Supramolecular Hydrogels with Multi-Cylindrical Lamellar Bilayers: Swelling-Induced Contraction and Anisotropic Molecular Diffusion

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Abstract

Novel, supramolecular, anisotropic hydrogels (called MC-PDGI gels) are presented in this study. These MC-PDGI gels consist of multi-cylindrical lipid bilayers aligned in a uniaxial manner and embedded in a soft hydrogel matrix. The bilayers and the hydrogel interact weakly due to hydrogen bonding. These MC-PDGI gels swell after exposure to water, which causes their volume and diameter to increase while simultaneously causing their length to decrease. This anisotropic swelling-induced contraction behavior is the result of competition between the isotropic elasticity of the hydrogel matrix and the interfacial tension of the lipid bilayers. Moreover, the MC-PDGI gels exhibit unique quasi one-dimensional diffusion behavior owing to the difficulty of molecular penetration through the multi-layered lipid bilayers. These materials would be useful for prolonged drug release or as an actuator.

Key words

gel; bilayer; anisotropy; swelling; diffusion

Highlights

· Supramolecular MC-PDGI gels consisting of multi-cylindrical lipid bilayers embedded in a soft hydrogel matrix have been created.

· The lipid bilayers in the MC-PDGI gels are aligned in a uniaxial manner due to strong shearing.

· The MC-PDGI gels show swelling-induced contraction behavior.

· Quasi 1-dimentional molecular diffusion has been observed in the anisotropic MC-PDGI gels.

Introduction

Lipid bilayer membranes, which are sheet-like dynamic assemblies of amphiphilic molecules, are one of the most basic components of biological systems.[1] A bilayer works as a barrier for the separation of ions and molecules, while also acts as a soft membrane surrounding cells and organelles in the body. Moreover, controlled molecular transport functionality can be added to the bilayer using various membrane proteins. Such a lipid bilayer structure allows for the membrane to undergo dynamic biological phenomena such as cell division.

Inspired by biological lipid bilayers, numerous artificial functional materials containing biological or synthetic lipid bilayers have been proposed for use in future bio-sensors, drug carriers, and gel/bilayer composite applications.[2-6] Our group has previously created sheet-like PDGI/polyacrylamide (PAAm) hydrogels consisting of periodically stacked monodomain poly(dodecyl glyceryl itaconate) (PDGI) bilayer sheets embedded in a PAAm hydrogel matrix.[7-8] The periodic PDGI bilayer induces the bright structural color of the gel like soft photonic crystals based on phase-separated structure of block copolymers.[9-11] The structural color of the PDGI/PAAm gel is widely tunable from red to blue by small stress.[12-13] If the PAAm moiety in the gel is chemically modified, the structure color the gel is also tunable by various external stimuli such as temperature and pH.[13-14] Anisotropic orientation of the bilayers in the gels leads to anisotropic deformation such as one-directional swelling and quasi one-directional contraction upon uniaxial stretching.[7,15] These hydrogels also show extremely high fatigue resistance because of the sacrificial bond effect of the bilayer.[16] PDGI/PAAm hydrogels are synthesized from dodecyl glyceryl itaconate (DGI) as a polymerizable lipid, acrylamide (AAm), and some other additives. An aqueous solution of these molecules, called a gel precursor solution, is injected into a rectangular reaction cell (0.5-1 mm in thickness) with high shear rate to form uniaxial DGI bilayers along the cell wall. Finally, co-current polymerization of DGI and AAm is performed to immobilize the lamellar

structure of the polyDGI (PDGI) inside the PAAm network.[17] The PDGI layers and the PAAm network weakly interact through hydrogen bonds to maintain the structural integrity of the gel, which has been confirmed from the absorption peak shift of hydroxyl group (-OH) of DGI and amide group (-$CONH_2$) of AAm observed with infrared spectroscopy.[18]

Here, we describe the swelling-induced contraction and quasi one-dimensional diffusion of PDGI/PAAm gels formed into string-like shapes (as opposed to the reported rectangular sheet shape). To synthesize these string PDGI/PAAm gels, a gel precursor solution was suctioned into a polyethylene tube (instead of the rectangular cell) at a high shear rate (approximately 1,300 s^{-1}) to align the DGI lamellar bilayers along the inner wall of the tube. The gels were then synthesized by the co-current UV polymerization of DGI and AAm.

