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COMMUNICATION

Quasi-Unidirectional Shrinkage of Gels with Well-Oriented Lipid Bilayers upon Uniaxial Stretching

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The PDGI/PAAm gels with well oriented lipid bilayers show quasi-unidirectional shrinkage upon uniaxial stretching along bilayers. They shrink largely parallel to bilayer but slightly perpendicular to bilayer in order not to increase bilayer area and its interfacial energy. Such anisotropic deformation can be well-modelled based on classical theories for gel networks and lipid layers.

Generally, gels have isotropic network structure and show isotropic deformation as shown in Figure 1(a). One of typical example is free swelling. When isotropic gels are immersed in solvents, deformation (swelling) ratio of each direction α is ideally same. Also, uniaxial stretching is frequently-performed experiments. Note that gels' Poisson's ratio is very close to 0.5 if solvent exchange is not accompanied to the deformation [1]. When gels are uniaxially stretched in x -axis with the deformation ratio of λ , they similarly shrink in y and z -axis with the deformation ratio of $\lambda^{-0.5}$. On the other hand, if any restriction is introduced to gels, deformation of such gels does not follow the formulas of isotropic gels [2-5]. For example, when a hydrogel having liquid crystalline structure was put under magnetic field, orientation of liquid crystal induces anisotropic swelling of the gel [2]. A spherical gel surrounding a hard core shows water content distribution at equilibrium state due to swelling constraint near a core [3]. If the gel with patterned cross-linking distribution swells, many bumps are formed on its surface due to swelling degree distribution [4].

As a kind of the gels having such restrictions, a PDGI/PAAm gel with thousands of monodomain lamellar bilayer has been reported [6-9]. This gel consists of hard, uniaxially-oriented sheet-like poly(dodecyl glycidyl itaconate)(PDGI) lipid bilayers fixed within soft PAAm gel as matrix. Structure of a PDGI/PAAm gel is shown in Figure 1(b). Monodomain PDGI bilayer structure is realized by applying strong shear when the gel precursor solution is poured into

a mould [6]. This gel shows brilliant structural colour due to its well-oriented and periodic lamellar structure. This colour can be modulated by external stimuli such as mechanical force [6,8], pH and temperature [9].

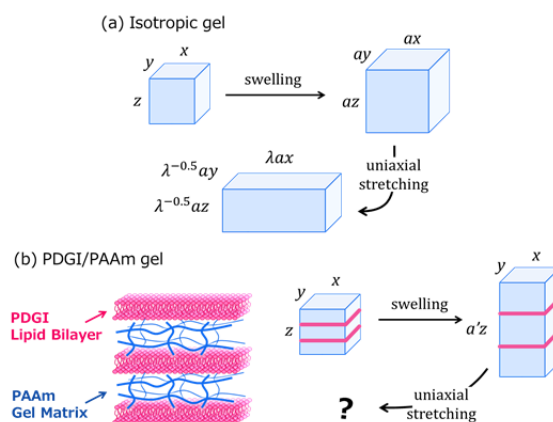


Figure 1: (a) Size change of an isotropic gel upon swelling and uniaxial stretching. (b) The structural model and unidirectional swelling behaviour of a PDGI/PAAm gel with hard monodomain lipid bilayers in soft gel matrix.

One of the most remarkable behaviour of a PDGI/PAAm gel is unidirectional swelling, shown in Figure 1(b) [6]. When the PDGI/PAAm gel with oriented PDGI bilayer in x - y plain is swollen in water, this gel swells only along z -axis, which is perpendicular to the bilayer plain. Such unidirectional swelling of gels with layered structure has been also reported by Kang *et al.* [10]. This strange phenomenon is because increasing area of bilayer is energetically unfavourable. The amorphous PAAm gel layers tend to keep their "shape" during swelling as explained above, whereas lipid bilayers tend to keep their "area" upon deformation to maintain low surface

energy. If a PDGI/PAAm gel swells in x or y -axis, this process always accompanies area expansion of bilayer, which is energetically unfavourable. As a result, a PDGI/PAAm gel tends to swell only along z -axis. More precisely, Wang *et al.* have proposed the simple theoretical model to explain this anisotropic swelling of PDGI/PAAm gels [11].

As such anisotropic PDGI/PAAm gels show anisotropic swelling due to bilayers, they also should show anisotropic deformation upon uniaxial stretching. Although this prediction is interesting in physical viewpoint, no study for this subject has been reported. Thus, the aim of this study is to investigate how PDGI/PAAm gels deform anisotropically upon uniaxial stretching. In this paper, we investigate deformation behaviour of the PDGI/PAAm gels upon uniaxial stretching by experiment firstly, then establish the theoretical model to explain these experimental phenomena.

