Supporting Information for

Swelling-induced Long-range Ordered Structure Formation in Polyelectrolyte Hydrogel

Md. Arifuzzaman[a], *Zi Liang Wu*[a], *Takayuki Kurokawa*[b,c], *Akira Kakugo*[b,d], *and Jian Ping Gong*[b,c*]

[a] Laboratory of Soft and Wet Matter, Division of Biological Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

[b] Laboratory of Soft and Wet Matter, Faculty of Advanced Life Science, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

[c] Creative Research Institution (CRIS), Hokkaido University, Sapporo 001-0021, Japan

[d] PRESTO, Japan Science and Technology Agency (JST)

[*] Corresponding author: E-mail: gong@mail.sci.hokudai.ac.jp

Keywords: Hydrogel, mechanical instability, semi-rigid polymer, polyion complexation, long-range ordered structure

Results and discussion section

Birefringence in the as-prepared gels:

In the as-prepared state, the PBDT-containing PDMAPAA-Q gels exhibit birefringence that is always irregular even if the sample fixed onto the stage of the polarizing optical microscope is rotated [Figure S1]. Moreover, when a small compressive strain (e.g., about $\varepsilon = 0.1$) is applied on the as-prepared gel, the level of birefringence increases to some extent within the same order. However, the birefringence pattern remains irregular. Therefore, it is concluded that the millimeter-scale ordered structure is absent in the as-prepared state. PAMPS and PAAm gels also exhibit birefringence in their as-prepared state in the presence of PBDT, which is susceptible to orientation even under a very small shear/strain.[S1,S2] In order to emphasize this, we synthesized the PDMAPAA-Q gel in the presence of a flexible anionic polymer chain PAMPS; crossed POM observations revealed that this gel does not exhibit birefringence in the as-prepared state [Figure 3b(i)].

Influence of swelling kinetics on ordered structure formation:

Since the mechanical instability originates from the large mismatch in the degree of swelling between the surface layer and the inner layer of the gel, the *creasing* should be strongly dependent on the rapid swelling kinetics.[S3,S4] To confirm this, we reduced the rate of swelling by allowing the gels to swell in a confined chamber filled with water vapor, where humidity was controlled. In the chamber, which was equilibrated to 80–90% humidity, it took about seven days for the gel to swell up to 95−97% of its equilibrium swelling size. Such slow-swelling kinetics suppressed the mismatch in the swelling ratio between the surface layer and the inner layer, and thus, no mechanical instability occurred. As shown in Figure S3, after satisfactory swelling in the confined chamber, the intensity of the initial irregular birefringence became weaker [Figure

S3(b)] compared to that for the as-prepared state [Figure S3(a)]. Then, the partially swollen gel was immersed in sufficient water to confirm the completion of water uptake by the gel. Subsequent POM observation in the direction normal to the surface revealed the irregular orientation of PBDT in the equilibrium state [Figure S3(c)], which was completely different from that in the case of the sample directly swollen in water. This investigation confirmed that surface creasing is the origin of the ordered molecular orientation of PBDT and demonstrated the importance of swelling kinetics in the formation of such a gigantic ordered structure inside the gel.

References

(S1) T. Funaki, T. Kaneko, K. Yamaoka, Y. Oshedo, J. P. Gong, Y. Osada, Y. Shibasaki,and M. Ueda, *Langmuir*, 2004, **20**, 6518.

(S2) Z. L. Wu, D. Sawada, T. Kurokawa, A. Kakugo, W. Yang, H. Furukawa, and J. P. Gong, *Macromolecules*, 2011, **44**, 3542.

(S3) T. Tanaka, S.-T. Sun, Y. Hirokawa, S. Katayama, J. Kucera, Y. Hirose, and T. Amiya, *Nature* (London), 1987, **325**, 796.

(S4) M. Guvendiren, S. Yang, and J. A. Burdick, *Adv. Func. Mater.*, 2009, **19**, 3038.