Experimental

Materials: Dodecyl glyceryl itaconate (DGI; n-$C_{12}H_{25}OCOCH_2C(=CH_2)COOCH_2CH(OH)CH_2OH$) was synthesized as previously reported.[6] Acrylamide (AAm) (Junsei Chemical Co., Ltd., Japan), *N*,*N*'-methylenebis(acrylamide) (MBAA) (Wako Pure Chemical Industries, Ltd., Japan), Irgacure 2959 (BASF SE, Germany), sodium dodecyl sulfate (SDS) (MP Biomedicals Inc., USA), methylene blue (MB) (Wako Pure Chemical Industries, Ltd., Japan), and polyethylene glycol (PEG; number average molecular weight M_n: 21,170) (Wako Pure Chemical Industries, Ltd., Japan) were used without further purification.

Gel preparation: Multi-cylindrical PDGI/PAAm gels were synthesized following a previously published synthesis of sheet-like PDGI/PAAm gels.[7] In brief, 0.1 M DGI, 0.025 mM SDS, 2 M AAm, 2.1 mM MBAA (as a cross-linker of AAm), and 2 mM Irgacure 2959 (as a UV initiator) were dissolved in water. This precursor solution was poured into a 10 ml glass bottle and placed in a water bath at 55 °C for approximately 5 h, until stable lamellar DGI bilayers formed. The solution was then suctioned into a polyethylene tube (inner diameter: 1.0 mm,

length: approximately 30 cm) using a 10 mL plastic syringe under Ar. The flow rate of the sample solution was kept as high as possible (roughly 30 $cm \cdot s^{-1}$, shear rate of 1,300 s^{-1}) to induce bilayer orientation. Co-current polymerization of DGI and AAm was performed using 365 nm UV light irradiation (4 $mW \cdot cm^{-2}$) in the polyethylene tube for 8 h at 50 °C under an Ar atmosphere. After the polymerization, the MC-PDGI gel was removed from the tube using a metal wire. String PAAm gels were also prepared as a control group from 2 M AAm, 2.1 mM MBAA, and 2 mM Irgacure 2959 aqueous solutions using the same method.

Swelling ratio measurements: MC-PDGI or PAAm gels were swollen in water for at least 1 week and cut into 1-cm-long pieces. The sample length L_{ref} was measured using calipers, and the diameter D_{ref} was determined by polarized optical microscopy (POM) and ImageJ software. The cut samples were then immersed in 3–50 wt% PEG aqueous solutions for at least 3 days. The sample length L and diameter D after swelling were determined in a similar fashion. Axial expansion, radial expansion, and volume swelling ratios of the samples, defined as L/L_{ref}, D/D_{ref} and $V/V_{ref} = (LD^2)/(L_{ref}D_{ref}^2)$, respectively, were calculated based on these measurements.

Repeated swelling-deswelling measurements: The MC-PDGI gel was immersed in pure water for 2 days, and subsequently in 20 wt% PEG aqueous solution for 2 days; this cycle was repeated 3 times. Photos of the gel samples were collected at the end of each step. The length and diameter of the gels at each step were determined by image analysis with ImageJ software.

Small angle X-ray diffraction (SAXD) measurements: SAXD measurements were performed at the BL40B2 of SPring-8 (JASRI, Japan). The swollen MC-PDGI gel (diameter: 2.0 mm) was sliced into 1-cm-long pieces, and then covered by two kapton films to prevent drying. Samples were irradiated with 0.1 nm X-rays at room temperature for 20 s, and the diffraction pattern was recorded on an imaging plate (camera length: 2.308 m).

Polarized optical microscopy (POM): The swollen MC-PDGI gel (diameter: 2.0 mm) was cut into 1-cm-long pieces to observe the profile of the gel, and subsequently sliced into 1 mm cross-sections for cross-sectional viewing on a conventional slide glass without coverage. Samples were then studied using POM (Eclipse LV100POL, Nicon, Co.). Next, they were placed between orthogonally oriented polarizers with and without a 530 nm tint plate.

