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Hydrogels with Cylindrically Symmetric Structure at Macroscopic Scale by Self-Assembly of Semi-rigid Polyion Complex

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Abstract: A hydrogel with cylindrically symmetric structure at macroscopic scale has been developed by polymerization of a cationic monomer in the presence of a small amount of semi-rigid polyanion poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT) in a cylinder glass tube. The polyion complex radially aligns in the outer region of the synthesized cylinder gel. On the other hand, it orients in concentric and axial directions in the inner region. To the authors' knowledge, this is the first report of such millimeter-scale ordered structure developed in a polymeric hydrogel. We elucidate that homeotropic alignment on the glass wall is energetically favorable for the semi-rigid polyion complex, resulting in the radial orientation in the outer region. In the inner region, the oriented structures result from the monomer difffusion (due to the heterogeneous polymerization) that induces PBDT orientation perpendicular to the diffusion direction. The structured gels showing sensitive response of birefringence to external force are expected to find applications in optical sensors.

Introduction

Most bio-tissues are in a soft and wet gel-like state, containing a large amount of water. These hydrogels usually possess well-ordered structures at scales ranging from nanometers to milimeters given highly elaborate functions of living organisms.[1−4] For example, ciliary muscle in the eye with circular, longitudinal, and radial orientations enables the changes in lens shape for light focusing and regulates the flow of aqueous humor.[3] Thus, biomimetism and bioinspiration as tools for the design of structured hydrogels have received increasing attention in recent years, endowing the synthetic gels with particular photonic and electrical characteristics and potential applications in tissue engineering.[5−11] Osada developed hydrogels with shape memories by incorporation of crystalline molecules.[7] Tsujii introduced bilayer surfactant into hydrogels to generate iridescent color.[8] However, these works only succeeded in producing anisotropic domains at a sub-micrometer or micrometer level. Hydrogels with one integrated anisotropic structure at macroscopic scale, especially the cylindrically symmetric structure, are rarely reported.[7−11]

Macroscopically radial or concentric structure can be tuned in hydrogels by a facile reaction−diffusion process; the reaction and diffusion compete with each other and result in intricate spatial or temporal structures. Concentric Liesegang rings are usually generated in hydrogel, when the component in the solution out of the gel diffuses in and induces reaction to form precipate.[12,13] Dobashi and co-workers have successfully synthesized physically cross-linked gels with radial structure by dialysis of a rigid polyelectrolyte aqueous solution in a multivalent cation solution, where ion diffusion induces molecular orientation and physical gelation.[14,15] However, the physical gels thus obtained are generally turbid and lack stability, which affect their optical and mechanical utility.

Here, we report a hydrogel with cylindrically ordered symmetric structures by photo-polymerizing an isotropic precursor solution of a cationic monomer with a small amount of semi-

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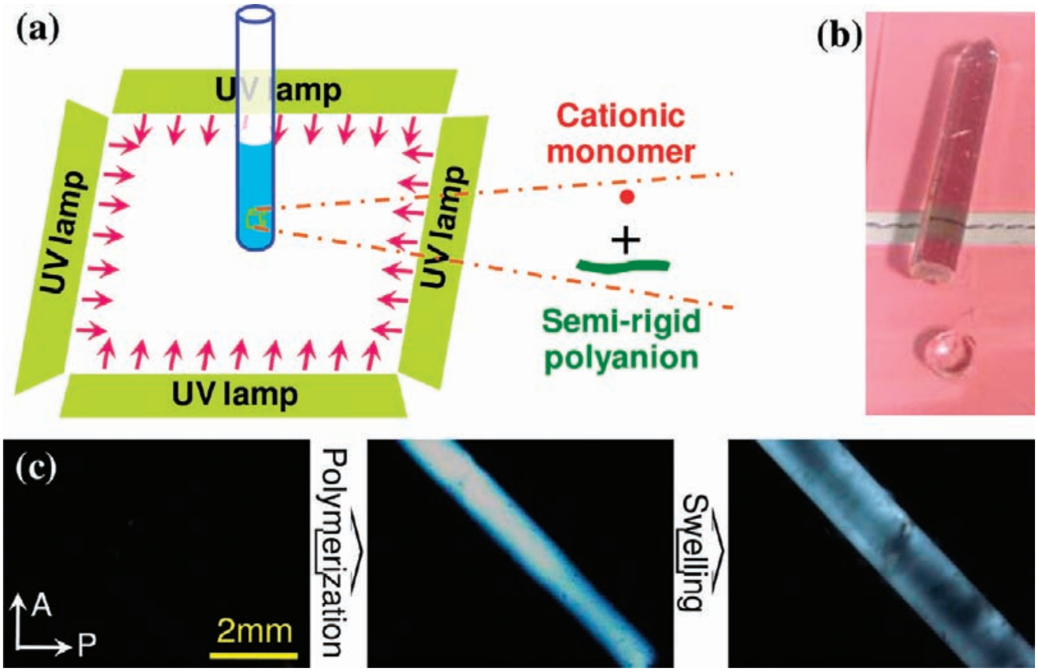