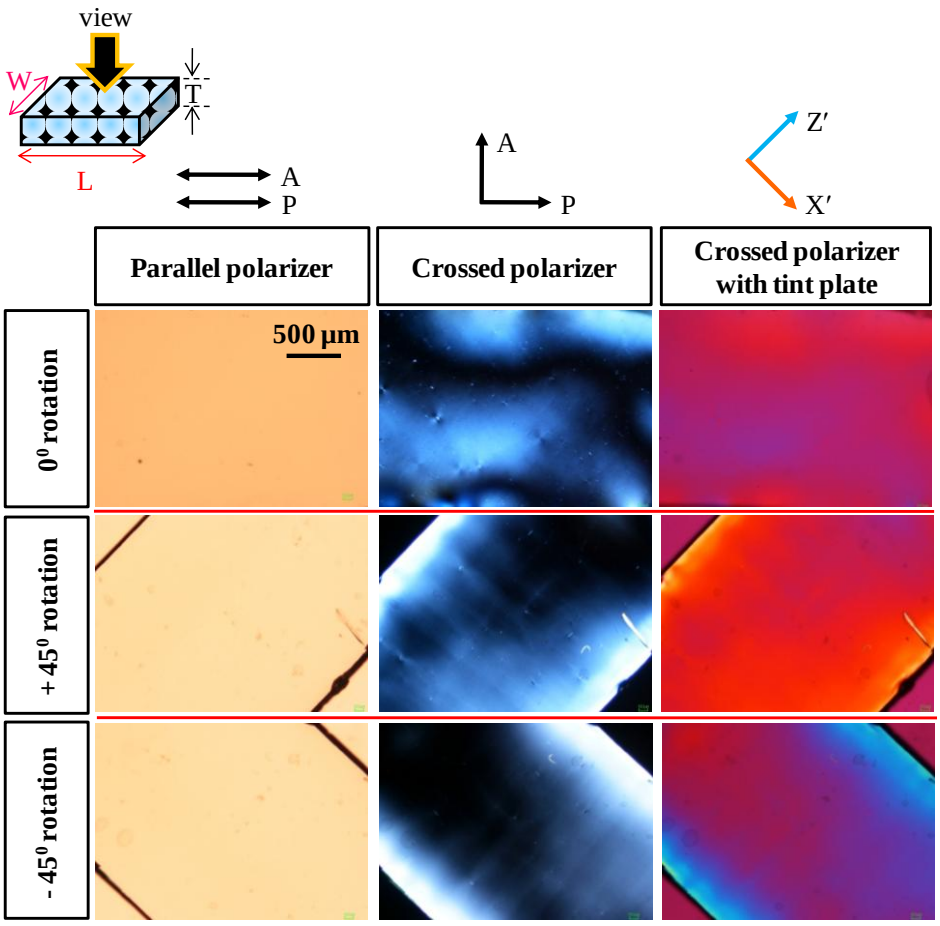

Figure S1. Flat surface and irregular birefringence pattern of the as-prepared PBDT-containing PDMAPAA-Q gel observed at different angles with respect to the polarizer. With the change in the angle, the birefringence pattern of the sample changed to some extent; however, a regular/ordered pattern was not observed. From these polarizing optical micrographs, it is easy to understand that before swelling, the surface of the gel is flat and the birefringence pattern is irregular, lacking any long-range periodicity. The dimensions of the as-prepared gel were about 6.0 mm (L) × 3.0 mm (W) × and 1.0 mm (T). The scale bar is the same for all the images in this figure.