Diffusion test: The PAAm gel and the MC-PDGI gel swollen in water (diameters: 2.1 mm and 2.0 mm, respectively) were cut into 2-cm- or 6-cm-long pieces. Methylene blue (MB, molecular weight MW: 319.85) was used as a model reagent to observe the diffusion behavior within the gels. Radius r of a MB molecule (or its aggregation) in pure water is roughly calculated as 0.3 nm based on its reported diffusion coefficient D (around 7×10^{-8} m^2s^{-1}) and the Stokes-Einstein equation $D = (k_BT)/(6\pi\eta r)$, where k_B is Boltzmann's constant, T is the absolute temperature, η is the viscosity of solvent.[19] This value is enough smaller than characteristic length, which can be considered as mesh size, of the 2 M PAAm gel $\xi = 2$ nm, suggesting MB can diffuse inside the PAAm matrix almost freely.[20] For testing in pure water, samples were immersed in an aqueous MB solution (6.25×10^{-4} M) for loading of MB for at least 10 days (see the Results and Discussion section for setup detail). The sample was covered by a Teflon net for protection from the rotating stirrer tip, and then placed in a 50 ml glass bottle filled with 23 mL of pure water. The solution was continuously stirred and circulated between the bottle and a UV/Vis spectrometer (UV-1800, Shimadzu Co.) with a Perista Pump (AC-2110II, Atto Co.). Time-lapse measurements of the absorbance I at 652 nm (which is near the 667 nm absorption peak of MB) were performed to determine the amount of MB diffused from the gels. Experiments were continued until the absorbance reached a constant maximum value (I_{max}). The percent of MB diffused from the sample was calculated as I/I_{max}. The diffusion time constant τ is defined as the time needed for the ratio of the remaining MB in the sample ($1- I/I_{max}$) to reach the value of $1/e$. For testing in the PEG

solution, the cut gels were first put in an aqueous solution of MB (6.25×10^{-4} M) for at least 10 days, and then placed in a 15 wt% PEG aqueous solution containing the same concentration of MB for an additional 10 days. The diffusion test was performed in this 15 wt% PEG aqueous solution instead of water, as previously described.

Results and Discussion

Figure 1(a) shows an image of string PDGI/PAAm gels swollen in pure water. They possessed bright structural colors, suggesting the formation of periodical PDGI lamellar bilayers with layer distances on the order of visible light wavelength. SAXD experiments were performed to determine the bilayer orientation in the gels, as shown in Figure 1(b–c). By exposing the side walls of the string PDGI/PAAm gels to X-rays, periodic diffraction patterns could be acquired along the meridian direction. Although the 1st order peak is hidden by the beam center, periodic 2nd to 5th order peaks are present, which correspond to monodomain lamellar structures oriented along the axial direction with average spacings of 208 nm. The samples were also studied by POM. When the string gels were set parallel to the polarizer, the resulting image was completely dark (Figure 1(d)), whereas a bright image was observed after a 45° rotation (Figure 1(e)). This corresponds to unidirectional bilayer alignment along the axial direction, which has also been revealed by SAXD measurements. After insertion of the 530 nm sensitive tint plate, the color of the image changed to orange (Figure 1(f)). The orange color in the image corresponds to the bilayer alignment from upper left to lower right. On the other hand, when the cross-section of the gel was observed with the tint plate (Figure 1(g)), an obvious cross pattern was present. The color of the upper right of the cross pattern was orange, which implies that bilayers exist in circular (non-radial) orientation in the cross-section of the gels. These SAXD and POM results clearly indicate tree-ring-like PDGI multilayers in the gel, with layer distances of 208 nm, as shown in Figure 1(h). As the thickness of single PDGI bilayer sheets is approximately 4 nm,[21] this observation suggests that an approximately

200-nm-thick PAAm gel layer and a 4-nm-thick PDGI bilayer are alternately stacked in the string PDGI/PAAm gels. Moreover, as the diameter of the swollen gels is approximately 2 mm, there should be ~5,000 cylindrical bilayers in the gels. Hereafter, we label our string PDGI/PAAm gels as multi-cylindrical PDGI/PAAm gels, or simply as MC-PDGI gels.

