Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for

Coupled instabilities of surface crease and bulk bending during fast free swelling of hydrogel

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Supplementary Methods

Preparation of hydrogel sheet

The positively charged gel was synthesized by radical polymerization of a cationic monomer, *N*-[3-(*N,N*-dimethyl amino)propyl] acrylamide methyl chloride quaternary (DMPAA-Q), and a chemical cross-linker, *N,N'*-methylenebis(acrylamide) (MBAA), in the presence of a small amount of semi-rigid polyanion, PBDT, as stress sensor. In order to synthesize the hydrogel film, the reaction cells were prepared by sandwiching a 1 cm wide silicone spacer (thickness: 3 mm) along the periphery between two parallel glass plates. The aqueous precursor solution contained 2.0 M DMAPAA-Q, 1.0 wt% PBDT, 2 mol% MBAA, and 0.15 mol% OA (the amount in mol% is related to DMAPAA-Q). After proper mixing, the pre-gel solution was injected into the reaction cells. UV irradiation from both sides of the reaction cell (UV light intensity is 3.9mW/cm^2) was performed for 6.0 h in an argon atmosphere at room temperature to form the gel.

Compression test

The compression measurements were performed on as-prepared and water-swollen gels using a tensile-compressive tester (Tensilon RTC-1310A, Orientec Co.). The as-prepared gel sheet was cut into specific dimensions (diameter: 10 mm; thickness: 3 mm) and compressed along the thickness direction of the samples at an extension rate of 0.3 mm/min. The swollen gel sheet was cut into specific dimensions (diameter: 10 mm; thickness: 6 mm) and compressed along the thickness direction of the sample at an extension rate of 0.6 mm/min. Tensile strain, ε, is defined as $(t-t_0)/t_0$, in which t_0 and t are the thickness of the gel before and during compression, respectively. The Young's moduli of the as-prepared and swollen samples were estimated from the stress-strain curves as 0.24 MPa and 0.11 MPa, respectively [Figure S1].

Mechanical properties of polyelectrolyte hydrogels with or without semi-rigid macromolecules

The PDMAPAA-Q hydrogel sheets containing PBDT molecules were synthesized like as mentioned above. Moreover, we synthesized PDMAPAA-Q gel (same composition without PBDT) as control. Then, the as-prepared samples were cut into specific dimensions (diameter: 10 mm; thickness: 3 mm) and immersed in water for 24 hours. After reaching the equilibrium state, the diameter and thickness of samples were measured for estimating swelling ratio. The swelling ratio is defined as x/x_0, in which x_0 and x are the diameter (D) or thickness (T) of the gel before and after swelling of the sample, respectively [Figure S2(a)]. In addition, we performed the compression test like as mentioned above. The stress-strain curves of the PDMAPAA-Q gels with or without PBDT molecules are shown in Figure S2(b).

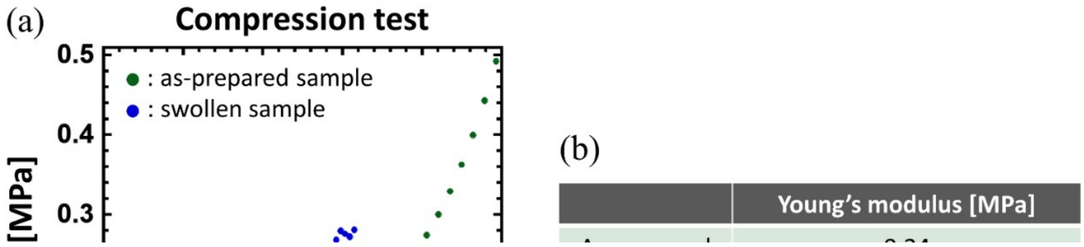
Preparation method of a thin hydrogel sheet fixed onto the saddle shaped substrate

A polyurethane rubber sheet was purchased from ASKUL corporation and cut into stripe shape (width: 15 mm, length: 150 mm, thickness: 1 mm). Then, the rubbers were stretched uniaxially along their longitudinal directions (strain: ε=0.3) and then glued together perpendicularly by the instant glue (Aron Alpha, TOAGOSEI CO., Ltd., Japan) [Figure S3(a)]. After that, a square shaped PBDT-containing PDMAPAA-Q gel (width: 13 mm, length: 13 mm, thickness: 0.5 mm) was glued onto the surface of the stretched rubber compound at the junction point [Figure S3(b)]. Finally, by releasing the stretching of the compound, a compressive stress was applied on the hydrogel, which induces a saddle shape transition [Figure S3(c)]. The curvature of saddle shape was estimated as 0.155 [1/mm] by the picture taken by digital photo camera [Canon, EOS Kiss X5].