Figure 1. (a) Scheme of experimental setup for synthesis of cylindrical gel with ordered structures. Glass tube with precursor solution is placed vertically in the center of four UV lamps arranged in a square. (b) Appearance of gel swelled in 1 M sodium chloride aqueous solution. The disk piece is cut from the cylinder gel. (c) Polarizing micrographs of precursor solution in glass tube, as-prepared cylindrical gel, and swollen gel (QP-2.5-1).

rigid polyanion, poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT), in a cylindrical glass tube. The semi-rigid polyion complexes formed during polymerization of cationic monomer favor long-range homeotropic alignment on the surface of glass tube, forming a radial structure in the outer region of the synthesized cylinder gel. On the other hand, the complexes orient in concentric and axial directions in the inner region induced by the molecular diffuison during the heterogeneous polymerization due to the significant UV absorbance of PBDT. The two different orientation fields compete with each other and develop the complex cylindrical symmetric structure that is frozen by a subsequent chemical cross-linking process. Thus, a novel polymeric hydrogel is developed with millimeter-scale anisotropic structures of cylindrical symmetry. These gels show a sensitive response to external force by changing birefringence colors and are expected to find applications in mechano-optical sensing.

Results and Discussion

Hydrogels were synthesized by photo-polymerization at room temperature. A non-modified glass tube with a diameter of several millimeters, containing the precursor aqueous solution, was placed vertically in the center of four UV lamps arranged in a square (Figure 1a). The synthesized gels were coded as QP-C_Q-C_P, where C_Q was the concentration of cationic monomer *N*-[3-(*N*,*N*-dimethylamino)propyl]acrylamide methyl chloride quarternary (DMAPAA-Q) in M, and C_P is the concentration of PBDT in wt %. All the samples were synthesized with constant concentrations of the chemical cross-linker (3 mol %) and photo-initiator (0.15 mol %) (relative to monomer concentration).

The precursor solutions are optically isotropic, because C_P (0.2−1 wt %) used in this study is much lower than the critical concentration of nematic liquid crystal, C_{LC}*, of 2.2 wt %.[16,17] However, the as-prepared hydrogels are transparent (Figure 1b) and exhibit strong birefringence observed under polarizing optical microscope (POM), indicating that ordered structure is formed during the polymerization (Figure 1c). This ordered structure is well maintained after swelling, both in pure water or simple salt solution.[18] In the following, all the integrated samples we used are swelled in 1 M sodium chloride (NaCl) aqueous solution to prevent overswelling due to the nature of polyelectrolyte gel. The disk-shaped specimens cut from swollen cylinder gels exhibit a clear millimeter-scale Maltese cross that does not change while rotating the sample, indicating that a cylindrically symmetric structure was formed during the polymerization (Figure 2a).

Poly(DMAPAA-Q) gels synthesized without PBDT are transparent and without birefringence. Furthermore, the PBDT-containing gels synthesized with anionic monomer 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and neutral hydroxyethyl acrylate (HEA) also show no birefringence. Thus, the above oriented structure in PBDT-contained poly(DMAPAA-Q) hydrogels is related to the electrostatic interaction between the polycation and oppositely charged semi-rigid PBDT that triggers the self-assembly and orientation.[19−21]

To characterize the organized structure of PBDT in detail, the gels are observed under POM with insertion of a 530 nm tint plate. The swollen disk gel QP-2-1 shows different birefringent colors in the inner and outer regions, implying