When the as-prepared MC-PDGI gel is immersed in water, it exhibits a unique combination of expansion and contraction behavior along different axes due to its absorption behavior. **Figure 2(a, b)** shows images of the MC-PDGI gel in as-prepared and equilibrium states in water. The volume and diameter of the MC-PDGI gel expanded 2.0 and 1.6 times after swelling, respectively, whereas the length of the gel obviously contracted to 0.77 times its original length by swelling. To systematically investigate such anisotropic swelling behavior, the volume swelling ratio of the MC-PDGI gel was precisely controlled by immersing them in PEG (Mn: 21,170) aqueous solutions of varying concentrations, c_{PEG}. The degree of swelling of the gels is generally determined by the competition of network elasticity and osmotic pressure differences between gels and the surrounding bath solutions.[22–23] Addition of PEG to the bath solution effectively increases its osmotic pressure and therefore suppresses the swelling of gels.[24] We measured volume V, diameter D, and length L of the MC-PDGI/PAAm gels soaked in water and PEG solutions. **Figure 3(a,b)** shows the dependences of the swelling ratio V/V_{ref}, radial expansion ratio D/D_{ref}, and axial expansion ratio L/L_{ref} for the MC-PDGI gel and the PAAm gel on the PEG concentration, where X_{ref} ($X = V, D, L$) denotes the corresponding variable for the gel swollen in pure water. The string PAAm gel contracted almost equally in both the radial and axial directions after immersion in the PEG solutions, whereas the MC-PDGI gel showed unique anisotropic de-swelling behavior. As shown in Figure 3(c), when c_{PEG} was lower than 10 wt%, the MC-PDGI gel contracted in the radial direction but expanded in the axial direction by de-swelling. Increasing c_{PEG} further caused the gel to contract in both directions, but more so in the radial direction. If the MC-PDGI gel is repeatedly immersed in pure water and aqueous PEG

solution, this expansion-contraction cycle can be repeated many times. For example, if the 20 wt% PEG solution was used, 13% of the repeatable length change on average was observed, as shown in Figure 3(d).

The reason for swelling-induced contraction of MC-PDGI gels can be discussed in reference to our previous report regarding the deformation mechanism of sheet-like PDGI/PAAm gels.[15] Polymer gels are rubbery materials and prefer isotropic deformation to minimize the total elastic energy.[23] On the other hand, lipid bilayers behave like 2-D liquids and prefer to deform without a corresponding area change.[25] Area changes of the lipid bilayers induce disordered molecular packing, which is energetically unfavorable. MC-PDGI gels consist of isotropic PAAm networks and multi-cylindrical PDGI bilayers aligned along their side walls. Deformation of a PAAm matrix and PDGI bilayers in a MC-PDGI gel is completely coupled since they are weakly interacted via hydrogen bonds. Prior to starting the discussion, it is assumed as a precondition that existence of PDGI bilayers does not significantly affect intrinsic physical properties of a PAAm matrix. Validity of this assumption is suggested by our previous results, which is that the elastic modulus of the sheet-like PDGI/PAAm gels perpendicular to the lamellar layers, $E_{\perp}$, is similar to that of a PAAm gel.[7] In consideration of anisotropic structure of hard PDGI and soft PAAm, $E_{\perp}$ of the sheet-like PDGI/PAAm gel should be determined mainly by the PAAm matrix inside it. The similar $E_{\perp}$ of the PDGI/PAAm gel and the PAAm gel implies that intrinsic physical property of a PAAm matrix in a PDGI/PAAm gel is quite similar to that of a sole PAAm gel, and not affected by a presence of PDGI bilayers.

When an MC-PDGI gel swells in its good solvent, the area expansion ratio of each cylindrical bilayer A/A_{ref} should be equal to $(DL)/(D_{ref}L_{ref})$. L/L_{ref} of the MC-PDGI gel and the PAAm gel as a function of their D/D_{ref} is shown in **Figure 4**. Pure gels without bilayers should satisfy $L/L_{ref} = D/D_{ref}$ to maintain isotropy, while pure bilayers should follow $A/A_{ref} = 1$ (or $L/L_{ref} = (D/D_{ref})^{-1}$) to maintain a constant bilayer area. Data of the PAAm gel are

