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## **Anisotropic Hydrogel Based on Bilayers: Color, Strength, Toughness, Fatigue Resistance**

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## **ABSTRACT**

In this highlight, we introduce a novel anisotropic hydrogel with a perfect 1D photonic crystal structure based on the uni-axial alignment of lamellar bilayers. The gel was synthesized in a one-pot polymerization from a precursor solution containing polymerizable surfactant (dodecyl glyceryl itaconate: DGI), acrylamide, and cross-linker. By applying shear flow to the precursor solution, lamellar bilayers of self-assembled DGI were aligned in one direction parallel to the substrate surface. The polymerized lamellar bilayers were stacked periodically and entrapped in the polyacrylamide matrix to give a hydrogel with 1D photonic crystal structure. This hydrogel, containing 94-95 wt% water and 1.0-1.5 wt% bilayer molecules, shows perfect one-dimensional swelling, strong anisotropy in the elastic modulus, and magnificent structural color by multilayer interference according to Bragg's law of diffraction. Owing to the softness and large deformability, the color of the gel can be reversibly tuned by both compressive and tensile mechanical stimuli over the entire wavelength range of visible color. The single-domain lamellar bilayer not only diffract light, but also serves as reversible sacrificial bonds that dissociates upon deformation, exhibiting large hysteresis as an energy dissipation mechanism, which gives the gel high tensile strength and fatigue resistance. Both the molecular dissociation and lipid-like mobile nature of DGI molecules in the bilayers dramatically enhance the resistance against crack propagation by the formation of extra-ordinary blunting, which gives the gel an extraordinarily high toughness.

## 1. Introduction

Biological soft tissues have two structural characteristics. One is their water-containing structures. Most of soft tissues contain 50-85 wt% water by volume. The hydroscopic structure enables biological soft tissues to serve as a medium for dynamic vital activities. The other is their well-defined hierarchical structures ranging from the molecular scale to the macroscopic scale. The fact that biological soft tissues contain suitable amount of water to ensure molecular mobility and at the same time they possess sophisticated structures is the true nature which enables biological tissues to create superb performances.<sup>1-5</sup> For example, the fast and robust contraction of muscle in a specific direction is owing to their hierarchical structure, where actins and myosin form the liquid crystalline anisotropic structure called sarcomere.<sup>5-7</sup>

Polymer hydrogel is also a water-containing substance, categorized as *soft and wet matter* the same as biological soft tissues. They are expected to simulate biological tissues, such as muscles, cartilages, etc.<sup>8-13</sup> However, most of the artificially created hydrogels are amorphous in structure with random cross-linking of hydrophilic polymer chains. Due to the [lack](#) of any sophisticated structure, hydrogels do not show any superb function as living bodies do. Introducing living-body like sophisticated structures, either by conventional equilibrium chemistry or by novel non-equilibrium chemistry, into synthetic polymer hydrogels would be the next challenge for gel scientists.

In this article, we highlight on an anisotropic hydrogel system that contains macroscopic, single-domain, periodical stacking of integrated microscopic lamellar bilayers inside the polymer matrix of the hydrogel. This hydrogel is synthesized by combining the self-assembly process of surfactant-like molecules (equilibrium chemistry) and the mechanical shear to the precursor solution of the gel (non-equilibrium chemistry). Periodical stacking of the bilayers in the hydrogel selectively diffract visible light to exhibit magnificent structural color. Due to the uniaxial orientation of the bilayer, the hydrogel possesses superb

functions that have never been realized before, such as the one-dimensional swelling, anisotropic Young's modulus, anisotropic molecular permeation and diffusion. Furthermore, the rigid and brittle bilayers also serve as reversible sacrificial bonds to ensure excellent mechanical performance of the hydrogel such as high strength and toughness, self-recovery, and high fatigue resistance. The hydrogel exhibits excellent color tuning ability over a wide spectrum range by mechanical stimuli.

## 2. A hydrogel system containing bilayer membranes

Dodecyl glyceryl itaconate (DGI:  $n\text{-C}_{12}\text{H}_{25}\text{OCOCH}_2\text{C}(\text{=CH}_2)\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ) is an amphiphilic molecule containing a polymerizable vinylic double bond in the hydrophilic end (**Figure 1a**). DGI has a very low solubility in water and the Krafft point is about 43°C. When the concentration exceeds its critical micelle concentration, DGI molecules tend to self-assemble into aggregated structures in aqueous phase at the temperature above the Krafft point.<sup>14-17</sup> Pure DGI self-assembles into onion-like bilayer membrane structures or multi-lamellar vesicles. In presence of ionic surfactants (sodium dodecyl sulfate: SDS), these bilayer membranes change into lamellar structures with periodical spacing depending on the concentrations of the surfactants (**Figure 1b**). The lamellar bilayer domains are randomly oriented to give isotropic solution on the macroscopic scale. Tuning of the periodical stacking distance of bilayers can induce iridescent color of the solution due to Bragg diffraction of randomly oriented lamellar bilayer domains in macroscopic scale of bulk solution.

Tsujii *et al* initially developed a hybrid hydrogel system consists of polyacrylamide (PAAm) network and PDGI bilayers.<sup>16</sup> The PDGI/PAAm hydrogel was prepared by simultaneous free radical polymerization from aqueous solution of DGI, sodium dodecyl sulfate (SDS), acrylamide (AAm) as monomer, MBAA (*N,N'*-methylenebis acrylamide) as cross-linker, and Irgacure 2959 as initiator. Since the bilayer structure is maintained even in this aqueous solution and DGI molecules contain polymerizable vinylic double bond, the

bilayer structure of the polymeric-DGI (PDGI) is immobilized and stabilized inside the polyacrylamide (PAAm) network structure after polymerization (**Figure 1b**). It has been elucidated that DGI is homo-polymerized and entrapped in the PAAm network without forming covalent bonds with PAAm and the cross-linker (MBAA).<sup>18</sup> The gel exhibits iridescent multi-colors, and is isotropic in macroscopic scale, similar to the precursor solution.<sup>16,17</sup>

### 3. Shear-induced uni-axial orientation of bilayer sheets in hydrogel

Recently, *Haque et al.* have developed a method to synthesize anisotropic PDGI/PAAm hydrogel by applying a strong shear to the precursor solution, in which the lamellar bilayers are aligned uni-axially along the substrate up to the macroscopic scale.<sup>19</sup> Aqueous solution containing prescribed amounts of DGI, 0.025 mol% SDS (molar percentage is in relative to DGI), 2 M AAm, 0.05-0.1 mol% MBAA, and 0.1 mol% Irgacure 2959 (the molar percentages are relative to AAm) was left to stand in a water bath at 55°C for about 4 h until the formation of stable lamellar bilayers. The solution was purged in an argon atmosphere to remove the dissolved oxygen. The precursor solution was injected, with a pipette, into the 500- $\mu\text{m}$ -thick reaction cell of 10 cm length and 1 cm width. The injection speed of the solution was about 5  $\text{cm s}^{-1}$ , corresponding to a shear rate of 200  $\text{s}^{-1}$ . As the precursor solution contained randomly oriented micro-domains of stable lamellar bilayers, the strong shear induced the bilayer micro-domains to align in one direction parallel to the glass substrates in the cm-scale (**Figure 1c**). By UV polymerization for 8 h at 50°C under an argon gas atmosphere, the uni-axial lamellar structure of PDGI was immobilized and stabilized inside the PAAm network. Therefore, an anisotropic hydrogel film (thickness: 500  $\mu\text{m}$ , length: 10 cm, width: 1 cm) was obtained in which lamellar bilayer sheets oriented parallel to the wide surface of the film. At the as-prepared state, the sheet-shaped anisotropic PDGI/PAAm gel films are almost transparent and show Bragg's diffraction in ultra-violet wavelength band ( $\lambda_{\text{max}} < 350 \text{ nm}$ ), but

after reaching equilibrium swelling in water, they exhibit excellent visible color ( $\lambda_{\max} = 400\text{-}700\text{ nm}$ ).<sup>19</sup>