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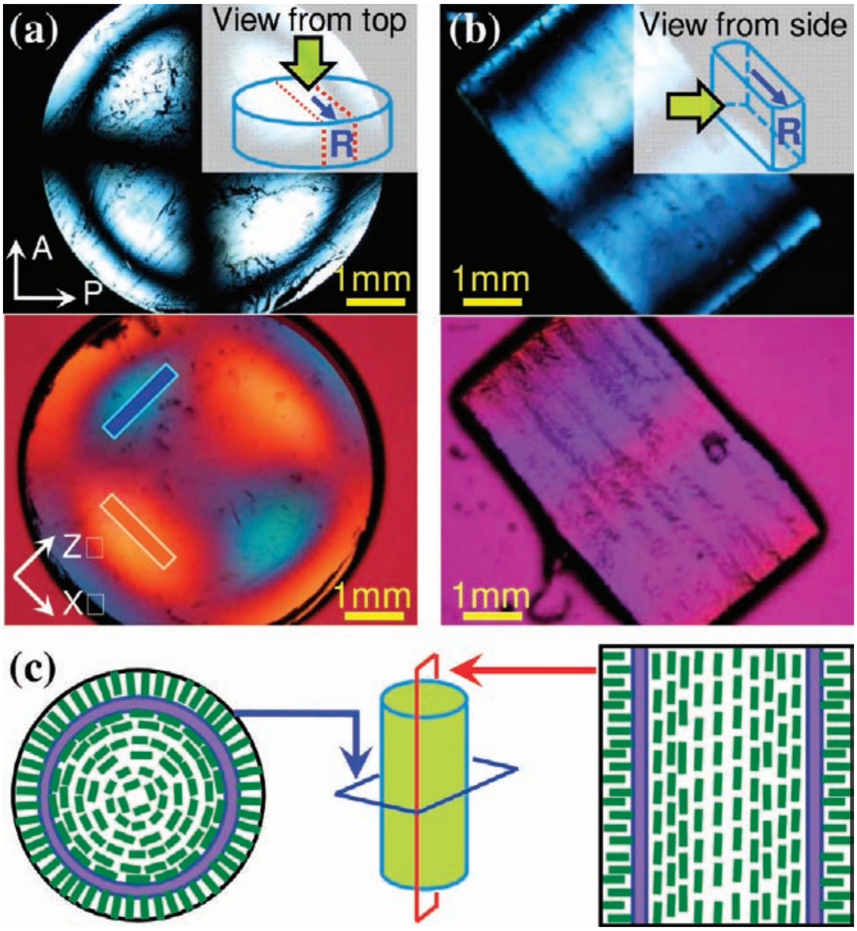


Figure 2. Polarizing micrographs of gel QP-2-1 swelled in 1 M NaCl aqueous solution and schematic structures of PBDT in the synthetic gel. Micrographs of disk gel observed from the top (a) and its central slice observed from the side (b) under microscope with crossed polarizers and insertion of 530 nm tint plate. The insets show the specimen position for the observation and observation direction; the central slice cut from the disk gel as guided by red dotted line. (c) A proposed microstructure of hierarchically oriented PBDT in the cross section and axial plane of polymeric gels.

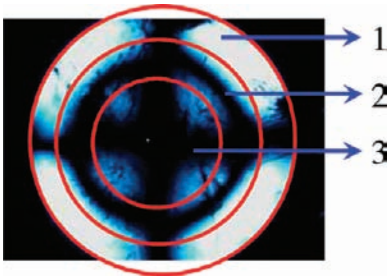
different molecular orientations in these two regions (Figure 2a). The flexible polycation with much shorter persistence length entwines on the semi-rigid PBDT;[22] thus, the birefringence should mainly be attributed to oriented PBDT. According to the birefringent colors of PBDT aqueous solution under shearing, we find that PBDT is a positive liquid crystal.[16,23] It shows blue and orange colors if oriented in southwest and northwest directions, respectively.[24] Thus, the birefringent micrograph of the disk gel demonstrates that PBDTs orient radially in the outer region and form a concentric structure in the inner region. This is also confirmed by the small-angle X-ray scattering results (Figure S1, Supporting Information). Between the two different alignment regions, there is a transition zone that appears as a black ring within the huge Maltese cross. PBDT is randomly oriented rather than absent in this region, which is confirmed by the elemental analysis (Table 1).