consistent with those of an isotropic gel (slope = 1), while those of the MC-PDGI gel are between those of an isotropic gel and an ideal bilayer (slope = -1). This result suggests that the natures of both PAAm networks and PDGI bilayers dominate the anisotropic deformation of MC-PDGI gels. Upon swelling, an MC-PDGI gel must change its swelling ratio $V/V_{ref} = (D^2L)/(D_{ref}^2L_{ref})$ while maintaining $A/A_{ref} = (DL)/(D_{ref}L_{ref})$ constant as best as possible. In order to realize such swelling, D should increase during the swelling process (volume increase), whereas L should decrease, which is consistent with the swelling-induced contraction of the MC-PDGI gel. Such anisotropic swelling of MC-PDGI gels is reminiscent of liquid crystal (LC) elastomers, which are rubbery materials containing ordered mesogenic units.[26-28] If the LCs in an LC elastomer has long-range order, its anisotropic mechanical and physical properties arise owing to the coupling of the anisotropic mesogenic structure and isotropic rubber elasticity. In this study, our PDGI/PAAm gels could be considered as lyotropic smectic A LC elastomers. The PDGI lamellar lipid bilayer in MC-PDGI gels can be deemed as a smectic A lyotropic LC, and the coupling of the anisotropic LC structure and isotropic gel structure causes anisotropic swelling of the MC-PDGI gels.

In addition to the swelling anisotropy, the MC-PDGI gels show unique quasi one-dimensional diffusion, as shown in **Figure 5**. In an ideal case, a conventional gel will absorb solvent equally from all of its interface during swelling. In the case of MC-PDGI gels, however, this behavior occurs preferentially at the edge of the gels in the early stages of swelling. This unique behavior arises from the multi-cylindrical bilayers in the gels. Because the inner part of the PDGI bilayer membrane is hydrophobic, penetration of water or other hydrophilic molecules through the PDGI bilayers is hindered.[29] Considering the multi-cylindrical bilayer structure in the gels (Figure 1), diffusion of water molecules along the axial direction may be free because water molecules can diffuse almost freely inside PAAm gels,[30] whereas the diffusion along the radial direction should be more difficult since the bilayers hinder this behavior. Inspired by this result, we subsequently performed

molecular diffusion test inside the MC-PDGI gel. It is expected that hydrophilic molecules such as water can diffuse freely along the axial direction of the MC-PDGI gels, but hardly diffuse along the radial direction of the gels due to their multi-cylindrical bilayers.

In order to confirm this assumption, MB as a model reagent was loaded into the string PAAm gel and the MC-PDGI gel with lengths of 2 cm or 6 cm, respectively, and the gels containing MB were immersed in pure water to observe the diffusion behavior of MB. The amount of MB diffusion from the gels to the outside was monitored by measuring the absorbance I of the surrounding solution, which should be proportional to the amount of MB diffused from gels, as shown in Figure 5(b). In this work, we normalized I to I_{max}, which is the maximum I for each measurement; therefore, I/I_{max} denotes the ratio of diffused MB from the gels. Note that in pure water MB (or its aggregation) is enough smaller than mesh size of the PAAm matrix, as discussed in the experimental part. Figure 5(c) shows I/I_{max} of the samples as a function of time. Diffusion of MB out of the PAAm gel was completed within 1 h, while this process took approximately 2 days for the MC-PDGI gels. To index the diffusion time, we define the time constant τ as the time at which the ratio of remaining MB in a gel ($1-(I/I_{max})$) reaches $1/e$. The values of τ for the two MC-PDGI gels (91.4 min for 2-cm samples and 98.4 min for 6-cm samples) are approximately 4 times larger than that of the PAAm gel (22.8 min), suggesting that the cylindrical bilayers effectively retard MB diffusion through the side wall. However, τ had no significant dependence on the gel length in this case, suggesting that the diffusion through the side wall undesirably dominates the drug release of MC-PDGI gels. Compared to its as-prepared state, the area of the bilayer in the MC-PDGI gel expanded 1.24 times after swelling in water, which may generate defects in the bilayers through which MB molecules can freely pass. To suppress defect generation, we used a 15 wt% PEG aqueous solution instead of water for both the loading and diffusion of MB. The bilayers area expanded 0.81 times in this solution, implying that swelling-induced defect generation can be neglected under these conditions. Figure 5(d) shows the diffusion results of

