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Quasi-unidirectional shrinkage of gels with well-oriented lipid bilayers upon uniaxial stretching†

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

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

One kind of gel having such restrictions, the PDGI–PAAm gel with thousands of monodomain lamellar bilayers, 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 the matrix. The structure of a PDGI–PAAm gel is shown in Fig. 1(b). The monodomain PDGI bilayer structure is realized by applying a 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]

One of the most remarkable behaviours of a PDGI–PAAm gel is unidirectional swelling, shown in Fig. 1(b).[6] When the PDGI–PAAm gel with an oriented PDGI bilayer in the x–y plain is swollen in water, this gel swells only along the z-axis, which is perpendicular to the bilayer plain. Such unidirectional swelling of gels with a layered structure has been also reported by Kang *et al.*[10] This strange phenomenon is because increasing the area
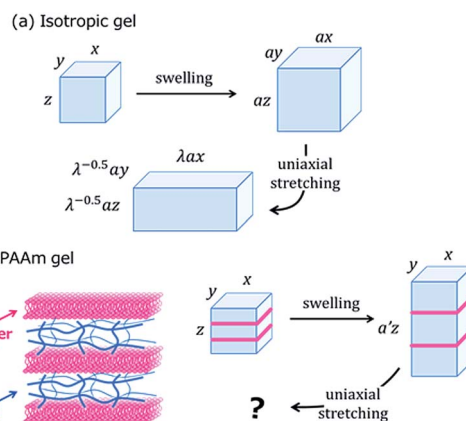
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Fig. 1 (a) Size change of an isotropic gel upon swelling and uniaxial stretching. (b) The structural model and unidirectional swelling behaviour of a PDGI–PAAm gel with hard monodomain lipid bilayers in the soft gel matrix.

of the 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 a low surface energy. If a PDGI–PAAm gel swells along the x or y-axes, this process is always accompanied by an area expansion of the bilayer, which is energetically unfavourable. As a result, a PDGI–PAAm gel tends to swell only along the z-axis. More precisely, Wang and Hong have proposed a simple theoretical model to explain this anisotropic swelling of PDGI–PAAm gels.[11]

As such anisotropic PDGI–PAAm gels show anisotropic swelling due to the bilayers, they also should show anisotropic deformation upon uniaxial stretching. Although this prediction is interesting from the physical point of view, 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 the deformation behaviour of PDGI–PAAm gels upon uniaxial stretching by experiments first, then we establish the theoretical model to explain these experimental phenomena.

For the sample, a monodomain PDGI–PAAm gel was prepared as reported previously.[6] Briefly, 0.1 M of dodecyl glycidyl itaconate as the polymerizable lipid, 2.5 mM of sodium dodecyl sulfate (SDS) as the additive, 2 M of acrylamide as the monomer, 0.1 mol% of N,N'-methylene(bis)acrylamide as the cross-linker and 0.1 mol% of IRGACURE 2959 as the 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 a silicone rubber spacer (thickness = 0.5 mm). The 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 under strong shear. Polymerization of PDGI and PAAm was then immediately carried out by irradiation with a 365 nm UV light for 8 h. After polymerization, the gel was immersed in pure water for 3 d to remove any residual chemicals.

Here, we chose the water swelling state (just before stretching) as the reference state of gels, and defined λ_i ($i = x, y$ or z) as the deformation ratio of the reference gels along the x, y and z-axes caused by uniaxial stretching. Both sides of the gel samples were fixed by two clips and uniaxially stretched along the x-axis slowly by hand to several desired deformation ratios, 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 Fig. S1 of the ESI† for stress relaxation tests). λ_y was determined by direct measurement of the gel width analysed from the pictures of the deformed gels shown in Fig. 2(a). λ_z was determined by reflection spectrum measurements of the gels with a Hamamatsu Photonics KK, C10027 device.[6,8] The 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 for the measurement and raw spectra are shown in Fig. 2(b) and (c), respectively). As a change of d should be proportional to a change of gel thickness along the z-axis, λ_z can be calculated as $\lambda_z = \dfrac{d}{d_0}$, where d_0 is d in the reference state. At any λ_x, the calculated change of gel
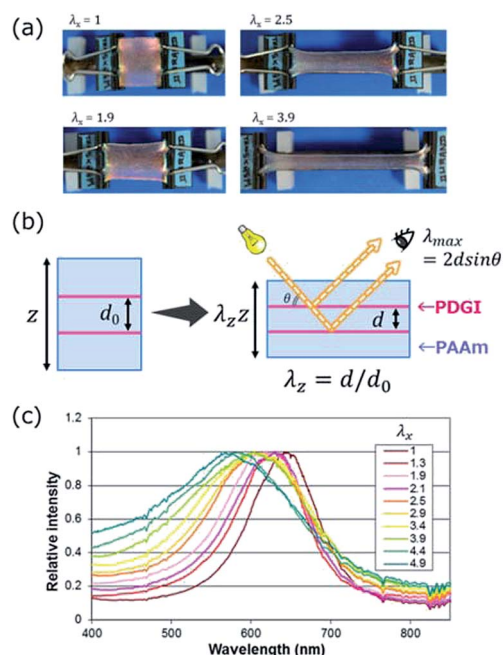

