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

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Abstract

A millimeter-scaled periodic structure is created in a polyelectrolyte hydrogel by the rapid-heterogeneous swelling process, and is frozen by the polyion complexation of the polyelectrolyte network with the oppositely charged, *semi-rigid* polyelectrolyte. The hydrogel is synthesized from a cationic monomer, *N*-[3-(*N,N*-dimethylamino)propyl] acrylamide methyl chloride quaternary (DMPAA-Q), in the presence of a small amount of the oppositely charged poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) that has a *semi-rigid* nature. During swelling process, surface *creasing* due to the large mismatching of swelling degree between the surface layer and the inner one of the poly DMAPAA-Q (PDMAPAA-Q) gel occurs, which induces highly oriented semi-rigid PBDT molecules along the tensile direction of the crease pattern. In accompany with the evolution of surface creasing, a lattice-like periodic birefringence pattern is formed, which is frozen permanently by the strong polyion complex formation, even after the surface instability pattern of the gel disappears completely throughout the dynamic coalescence. In this work we rationally clarified that formation of such a long-range ordered non-equilibrium structure in the polyelectrolyte hydrogel by the rapid-heterogeneous swelling process requires the following three indispensable conditions: (i) swelling-induced surface creasing; (ii) polyion complex formation; and (iii) a semi-rigid or rigid dopant. This sort of non-equilibrium structure formation mechanism may help understand how biomacromolecules that are rigid polyelectrolytes, such as microtubules and actin filaments, form rich architectures during the growth of biological organs.

Introduction

Biological soft tissues contain a certain amount of water that ensures molecular mobility and at the same time, possess a sophisticated structure that enables them to exhibit outstanding performances over a wide range of physiological functions.¹⁻⁴ Among all, intricate structural pattern found in the human brain, the intestine, and leaves, are believed to be formed via non-equilibrium, dynamic process during the growth,^{5,6} which are frozen by the physical/chemical interaction among the molecules.^{7,8} Elucidation of the mechanism of such structure formation induced by non-equilibrium chemistry in living bodies is an attractive research topic. Furthermore, introducing sophisticated structures into hydrogels,⁹⁻¹² which are soft, wet materials similar to the biological tissues, by the non-equilibrium process is one of the ultimate challenges for polymer scientists.

In our previous study, we found that a piece of sheet-like polyelectrolyte gel containing an oppositely charged semi-rigid polymer exhibits a periodic birefringence pattern after full swelling in water.¹³ Such a well-ordered structure with millimeter-scale periodicity was initially formed in a polyelectrolyte gel with a dilute concentration (water content > 90 wt%). Although some plausible explanation for the structure formation could be derived, the exact structure formation mechanism remains a mystery.

In this study, we showed that the periodic birefringence pattern, representing an ordered orientation of the semi-rigid poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) molecules, developed during swelling of the hydrogel. Further, we found that the surface mechanical instability induced by the rapid-heterogeneous swelling, the *semi-rigid* nature of the dopant macromolecule, and polyion complex formation are the three indispensable requirements

for the formation of such ordered structure. This study reveals a novel strategy for introducing a long-range ordered structure in amorphous hydrogels through dynamic mechano-complexation coupling in a non-equilibrium process. This strategy can be applied to soft, wet systems in a variety of contexts, namely, for developing various ordered structures with macroscale correlation by proper design of the hydrogel geometry. Furthermore, rigid or semi-rigid macromolecules such as deoxyribonucleic acid (DNA), microtubules (MTs), and actin filaments (F-actin) are ubiquitous in living organisms. These biomacromolecules form rich architectures through self-assembly or via physical/chemical interactions with other species. The mechanism of non-equilibrium structure formation elucidated in this study might provide scientific insights into the formation of rich architectures by these biomacromolecules during the growth of biological organs.

Experimental

Materials:

PBDT, a water-soluble *semi-rigid* polyanion, was synthesized by an interfacial polycondensation reaction.¹⁴ The synthesized PBDT had an average molecular weight M_w of about 1.6×10^6 g/mol and a liquid crystalline critical concentration C_{LC}^* of 2.8 wt% in aqueous solution.^{13,15,16} The cationic monomer, *N*-[3-(*N,N*-dimethylamino)propyl]acrylamide methyl chloride quaternary (DMPAA-Q) (Kohjin Co. Ltd. Japan), the anionic monomer, 2-acrylamido-2-methylpropanesulfonic acid (AMPS) (Tokyo Kasei Co. Ltd.), the neutral monomer, Acrylamide (AAm) (Junsei Chemical Co. Ltd. Japan), and the photoinitiator, 2-oxoglutaric acid (OA) (Wako Pure Chemical Industries Ltd. Japan), were used as received without further purification. *N,N'*-methylenebis(acrylamide) (MBAA) (Wako Pure Chemical Industries Ltd. Japan) was recrystallized from ethanol and used as a chemical cross-linker. For all

the experiments, deionized water, purified using 0.22 μ m and 5 μ m membrane filters, was used.