Next, the disk gel is cut into slices parallel to the axis of cylinder gel to observe PBDT alignment in the axial plane of gel. The birefringent image indicates that PBDT aligns radially in the outer region, perpendicular to the glass surface, whereas it orients parallel to the axial direction in the inner region (Figure 2b). The former is consistent with the observation in Figure 2a; however, the latter seems contradictory with the result in Figure 2a that shows a concentric structure in the inner region. This contradiction could not be explained by the formation of a helix structure, since the gel slices become absolutely dark

Table 1. Elemental Analysis Results of Gel QP-2.5-0.5 Swelled in 1 M NaCl Aqueous Solution (Swelling Ratio of the Gel (w/w) Is Also Shown)

sample no.[a]	C %	H %	N %	S %	WQ/WP[b]	swelling ratio
1	41.23	7.69	10.73	0.08	121.5	4.48
2	40.12	7.88	10.45	0.09	105.1	4.78
3	38.3	7.53	9.97	0.1	89.6	5.15

[a] Samples from different parts of swollen disk gels, as shown in the following scheme. [b] Mass ratio of poly(DMAPAA-Q) to PBDT estimated from the values of N and S. The mass ratio in feed was 103.3.



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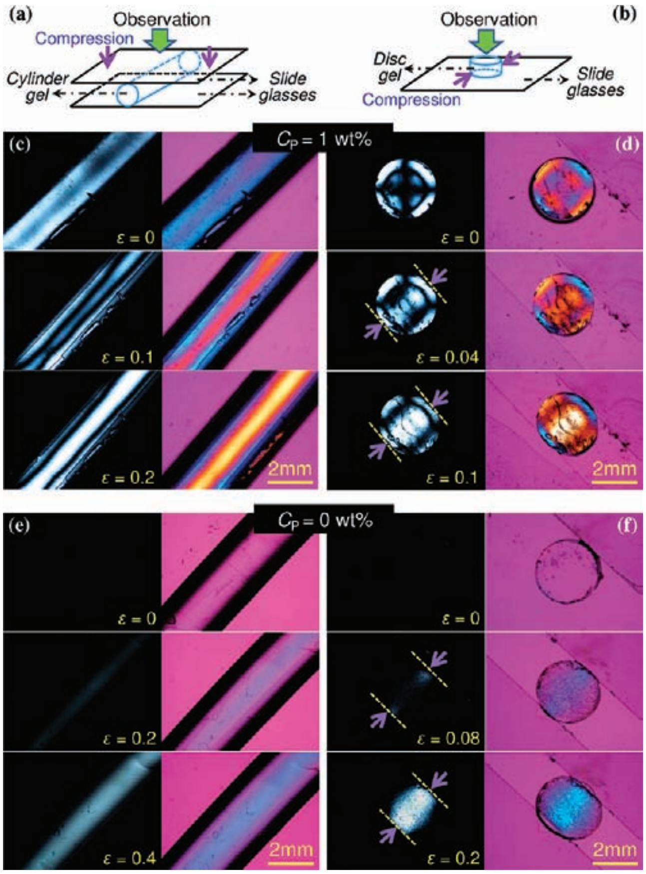

Figure 3. Birefringence change of the swollen gel QP-2.5-1 and QP-2.5-0 under compression in radial direction. Schematic illustration of the compression and observation for (a) cylindrical gel and (b) disk gel. Crossed polarizing micrographs of QP-2.5-1 (c,d) and QP-2.5-0 (e,f). The right columns are observed with the insertion of a 530 nm sensitive tint plate. The related strain, ε, is noted in the figure.

only when the gel axis is parallel to the polarizer or analyzer. Furthermore, it is not due to the internal stress of the gel; the PBDT-containing disk gels retain their birefringence without weakening after being cut into several thin pieces (Figure S2, Supporting Information). Although the swelling of cylindrical gels commonly produces a certain internal stress, it is too small to generate birefringence (the swollen gels without PBDT are optically isotropic). Thus, PBDT is organized in two orthogonal directions in the inner region, partially forming concentric structure and partially aligning with the axial direction.[25] The proposed structure model is shown in Figure 2c.