Swelling experiment of the gel fixed onto saddle-shaped and flat substrate

Each sample was immersed in a large excess of water. Blue dye, Alcian blue(0.05 wt %), was added in the water to acid the visualization of the surface crease pattern. After reaching equilibrium state (~600 s), the samples were taken out from the solution and photographed with a digital camera and then observed with an optical microscope [Figure 4]. The thickness of gel changed from 0.5 mm to 1.15 mm. We should notice that the gel sheets homogeneously adhered to the polyurethane substrate without any delamination even after swelling.

Supplementary Figures



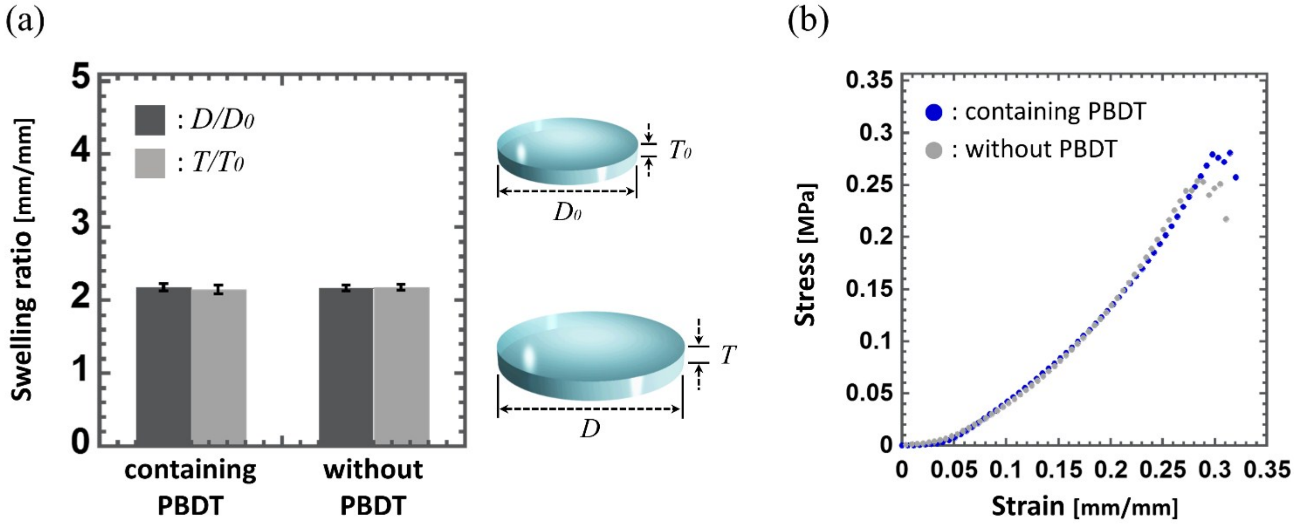


Figure S1| Compression test of as-prepared and swollen samples. (a) stress-strain curves of positive charged hydrogel containing anionic semi-rigid polymer. Green dots and blue dots represent the as-prepared state and swollen state, respectively. Compression strain, ε, is defined as (t_0－t)/t_0, in which t_0 and t are the thickness of the gel before and during compression, respectively. (b) Young's modulus of the gel on as-prepared state (green) and swollen state (blue).

Figure S2| Mechanical properties of PDMAPAA-Q gel with or without PBDT molecules. (a) Swelling ratio of PDMAPAA-Q gel with or without PBDT molecules. The dark gray and light gray bars represent the swelling ratio of diameter and thickness, respectively. (b) Stress-strain curves of compression test of PDMAPAA-Q gel with (blue dots) and without (gray dots) PBDT molecules. The two strain-stress curves show no distinct difference. These results show that PBDT molecules do not influence the swelling and mechanical properties of the PDMAPAA-Q gel.