For the sample, the monodomain PDGI/PAAm gel was prepared as reported [6]. Briefly, 0.1 M of dodecyl glycidyl itaconate as polymerizable lipid, 2.5 mM of sodium dodecyl sulfate (SDS) as additive, 2 M of acrylamide as monomer, 0.1 mol% of N,N' -methylene(bis)acrylamide as cross-linker, and 0.1 mol% of IRGACURE 2959 as initiator were added to pure water, and gently mixed at 55 °C for 3 hours. The glass mould was prepared from two glass plates (thickness = 3 mm) separated by silicone rubber spacer (thickness = 0.5 mm). Length and width of the space in the mould were 90 mm and 20 mm, respectively. Then the solution was poured into the glass mould with strong shear. Polymerization of PDGI and PAAm was then immediately carried out by irradiation of 365 nm UV light for 8 h. After polymerization, the gel was immersed in pure water for 3 d to remove any residual chemicals.

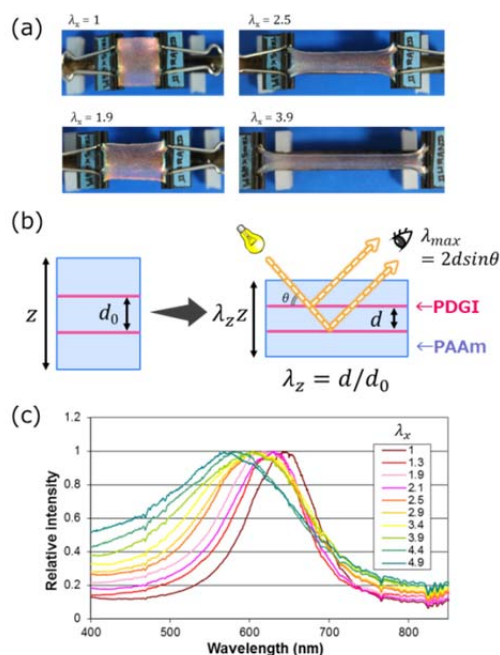


Figure 2: (a) Excerpted pictures of the deformed PDGI/PAAm gel. λ_y was determined by direct measurement of gel width. (b) Concepts how to determine λ_z . λ_z can be indirectly determined from layer distance d , which can be measured by the reflection spectra with Bragg's law. (c) Reflection spectra of the deformed gels with several λ_x . In this experiment, θ was 60°.

Here, we chose water swelling state (just before stretching) as reference state of gels, and defined λ_i ($i = x, y$ or z) as deformation ratio of reference gels in x, y, z -axis caused by uniaxial stretching. Both sides of gel samples were fixed by the two clips and uniaxially stretched along x -axis slowly by hand to several desired deformation

ratio λ_x . Here, it should be noted that the following measurements of λ_y and λ_z have been done after waiting for more than 90 s until complete relaxation (see Figure S1 of Supplementary Information for stress relaxation test). λ_y was determined by direct measurement of gel width analysed from the pictures of the deformed gels shown in Figure 2(a). λ_z was determined by reflection spectrum measurement of the gels with a Hamamatsu Photonics KK, C10027 device [6, 8]. Distance of two adjacent lamellar sheets d for each λ_x was calculated from the peak wavelength of the reflection spectra by using Bragg's law (concept of the measurement and raw spectra are shown in Figure 2(b) and (c), respectively). As change of d should be proportional to change of gel thickness in z -axis, λ_z can be calculated as $\lambda_z = \frac{d}{d_0}$, where d_0 is d in reference state. At any λ_x , calculated change of gel volume $\lambda_x \lambda_y \lambda_z$ is almost 1, which verifies accuracy of our measurements of λ_y and λ_z (see Figure S2 of Supplementary Information).

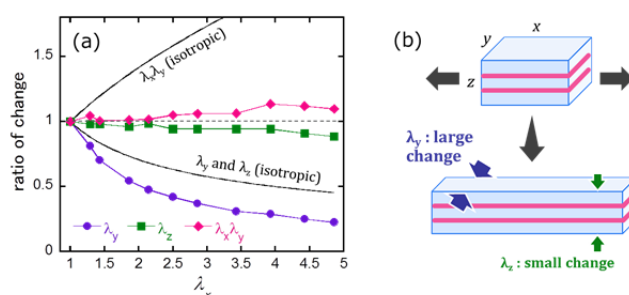


Figure 3: (a) Changes of λ_y , λ_z and $\lambda_x \lambda_y$ of the uniaxially-stretched PDGI/PAAm gel upon changing the deformation ratio in x -axis λ_x . (b) An illustration of a uniaxially-stretched PDGI/PAAm gel. It remarkably shrinks in y -axis but slightly in z -axis.