#### 4. Hierarchical structure and anisotropic property

The anisotropic PDGI/PAAm hydrogel contains single-domain, lipid-like PDGI lamellar structure stacked inside the PAAm matrix. The thickness of one PDGI bilayer is  $4.7\text{ nm}$ <sup>14</sup> and that for PAAm layers varies between  $150\text{-}300\text{ nm}$  depending on the DGI concentration and the swelling degree of PAAm networks.<sup>19,20</sup> The hydrogel contains  $94\text{-}95\text{ wt\%}$  water,  $1.0\text{-}1.5\text{ wt\%}$  PDGI, and  $4\text{ wt\%}$  PAAm at swollen state. The photographs of the PDGI/PAAm gels prepared at various DGI concentrations are shown in **Figure 2a**. The gels exhibit magnificent structural color due to the homogeneous Bragg's diffraction by the multi-lamellar planes (**Figure 2a**). The very pure color of the gel over cm-scale indicates that the PDGI bilayers, *nanometer* in thickness, are periodically stacked in the PAAm network with a *macroscopic* ordering. This is in sharp contrast to the PDGI/PAAm gel synthesized with no shear or weak shear, which shows multi-colors and/or iridescence due to random orientation of the micro-scale bilayer domains in the macroscopic bulk gel.<sup>16</sup> The uni-axially oriented bilayer structure of the PDGI/PAAm gel is also confirmed by the transmission electron microscope (**Figure 2b**) observation, small angle X-ray scattering (**Figure 2c**), and polarized optical microscope (POM).<sup>19,20</sup>

Owing to the global uni-axial orientation of the lamellar bilayers, the gel has a strong anisotropy in its macroscopic properties. This is clearly observed from the anisotropic swelling of the PDGI/PAAm gel at various concentrations of DGI (**Figure 3a**). At zero concentration of DGI, the PAAm gel possesses identical swelling ratios in the three different directions. However, by incorporating DGI, the swelling ratio of the sheet gels along the length ( $L_1/L_0$ ) and width ( $W_1/W_0$ ) axes decrease sharply, whereas that along the thickness axis ( $T_1/T_0$ ) increases sharply above  $0.07\text{ M}$  of DGI. The swelling anisotropy is enhanced by

further increase in the DGI concentration; above a critical DGI concentration of 0.10 M, the swelling ratio in the thickness direction ( $T_1/T_0$ ) saturated to a constant value, whereas no swelling was observed at all in the length and width directions of the sheet-shaped sample ( $L_1/L_0=1$ ,  $W_1/W_0=1$ ). That is, above 0.10 M DGI concentration, the lamellar bilayers formed continuous structure in the gel. Therefore, the gel swelled only in the direction perpendicular to the plane of the PDGI lamellar bilayers because the PAAm network can swell freely only in this direction but in the other two directions (parallel to the plane of the PDGI lamellar bilayers), the swelling of PAAm was completely restricted by the rigid lamellar bilayers. As shown in **Figure 3a**, no difference was observed between the swelling ratios in the length and width directions of the sample, *i.e.*, parallel to the lamellar layers, indicating that the shear flow did not cause any in-plane anisotropy.

Above the critical DGI concentration that continuous lamellar bilayers were formed, water cannot diffuse perpendicular to the lamellar plane due to impermeable nature of the bilayer membrane, so swelling occurred due to the water diffusion parallel to the lamellar plane. This anisotropic diffusion is demonstrated in **Figure 3b** that shows swelling kinetics of the PDGI/PAAm gel with a DGI concentration of 0.1 M, above the critical concentration. The swelling ratio along the thickness axis ( $T_1/T_0$ ) increased with the progress of time whereas no swelling is observed at all along the length axis ( $L_1/L_0=1$ ). **Figure 3b** also shows that the swelling process was very slow since the characteristic length of swelling in this case was not the thickness but the width of the sheet-shaped sample ( $W_0= 0.8$  cm).<sup>21</sup> Therefore, the anisotropic swelling in the gel is attributed to the formation of 1D crystal structure of PDGI bilayer membrane.

Concomitant with the appearance of the anisotropic swelling, the PDGI/PAAm gel showed strong anisotropy in its mechanical properties. The elastic modulus of the gel along the lamellar layer direction ( $E_{\parallel}$ ) and perpendicular to the lamellar bilayer direction ( $E_{\perp}$ ) are



shown in **Figure 3c**. The original PAAm gel possessed an isotropic elastic modulus ( $E_{\parallel} \cong E_{\perp}$ ). However, by adding DGI, a sharp rise in  $E_{\parallel}$  could be observed, whereas  $E_{\perp}$  did not change significantly. The dramatic increase in  $E_{\parallel}$  led to anisotropy in the elastic modulus, with the value of  $E_{\parallel}$  being one order of magnitude higher than  $E_{\perp}$ . As the PDGI lamellar bilayers formed continuous single domain,  $E_{\perp}$  arose primarily from the very low modulus of PAAm network, whereas  $E_{\parallel}$  arose from both the PAAm network and rigid PDGI bilayers, which had probably a very high modulus. The single-domain lamellar structure made it possible to estimate the tensile elastic modulus of the PDGI bilayer ( $E_{\text{PDGI}} \sim 4$  MPa) from  $E_{\parallel}$  by using a stratified layer structure model of a composite material composed of two alternate layers, one is hard and the other soft, where the PDGI lamellar bilayer was considered as the hard layer and the PAAm networks as the soft layer.<sup>19,22,23</sup>