Synthesis of the sheet-like polyelectrolyte gels:

To synthesize the poly DMAPAA-Q (PDMAPAA-Q) gel containing PBDT, an aqueous solution was prepared by mixing the cationic monomer, DMAPAA-Q (2.0 M), the *semi-rigid* anionic polymer, PBDT (1.0 wt%), the chemical cross-linker, MBAA (2.0 mol%), and the photoinitiator, OA (0.15 mol%) together (the amount in mol% is related to the cationic monomer concentration). After proper mixing, the precursor solution was poured into a reaction cell consisting of a 1.0 mm thick rectangular silicone rubber frame sandwiched between a pair of parallel glass plates. Before polymerization, the precursor solution was transparent and completely amorphous because the PBDT concentration was much lower than the liquid crystalline critical concentration ($C_{LC}^* = 2.8$ wt%). In the precursor solution the charge ratio of PBDT to DMAPAA-Q was 0.02, which was far below the stoichiometric value. Radical polymerization was effected by UV irradiation from both sides of the glass reaction cell for 6.0 h at room temperature in argon atmosphere. Other gels with sheet-like shapes [poly AMPS (PAMPS) and poly AAm (PAAm) gels in the presence of the *semi-rigid* anionic polymer PBDT and PDMAPAA-Q gel in the presence of the *flexible* anionic polymer PAMPS] were synthesized by using the same method and conditions.

Swelling of the polyelectrolyte gels:

After prolonged UV polymerization, the sheet-like gels (about 45 \times 45 \times 1.0 mm³) were carefully removed from the glass reaction cell and cut into specific dimensions (about 6.0 \times 3.0 \times 1.0 mm³) using a mechanical gel cutter (Dumb Bell Co. Ltd.). Then, the gels were immediately immersed in water for spontaneous swelling. The volume of water (~200 mL) was kept constant for every sample. In the case of slower kinetics, to decrease the rate of swelling, a confined metal chamber

in which equilibrated humid conditions were successfully maintained for a long time was used.

Measurement of swelling kinetics:

At room temperature, a set of as-prepared gels with dimensions of about $6.0 \times 3.0 \times 1.0 \text{ mm}^3$ were immersed together in a large quantity of water for swelling. The increased mass of the samples at different swelling times (t) was recorded by measuring the weight of the samples on an electronic balance (Shimadzu Co., Kyoto, Japan). The relative swelling ratio, q (g/g), is defined as the ratio of the weight of the gel swollen for different time lengths to its weight in the as-prepared state.¹⁷

Polarizing optical microscope (POM) observation:

The surface morphology and the birefringence of the gels in the as-prepared state, during swelling, and finally in the equilibrium swelling state were observed under a polarizing optical microscope (POM) (Nikon, Eclipse, LV100POL) in the parallel and crossed polarization modes, respectively, at room temperature. To determine the orientation direction of the rod-like PBDT molecules or their fibrous bundles, the samples were also observed under a crossed POM with a 530 nm sensitive tint plate. The change in the surface morphology of the gels during unrestricted and rapid swelling was observed under POM with a parallel polarizer at room temperature. To observe such a swelling-induced surface instability *crease* pattern, the surface of the as-prepared gels was fully covered with an aqueous solution of 0.05 wt% Alcian blue (Wako Pure Chemical Industries Ltd. Japan). Therefore, the crease pattern with its sharp boundary was clearly observed in the gel during swelling. Images were captured by a digital camera coupled with the microscope.

Results and discussion

To elucidate the correlation between the surface *creasing* and the *semi-rigid* molecular orientation at different swelling times in water, we observed the sample under a polarizing optical microscope (POM) in three different modes: a parallel polarization mode to identify the surface morphology [Figure 1, column (i)], a crossed polarization mode to identify the birefringence [Figure 1, column (ii)], and a crossed polarization mode with a 530 nm sensitive tint plate to identify the orientation of the semi-rigid PBDT molecules [Figure 1, column (iii)]. The schematic orientation of the PBDT molecules is shown in Figure 1, column (iv).

The as-prepared PBDT-containing PDMAPAA-Q gel was always transparent with a smooth surface [Figure 1a(i)] and exhibited irregular birefringence [Figure 1a(ii, iii)] that was almost unchanged with the rotation of the sample on the POM stage (see Supporting Information, Figure S1).