Fig. 2 (a) Selected pictures of the deformed PDGI–PAAm gel. λ_y was determined by direct measurement of the gel width. (b) Schematic of the concept for determining λ_z. λ_z can be indirectly determined from the layer distance, d, which can be measured by the reflection spectra with Bragg's law. (c) Reflection spectra of the deformed gels with several λ_x values. In this experiment θ was 60°.

volume $\lambda_x\lambda_y\lambda_z$ is almost 1, which verifies the accuracy of our measurements of λ_y and λ_z (see Fig. S2 of the ESI†).

Fig. 3(a) shows the changes of λ_y and λ_z of the uniaxially-stretched PDGI–PAAm gel upon changing the deformation ratio along the x-axis, λ_x. The anisotropic PDGI–PAAm gel did not follow the formula for isotropic gels, and showed an abnormal deformation. In particular, λ_y remarkably decreased with the deformation ratio λ_x following the relationship $\lambda_y \propto \lambda_x^{-0.93}$, whereas λ_z slightly decreased with λ_x following $\lambda_z \propto \lambda_x^{-0.06}$. In other words, upon stretching along the x-axis, the PDGI–PAAm gel shrinks largely along the direction parallel to the bilayer but also slightly along the direction perpendicular to it, as shown in Fig. 3(b). Thus, this phenomenon can be called 'quasi-unidirectional shrinkage' upon uniaxial stretching. Such quasi-
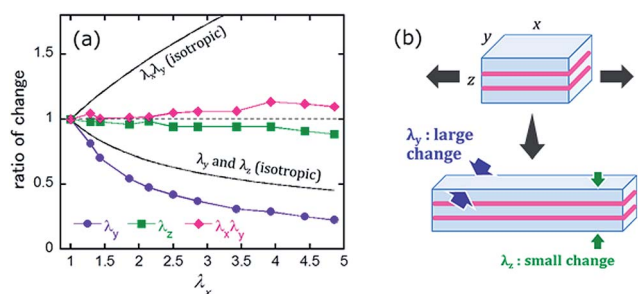

Fig. 3 (a) Changes of λ_y, λ_z and $\lambda_x\lambda_y$ of a uniaxially-stretched PDGI–PAAm gel upon changing the deformation ratio along the x-axis, λ_x. (b) Illustration of a uniaxially-stretched PDGI–PAAm gel. It remarkably shrinks along the y-axis but only slightly along the z-axis.

unidirectional shrinkage has been also reported by Finkelmann and Nishikawa using a monodomain thermotropic liquid crystal (LC) elastomer.[12] As their elastomer has modulus anisotropy, it mainly shrinks along the soft direction when stretched uniaxially. Our system, which can be called a mono-domain lyotropic LC gel having modulus anisotropy, seems to show a similar shrinkage to Finkelmann's system. However, surprisingly, our gel shrinks along the 'hard' direction, which is the opposite to their system.