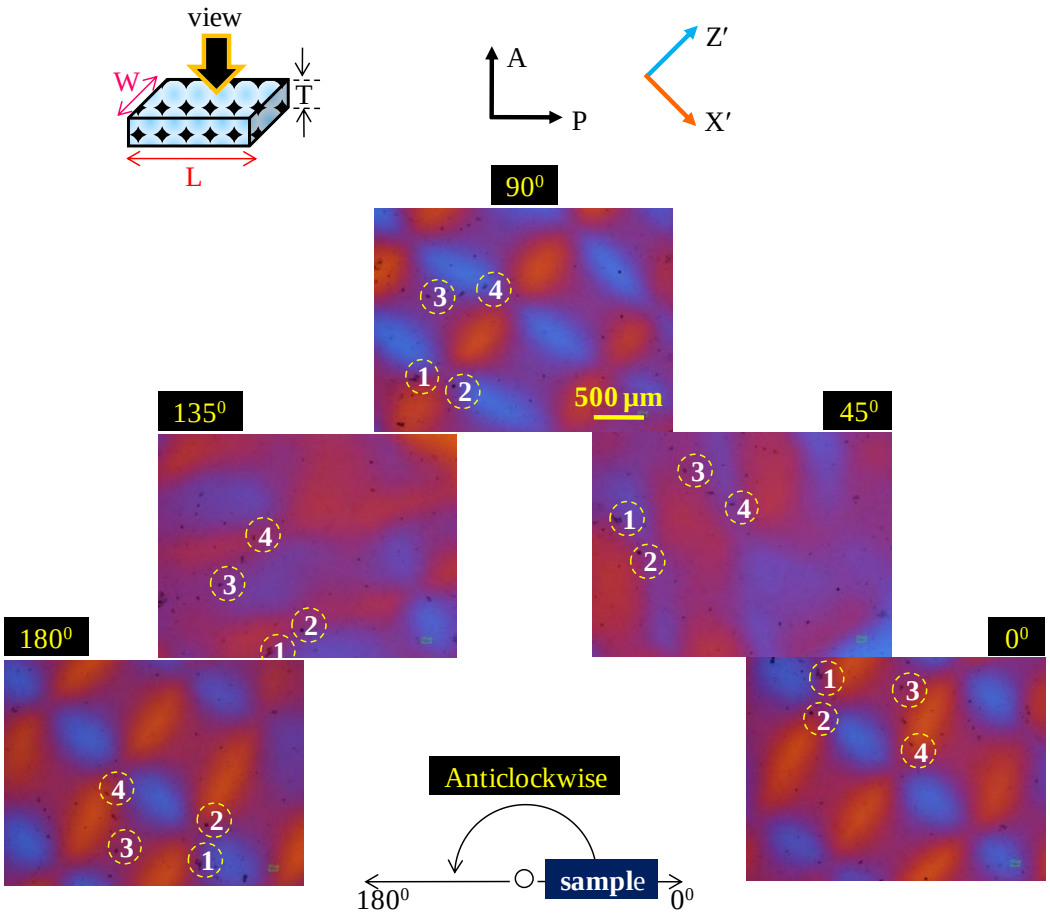

Figure S2. Birefringence patterns of the swollen PDMAPAA-Q gel containing PBDT observed under the polarizing optical microscope (POM) for anticlockwise rotation of the sample. The regular crossed birefringence pattern significantly changes to a heterogeneous one with every 45° rotation. From the above observation, it is clarified that the basic unit of entire birefringence pattern is a "*square*" where the semi-rigid PBDT molecules are orientated vertically with respect to the boundary of the square creasing unit. The numbers in the images are used as markers to identify the same spots on the gel surface during the sample rotation. All the images were recorded using a crossed POM with a 530 nm sensitive tint plate. The dimensions of the swollen gel were about 12.2 mm (L) × 6.5 mm (W) × 2.1 mm (T).

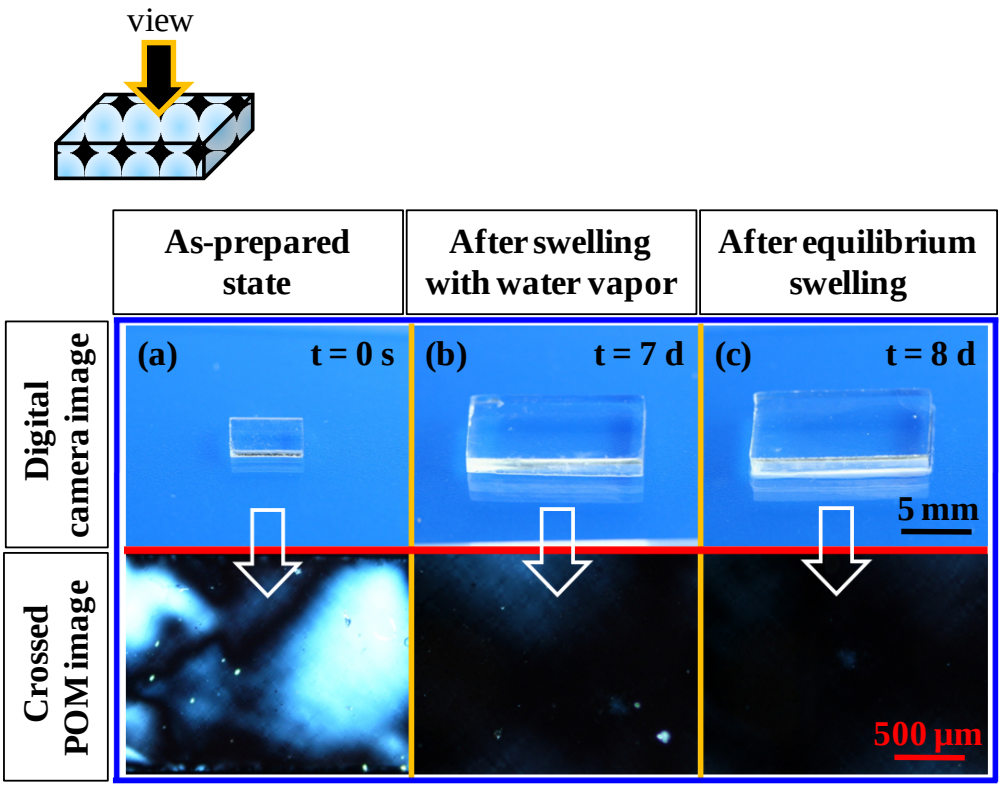

Figure S3. Influence of swelling kinetics on ordered structure formation in the polyelectrolyte gel. Crossed POM observations revealed that the gel exhibited significant birefringence in the as-prepared state (a). After sufficient swelling with water vapor in a confined chamber at a low swelling rate, the birefringence became very weak (b); finally, after the equilibrium swelling state was reached, the birefringence pattern became too weak to be recognized (c). The images in the first row were captured using a digital camera Canon DS126071, while those in the second row were recorded under the crossed POM. The duration of swelling in the confined chamber was seven days. Then, to confirm the completion of water uptake, the gel was immersed in sufficient water for another 24 h. A: analyzer, P: polarizer.

Caption of the Supporting Information movie files

Movie S1. Movie showing "leaf-like" birefringence pattern formation during the initial period of swelling, accompanied by the onset of surface instability creasing. The movie was recorded under a crossed Nicole film coupled with a stereomicroscope (Olympus, SZX-12). The frame rate was 15 fps (wmv: 2.75 MB).

Movie S2. Movie showing the growth of the *square* unit of "lattice-like" birefringence pattern with the progress of swelling. The movie was recorded under a crossed Nicole film coupled with a stereomicroscope (Olympus, SZX-12). The frame rate was 15 fps (wmv: 6.46 MB).