the 15 wt% PEG aqueous solution. The resulting τ increased by changing the solvent from water to PEG solution, and τ of the 6-cm MC-PDGI gel (2,380 min) was 3.7 times larger than that of the 2-cm sample (646 min). Moreover, images of the MC-PDGI gels after $t = 2.9\times10^3$ min (~2 d) of the diffusion process clearly show that the diffusion of MB occurs preferentially at the edges (Figure 5(e)). These results suggest that more sustained, unidirectional molecular diffusion can be achieved by suppressing bilayer expansion and defect formation. For ideal one-dimensional diffusion, the characteristic diffusion time of the 6-cm sample should be 9 ($=(6/2)^2$) times longer than that of the 2-cm sample, whereas the experimental result of the former was only 4 times larger than that of the latter.[31] This suggests that some leakage from the side wall still occurs even though the sample used was in the non-swollen state. This indicates that the lamellar bilayers of the gels immersed in 15 wt% PEG aqueous solution still contain some defects. Developing defect-free multi-cylindrical structures of PDGI lamellar bilayers will be the subject of future works.

In this paper, we explained that retardation of the MB diffusion in the MC-PDGI gels is caused by hindrance of MB diffusion through the cylindrical bilayers. Another possible explanation for this phenomenon is weak adsorption of MB molecules in the PDGI bilayers, which can make the MB diffusion slower. However, if the adsorption is the main reason of the slow MB diffusion in the MC-PDGI gels, sample length dependence on diffusion time should always appear irrespective of presence or absence of defects in the bilayers since the adsorption behavior of MB should not be affected by the defect formation in the bilayers. Thus, we conclude that hindrance of MB diffusion through the bilayers is dominant on the retardation of the MB diffusion in MC-PDGI gels.

Conclusions

We have successfully created supramolecular string PDGI/PAAm hydrogels (MC-PDGI gels) consisting of tree-ring-like PDGI lamellar bilayers embedded into a polyacrylamide gel

matrix. MC-PDGI gels possess unique anisotropic physical behaviors such as swelling-induced contraction and quasi one-dimensional diffusion, which arise from the coupling of the inherent characteristics of isotropic gels and anisotropic lipid bilayers. The anisotropic swelling behavior of MC-PDGI gels may be useful for future use in actuators. When an MC-PDGI gel and a common gel are immersed in PEG aqueous solutions, the length of the former increases while that of the latter decreases. By laminating these materials, a gel that bends in response to the osmotic pressure of the surrounding solution can be generated. Molecular diffusion tests of the MC-PDGI gels also suggest at the possibility of their use in prolonged drug-release applications. When drug molecules are loaded in an MC-PDGI gel and the gel is embedded in the body, drug gradually and continuously releases from the gel. Such sustained drug release helps to keep a desirable concentration of drugs in the body and to make the drug work more efficiently.

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Figure 1 (color both in print/on web). Structure evaluation of water-swollen MC-PDGI gels. (a) Visual appearance. (b) 2-D SAXD pattern (side view). (c) X-ray intensity (integrated along the meridian direction) as a function of $q = 4\pi\sin\theta/\lambda$ (nm^{-1}). (d-g) POM images under crossed polarizers; (d) side view of the sample in parallel to the polarizer; (e, f) after 45° rotation (e) without and (f) with the 530 nm sensitive tint plate; (g) cross-sectional view with the same tint plate. (h) Estimated multi-cylindrical structure of the MC-PDGI gels.