## 5. Mechanical strength and toughness

The PDGI/PAAm hydrogel possesses the structure that several thousands of rigid bilayers (1D photonic crystal) are uni-axially stacked periodically in the soft PAAm matrix (**Figure 1a**). This 1D photonic crystal structure not only gives bright structural color, similar to that in some biological systems, such as the iridophore of tropical fishes, octopus, squid, and beetle,<sup>24,25</sup> but also leads to the emergence of excellent mechanical functions. As is well-known, some extra-ordinary tough materials, such as nacre and abalone, are derived from their soft/hard multi-layered structure.<sup>22,26</sup> The PDGI/PAAm hydrogel also exhibited excellent tensile strength and toughness, as shown in **Figure 4**. The rigid bilayers in the soft polymer matrix sustain the tensile stress and they yield at a large stress due to the dissociation of the hydrophobic packing of PDGI molecules. The PDGI molecules recover to the association state after the removal of stress, as schematically shown in **Figure 4a**. Thus, the rigid bilayers serve as reversible sacrificial bonds to delocalize the stress and enhance the crack resistance at the crack tip, similar to that observed in the bones.<sup>27,28</sup> Accompanying with

the tensile deformation, the color of the gel changed from orange to blue, which is shown by the images taken at free-standing as well as the elongated state (**Figure 4a**). The tensile stress-strain curves for the PAAm gel, PDGI/PAAm gel having uni-axial bilayer structure, and the PDGI/PAAm gel without having uni-axial bilayer structure are shown in **Figure 4b**. The PAAm gel fractured at a tensile stress and strain of 38 kPa and 11 m/m, respectively, while the tensile fracture stress and strain of the PDGI/PAAm gel that has uni-axial bilayer structure are dramatically improved up to ~600 kPa and ~22 m/m, respectively, and a clear yielding is observed at low strain of the stress-strain curve. In sharp contrast, the PDGI/PAAm gel that has no bilayer structure shows a stress-strain curve without yielding, similar to that of the PAAm gel, only with a slight increase in the modulus and fracture stress. The dramatic enhancement of the tensile strength of the PDGI/PAAm gel is, therefore, attributed to the macroscopic single-domain bilayer structure inside the PAAm network.

The hysteresis behaviors for the PDGI/PAAm gel were observed by cyclic tensile test. As expected for a conventional chemically cross-linked gel that is purely elastic, no hysteresis loop appears in the single PAAm gel (**Figure 4c: inset**). On the contrary, PDGI/PAAm gel with bilayer structure shows strong hysteresis, indicating the energy dissipation and the structure change of the bilayer (**Figure 4c**). Before yielding, the hysteresis appears, indicating that the associated hydrophobic side groups of PDGI experience the plastic deformation under tensile stretching. Above the yielding strain, the polymer backbone of the PDGI that was in random coil conformation starts to be extensively elongated, so that the associated hydrophobic side groups are forced to dissociate, behaving like sacrificial bonds. The latter process absorbs a large amount of energy for hydration, which increases the resistance against crack propagation. To confirm the reversible nature of the sacrificial bond, the consecutive hysteresis cycles with the same sample at gradual increasing levels of maximum strain were performed. All the cycles follow the same loading curves and different unloading curves,

implying that the stiffness of the gel recovers to its initial state after each deformation cycle, which is a clear indication of self-recovery of the initial stiffness of the gel upon successive loading with a certain rest time. This behavior shows a complete absence of Mullins effect, in contrast with observations for the reported double network (DN) gels.<sup>29-31</sup> Significant hysteresis has been noted in the first loading cycle of DN gel, but no recovery was observed due to the permanent breaking of chemical bonds in the brittle polyelectrolyte PAMPS (2-Acrylamido-2-methyl- propanesulfonic acid) network structure.<sup>21,32</sup> So, the rigid PDGI bilayers in the PDGI/PAAm gel serve as the reversible sacrificial bonds whereas the brittle PAMPS network in the DN gel serves as irreversible sacrificial bond. It is worth noting that a recovery time (up to 30 min at a maximum strain of 6) is required between two successive cycles to achieve the original dimensions and stiffness of the PDGI/PAAm gel sample. Most of the stiffness and dimensions are recovered within 1 min and then the slow recovery process takes relatively longer time up to several 10 min.<sup>20</sup> This indicates two types of recovery processes of the structure. Both the quick and slow recovery of the strain is owing to the polymeric nature of PDGI and PAAm, driven by elastic and entropic restoring forces of PDGI backbone as well as PAAm network and the slow recovery of the strain is due to the strong hydrophobic interaction of the associated PDGI molecules. The recovery of the stress is attributed to the re-association (fast) and re-organization (slow) of the hydrophobic PDGI side groups driven by the high interfacial tension between PDGI hydrophobic chain and water. The hysteresis loop of the PDGI/PAAm gel at a fixed maximum strain is repeatable over a series of loading-unloading cycles, which is an indication of ‘fatigue resistance’ of such materials.<sup>20</sup>

Due to the lipid-like nature of the bilayers, the PDGI/PAAm gel showed a very high toughness, as observed by its high resistance against the propagation of a pre-existed crack in the pure shear fracture test (**Figure 5**). When the gel having an initial crack/notch (**Figure 5a**) is elongated (strain,  $\epsilon \sim 3$  or even more) perpendicular to the crack direction, a huge blunting

with an extra-ordinary pestle and/or trumpet shape occurs at the crack tip. As a result, there is no stress concentration at all in front of the crack tip, as revealed by the homogeneous blue shift of the gel color over the blunting and the whole stretching area (**Figure 5b,c**). After releasing the stress, the gel gradually returns back to the original dimension and color after several minutes, showing a very small crack propagation distance of about 1 mm (**Figure 5d**). The results are in sharp contrast to most conventional gels including DN gel and the PAAm gel, where the crack easily propagates at small strain ( $\epsilon < 1$ ). We assume that besides the yielding effect or molecular dissociation of the PDGI bilayers, the mobile or lipid-like nature of the bilayer is crucial to form the extra-ordinary blunting at the crack tip. The recovery of the bilayer structure driven mainly by elastic restoring force of the PDGI polymeric backbone, on the other hand, gives the solid-like nature of bilayers. The delicate balance between the liquid-like and solid-like natures of the PDGI chains during stressing and releasing make it extra-ordinarily tough and self-recoverable.

## **6. Color tuning by mechanical stimuli**

The PDGI/PAAm gel exhibits magnificent color in the visible wavelength region due to Bragg's diffraction. When the gel with an initial color of red was compressed perpendicular to the lamellar layer direction, blue shift in gel color is observed and the color returned to its initial state (red) after complete removal of the stress/strain. The photographs of the gel at various compression states and their corresponding reflection spectra are shown in **Figure 6**. The color as well as the reflection peak shifted from the red (~600 nm) to the blue (~415 nm) wavelength region with the increase of applied strain (0 to 0.64). During compression, most of the deformation localized only in the soft PAAm layers which cause a decrease in the PDGI bilayer distance and the corresponding blue shift of gel color is observed.