These gels with complex oriented structures show a sensitive response to external force. We observe the birefringence change of the cylinder and disk gels under compression in the radial direction, as shown in Figure 3a,b. The swollen cylinder gel QP-2.5-1 shows strong birefringence without compression; the birefringence color with tint plate indicates that axial direction alignment of PBDT predominates in the observation from the radial direction (Figure 3c). With applied compression, the central region changes birefringence color from blue to orange, indicating that the axial alignment is overwhelmed by the concentric direction one. This is because the compression enhances the concentric direction alignment of PBDT due to the lateral stretch and decreases the axial direction one due to the decrease in thickness. Furthermore, birefringence change of the disk gels is observed under compression from the two sides (Figure 3d). The micrographs show the circular symmetric Maltese cross and a black ring before compression. With applied compression force, the intensity and range of blue birefringence in the inner region gradually decrease; meanwhile the orange one increases. The compression promotes the alignment of PBDT perpendicular to the force direction due to the lateral stretch; thus, concentric alignment gradually changes from the circular to elliptical. The results are consistent with our proposed PBDT alignment model of synthesized gel in Figure 2c.

We should emphasize that the change of birefringence under compression does not result from the poly(DMAPAA-Q) matrix of the swollen gel, according to the results of the gel QP-2.5-0 synthesized without PBDT under compression (Figure 3e,f). The gel QP-2.5-0 is isotropic before compression, and the birefringence appears under a much larger strain than that of gel QP-2.5-1. Moreover, the birefringence color of the poly(DMAPAA-Q) gel is opposite to that of QP-2.5-1 since poly(DMAPAA-Q) is an optically negative polymer.[26] Thus, the strong birefringence of the PBDT-containing gel comes from the molecular orientation of PBDT that is an optically positive, semi-rigid polymer.

We next study the effects of C_P and C_Q on the structure of swollen gel. When 0.5 wt % $\leq C_P \leq$ 1 wt %, the disk gels show Maltese cross concomitant with a black ring. On the other hand, the birefringence just appears in the outer region and the inner region is isotropic, when $C_P <$ 0.4 wt % (Figure S3, Supporting Information). When $C_P >$ 1 wt %, gels shrink severely due to the condensation of polyion complex. The birefringence intensity of disk gels, both inside and outside the black ring, increases with C_P. However, the birefringence inside the black ring is much weaker than that of the outside at $C_Q =$ 2.5 M, while it is almost the same at $C_Q =$ 2 M (Figure 4a). The black ring position is studied by measuring the radius ratio (r/R) of the black ring r to the cylinder gel R. The r/R holds a constant value for the same C_Q, regardless of the change in C_P and gel diameters. However, it decreases with the increase in C_Q, $r/R =$ 0.75 and 0.6 for $C_Q =$ 2 and 2.5 M, respectively (Figure 4b). The dependence of r/R only on C_Q suggests that the polymerization kinetics is crucial for the orientation of PBDT in the gels.

What mechanism is responsible for the formation of such complex structure in the hydrogels? Primarily, homeotropic alignment on the glass wall seems to be energetically favorable for the semi-rigid polyion complexes, and thus form the radial structure in the outer region of synthesized gels. Similar results are observed in other LC complex systems consisting of sulfonic acid and amino groups.[27−29] High C_Q or high C_P should enhance this homeotropic alignment, making it well-oriented and long-range effective. On the other hand, why do PBDT and its polyion complex orient into concentric and axial directions in the inner region? Like other rigid polyelectrolytes, PBDT molecules form ordered structures by the diffusion of Ca^{2+}, similar to the process described by Dobashi.[14,15] We found that

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(25) A visualized evidence for the existence of axial alignment of PBDTs in the inner region of gel is the birefringent images of the gel QP-2-0.2 (Figure S3), of which the gel slice shows strong birefringence; however, the inner region of disk gel is isotropic observed from the top.

