Supporting Information

Flower-like Photonic Hydrogel with Superstructure Induced via Modulated Shear Field

Ya Nan Ye[1#], Md Anamul Haque[2,3#], Akane Inoue[4], Yoshinori Katsuyama[2] Takayuki Kurokawa[1,2] and Jian Ping Gong[1,2,5*]*

[1]Global Institution for Collaborative Research and Education (GI-CoRE), Hokkaido University, Sapporo 001-0021, Japan;

[2]Faculty of Advanced Life Science, Hokkaido University, Sapporo 001-0021, Japan;

[3]Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh;

[4]Graduate School of Life Science, Hokkaido University, Sapporo 001-0021, Japan;

[5]Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo 001-0021, Japan.

* T.K.: email, kurokawa@sci.hokudai.ac.jp.

* J.P.G.: email, gong@sci.hokudai.ac.jp.

Experiment

Gel preparation. The aqueous precursor solution consists of 0.1 M dodecyl glyceryl itaconate (DGI), 0.025 mol % sodium dodecyl sulfate relative to DGI, 2 M acrylamide (AAm), 2 mM N,N′-methylenebis(acrylamide) (MBAA) as a cross-linker, and 2 mM Irgacure 2959 as an initiator. The precursor solution was kept in a temperature-controlled water bath for ~5 h at 55 °C to dissolve monomeric DGI powders and stabilize lyotropic liquid crystalline phases of DGI. Then the precursor solution was loaded

between two coaxially aligned parallel disk plates of a customized rheometer. The upper plate made from crystal glass has a radius of R = 17.5 mm and the lower plate made of glass has a larger radius of 20 mm. The gap between these two plates was kept as t = 0.5 mm in this work. The shear flow was imposed by the rotation movement of the upper plate while the lower plate was fixed. The angular velocity ω used in this work ranges from 1.4 to 42.9 s^{-1}. The shear rate gradient across the plate radius was applied as $\dot{\gamma} = \omega r/t$, which gives a modulated anisotropic structure from center to edge of the sample. Where r is the radial distance from the center of the concentric circular plates. The rotation of the upper plate was performed for 20 s in all the experiments. After the cessation of shear flow, the precursor solution was polymerized in argon atmosphere through a UV polymerization system equipped with the shear device (details see **Figure S1** and **Figure 1C**). Then the polymerized gel was immersed into water for 1 week to reach swelling equilibrium.

Swelling measurement. The photonic disk gels equilibrated in water was cut into seven pieces along the radial direction. The distance r of each of the pieces from the centers is taken as the middle positions of gels, and each step was 2 mm. Each gel piece has a size of $L_0 \times W_0 \times T_0\ mm$, where the L_0 W_0 and T_0 are the length (5 mm), width (2 mm), and thickness, respectively (inset in **Figure 2D**). Then the gel pieces were immersed in 10 wt % PEG solution (Mn = 20000 g/mol) and the gels shrunk to a size of $L_1 \times W_1 \times T_1\ mm$ after reaching equilibrium. The size change ratios are $\lambda_L = L_0/L_1$ for lateral direction and $\lambda_T = T_0/T_1$ for

thickness direction. The size of the gels was measured by dial calipers. The anisotropy parameter was calculated as $(\lambda_L - 1)/(\lambda_T - 1)$ to represent the degree of orientation for lamellar structure from the center to the edge.

Small-angle X-ray Scattering. The SAXS measurements of photonic gel from center to edge from thickness direction were performed at beamline BL40B2 of synchrotron radiation X-ray facility SPring-8 (JASRI, Hyogo, Japan). The X-ray wavelength was 0.1 nm, and a sample-to-detector distance was 3.86 m. Both the X- and Y-pixel size of the detector were 100 μm. The X-ray exposure time was 10 s. The back scattering 2D patterns were recorded on an imaging camera. The 2D image was converted to 1D data using Fit2D analysis software. From the q^* value of the first-order peak, interlamellar spacing, d, was calculated as $d = 2\pi/q^*$.