Most of the tunable photonic polymer materials, synthesized so far, are limited to the color tuning either by chemical or physical stimuli such as temperature,<sup>33-40</sup> pH,<sup>40,41</sup> solvent

exchange,<sup>42,43</sup> etc. They are based on the incorporation of periodically packed colloidal particles in the polymer matrix, or on the formation of a porous polymer matrix by etching away the precursor colloidal particles. These three dimensional (3D) photonic crystalline materials are therefore isotropic in structure and remain poorly applicable for the devices which possess a complicated force field when need to detect a local deformation. Several attempts have been made for developing such mechano-responsive color tuning polymer materials based on isotropic colloidal crystal array.<sup>44-47</sup> However, they are also isotropic in structure, having poor color quality and weak mechanical response, and their color tuning ability covers narrow wavelength band ( $< 70$  nm) and is irreversible. In contrast, the current PGDI/PAAm gels exhibit magnificent structural color based on the one dimensional (1D) photonic crystalline structure. They are anisotropic in structure, mechanically strong (sustain a large deformation;  $\epsilon > 90\%$ ), and exhibit a large reversible color change over the entire visible region ( $\Delta\lambda_{\max} \sim 200$  nm).<sup>19</sup> However, once the gel is compressed and/or stretched, a long time (2-30 min) is required to regain its original color and dimensions, which limits its applicability.<sup>20</sup>

The mechanical response time of the PDGI/PAAm hydrogel is dramatically improved by applying double network principle.<sup>29</sup> According to the DN principle, a 2<sup>nd</sup> PAAm network is introduced into the existing 1<sup>st</sup> PAAm network layers of the PDGI/PAAm hydrogel to obtain a so-called PDGI/PAAm<sup>2</sup> hydrogel. Due to the additional osmotic swelling pressure of the second PAAm, the macroscopic single domain of the lamellar bilayer is destroyed into many small/discontinuous micro-domains upon swelling. The resulting PDGI/PAAm<sup>2</sup> hydrogel exhibits rubber-like elastic behavior with negligible hysteresis.<sup>21</sup> The PDGI/PAAm<sup>2</sup> gel, which is initially almost transparent, exhibits color at low tensile strain, and the color changes from red to blue-violet with the gradual increase in strain (**Figure7a**). This color change is rapid and reversible, *i.e.*, the gel changes its color under an applied tensile stress and

then returns to its initial color and dimensions immediately following the quick release of the strain. This color tuning phenomenon can be repeated for many times and the gel behaves like an elastic rubber during stretching and releasing. Since elongation accompanies with the decrease in gel thickness, *i.e.*, compressive deformation perpendicular to stretching direction, the inter-bilayer distance,  $d$ , decreases with elongation.<sup>21</sup> As a result, lower wavelength light is reflected and consequent blue shift of color is observed. The wavelengths at maximum of the reflection spectra taken at various tensile strains ( $\lambda_{\text{max;ten}}$ ) show a non-linear decrease with the increase of tensile strain ( $\epsilon_{\text{ten}}$ ) and returns back in the similar way on releasing of strain (**Figure 7b**), indicating the reversibility in agreement with the reversible color change. The mechanical response time on the reverse process or recovery time of the PDGI/PAAm<sup>2</sup> gel just after complete removal of stress/strain is negligible (**Figure 7c**). The color and dimensions of the gel return immediately following the unloading at a high destretching velocity (200 mm/min). This is in sharp contrast to the PDGI/PAAm gel which takes about 900s (**Figure 7c**). A rainbow-like complete visible spectrum (red to violet) was observed in the PDGI/PAAm<sup>2</sup> gel under a compressive strain gradient from 0 to 0.6, which might enable to detect an uneven force distribution (**7d**). At lower compressive strain region ( $\epsilon_{\text{com}} \sim 0.2$ ), the inter-bilayer distance decreases a little which satisfy to diffract the light corresponding to the red wavelength band. With further increase in strain, the color gradually shifts to blue-violet ( $\epsilon_{\text{com}} \sim 0.45$ ) region due to decrease in the corresponding interbilayer distance. At high compressive strain ( $\epsilon_{\text{com}} > 0.5$ ), the bilayer distance becomes too small which diffracts light beyond the visible region and the gel become transparent in this region.

## 7. Deformation based color display

The PDGI/PAAm gel has the superb ability change its color at a localized stress and/or strain. Therefore, the gel could simply detect the macroscopic surface roughness for example coin or any particular engraving surface. Because, when the PDGI/PAAm gel was compressed on an

uneven or engraved hard surface, the roughness or particular engraving of that surface appeared in the gel as different color depending on the surface topography and compressive strain. As shown in **Figure 8**, the letters 'LSW' appeared distinctly in the gel as different color, from green to blue with the increase of strain, while the gel was compressed on a rubber seal (top) engraved with letters 'LSW'. The compressive strain exerts only in the engraved 'LSW' region and blue shift of color in the deformed portion appeared in the gel as different color and a larger strain causes a larger blue shift. This feature of the gel could provide an application as deformation based display of different color.

## **8. Conclusions**

By incorporating uni-axially oriented PDGI lamellar bilayers (1D photonic crystal) into the amorphous PAAm hydrogel, the hydrogel, containing 94-95wt% water, exhibits robust multi-functions that an amorphous hydrogel never possesses, such as beautiful structural color, one-dimensional swelling, anisotropic modulus, stress induced color tuning, excellent mechanical strength, extra-ordinarily high toughness, and high fatigue resistance. This hydrogel is an excellent model system to demonstrate how a very simple hierarchical structure could derive superb functions. The unique polymeric DGI bilayer structure, in which the main chain of polymeric DGI has a random coil conformation while the side chains are physically associated ordered structure, is responsible for the emergence of these superb multi-functions. When the unique bilayers form single-domain lamellar structure in the hydrogel, the stress applied to the macro-scale hydrogel is effectively transferred to the nano-scale bilayers. As a result, the deformation resistance at small strain has an energetic origin against the ordered structure change of the DGI side chain packing while that at large deformation has an elastic-origin against the decrease in the main chain entropy. Both the side chain molecular association and main chain elasticity of the polymeric DGI are indispensable for the bilayers to serve as reversible sacrificial bonds to toughen the hydrogel and to show high fatigue

resistance. Moreover, the rubber-like elastic deformability and the color tuning ability of this photonic material could derive a new class of soft tactile sensor or mechanical sensor. This type of sensor material could detect a local deformation of some mechanical devices that experience a force gradient by the external mechanical stimuli.