When a sample of the as-prepared gel, $6.0 \times 3.0 \times 1.0 \text{ mm}^3$ in size, was immersed in water, rapid swelling of the gel commenced immediately and polygonal patterns appeared on the gel surface, with clear lines that corresponded to the borders of the crease patterns [Figure 1b(i)]. Simultaneously with the appearance of the polygonal patterns, the entire irregular birefringence pattern rapidly changed into numerous distinct small domains (about 200–300 μm in length) having leaf-like shapes. These leaf-like patterns always appeared around the borderlines of the crease patterns [Figure 1b(ii) and see Supporting Information, movie S1]. The birefringence of the PDMAPAA-Q gel containing PBDT is related to the orientation of the semi-rigid PBDT molecules, which is typical of that of a positive liquid crystal.^{15,16,18-21} From the characteristic birefringence colors in the presence of the 530 nm sensitive tint plate [Figure 1b(iii)], we

concluded that the PBDT molecules are aligned perpendicular to the borderlines, as illustrated in [Figure 1b\(iv\)](#).

As the swelling time increased, these polygonal surface patterns coalesced into larger ones c.a. 1.0 mm in length [[Figure 1c\(i\)](#)], exhibiting even more clear, lattice-like borders corresponding to the cubic packing of the *convex* creases. Consistent with this surface pattern evolution, the leaf-like domains in the birefringence image coalesced into larger ellipsoidal domains, with the borderline as the long axis of the ellipsoid and the PBDT molecules oriented vertically to this axis [[Figure 1c\(iii\)](#)]. After prolonged swelling, the surface crease pattern disappeared along with the lattice-like borders, and the gel surface became smooth and flat [[Figure 1d\(i\)](#)], while the birefringence pattern remained even after reaching the equilibrium swelling state, keeping with the high periodicity [[Figure 1d\(ii, iii\)](#)].

To further confirm the lattice-like symmetry of the oriented structure, the angle dependence of the finally stable birefringence pattern was investigated. With every 90° rotation, the same periodic birefringence pattern appeared, while the pattern became less regular with a 45° rotation in the clockwise or anticlockwise direction (see [Supporting Information, Figure S2](#)). These observations confirmed that the gel has a periodically ordered structure with a square-shaped lattice unit, whereupon the PBDT molecules orient vertically with respect to the lattice boundary. One of the periodical units in the equilibrium state is highlighted by the dashed boxes in [Figure 1d\(ii, iv\)](#). Thus, our previously proposed structure needs modification.¹³

Next, we carried out a more quantitative investigation of the correlation between the swelling kinetics and the ordered structure formation in the gel. For a diffusion-limited process,

the characteristic swelling time is determined by the smallest dimension of the sample, which in the present case is the sample thickness. The time profile of the swelling ratio q in terms of the weight change of the gel relative to the as-prepared state is shown in [Figure 2\(a\)](#). The gel swelled rapidly and reached its equilibrium swelling state within 20 min [[Figure 2\(a\) inset](#)]. Evolution of the surface morphology and the birefringence pattern after the initial 600 s are shown in [Figure 2\(b\)](#) and [Figure 2\(c\)](#), respectively. As shown in [Figure 2\(b\)](#), bumped irregular polygons appeared on the surface during the initial period of the swelling process (~ 30 s). With the advancement of swelling (~ 200 s), the irregular polygons fused rapidly to form regular patterns with lattice borderlines. In order to characterize the coalescence of the surface crease patterns, we define n_{JP} as the density of junction point (the number of crossover junction points of the creases per square millimeter area), where at least three bumps coexist. The value of n_{JP} decreased very rapidly with time and finally reduced to zero after a swelling time of about 400 s [[Figure 2\(b\)](#)].

The leaf-like birefringence pattern appeared at around 60 s and became regular at around 200 s [[Figure 2\(c\)](#)] like a symmetric lattice. The leaf length or the length of the lattice unit L_s increased gradually with the swelling time [[see Supporting Information, movie S2](#)], reaching a constant value of 1.1 mm at around 400 s [[Figure 2\(c\)](#)], which was approximately the same time taken for the disappearance of the surface crease pattern.

From the above observations, we conclude that a periodic birefringence pattern is formed during the swelling process and that it is correlated to surface creasing. The latter is often transient in nature during the swelling of hydrogels, especially in the case of polyelectrolyte hydrogels that have a very high osmotic swelling pressure.²²⁻³⁹ The rapid swelling of the surface layer causes a large difference in the degree of swelling between the surface and the inner layer

of the gel; this *spatial mismatch* results in compressive strain in the surface layer and leads to *transient* creasing instability in the surface layer.²²⁻³⁹ Theoretical and experimental studies indicate that the onset of creasing is only related to the effective compressive strain experienced by the surface layer, irrespective of the modulus and thickness of the mismatched layers, while the characteristic spacing between the creases increases with the surface layer thickness. The critical value of compressive strain for the creasing instability, ε_c , is reported as 0.35.^{22,24,29,35-39} At the initial stage of swelling, the high osmotic swelling pressure induces rapid swelling to satisfy $\varepsilon > \varepsilon_c$; thus, creasing instability occurs and polygonal patterns appear. With the advancement of swelling, the thickness of the surface swollen layer increases, and this leads to coalescence and eventual disappearance of the crease patterns at equilibrium swelling because of the disappearance of the swelling mismatch. It is interesting that in the present case, before disappearing, the polygonal patterns coalesce to form cubic patterns instead of hexagonal patterns, which is the previously reported mode at the instability onset.^{22,23}