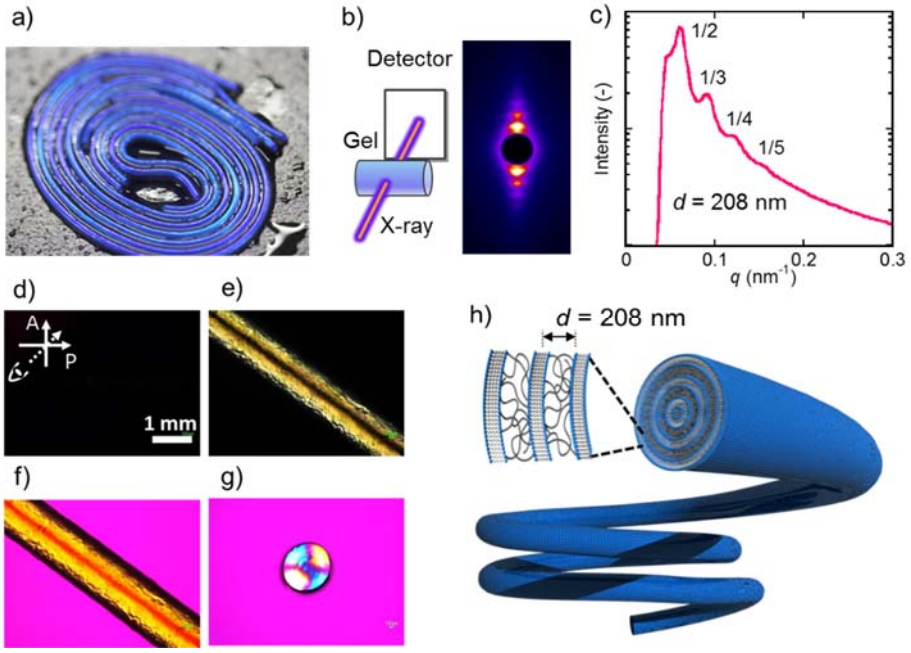


Figure 2 (color only on web). Images of a MC-PDGI gel in (a) as-prepared and (b) water-swollen states. Brightness and contrast of the pictures were optimized to clarify the sample shape.

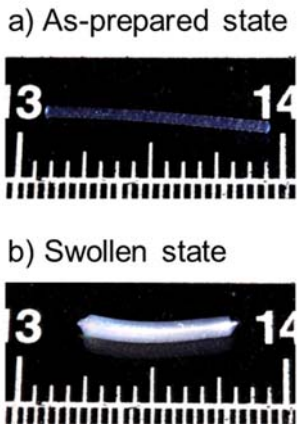


Figure 3 (color only on web). (a, b) Swelling ratios of the PAAm gel and the MC-PDGI gel as a function of PEG concentration. (c) MC-PDGI gels immersed in various PEG solutions. (d) Cyclic deformation of the MC-PDGI gel by alternating immersion in water and 20 wt% PEG aqueous solution.

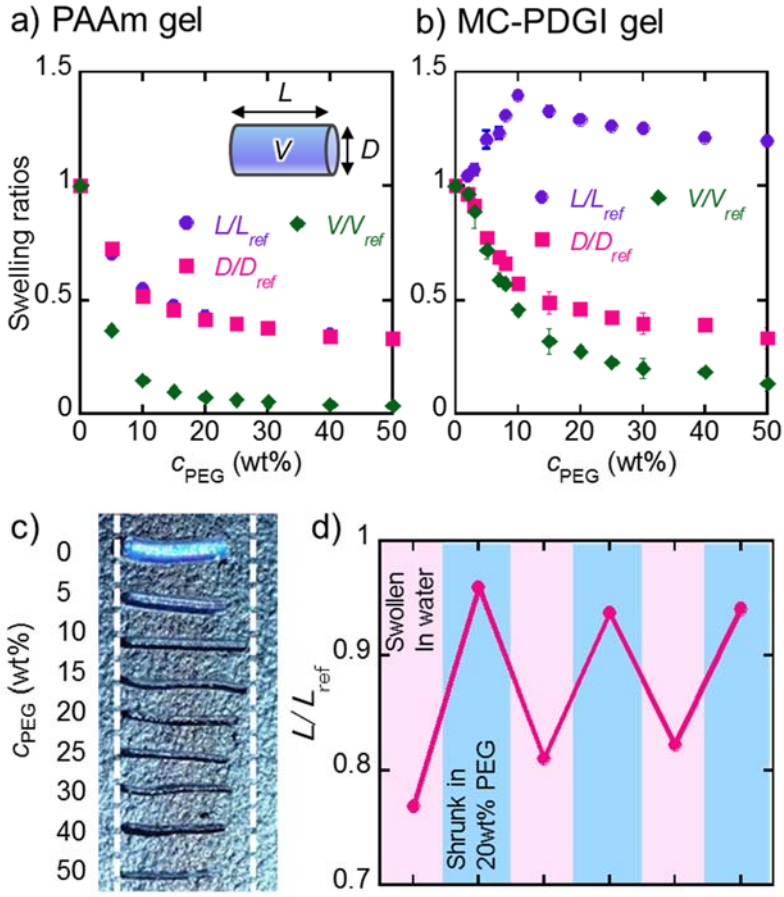


Figure 4 (color only on web). L/L_{ref} of the PAAm gel and MC-PDGI gel as a function of D/D_{ref}. Data of an isotropic ideal gel should follow the solid line, whereas data of an ideal bilayer should follow the dashed line.