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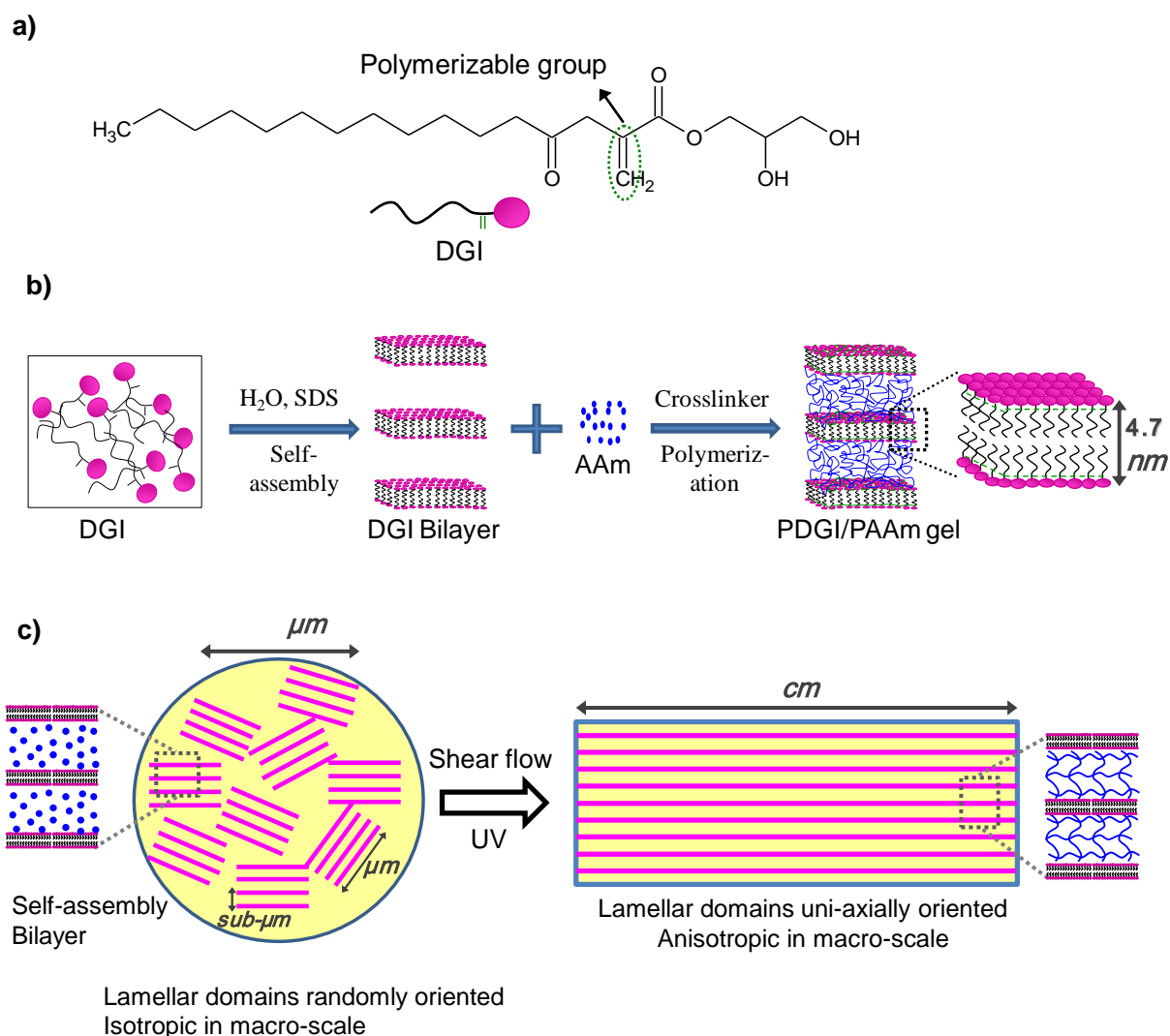