We also found that the size of the millimeter-scale periodicity increased linearly with the sample thickness but did not change with the formulation of the gel, such as the concentrations of the cationic monomer and the semi-rigid anionic polymer in the precursor solution.¹³ These results are in agreement with the feature of the creasing instability.³⁵⁻³⁹

To confirm that the surface creasing originated only from the rapid swelling of the polyelectrolytic gel PDMAA-Q and that the semi-rigid PBDT did not play a role in the same, we studied the swelling behavior of the PDMAA-Q hydrogel without PBDT [Figure 3(a)]. No birefringence was observed in the as-prepared state [Figure 3a(i)], indicating the amorphous nature of the PDMAA-Q hydrogel. A transient surface crease pattern and birefringence pattern

similar to those for PDMAA-Q containing PBDT [Figure 1c(ii)] were observed at the initial stage of swelling, although the birefringence pattern was relatively weak [Figure 3a(ii)]. However, both the patterns disappeared at equilibrium swelling [Figure 3a(iii)]. This result indicated that the periodic birefringence pattern is induced by the creasing instability of the PDMAA-Q gel, while the strong polyion complexation between the positively charged PDMAA-Q network and the negatively charged semi-rigid molecule PBDT freezes the birefringence pattern. Certainly, polyion complexation is enhanced by the outward diffusion of the mobile counterions (Na^+ and Cl^-) from the gel to the solvent environment during the swelling process,⁴⁰⁻⁴² which stabilizes the molecular orientation inside the gel. Thus, the intense polyion complexation between PDMAA-Q and PBDT freezes the periodic molecular orientation induced by the mechanical instability.

Furthermore, we have clarified that the *semi-rigid* nature of PBDT plays an indispensable role in the stabilization of the birefringence pattern. As shown in Figure 3(b), PDMAA-Q hydrogel containing a negatively charged *flexible* linear polymer, polyAMPS (PAMPS), exhibited no birefringence in the as-prepared state [Figure 3b(i)], while the crease pattern and birefringence pattern appeared transiently during swelling [Figure 3b(ii)]. However, both patterns disappeared well ahead of the equilibrium swelling state [Figure 3b(iii)]. This result suggests that the semi-rigid nature of the PBDT plays an important role in maintaining the highly oriented structure in the gel. As has been elucidated, mesoscopic fibrous bundles formed from semi-rigid PBDTs are very sensitive to external stress/strain and show a stronger birefringence owing to specific molecular orientation than do the flexible molecules.⁴³ The strong birefringence observed in Figure 1 indicates that the semi-rigid PBDT forms long and rigid fibrous bundles in the tensile direction of creasing, almost vertical to the borders of the crease patterns.

We also confirmed the effect of polyion complexation by investigating the like-charged combination. The gel synthesized from an anionic monomer, AMPS in the presence of the semi-rigid PBDT also exhibited certain birefringence in the as-prepared state [Figure 3c(i)] and an creasing instability pattern when exposed to water [Figure 3c(ii)]. However, after sufficient (equilibrium) swelling, both the surface instability and birefringence pattern disappeared [Figure 3 c(iii)]. Such an amorphous phenomenon can be explained by the absence of polyion complexation between the semi-rigid anionic PBDT and the chemically cross-linked negatively charged PAMPS. We also confirmed that in the absence of creasing instability, for example, in the case of the PDMAAA-Q gel swollen with water vapor (see Supporting Information, Figure S3) or the neutral PAAm gel, no periodic birefringence pattern appeared, even though these gels contained PBDT [Figure 3(d)]. Table 1 summarizes the results obtained for various systems.

Conclusion

In conclusion, a long-range periodic structure is induced during the swelling of the polyelectrolyte gel, concomitantly with the occurrence of surface *creasing*, a transient process related to the mechanical instability during the free and rapid swelling of polyelectrolytic gels in water. The mismatch in the swelling ratio between the surface layer and the inner layer of the gel induces creasing instability, which exerts tension on the semi-rigid molecules vertical to the borderline of the crease patterns. Thus, the molecules orient along the tensile direction and exhibit strong periodic birefringence. The molecular orientation is fixed simultaneously by the strong ion complexation between the two oppositely charged components and the formation of a lateral fibrous bundle from these components; the *semi-rigid* nature of the dopant molecules is indispensable for the fibrous bundle formation. Thus, the strong birefringence pattern is frozen even after the disappearance of the surface creasing instability. Figure 4 illustrates the mechanism

of formation of the swelling-induced ordered structure in the polyelectrolyte gel.