Experiment equipment

The customized rheometer was made based on the rheometer of Thermo Scientific (**Figure S1C**). The developed accessories consist of three sections: temperature control system, UV radiation system, argon protection system. The scheme of equipment set-up was shown in **Figure S1A**. The geometry used in the experiment was parallel plates. The upper plate radius R is 17.5 mm, which is smaller than that of the lower plate (20 mm). The material for the upper plate was crystal glass while the lower plate was a transparent glass plate for UV radiation. The temperature control was achieved by a water circulation bath. The UV-light was loaded from bottom of temperature control systems (**Figure S1B**). In addition, a

cup was made to seal the space between the upper and lower plates and then the protection argon gas was injected into the cup during polymerization (**Figure S1B** and insert of **Figure S1C**).

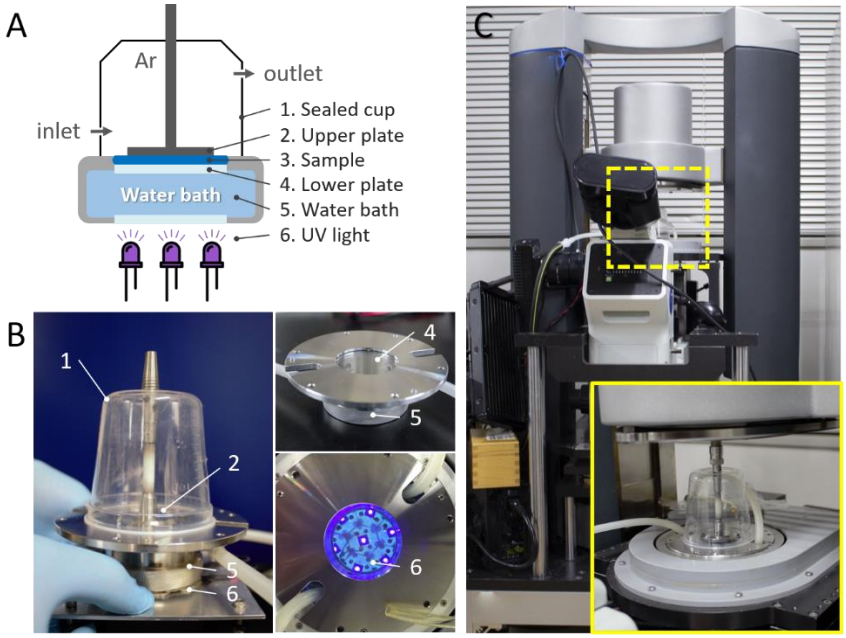

Figure S1. Sketch and photos of the customized rheometer. (A) Sketch of the equipment setup of the customized rheometer. (B) Photos for the main parts taken outside of the rheometer for clarity: argon protection system by a sealed cup (No.1 in figure), shear loading by coaxially aligned parallel plates (No.2 and 4), temperature control system (No.5) and UV irradiation system (No.6). (C) Overview of the equipment setup of the customized optical rheometer. The inset is the magnification of the main part.

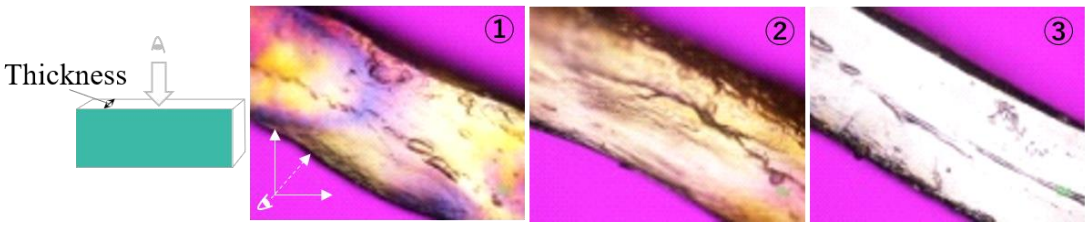

Figure S2. POM images with 530 nm sensitive tint plate measured at different distances from the centers shown in Figure 2A. The distances from centers are 4, 10, and 12 mm for position 1, 2, and 3, respectively. The observation was performed in the thickness direction. The gel was prepared with an angular velocity of 11.4 rad/s at 55 ℃ for 20 s.