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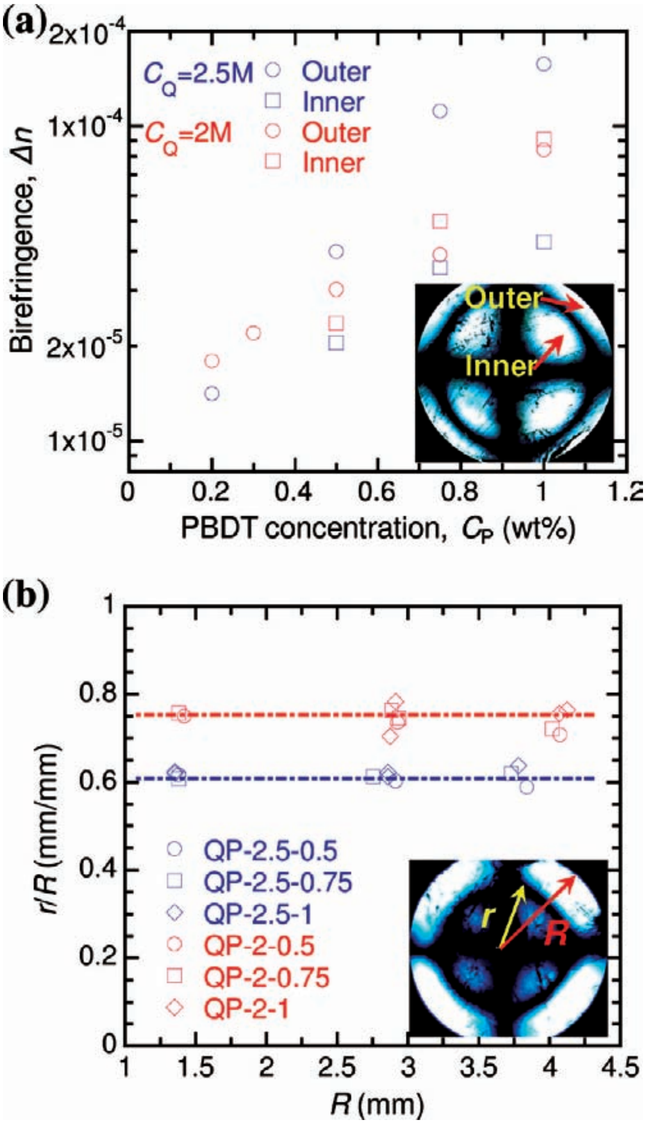

Figure 4. (a) Birefringence of the outer and inner region for swollen gels synthesized with different C_Q and C_P (diameter of swollen gel ~5.8 mm). (b) Ratio between the radius of black ring and the radius of swollen gel synthesized with different C_Q, C_P, and gel diameters.

the anionic PBDT aligns perpendicular to the diffusion direction of cationic ion; a similar result was reported by Stupp and co-workers.[30] Thus, we consider that the orientation of PBDT polyion complex in the inner region might result from cationic molecular diffusion if a heterogeneous polymerization occurs.

To validate this hypothesis, we study the absorbance of the reaction components. PBDT shows significant absorbance of UV light at wavelength less than 370 nm that fully covers the absorbance band (~325 nm) of the photo-initiator (Figure 5). The wavelength of UV that we used for photo-polymerization is ~365 nm. Thus, a UV intensity gradient is built in the polymerization solution, resulting in the heterogeneous polymerization.[31−33] The outer region with high UV intensity has a relatively fast reaction kinetics; thus, the cationic monomer should diffuse from the inner region to the outer because of the concentraion gradient (the diffusion of PBDT and polycation is much slower than that of cationic monomer and therefore

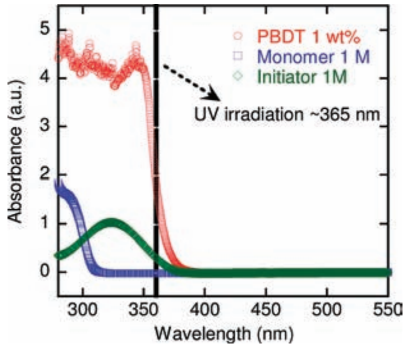

Figure 5. Absorbance spectra of the reaction components. Aqueous solution of each component is poured into standard quartz cell with 1 mm thickness to measure the absorbance by UV−vis spectrophotometer (Hitachi U-3000). The wavelength of UV used for photo-polymerization (~365 nm) is also noted in the figure.