These results might help derive a novel strategy for introducing an ordered structure in soft, wet systems using rigid macromolecules, coupling with mechanical instability and ion complexation.

Electronic Supporting Information (ESI) available

Brief discussion on (i) the POM observations of the as-prepared state, (ii) experimental results by the controlled (slow) swelling kinetics, and (iii) movie files recorded during rapid swelling are presented in the Electronic Supporting Information.

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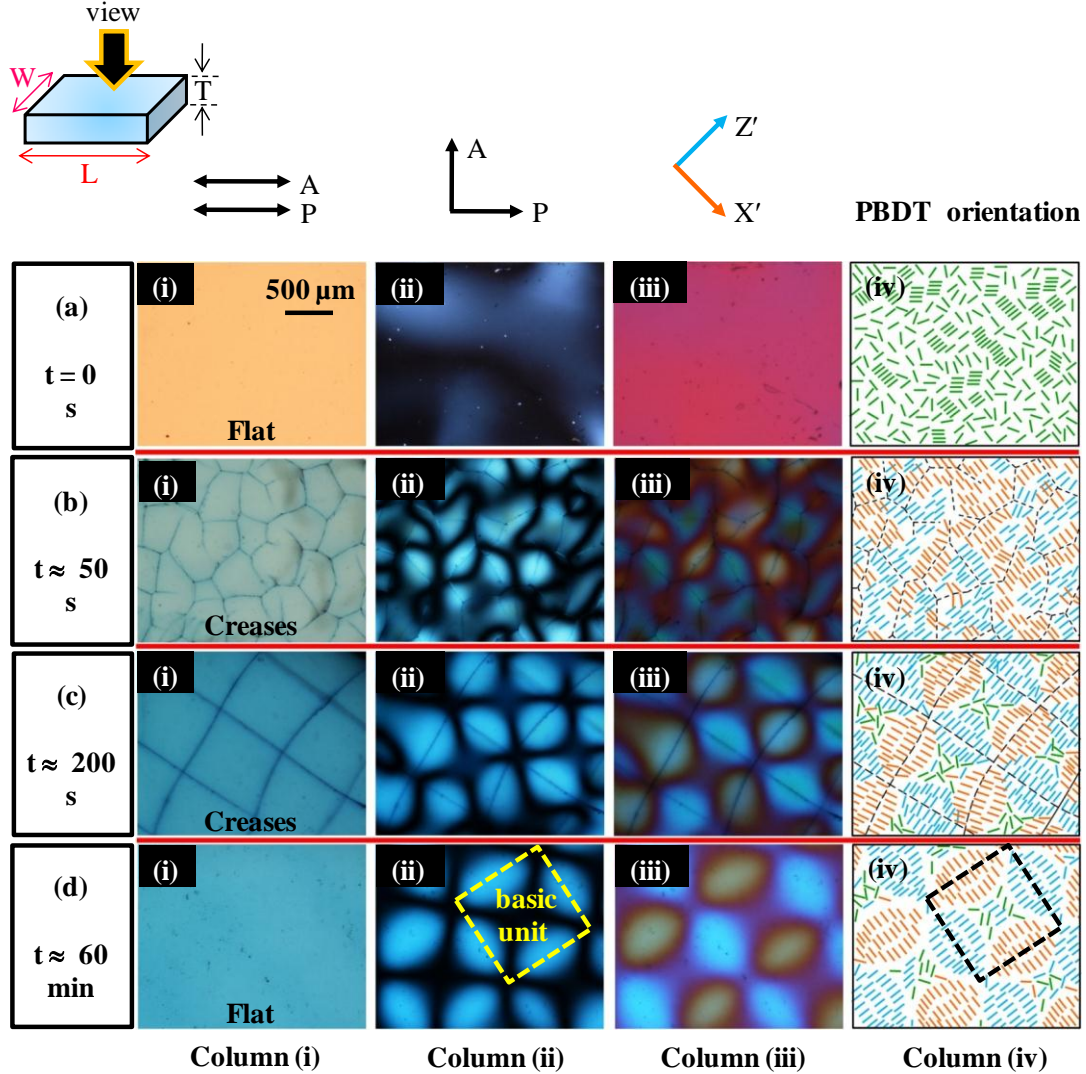