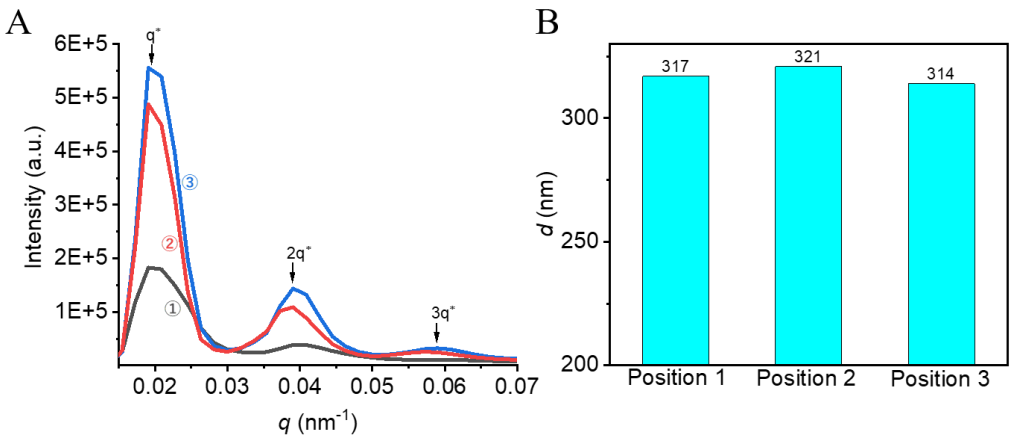

Figure S3. (A) The integrated one-dimensional (1D) SAXS intensity profiles from 2D small-angle X-ray scattering images and (B) the corresponding *d*-spacing at different distances from the centers shown in Figure 2A. The *d* is calculated by $d = 2\pi/q^*$. Where q^* is the first peak position in the 1D scattering profile.

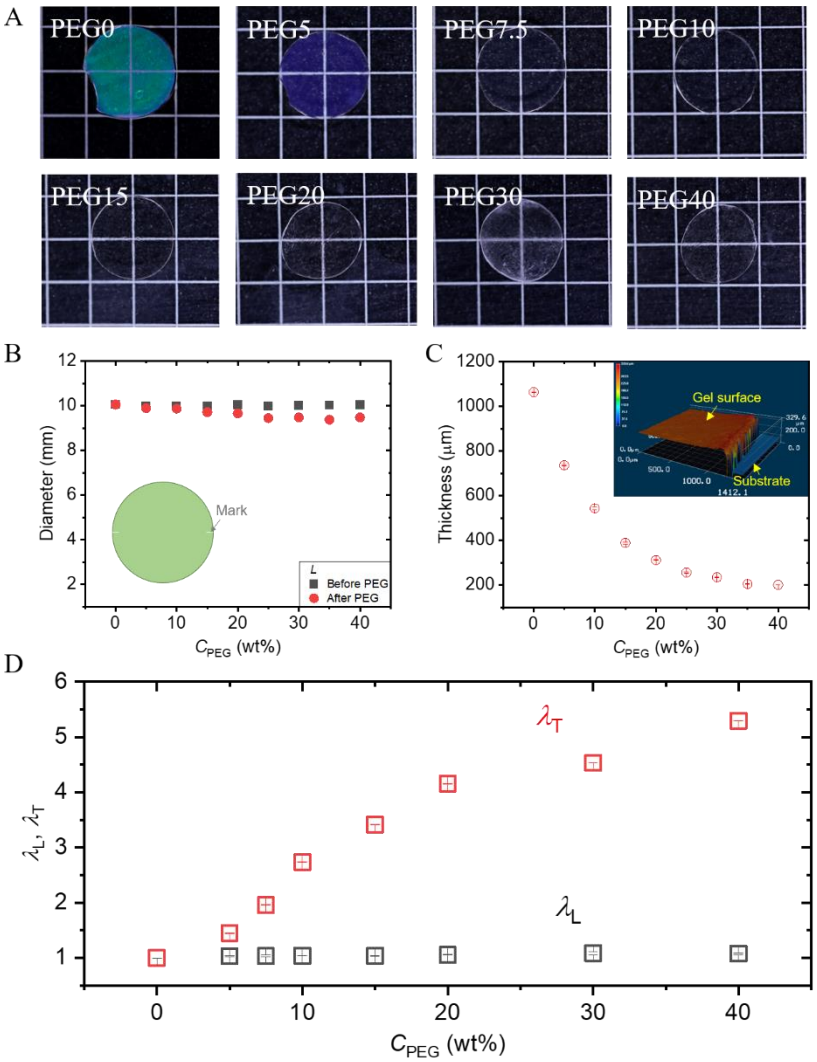

Figure S4. (A) Photographs of photonic hydrogels with perfect aligned lamellar structure immersing in different PEG aqueous solutions. The gel was prepared based on previous method.[1] The numbers after the letters "PEG" are the PEG weight percent in aqueous PEG solution. The mesh size of background lattice is 5 mm. (B) The diameter of disk gels at various PEG solution. Due to the imperfect disk shape of the gels, two marks were made on the gels by cutting. The diameters of the gels were measured near the marks. The inset represents schematic of the gels with cutting marks. (C) The thickness of the gels at various PEG solution. The inset represents

