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ARTICLE

Dual Network Formation in Polyelectrolyte Hydrogel via Viscoelastic Phase Separation: Role of Ionic Strength and Polymerization Kinetics

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ABSTRACT: In this Article, we report a systematic research on a hydrogel with dual networks of 10^4 times difference in mesh sizes. The structure was developed by polymerizing a cationic monomer *N*-[3-(*N*,*N*-dimethylamino)propyl] acrylamide methyl chloride quarternary (DMAPAA-Q) in the presence of a small amount of semirigid polyanion, poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT). During the polymerization, polyion complexes were formed, which caused viscoelastic phase separation (VPS) due to the self-assembly of the semirigid polyion complexes, whereupon the dynamic coupling of phase separation and gelation is crucial for the structure formation. When PBDT was above its overlap concentration ($C_{\mathrm{PBDT}} > C^*$), a critical concentration of cationic monomer, $C_{\mathrm{Q}} \approx 1.5$ M, was observed, below which VPS occurred and turbid hydrogels with the dual network structure were formed, whereas above which, a transparent, anisotropic hydrogel was formed. It has been elucidated that the critical effect of C_{Q} on the VPS process is through the ionic strength mechanism. That is, the abundant unreacted cationic monomer at high C_{Q} behaves as a simple salt that screens the electrostatic interaction between the polycation and PBDT and therefore suppresses the occurrence of the phase separation. Furthermore, we investigated the effects of reaction kinetics on the VPS and the microstructure of gels by changing the concentrations of photoinitiator and chemical cross-linker. The dual network gels possess controllable turbidity degrees and mesh sizes corresponding to different quench depths of the phase separation. On the basis of these results, as well as in situ observation of the structure formation during the polymerization, we proposed a detailed mechanism for the formation of dual networks and the anisotropic hydrogels.

Introduction

Most biotissues are in a soft gel-like state and have mesoscopically well-ordered structures that give robust functions to living organisms.[1−4] For example, myosin shows a liquid-crystalline (LC) structure in sarcomere, contributing to the formation and smooth motion of muscle fibers.[3] Collagen fibrils (type III) form a micrometer-scale reticulum in the extracellular spaces of reticular connective tissue, which act as a scaffold for cells and ground substance.[4−6] These highly sophisticated structures of soft biotissues inspire researchers to develop versatile soft materials with special microstructures and functions. There have been several attempts to introduce well-ordered structures to synthetic hydrogels that are generally amorphous with a nanometer-scaled network. However, the efforts are mainly focused on anisotropic gels with LC domains, which show smart functions such as anisotropic shrinkage and generation of iridescent color.[7−13] Hydrogels with more complicated composite structures, especially the mesoscopically reticular structure, are hardly realized.

Recently, we reported a novel hydrogel with a micrometer-scaled network-like structure of a semirigid polyion complex, nested in a nanometer-scaled network.[14] This hydrogel was developed by polymerizing a cationic monomer *N*-[3-(*N*,*N*-dimethylamino)propyl] acrylamide methyl chloride quarternary (DMAPAA-Q) in the presence of a small amount of semirigid polyanion poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT) as dopant. During the polymerization of cationic monomer, the polycations form a complex with semirigid PBDT through electrostatic interaction. Then, self-assembly and viscoelastic phase separation (VPS) of the polyion complexes compete with each other and render the micrometer-scaled network-like structure, which is permanently frozen by the subsequent cross-linking reaction between polycation chains.

VPS produces a characteristic network-like structure in dynamically asymmetric mixtures, especially for a deep quench.[15−17] During the VPS, the phase with slower dynamics cannot catch up with the fast domain deformation and selectively sustains the mechanical stress, forming a transient network structure. In our case, viscosity asymmetry resulted from the formation of polyion complexes and further self-assembled aggregates with much higher viscosity than the base solution. Although only 0.5−2 wt % PBDT is adopted, the minority PBDT-rich phase forms a complete and clear network-like structure during the VPS.

Additionally, we found that this dual network structure was formed at a relatively low concentration of cationic monomer. If the monomer concentration C_{Q} is relatively high, then severe phase separation disappears and transparent gel with anisotropic structure of 1−3 mm in size is obtained.[18,19] C_{Q} seems to be critical for the occurrence of phase separation; however, the essential reason is still a puzzle. Furthermore, how do the reaction kinetics, which are determined by the concentrations of photoinitiator and chemical cross-linker, affect the microstructure of gels remains an open question.

In this Article, we report the systematic research on the characterization of the structure of this polyion complex hydrogel and develop a framework for the understanding of the underlying mechanism of this phenomenon. Effects of polymerization

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kinetics and ionic strength on the occurrence of phase separation and the microstructure of synthesized gels are studied through changing the components concentrations and adding sodium chloride to the precursor solutions, respectively. We elucidate how the different processes dynamically couple to each other during the polymerization. The crucial factors for self-assembly and phase separation as well as the determinant of polyion complex stability are also discussed.