Figure 1. Time evolution of surface morphology and ordered structure formation for PBDT-containing PDMA-PAA-Q hydrogel during swelling in water. The observation was performed under the polarizing optical microscope (POM). The images presented in column (i), observed under the parallel polarizer, shows the surface morphology of the gel; column (ii), observed under the crossed polarizer, shows the birefringence of the gel; column (iii), observed under the crossed polarizer with a 530 nm sensitive tint plate, shows the molecular orientation direction. Column (iv) is a schematic illustration of the orientation of semi-rigid PBDT molecules, where the green single bars represent the weak molecular orientation of PBDT, while the blue and orange bars indicate strong/highly ordered orientation. To visualize the surface morphology, the as-prepared gel was swollen in water containing a dye Alcian blue. The dimensions of the as-prepared gels were about 6.0 mm (L) \times 3.0 mm (W) \times 1.0 mm (T). A: analyzer, P: polarizer, X' and Z' : fast and slow axes of the tint plate, respectively. All the images are shown on the same scale as in a(i).

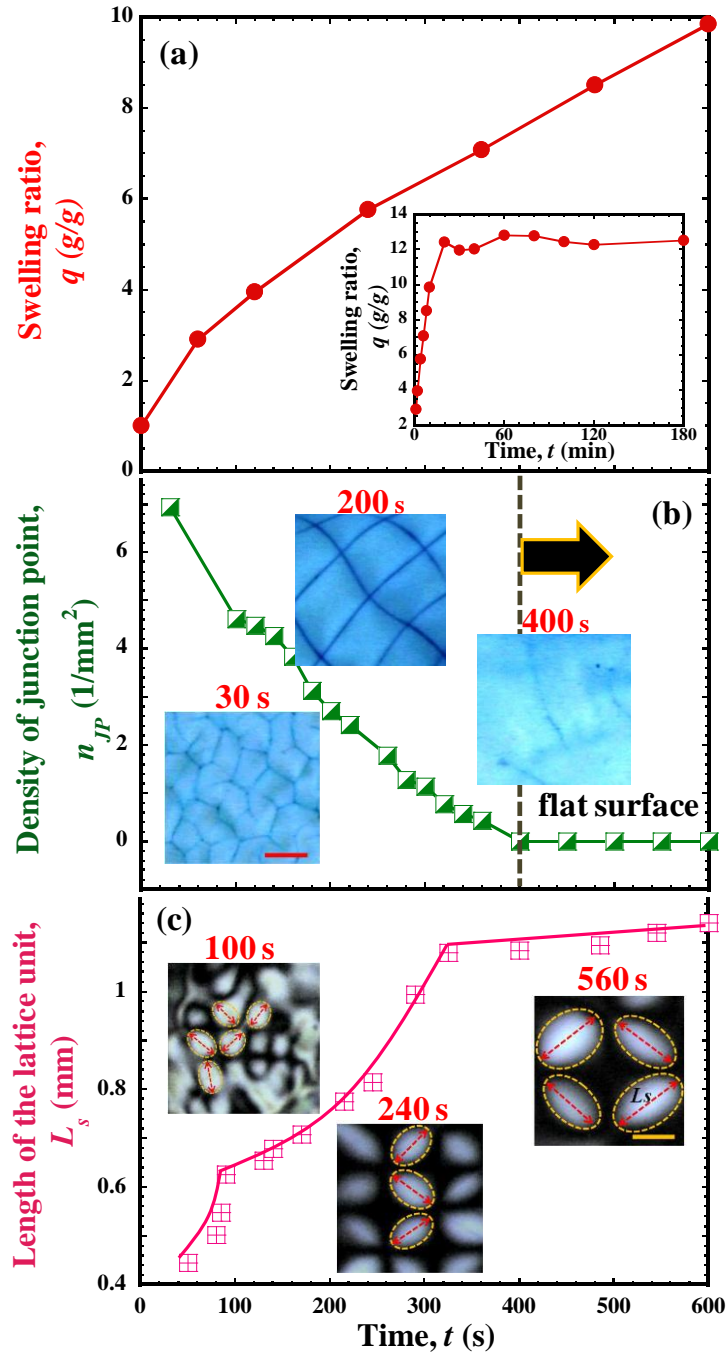


Figure 2. Time profiles of swelling ratio (q) relative to the as-prepared state (a), density of junction point (n_{JP}) of the crease patterns on the surface (b), and the length of the lattice unit (L_s) of the birefringence images (c) of the PBBDT-containing PDMA PAA-Q gel during swelling in water. Inset graph in (a) represents the identical swelling process of the gel for a prolonged period. Images in (b) and (c) were observed by a POM with a parallel and crossed polarizer, respectively. The scale bar in the inset images represents $500 \mu\text{m}$, and all the images are shown on the same scale.