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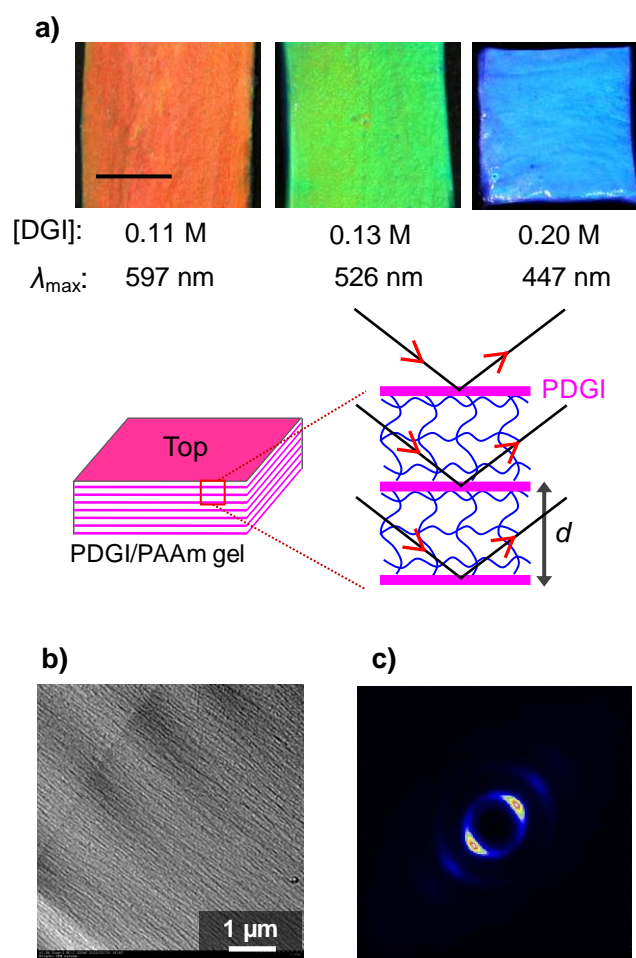
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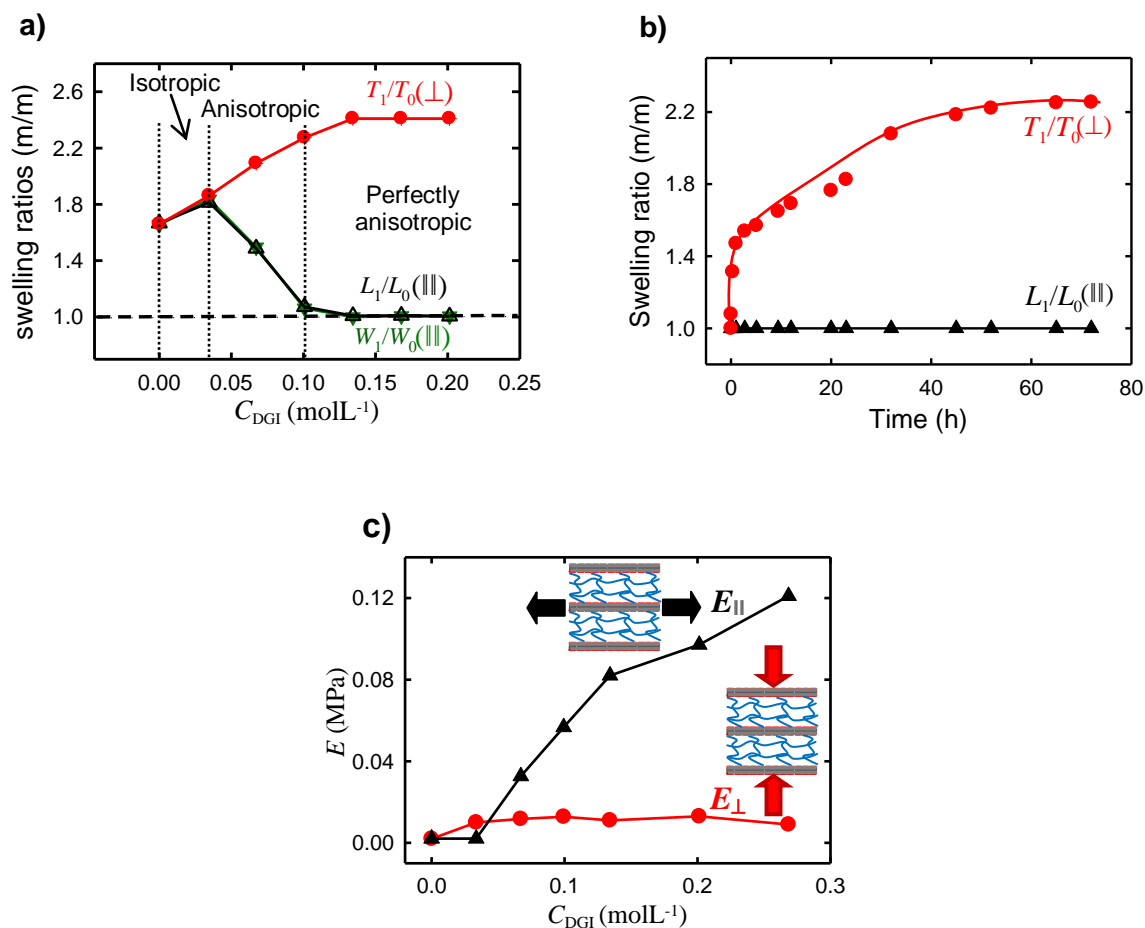
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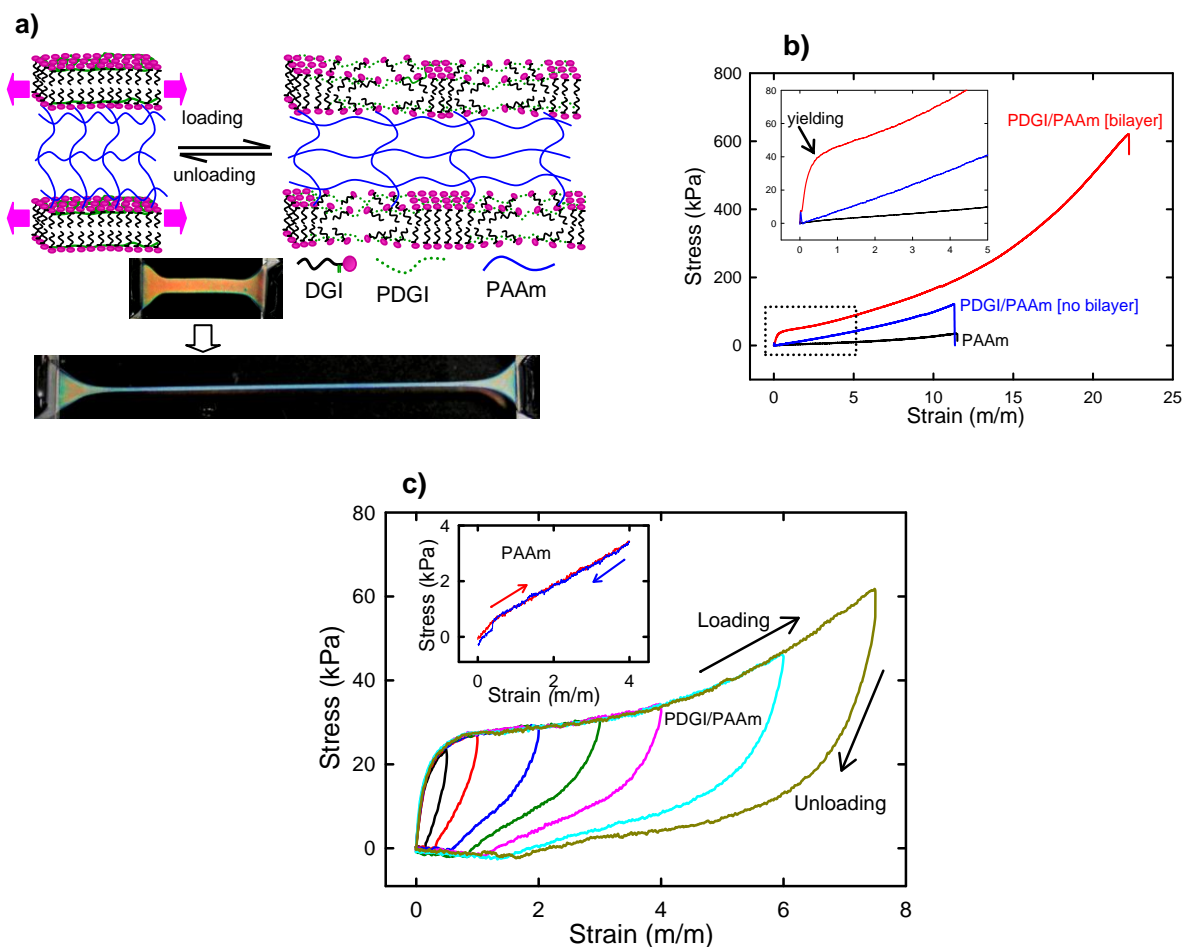
**Figure 1:** a) Molecular structure of dodecyl glyceryl itaconate (DGI) containing polymerizable double bond. b) In presence of an ionic surfactant sodium dodecyl sulfate (SDS), DGI molecules self-assemble into lamellar bilayer structure in water. This structure is retained in aqueous solution of acrylamide (AAm) in presence of cross-linker and initiator. By polymerization, polymeric DGI (PDGI) lamellar bilayers are entrapped inside the amorphous polyacrylamide (PAAm) network and the hybrid PDGI/PAAm hydrogel is obtained. c) Prior to the polymerization, randomly oriented self-assembled lamellar bilayer domains are aligned in one direction (anisotropic in macro-scale) by shear flow to the precursor solution.



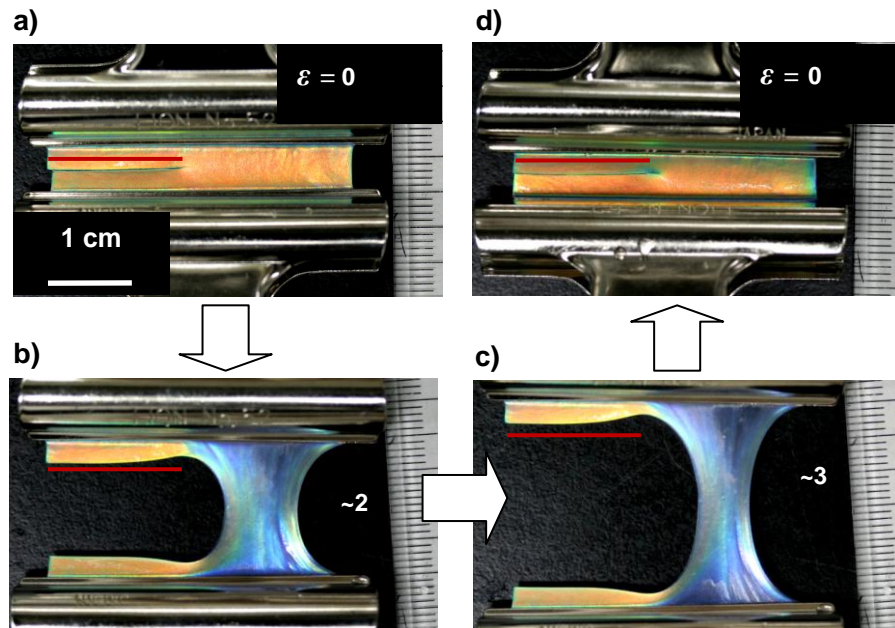
**Figure 2:** a) Photographs of PDGI/PAAm gel prepared at various concentrations of DGI (0.11, 0.13, and 0.2 M). The AAm and cross-linker (MBAA) concentration were 2 and 0.001 M, respectively. The lamellar bilayers are parallel to the screen as well as top of the 3D illustration of the gel. The gels exhibit magnificent structural color due to the Bragg's diffraction by the multi-layer reflection of visible light. The wavelength at maximum of the reflection spectrum ( $\lambda_{\max}$ ) was measured by fixing the Bragg's angle as  $60^\circ$ . The scale bar is 5 mm. b) Transmission electron microscope (TEM) image shows the clear uni-axial pattern of bilayers in the cross section of the gel. c) Small angle X-ray scattering (SAXS) image of the gel demonstrates perfectly anisotropic diffraction patterns. X-ray radiation was exposed at the cross-section of the gel, *i.e.*, parallel to the bilayer sheets. [Reproduced with permission from Ref. 19 (a) and 20 (b,c)].