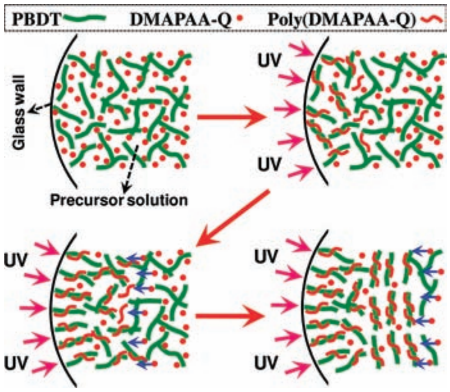

Figure 6. Mechanism for the formation of cylindrically symmetric structure during the photo-polymerization of a cationic monomer DMAPAA-Q in the presence of semi-rigid polyanion PBDT as dopant. The precursor solution is optically isotropic because of $C_P \ll C_{LC}^*$. Due to strong UV absorbance of PBDT, the polymerization started from the surface of the glass tube, and large amounts of polycations are produced in the outer region that interact with PBDT to form polyion complex. These semi-rigid complexes favor long-range homeotropic alignment on the glass wall. Simultaneously, a concentration gradient along the radial direction is built up. Thus, monomer diffuses from the inner region to the outer region. This monomer diffusion induces the polyion complex orientation perpendicular to the diffusion direction to form a concentric structure in the inner region. The different oriented structures are frozen by the subsequent cross-linking reaction. As a result, the polymeric hydrogels with macroscopically cylindrical symmetric structure are formed.

negligible). This is confirmed by the elemental analysis of the component distributions in the synthesized gels (Table 1). The inner region has relatively small mass ratio of poly(DMAPAA-Q) to PBDT and large swelling ratio, indicating the occurrence of monomer diffusion from the inner region to the outer. We further found that when the gel QP-2-1 is synthesized by thermal polymerization, the inner region of the disk gel is isotropic due to the homogeneous polymerization in the whole sample.

On the basis of these results, we propose a mechanism for the cylindrically symmetric structure formed in synthetic gels (Figure 6). The precursor solution is isotropic. After photo-polymerization, the outer region has a higher polymerization kinetics, where the polymerized polycations interact with PBDT

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to form polyion complex. Due to the interfacial interaction of complex and the glass tube, the polyion complexes homeotropically align perpendicular to the glass wall to form a radial structure in the outer region. The polymerization in the inner part of glass tube is retarded due to the significant UV absorbance of PBDT, which leads to the heterogeneous polymerization, the concentration gradient, and the diffusion of cationic monomer and polycation.[31−33] The diffusion of monomer induces polyion complex to orient perpendicular to the diffusion direction and form the concentric as well as the axial alignments in the inner region (the latter is not shown in Figure 6). With the diffusion of cationic monomer PBDT in the inner region preferentially aligns parallel to the axial; when $C_P > 0.4$ wt %, it orients simultaneously in another relatively stable direction in the confined geometry to form a concentric structure. The oriented structures of PBDT are frozen by the cross-linking reaction, resulting in the polymeric hydrogels with cylindrically symmetric structure up to a macroscopic scale.

Now, we consider the effects of C_Q and C_P (the reaction kinetics) on the alignment-region segmentation. The solutions with a constant C_P hold the same UV gradient, despite having different C_Q. High C_Q, corresponding to relatively large amounts of polycations and strong ionic strength, merits the homeotropic alignment of polyion complex on the glass wall by increasing the thickness and birefringence in the outer region of synthesized gels (Figure 2). The effect of C_P is more complex. High C_P also favors the homeotropic alignment; however, it simultaneously promotes the molecule diffusion and orientation in the inner region by increasing the UV intensity gradient. The two contrary effects might result in the constant alignment-region segmentation if the gels are synthesized with the same C_Q (Figure 2b).

Conclusions

In summary, a cylindrical hydrogel with macroscopically symmetric structures, radial-concentric complex structure, has been developed by a facile polymerization of a cationic monomer with a semi-rigid polyanion PBDT as dopant. During the polymerization, PBDT forms a polyion complex with oppositely charged polycation. The semi-rigid polyion complex radially (homeotropically) orients in the outer region of the gel due to the interfacial interaction with the glass wall. In the inner region, it orients in concentric and axial directions, because the heterogeneous polymerization (due to UV absorbance of PBDT) leads to monomer diffusion and the polyion complexes orient perpendicular to the diffusion direction. To the authors' knowledge, this is the first report of chemically cross-linked polymeric hydrogels at macroscopic scale with symmetric structure developed by controlling the self-assembly direction during heterogeneous polymerization. The structured gels showing sensitive response to applied force by changing birefringence colors are expected to find applications in mechano-optical sensors and open avenues in developing biomimetic hydrogels with intricate complex structures.

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Supporting Information Available: Experimental details, SAXS measurement of swollen disk gel QP-2.5-0.5, POM images of the gel QP-2-0.75 after being cut into slices, and structure characterization of the gel QP-2-0.2 synthesized with relatively low PBDT concentration. This material is available free of charge via the Internet at http://pubs.acs.org.

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