the 3D laser microscope image showing the surfaces of gel (red profile) and the glass substrate (blue profile). The thickness is calculated as the distance between the above two surfaces. (D) The shrink ratio, in lateral direction $\lambda_L = L_0/L_1$ and thickness direction $\lambda_T = T_0/T_1$ as a function of PEG concentrations. Here L_0 and T_0 are the diameter and thickness of gels equilibrated in water, respectively. The L_1 and T_1 are the diameter and thickness of gels equilibrated in aqueous PEG solution, respectively. As increasing of the C_{PEG}, the gel only shrunk in thickness direction so that $\lambda_T > 1$ and $\lambda_L = 1$, resulting in the $(\lambda_L - 1)/(\lambda_T - 1) = 0$.

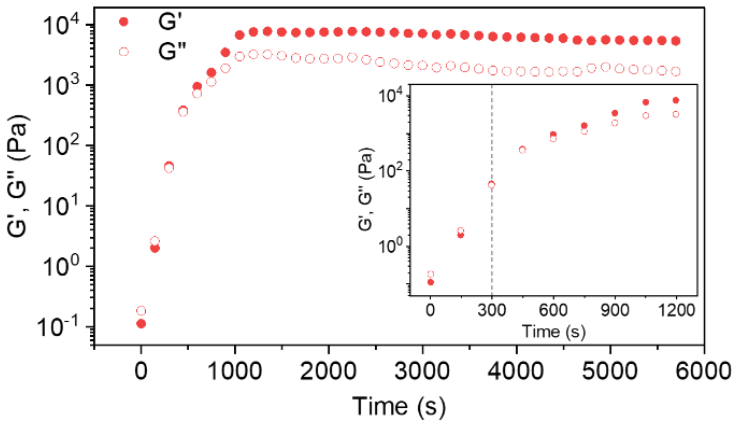

Figure S5. Experiment to study the the gelation process by UV polymerization using the customized rheometer. A shear was applied to the precursor solution with an angular velocity of 11.4 rad/s at 55 ℃ for 20 s. After the shear cessation, the solution was irradiated via UV and the storage modulus G′, loss modulus G″ vs UV irradiation time were recorded. The threshold of gelation, defined at $G' = G''$, was 300 s, and the gelation was completed at ~1000 s.

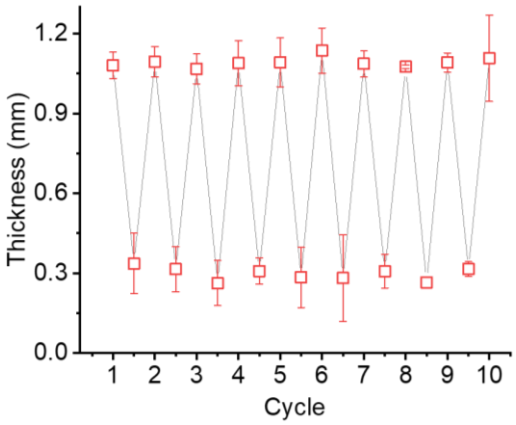

Figure S6. Repeatability of the flower blooming and fading by measuring the thickness change of flower cut at position 3 in Figure 2A alternatively equilibrated in water and 10 wt % PEG aqueous solution. The gel was prepared at an angular velocity of 11.4 rad/s at 55 ℃ for 20 s.

Reference

(1) Ilyas, M.; Haque, M. A.; Yue, Y.; Kurokawa, T.; Nakajima, T.; Nonoyama, T.; Gong, J. P. Water-Triggered Ductile-Brittle Transition of Anisotropic Lamellar Hydrogels and Effect of Confinement on Polymer Dynamics. *Macromolecules* **2017**, *50* (20), 8169–8177.