**Figure 3:** Anisotropic behaviors of the PDGI/PAAm gel. a) Swelling, perpendicular ( $\perp$ ) and parallel ( $\parallel$ ) to the lamellar layer, increased and decreased, respectively, with increasing DGI concentration while both reach to limiting values ( $\perp$ , 2.4 and  $\parallel$ , 1.0).  $L_1/L_0$ ,  $W_1/W_0$  are the swelling ratios parallel and  $T_1/T_0$  is that perpendicular to the lamellar layers where  $L_0$ ,  $W_0$ , and  $T_0$  are the length, width and thickness of the gel sample at the as-prepared state and  $L_1$ ,  $W_1$ , and  $T_1$  are those in the equilibrium swelling state, respectively. b) Swelling kinetics of the PDGI/PAAm gel ( $[\text{DGI}]=0.1 \text{ M}$ ) increases with time along the thickness axis (perpendicular to the bilayers,  $T_1/T_0$ ), while no swelling at all along the length axis (parallel to the bilayers,  $L_1/L_0$ ). The gel dimension is  $40 \times 8 \times 0.5 \text{ mm}^3$ . c) DGI concentration dependence of overall elastic modulus of PDGI/PAAm gels in parallel to lamellar layers ( $E_{\parallel}$ ) and perpendicular to lamellar layers ( $E_{\perp}$ ). [Reproduced with permission from Ref. 19 (a,c) and 21 (b)].

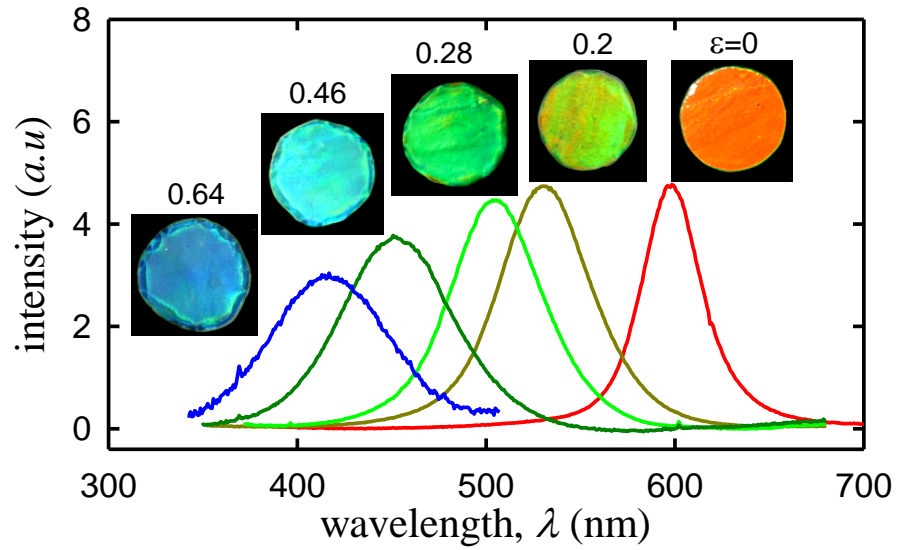


**Figure 4:** a) An illustration of the fracture process of the bilayers on uniaxial elongation in the direction parallel to the bilayers direction and the photographs of the PDGI/PAAm gel at normal as well as elongated state (strain  $\sim 4$ ). The color change of the gel is changed from orange to blue upon elongation, where the lamellar bilayers are in parallel to the screen. b) Nominal stress as a function of strain at a stretching velocity of 200 mm/min for the PAAm gel, PDGI/PAAm gel with and without lamellar bilayer structure. The tensile deformation was performed along the lamellar bilayers direction as indicated by the illustration and images (a). The concentration of DGI, AAm and MBAA at preparation were 0.13, 2.0 and 0.002 M, respectively. c) Tensile loading-unloading curves of the PDGI/PAAm gel (blue) exhibit as hysteresis. The hysteresis cycles are repeated with the same sample at increasing levels of maximum strain. All the loading curves are followed to their previous loading curve up to the maximum strain achieved in the previous one. There is no hysteresis for the pure PAAm gel which is also shown in the inset figure. Sample thickness:  $\sim 1.0$  mm. [Reproduced with permission from Ref. 20].