Figure 3(a) shows changes of λ_y and λ_z of the uniaxially-stretched PDGI/PAAm gel upon changing the deformation ratio in x -axis λ_x . The anisotropic PDGI/PAAm gel did not follow the formula for isotropic gels, and showed abnormal deformation. In particular, λ_y remarkably decreased with deformation ratio λ_x following the relationship of $\lambda_y \propto \lambda_x^{-0.93}$, whereas λ_z slightly decreased with λ_x following $\lambda_z \propto \lambda_x^{-0.06}$. In other words, upon stretching along x -axis, the PDGI/PAAm gel shrinks largely in direction parallel to bilayer but slightly in direction perpendicular to bilayer like shown in Figure 3(b). Thus, this phenomenon can be called 'quasi-unidirectional shrinkage' upon uniaxial stretching. Such quasi-unidirectional shrinkage has been also reported by Finkelmann *et al.* using monodomain thermotropic liquid crystal (LC) elastomer [12]. As their elastomer has modulus anisotropy, it mainly shrinks along soft direction when stretched uniaxially. Our system, which can be called monodomain lyotropic LC gel having modulus anisotropy, looks to show similar shrinkage to Finkelmann's system. However, surprisingly, our gel shrinks along 'hard' direction, which is opposite to their system.

To understand the reason of unidirectional shrinkage and the difference in shrinking direction of the PDGI/PAAm gels, we took notice on change of PDGI bilayer area. This is because not uniaxial deformation ratio but area expansion ratio is important for considering mechanics of lipid membranes [13-14]. For this reason, we also calculated change of $\lambda_x \lambda_y$, which corresponds to area expansion ratio of PDGI bilayer, with change of λ_x . The results are also shown in Figure 3(a). Though isotropic gels should follow $\lambda_x \lambda_y \propto \lambda_x^{0.5}$, the anisotropic PDGI/PAAm gel followed the different relationship of $\lambda_x \lambda_y \propto \lambda_x^{0.07}$, which has quite small value of

exponent. This strange deformation behaviour of the PDGI/PAAm gel suggests that it deforms with keeping minimum change of bilayer area. This conclusion is convincing if we imagine expansion of conventional lipid layers. Generally, expansion of layer area requires large energy due to generation of extra hydrophobic interface between water and layer [13]. On the other hand, flow and deformation of lipid layer without changing its area accompany negligible free energy change. Therefore, if only deformation of PDGI bilayers is considered, the most energetically-suitable way for the PDGI/PAAm gel stretched along x -axis is shrinkage along y -axis accompanied by flow of bilayers to avoid increase of bilayer area. It is noted that although PDGI molecules are not monomer but polymer, PDGI bilayers probably can flow freely. This is because polymerization degree of PDGI is just in order of 100 and it is not chemically connected to the PAAm network [15].

Based on these findings, we tried to establish simple theoretical models for such quasi-unidirectional shrinkage of the PDGI/PAAm gels upon uniaxial stretching. Helmholtz free energy change per unit volume ΔF_{total} (J/m^3) of conventional neutral gels upon deformation is sum of two contributions; those are mixing term and elastic term of network [16-17]. In our case, as volume change of the gels due to elongation is negligible, mixing term can be ignored. In addition, as the PDGI/PAAm gel contains bilayers, elastic term of bilayers also should be considered. As a result, we obtain ΔF_{total} (J/m^3) of the PDGI/PAAm gels upon uniaxial deformation as:

$$\Delta F_{total} = \Delta F_{el,g} + \Delta F_{el,d} \quad (1)$$

where $\Delta F_{el,g}$ and $\Delta F_{el,d}$ are the elastic terms of gels and PDGI bilayers, respectively. For $\Delta F_{el,g}$, we simply adopt classical Neo-Hookean rubber elasticity theory as:

$$\Delta F_{el,g} = \frac{E_{gel}}{6} (\lambda_x^2 + \lambda_y^2 + (\alpha' \lambda_z)^2 - (2 + \alpha')) \times \frac{d_0 - d_{dgi}}{d_0} \quad (2)$$

where E_{gel} (Pa) is Young's modulus of the PAAm layer, α' is the swelling ratio of the PDGI/PAAm gels along z -axis (see Figure 1), and d_{dgi} (m) is thickness of single PDGI bilayer [16-17]. The reason of coefficient α' before λ_z is because the PAAm network is already pre-stretched α' times along z -axis at reference state due to unidirectional swelling. The final $(d_0 - d_{dgi})/d_0$ means volume fraction of PAAm matrices in the PDGI/PAAm gel.