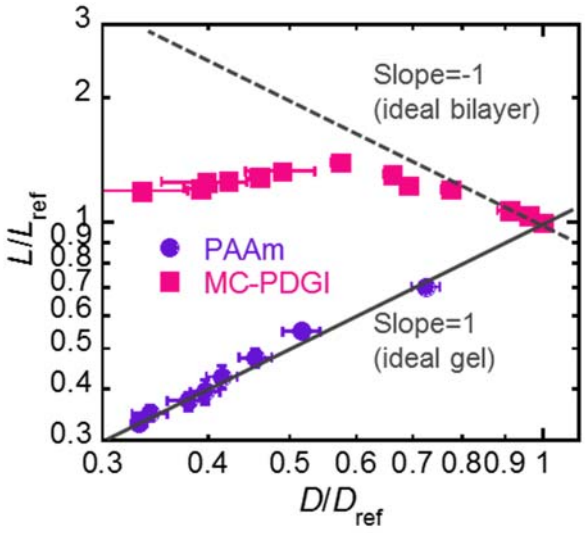
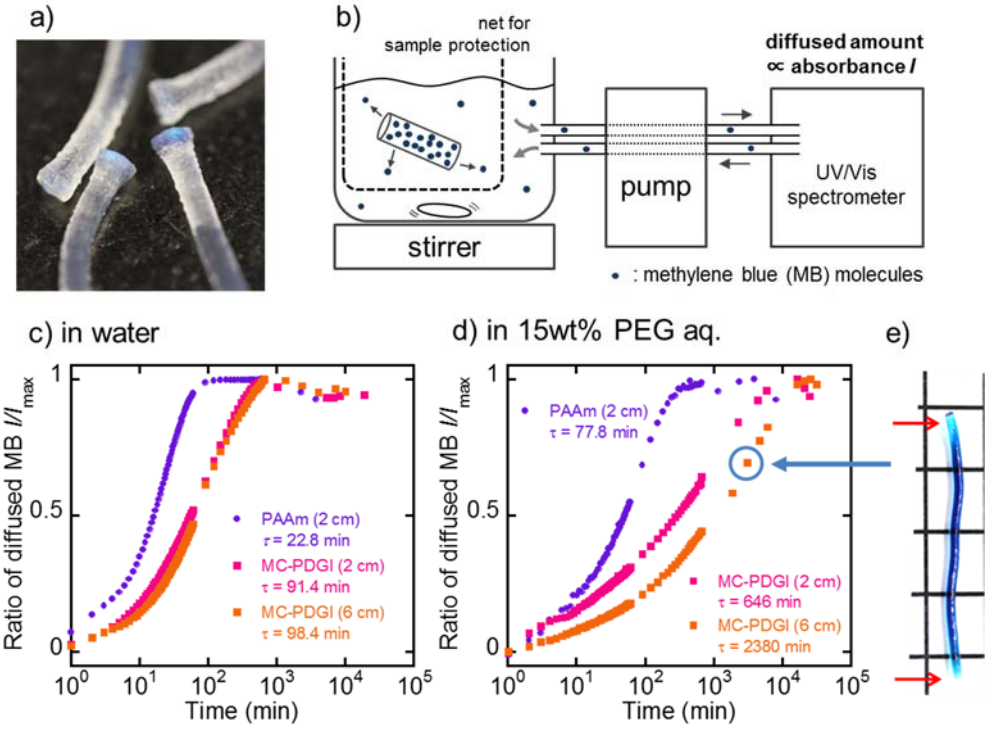


Figure 5 (color both in print/on web). Anisotropic diffusion of the MC-PDGI gels. (a) A photo of the initial swelling process of the MC-PDGI gels in pure water. (b) Experimental setup for the diffusion test. (c) Diffusion ratio I/I_{max} of MB from the PAAm gel and the MC-PDGI gel (sample length: 2 cm or 6 cm, respectively) in pure water, and (d) that in 15 wt% PEG solution as a function of time. (e) MC-PDGI gels (length: 6 cm) during diffusion experiments in PEG solution ($t = 2.9\times10^3$ min).



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Supramolecular Hydrogels with Multi-Cylindrical Lamellar Bilayers: Swelling-Induced Contraction and Anisotropic Molecular Diffusion

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