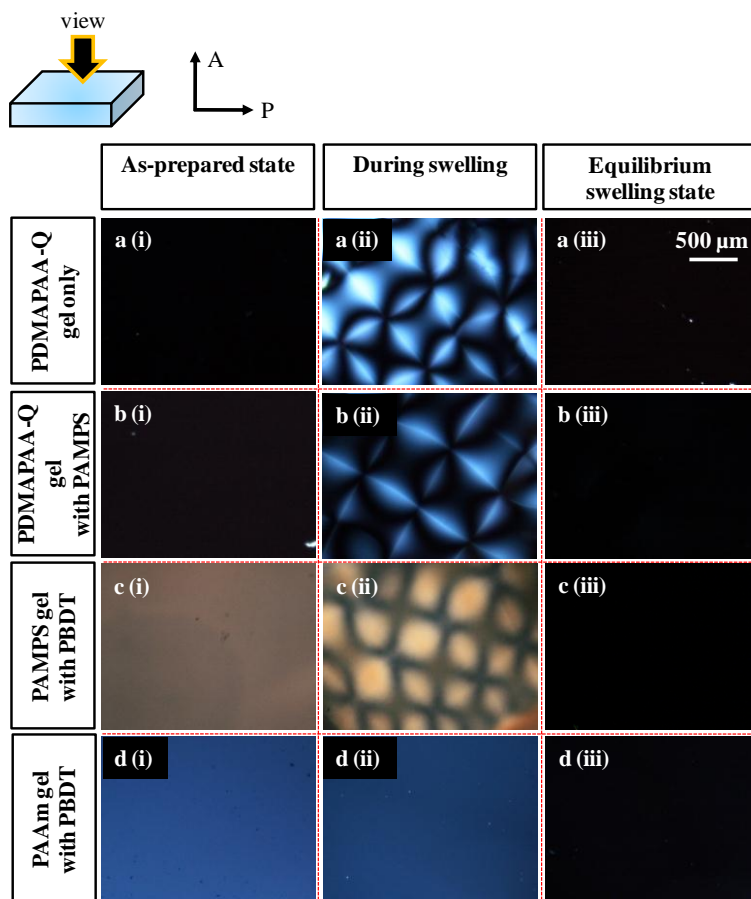


Figure 3. Effect of surface instability, polyion complexation, and rigidity of the dopant molecule on the regular-stable birefringence pattern formation in the hydrogel during the swelling process. The positively charged PDMA PAA-Q gel alone [a(i)] or in the presence of the negatively charged *flexible* dopant PAMPS [b(i)] exhibits almost no birefringence in the as-prepared state. Upon swelling, a transient birefringence pattern appears in the gels [a(ii) and b(ii)] because of the surface *creasing* instability. However, both the gels become amorphous well ahead of equilibrium swelling [a(iii) and b(iii)]. In presence of the negatively charged *semi-rigid* PBDT, the as-prepared anionic PAMPS and neutral PAAm gels exhibit weak birefringence patterns [c(i) and d(i), respectively]. During swelling, the birefringence pattern in the PBDT-containing PAMPS gel changes into numerous leaf-like patterns [c(ii)] because of the strong surface *creasing* instability [same as the PBDT-containing PDMA PAA-Q gel in Figure 1c(ii)]. In contrast, the birefringence pattern remains almost unchanged in the PBDT-containing PAAm gel [d(ii)] since there is no significant surface instability. However, after equilibrium swelling, both the PAMPS and PAAm gels containing PBDT show completely amorphous characteristics [c(iii) and d(iii), respectively] owing to the absence of polyion complexation. In all the cases, the dimensions of the as-prepared gels are the same as those in Figure 1. A: analyzer, P: polarizer. All the images are shown on the same scale as in a (iii).