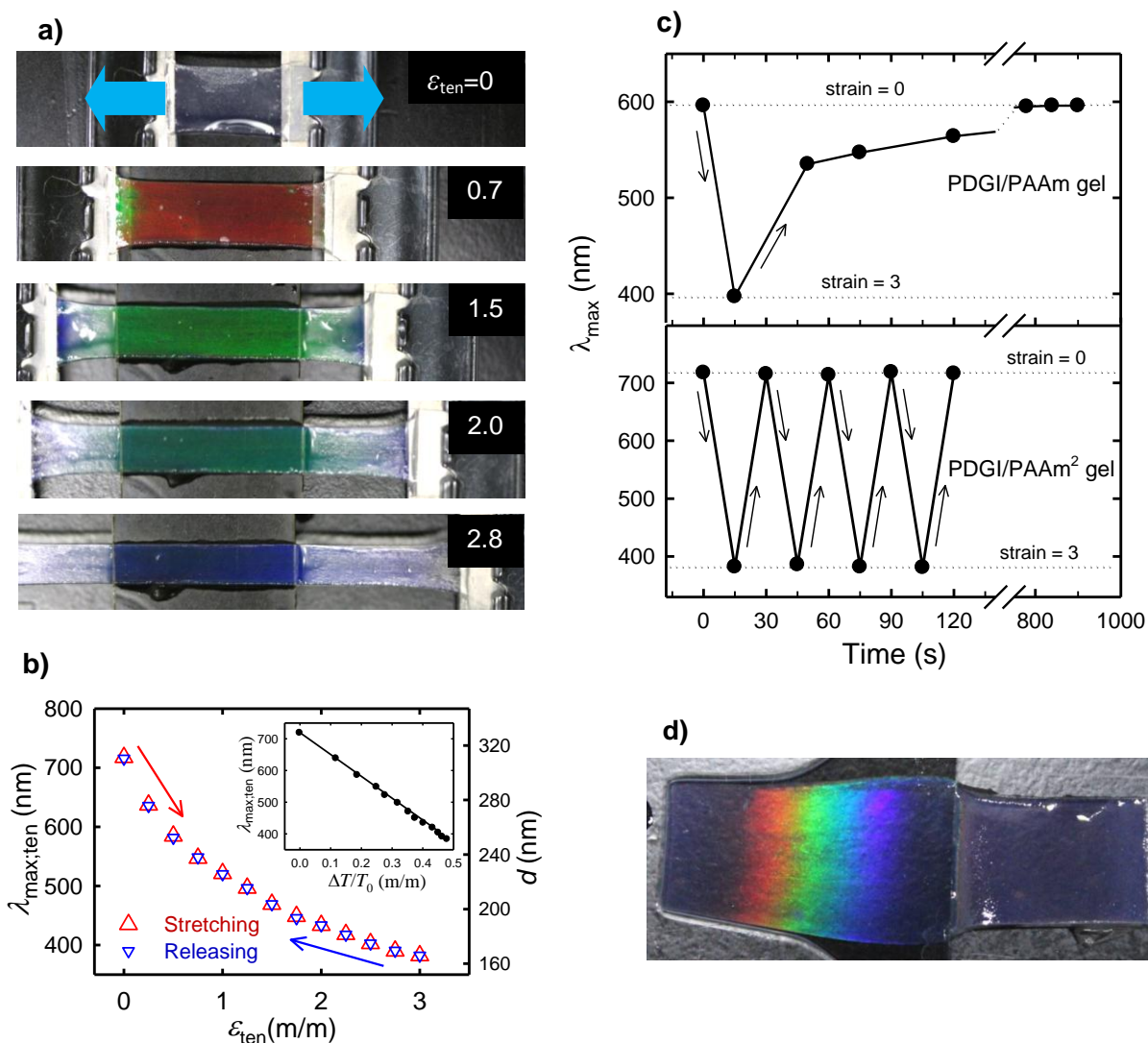


**Figure 5.** Images demonstrating the extra-ordinarily high crack resistance of the PDGI/PAAm gel during a pure shear fracture test. The lamellar bilayers are parallel to the screen. The PDGI/PAAm gel (0.10 M DGI) was cut to have an initial sharp notch/crack along the longitudinal direction (a). The gel is stressed perpendicular to the crack direction up to a strain ( $\varepsilon$ ) of about 3 or even more. A huge blunting occurs in front of the crack tip and it completely suppresses the stress concentration, as shown by the homogenous structural color change of the gel over the blunting as well as whole stretching area (b, c). After release of stress, the gel finally returns to its original dimensions and color after several min (d). This phenomenon is reversible and can be repeated for many times. Sample thickness:  $\sim 1.0$  mm. [Reproduced with permission from Ref. 20].





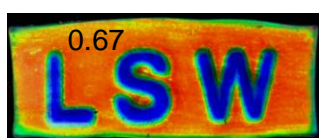
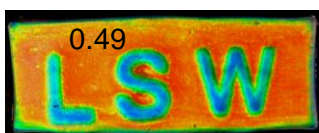
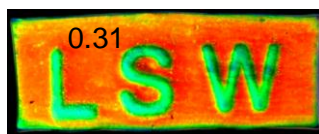
**Figure 6:** a) The PDGI/PAAm gel exhibits a color shift from red to blue upon gradual increase in compressive strain (right to left) perpendicular to the lamellar layer, and corresponding reflection spectra showing the peak position shift from higher to lower wavelength. The reflection spectrum was measured by fixing the Bragg's angle as  $60^\circ$ . Sample thickness:  $\sim 1.2$  mm. [Reproduced with permission from Ref. 19].



**Figure 7:** a) The photographs of the PDGI/PAAm<sup>2</sup> gel taken at different tensile strains ( $\epsilon_{\text{ten}}$ ) show the shift of gel color from transparent to blue-violet via red and green with gradual increase in strain. b) The wavelength at maximum of the reflection spectrum at various tensile strains ( $\lambda_{\text{max};\text{ten}}$ ) and bilayer distance,  $d$ , decreases nonlinearly with stretching, *i.e.*, the increase in tensile strain ( $\epsilon_{\text{ten}}$ ) and follows the same way on releasing the strain (in the reverse of stretching) indicating the reversibility.  $\lambda_{\text{max};\text{ten}}$  decreases linearly with the relative change of sample thickness ( $\Delta T/T_0$ ) perpendicular to the stretching direction at corresponding tensile strain (inset). c) The shift in peak position with stretching and de-stretching cycles for the PDGI/PAAm gel (top) and PDGI/PAAm<sup>2</sup> gel (bottom) against time. For PDGI/PAAm<sup>2</sup> gel, the every complete cycle is reproducible for several times with an elapsed time of 30 s in each cycle. d) The PDGI/PAAm<sup>2</sup> gel shows a complete visible spectra (rainbow-like) by applying a compressive strain gradient ( $\epsilon_{\text{com}} = 0$  to 0.6) on the gel with a transparent glass plate. [Reproduced with permission from Ref. 21].



Rubber seal



Gel compressed on  
rubber seal

**Figure 8:** Rubber seal engraved with LSW (top most) and the change of color display of PDGI/PAAm gel sheet, being compressed on the seal, through engraved ‘LSW’ from yellowish green to blue upon increasing strain (top to bottom). [Reproduced with permission from Ref. 19].

## Author's Profile

### Md. Anamul Haque



Md. Anamul Haque graduated in Master of Science from University of Dhaka, Bangladesh in 2008. He achieved the PhD degree from Hokkaido University, Japan in 2011. During doctoral research, he has carried the research on the creation of an anisotropic hydrogel with well define hierarchical structure. Now he is concentrating on high functionalization of the anisotropic hydrogel such as role of sacrificial bond on toughness, multi stimuli color sensor.

### Takayuki kurokawa



Takayuki Kurokawa graduated in polymer science from Hokkaido University, Japan in 2000. He received his PhD for study on Effect of Polymer Dynamics on Friction of Gels from Hokkaido University in 2005. He joined RIKEN, Japan as a postdoctoral researcher, then Creative Research Institution at Hokkaido University as an assistant professor since 2009. He focuses on functions of polymer gels, such as mechanical property, permeability, and biological property.

### Jian Ping Gong



Jian Ping Gong is the professor of Faculty of Advanced Life Science, Hokkaido University. She gained her Doctor of Engineering from Tokyo Institute of Technology and joined the faculty at the Hokkaido University in 1993. She received Wiley Polymer Science Award (2001), The Award of the Society of Polymer Science Japan (2006), and the Chemical Society of Japan Award (2011). She serves on the editorial and advisory boards of *Soft Matter*, *Macromolecules*, *Biointerphases*, and *Asia Materials*. Gong is currently concentrating on the researches of novel hydrogels with high mechanical performances and its application as biomaterials.