For $\Delta F_{el,d}$, we consulted elastic lipid membranes. According to the literature [14], Helmholtz free energy change per single lipid molecule upon membrane extension $\Delta\mu$ (J) can be roughly estimated as:

$$\Delta\mu = \frac{\gamma}{a} (a - a_0)^2 \quad (3)$$

where γ ($N m^{-1}$) is interfacial tension, a (m^2) is interfacial area occupied by single lipid molecule, and a_0 is a in initial state, which should be the optimum interfacial area. Under the assumption that area expansion ratio of a whole membrane $\lambda_x \lambda_y$ is equal to that of each single molecule a/a_0 , Eq. 3 can be rewritten as:

$$\Delta\mu = \frac{\gamma}{\lambda_x \lambda_y} a_0 (\lambda_x \lambda_y - 1)^2 \quad (4)$$

Single PDGI bilayer sheet having unit surface area at the initial state consists of $2/a_0$ of PDGI molecules (the coefficient 2 is because of 'bi'-layer). Also, volume of single PDGI bilayer sheet with unit surface area is $1 \times 1 \times d_{dgi}$. Hence, $\Delta F_{el,d}$ ($J m^{-3}$), which is free energy change of the PDGI bilayers per unit volume of the PDGI/PAAm gel, can be calculated as:

$$\Delta F_{el,d} = \Delta\mu \frac{2}{a_0 d_{dgi}} \times \frac{d_{dgi}}{d_0} = \frac{2\gamma}{\lambda_x \lambda_y d_0} (\lambda_x \lambda_y - 1)^2 \quad (5)$$

The d_{dgi}/d_0 in the second term means volume fraction of the PDGI bilayers in the PDGI/PAAm gel. Substituting Eqs. 2 and 5 to Eq. 1 and using the relationship of $\lambda_x \lambda_y \lambda_z = 1$, we finally obtain:

$$\Delta F_{total} = \frac{E_{gel}}{6d_0} \left(\lambda_x^2 + \lambda_y^2 + \left(\frac{\alpha'}{\lambda_x \lambda_y} \right)^2 - (2 + \alpha') \right) (d_0 - d_{dgi}) + \frac{2\gamma}{\lambda_x \lambda_y d_0} (\lambda_x \lambda_y - 1)^2 \quad (6)$$

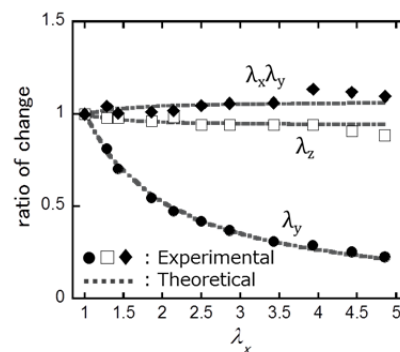


Figure 4: Theoretical fitting results of λ_y , $\lambda_z (=1/\lambda_x \lambda_y)$ and $\lambda_x \lambda_y$ of the uniaxially-stretched PDGI gel upon changing λ_x , based on Eq.(6) using $\gamma=10.0$ mN/m. Dashed lines and symbols represent model fitting curves and real experimental results, respectively.

Using experimental parameters of $d_0=251$ nm, $d_{dgi}=4.7$ nm [18], $\alpha'=2.1$ and $E_{gel}=0.01$ MPa (roughly estimated from the compression test shown in ref.6), we calculated the λ_y which gives the lowest ΔF_{total} for various λ_x using numerical calculation technique with γ as the fitting parameter. Figure 4 shows the fitting results of λ_y , λ_z and $\lambda_x \lambda_y$ dependence on λ_x . If $\gamma = 10.0$ mN m^{-1} was used, the fitting lines almost overlapped with the experimental results. This value of γ is comparable to the reported values of $\gamma \sim 10 \sim 100$ mN/m for some synthetic or natural lipid membranes [13-14]. These facts confirm the adequacy of our simple theory.

Finally, we should make comments about difference between the result of this work and our previous work [7]. This time we observed almost no colour change upon stretching. On the other hand, in our previous work [7], we have shown uniaxial deformation-induced colour change. The reason of the difference is probably that in the previous work we measured the reflection spectra before relaxation whereas this work we did it after relaxation. We have confirmed that the colour of the gel changes upon fast uniaxial deformation, while it slightly changes upon slow deformation.

In conclusion, we have found quasi-unidirectional shrinkage of the PDGI/PAAm gels with well-oriented lipid bilayers. When they are stretched parallel to bilayer, they tend to deform along the direction perpendicular to bilayer without increasing bilayer area. The simple theoretical model based on elasticity of gel network and lipid layer can well explain such anisotropic deformation. In future, design and creation of novel lipid layer-gel composites showing unique, anisotropic deformation based on this theory is expected. Such materials are possibly applied to artificial muscle with unique motion.

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Notes and references

† Electronic Supplementary Information (ESI) available: [Stress relaxation experiment and gel volume change upon deformation]. See DOI: 10.1039/c000000x/

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Table of Contents:

The hydrogels with well-oriented lipid bilayer showed strange, unique deformation upon uniaxial stretching, which can be explained with a simple theoretical model.