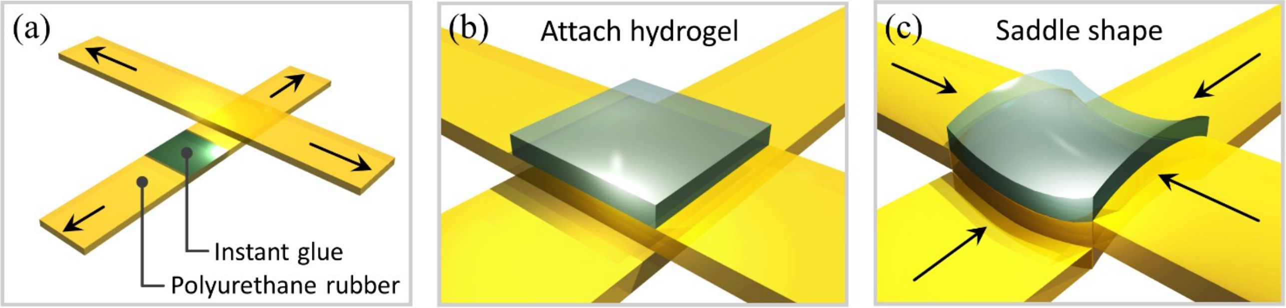


Figure S3| Preparation method of a thin hydrogel sheet with the saddle shape induced by mechanical mismatching with the substrate. (a) Two polyurethane rubber sheets (width: 15 mm, length: 150 mm, thickness: 1 mm) were stretched uni-axially along their longitudinal directions (strain: $\varepsilon=0.3$) and then glued together perpendicularly, forming a residually stressed compound. (b) A square-shaped hydrogel (width: 13 mm, length: 13 mm, thickness: 0.5 mm) was glued onto the surface of the stretched rubber compound at the junction point. (c) By releasing the stretching of the compound, a compressive stress was applied on the hydrogel, which induces a saddle shape transition.

Appendix 1.

Under the suitable coordinate system, we assume that the middle layer can be expressed as follows by using two parameters, (x, y):

$$\vec{\Phi}(x,y)=\begin{pmatrix} u(x,y) \\ v(x,y) \\ w(x,y) \end{pmatrix}.$$

Then, the first fundamental quantities (E, F, G) and second fundamental quantities (L, M, N) of the middle layer can be described as follows:

$$E=\left\langle \vec{\Phi}_x \cdot \vec{\Phi}_x \right\rangle,\ F=\left\langle \vec{\Phi}_x \cdot \vec{\Phi}_y \right\rangle,\ G=\left\langle \vec{\Phi}_y \cdot \vec{\Phi}_y \right\rangle,$$

$$L=\left\langle \vec{\Phi}_{xx} \cdot \frac{\vec{\Phi}_x \times \vec{\Phi}_y}{\left|\vec{\Phi}_x \times \vec{\Phi}_y\right|} \right\rangle,\ M=\left\langle \vec{\Phi}_{xy} \cdot \frac{\vec{\Phi}_x \times \vec{\Phi}_y}{\left|\vec{\Phi}_x \times \vec{\Phi}_y\right|} \right\rangle,\ N=\left\langle \vec{\Phi}_{yy} \cdot \frac{\vec{\Phi}_x \times \vec{\Phi}_y}{\left|\vec{\Phi}_x \times \vec{\Phi}_y\right|} \right\rangle.$$

And, mean curvature (H) and Gaussian curvature (K) defined by the principal curvatures ($\lambda_{\pm}(x,y)$) are calculated as follows by using E, F, G, L, M, and N:

$$H=\frac{\lambda_+ + \lambda_-}{2}=\frac{GL+EN-2FM}{2\left(EG-F^2\right)},$$

$$K=\lambda_+\lambda_-=\frac{LN-M^2}{EG-F^2}.$$

If $H=0$ and $K<0$, the principal direction ($\vec{v}_{\pm}$) which is respect to $\lambda_{\pm}(x,y)$ can be obtained as follows:

$$\vec{v}_{\pm}=\frac{FN-GM}{EG-F^2}\vec{\Phi}_x+\left(\frac{GL-FM}{EG-F^2}\mp\sqrt{\frac{M^2-LN}{EG-F^2}}\right)\vec{\Phi}_y.$$

Then, an inner product of principal directions is 0 (*i.e.*,$\left\langle \vec{v}_+ \cdot \vec{v}_- \right\rangle=0$). Therefore, we can confirm that the principal directions are orthogonal to each other at any point in our system. That is, it is possible to choose a local orthogonal coordinate system as including the principal directions for any point on Ω.