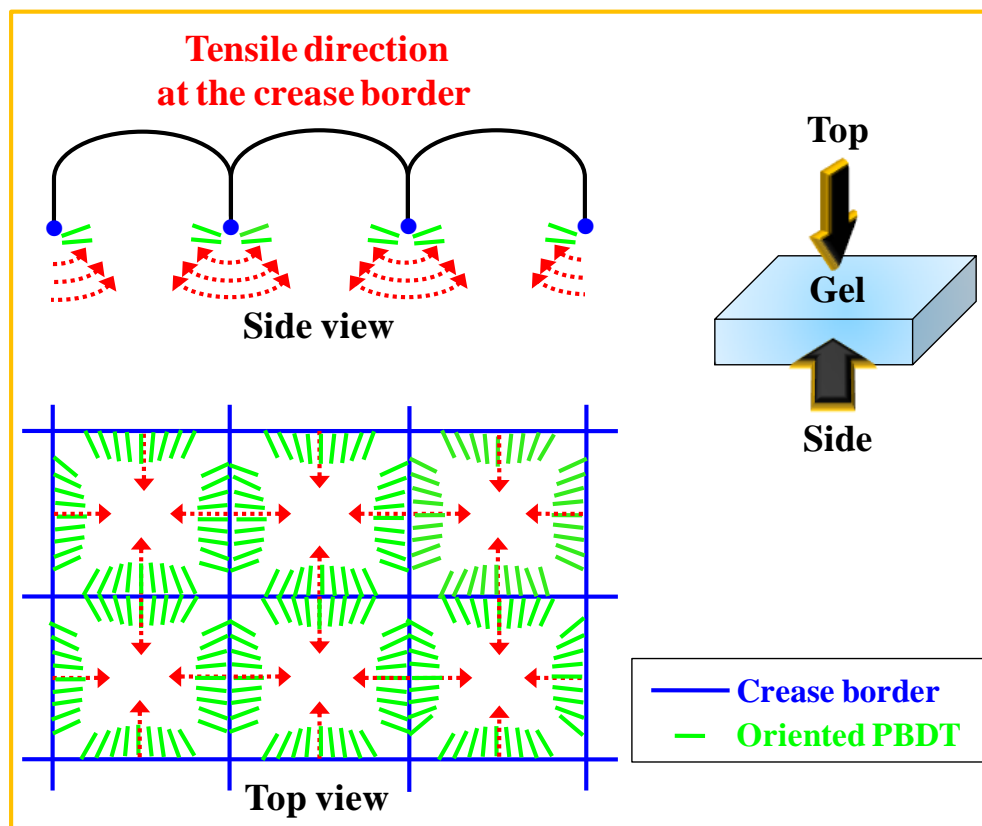


Figure 4. Mechanism of the formation of swelling-induced ordered structure in a polyelectrolyte gel containing a very small amount of an *oppositely* charged *semi-rigid* polyelectrolyte. When the sheet-like gel is immersed in water, rapid swelling occurs in the surface layer owing to the high osmotic pressure of the polyelectrolytic gel. The rapid swelling of the surface layer induces a large mismatch in the internal stress between the surface layer and the inner layer. Therefore, surface *creasing* instability occurs, which exerts tensile stress vertical to the boundary of the crease patterns and induces polymer network orientation. In the presence of an oppositely charged semi-rigid polyelectrolyte as the dopant, this polymer network orientation is frozen by the subsequent polyion complexation and fibrous bundle formation between the two oppositely charged components, which is stabilized by the removal of the low-molecular counterions through diffusion from the gel. Thus, the ordered structure remains even after the surface crease pattern completely disappears in the equilibrium swelling state. The dotted red arrows indicate the direction of tension induced by the formation of the crease pattern.

Table 1. Surface morphology and birefringence pattern of various hydrogels with different dopant molecules. Swelling-induced permanent and highly ordered macroscopic structure is obtained only for the PDMAPAA-Q gel containing PBDT. Here, the circles and crosses indicate “yes” and “no,” respectively. The symbols (+), (-), and (0) indicate positively charged, negatively charged, and neutral polymers, respectively.

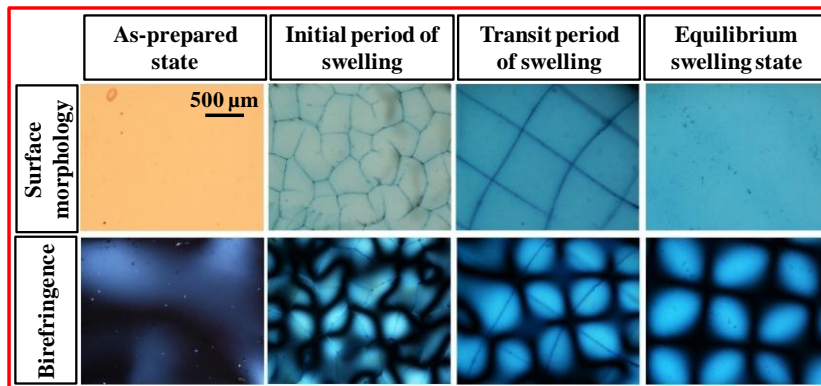
Hydrogel	Polyelectrolyte dopant	Crease pattern	Lattice-like birefringence	
			During swelling	At equilibrium
PDMAPAA-Q (+)	PBDT(-)	○	○	○
	PBDT(-)	×*	×	×
	PAMPS(-)	○	○	×
	None	○	○	×
PAMPS(-)	PBDT(-)	○	○	×
PAAm(0)	PBDT(-)	×	×	×

*Slow swelling in water vapor.

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

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Formation of a millimeter-scale long-range ordered structure in the polyelectrolyte hydrogel by the rapid-heterogeneous swelling process requires the following: (i) swelling-induced surface creasing; (ii) polyion complex formation; and (iii) a semi-rigid or rigid dopant. The structure formation mechanism may help understand how biomacromolecules that are rigid polyelectrolytes, such as microtubules and actin filaments, form rich architectures during the growth of biological organs.