-axis, vertical to the elongation axis). These newly formed alternating arrangements of rigid rod (fiber bundle) and soft polymer matrix should carry the stress at crack front and dramatically suppress the crack growth at large elongation. The crack tolerance of this gel will be reported by a separate paper.

4. EXPERIMENTAL SECTIONS

4.1 *Gel preparation*

PDGI/PAAm gel was prepared by simultaneous free radical polymerization from aqueous solution of 0.10 M dodecylglyceryl itaconate [DGI; $n\text{-C}_{12}\text{H}_{25}\text{-OCOCH}_2\text{C(=CH}_2\text{)COOCH}_2\text{CH(OH)CH}_2\text{OH}$], 0.025 mol% sodium dodecyl sulfate of DGI, 2 M acrylamide (AAm), 2 mM *N,N'*-methylenebis(acrylamide) (MBAA) as a cross-linker of AAm and 2 mM Irigacure as an initiator. Sheet-shape gel sample with 1D lamellar bilayer structure parallel to the sheet surface was achieved following the same procedure described in our previous paper.¹⁴ Briefly, *prior to* the polymerization, by applying a shear flow to the precursor solution, thousands of lamellar bilayers of self-assembled DGI were aligned in one direction parallel to the surface of glass substrate. After polymerization, bilayers of polymeric PDGI were stacked periodically and entrapped in the PAAm matrix to give an anisotropic and mechanically tough hydrogel. The single PAAm gel was prepared from 2 M AAm, 2 mM MBAA, and 2 mM Irigacure. The gels were swelled in water and attained equilibrium before using. The sample contained ~95 wt% water, and was ~1.2 mm thick.

4.2 *Tensile test*

Tensile stress-strain properties of the gel samples were analyzed with a commercial test machine (Tensilon RTC-1310A, Orientec Co.). *Prior to* the test, the sheet-shape bulk gel was cut with dumbbell shape standardized size [length = 50 mm, width = 5 mm, gauge length = 12 mm, gauge width = 2 mm] by the gel cutter (JIS-K6251-7). Longitudinal elongation ratio λ_x was obtained from optical extensometer. Two marking lines separated with a distance L_0 were made on the sample and the length between the marking line during elongation was measured. The true elongation ratio λ_x was estimated from the length ratio L/L_0 . Nominal stress (engineering stress), was calculated from the tensile force divided by the initial cross section area of the sample. The sample was elongated by the tensile machine at a cross-head velocity of 60 mm/min. The deformation rate is estimated as 0.08 s^{-1} .

4.3 *Small-Angle X-ray Scattering (SAXS)*

SAXS measurements of PDGI/PAAm gel were performed using two sets of beamlines with different ranges of scattering vector, q , were performed in high-brightness synchrotron radiation X-ray facility SPring-8 (JASRI, Hyogo, Japan). The first measurements at low q -range (for large scale structure), to observe the lamellar structure change, were performed at beamline BL40B2. The X-ray beam size was horizontal $500 \text{ } \mu\text{m}$ $\times$ vertical $500 \text{ } \mu\text{m}$. The X-ray wavelength was 0.15 nm , and sample-to-detector distance was 4.13 m . Both the X- and Y-pixel size of detector was $100 \text{ } \mu\text{m}$. The elongation axis was set vertical to the equatorial direction. The sample (width: 1 mm ; length: 20 mm [between clamps]; thickness: 1.2 mm) was fixed at the clamps of a computer controlled tensile deformation stage [Linkam, Model-10073A]. The stage was positioned in the X-ray irradiation setup to stretch the sample vertically. The gel was stretched, step-wisely, to various strains at a velocity of 60 mm/min (initial strain rate 0.05 s^{-1}). The X-ray exposure time

at each strain was 10 s. During the X-ray exposure, the sample was hold at the constant strain. The back scattering 2D patterns were recorded on an imaging camera. Two geometries of sample, the lamellar plane of gel was set to be parallel to the X-ray (**Figure 6a**), and the lamellar plane of gel was set to be vertical to the X-ray (**Figure S3a**), were measured. The 2D image was converted to 1D data using data analysis software (Fit2D, version 12_077).³⁴ From q value of first-order peak, inter-bilayer distance, d was calculated as $d = 2\pi/q$, where q is the modulus of scattering vector.

The second experiments at high q -range (for small scale structure) were performed at the same beamline mentioned above, SPring-8. The X-ray wavelength was 0.10 nm, and sample-to-detector distance was 1.74 m. The lamellar plane of gel was set to be perpendicular to the X-ray (**Figure 6b**). The sample (width: 5 mm; length: 16 mm [between clamps]; thickness: 1.2 mm) was fixed at the clamps of a computer controlled tensile deformation stage. The X-ray exposure time at each strain was 5 seconds. The back scattering 2D patterns were recorded on an imaging camera. Other conditions are the same with those of the first experiment.

The X-ray scattering of the pure PAAm gel was performed at the beamline BL05XU, SPring-8. The beam size was 200 μm (horizontal) x 128 μm (vertical). The X-ray wavelength was 0.1 nm, and sample-to-detector distance was 3.87 m. Both the X- and Y-pixel size of detector was 172 μm . The elongation axis was set vertical to the equatorial direction. The sample (width: 5 mm; length: 20 mm; thickness: 1.6 mm) was fixed at the clamps of a custom-made tensile deformation stage. The stage was positioned in the X-ray irradiation setup to stretch the sample vertically. The gel was stretched, step-wisely, to achieve various strains. The X-ray exposure

time at each strain was 10 s. During the X-ray exposure, the sample was hold at the constant strain. The back scattering 2D patterns were recorded on an imaging camera..

ASSOCIATED CONTENT

Supporting Information. Supporting figures, discussions and methods of experimental details such as reflection spectrum, measurement of transverse sample size at longitudinal elongation, optical observation, and scanning electron microscope (SEM) observation are described in supporting information.

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AUTHOR CONTRIBUTIONS

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