Appendix 2.

Here, we consider about the integral function of the compression energy. If we choose the local orthogonal coordinate system as including the principal directions, (x and y), the middle layer can be expressed by $\vec{\varphi}(x,y)=(x,y,w(x,y))^T$. In this case, $w(x,y)$ has the following futures, because the plane which consists of the principal directions contacts with the middle layer at the origin.

$$w_x(0,0)=w_y(0,0)=w_{xy}(0,0)=0,\quad w_{xx}(0,0)=\lambda_+,w_{yy}(0,0)=\lambda_- . \tag{S1}$$

Then, the outward unit normal vector at the origin of the middle layer ($\vec{n}(x,y)$) is given by

$$\vec{n}(x,y)\Big|_{(x,y)=(0,0)}=\frac{\vec{\varphi}_x\times\vec{\varphi}_y}{\left|\vec{\varphi}_x\times\vec{\varphi}_y\right|}\Bigg|_{(x,y)=(0,0)}=\begin{pmatrix}0\\0\\1\end{pmatrix}. \tag{S2}$$

Now, let us consider about the outward unit normal vector to t-level layer ($\vec{\eta}(x,y)$) at origin. From eq (3), the following equations can be obtained:

$$\vec{\phi}_x(x,y)=\vec{\varphi}_x(x,y)+ks_x(x,y)\vec{n}+ks(x,y)\vec{n}_x,$$

$$\vec{\phi}_y(x,y)=\vec{\varphi}_y(x,y)+ks_y(x,y)\vec{n}+ks(x,y)\vec{n}_y,$$

where, k:=sin($\pi t/2h$) is constant with respect to (x,y). Therefore, the following equations can be obtained with the considering eq (S1).

$$\vec{\phi}_x(x,y)\Big|_{(x,y)=(0,0)}=\begin{pmatrix}1-k\lambda_+s\\0\\ks_x\end{pmatrix},\quad \vec{\phi}_y(x,y)\Big|_{(x,y)=(0,0)}=\begin{pmatrix}0\\1-k\lambda_-s\\ks_y\end{pmatrix}.$$

As a result, we can describe the outward unit normal vector ($\vec{\eta}(x,y)$) to t-level layer at (x,y)=(0,0) as follows:

$$\vec{\eta}(x,y)=\frac{\vec{\phi}_x\times\vec{\phi}_y}{\left|\vec{\phi}_x\times\vec{\phi}_y\right|}=\frac{1}{\sqrt{\Psi_1^2+\Psi_2^2+\Psi_3^2}}\begin{pmatrix}\Psi_1\\\Psi_2\\\Psi_3\end{pmatrix}, \tag{S3}$$

where,

$$\begin{pmatrix}\Psi_1\\\Psi_2\\\Psi_3\end{pmatrix}=\begin{pmatrix}-k(1-k\lambda_-s)s_x\\-k(1-k\lambda_+s)s_y\\(1-k\lambda_+s)(1-k\lambda_-s)\end{pmatrix}. \tag{S4}$$

Finally, from eqs. S2-S4, we can calculate A^{-1} in the main text as follows:

$$\langle\vec{n}\cdot\vec{\eta}\rangle=\frac{1}{A}=\frac{1}{\sqrt{\Psi_1^2+\Psi_2^2+\Psi_3^2}}\left\langle\begin{pmatrix}0\\0\\1\end{pmatrix}\cdot\begin{pmatrix}\Psi_1\\\Psi_2\\\Psi_3\end{pmatrix}\right\rangle=\left\{\left(\frac{ks_x}{1-k\lambda_+s}\right)^2+\left(\frac{ks_y}{1-k\lambda_-s}\right)^2+1\right\}^{-1/2}.$$