To understand the reason for the unidirectional shrinkage and the difference in shrinking direction of PDGI–PAAm gels, we studied the changes of the PDGI bilayer area. This is because not the uniaxial deformation ratio but the area expansion ratio is important when considering the mechanics of lipid membranes.[13,14] For this reason, we also calculated the change of $\lambda_x\lambda_y$, which corresponds to the area expansion ratio of the PDGI bilayer with changes of λ_x. The results are also shown in Fig. 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 a small value of the exponent. This strange deformation behaviour of the PDGI–PAAm gel suggests that it deforms while keeping the change of bilayer area to a minimum. This conclusion is convincing if we imagine the expansion of conventional lipid layers. Generally, an expansion of layer area requires a large energy due to the generation of an extra hydrophobic interface between water and the layer.[13] On the other hand, flow and deformation of the lipid layer without changing its area is accompanied by a negligible free energy change. Therefore, if only the deformation of the PDGI bilayers is considered, the most energetically-suitable way for the PDGI–PAAm gel to stretch along the x-axis is to shrink along the y-axis accompanied by a flow of bilayers to avoid the increase of bilayer area. It is noted that although PDGI molecules are not monomers but polymers, PDGI bilayers probably can flow freely. This is because the polymerization degree of PDGI is just in the 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 a quasi-unidirectional shrinkage of the PDGI–PAAm gels upon uniaxial stretching. The Helmholtz free energy change per unit volume, ΔF_{total} (J m^{-3}), of conventional neutral gels upon deformation is the sum of two contributions: the mixing term and elastic term of the network.[16,17] In our case, as the volume change of the gels due to elongation is negligible, the mixing term can be ignored. In addition, as the PDGI–PAAm gel contains bilayers, the elastic term of the bilayers also should be considered. As a result, we obtain ΔF_{total} (J m^{-3}) of the PDGI–PAAm gels upon uniaxial deformation as:

$$\Delta F_{total} = \Delta F_{el\_g} + \Delta F_{el\_d} \tag{1}$$

where ΔF_{el_g} and ΔF_{el_d} are the elastic terms of the gels and PDGI bilayers, respectively. For ΔF_{el_g}, we simply adopt classical neo-Hookean rubber elasticity theory as:

$$\Delta F_{el\_g} = \frac{E_{gel}}{6}\left(\lambda_x^2 + \lambda_y^2 + (\alpha'\lambda_z)^2 - (2+\alpha')\right) \times \frac{d_0 - d_{dgi}}{d_0} \tag{2}$$

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

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

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

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

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

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

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

The d_{dgi}/d_0 in the second term indicates the volume fraction of the PDGI bilayers in the PDGI–PAAm gel. By substituting eqn (2) and eqn (5) into eqn (1) and using the relationship $\lambda_x\lambda_y\lambda_z = 1$, we finally obtain:

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

Using the experimental parameters $d_0 = 251$ 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 values using a numerical calculation technique with γ as the fitting parameter. Fig. 4 shows the fitting results of the 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 $\gamma \sim 10$–100 mN m^{-1} for some synthetic or natural lipid membranes.[13,14] These facts confirm the adequacy of our simple theory.
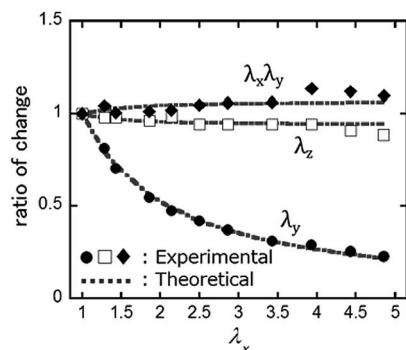
Fig. 4 Theoretical fitting results of λ_y, λ_z ($= 1/\lambda_x\lambda_y$) and $\lambda_x\lambda_y$ of the uniaxially-stretched PDGI gel upon changing λ_x based on eqn (6) using $\gamma = 10.0$ mN m^{-1}. Dashed lines and symbols represent model fitting curves and real experimental results, respectively.

Finally, we should comment on the difference between the results 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 changes. The reason for this difference is probably that in the previous work we measured the reflection spectra before relaxation, whereas in 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 a quasi-unidirectional shrinkage of the PDGI–PAAm gels with well-oriented lipid bilayers. When they are stretched parallel to the bilayer, they tend to deform along the direction perpendicular to it without increasing the bilayer area. A simple theoretical model based on the elasticity of the gel network and lipid layer can well explain such an anisotropic deformation. In the future, the design and creation of novel lipid layer–gel composites showing unique and anisotropic deformations based on this theory are expected. Such materials could possibly be applied to artificial muscles with unique motions.

Acknowledgements

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