Experimental Section

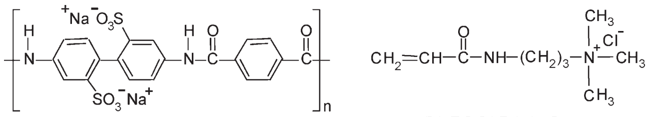
1. Synthesis of Poly(DMAPAA-Q) Gels Containing PBDT. PBDT, a water-soluble semirigid polyanion, was synthesized by an interfacial polycondensation reaction.[20] The weight-average molecular weight, M_w, and polydispersity (M_w/M_n) of PBDT were 1.8×10^6 and 1.2, respectively. Its aqueous solutions show a significantly low critical concentration of nematic liquid crystal, C_{LC}* of 2.2 wt %, much lower than those of common lyotropic LC macromolecules.[21,22] For example, the synthetic sulfonated poly(*p*-phenylene terephthalamide) with an elementary molecular structure similar to that of PBDT has a C_{LC}* of ~17 wt %.[23] The quite low C_{LC}* of PBDT should be attributed to its high M_w, intrinsic structural rigidity, and polyelectrolyte nature. The cationic monomer DMAPAA-Q (Kohjin) and the radical photoinitiator 2-ketoglutaric acid (Wako Pure Chemical Industries) were used as purchased without further purification. *N*,*N*′-Methylenebisacrylamide (MBAA) (Wako Pure Chemical Industries) was recrystallized from ethanol and used as a chemical cross-linker. Chemical structures of the components are shown in Scheme 1. Water was deionized and purified with 0.22 μm and 5 μm membrane filters before use. Aqueous solutions with a prescribed amount of PBDT, DMAPAA-Q, MBAA, and 2-ketoglutaric acid were prepared and poured in reaction cells consisting of a pair of parallel glass plates with 1 mm spacing. Gels synthesized in the presence of simple salt were carried out in the same way; a prescribed amount of sodium chloride (NaCl) was added into the precursor solutions. Photopolymerization was carried out at room temperature under an argon atmosphere with an ultraviolet (UV) lamp for 6 h. These as-prepared gels were immersed in a large amount of water for 1 week to reach an equilibrium state.

Samples of hydrogels were noted as QP-C_Q-C_{PBDT}-C_{MBAA}-C_{Init}, where C_Q is the monomer concentration in M, C_{PBDT} is the PBDT concentration in wt %, and C_{MBAA} and C_{Init} are the concentrations of cross-linker (MBAA) and initiator (2-ketoglutaric acid) in mol % (against DMAPAA-Q), respectively.

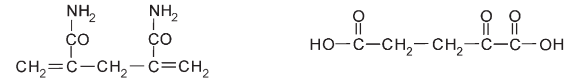
2. Characterization. The absorbance of as-prepared gels and precursor solutions was measured at a wavelength of 550 nm by a model 680XR plate reader (Bio-Rad). The absorbance value is the average of five measurements at different spots on one sample. All precursor solutions are transparent with absorbance that is quite low, < 0.04. If the absorbance of as-prepared gels is > 0.1, then the turbidity can be judged by the naked eye, and phase separation is presumed to have occurred during the polymerization.

The morphologies of the as-prepared and swollen gels were observed under microscope with parallel and crossed polarizers (Olympus, BH-2) at room temperature. Images were captured by a digital camera coupled to the microscope. The characteristic lengths of the network-like structures were extracted by Fourier transformation using the software NIH Image J. The birefringence, Δn, was measured from the retardation values using a crossed polarizing microscope with a Berek compensator. Δn was obtained as the average of five or six measurements at different points for each sample. Additionally, structural evolution was observed in situ by microscope with parallel and crossed polarizers during the photopolymerization process. The reaction cell consists of a pair of glass plates with 1 mm spacing. Samples were taken out at different reaction times and observed for 1 to 2 min; then, polymerization resumed to the completion.

Scheme 1. Chemical Structures of (a) Semi-Rigid Polyanion, PBDT, (b) Cationic Monomer, DMAPAA-Q, (c) Chemical Cross-Linker, MBAA, and (d) Photo-Initiator, 2-Ketoglutaric Acid



(**a**) PBDT (**b**) DMAPAA-Q



(**c**) MBAA (**d**) 2-ketoglutaric acid

The surface morphologies of as-prepared and swollen gels were observed by differential interference contrast microscope (Olympus BX50) at room temperature. The swelling degree of the gels, *q*, defined as the mass ratio of the sample in its swollen state to its dried state, was estimated. We obtained the dried samples by keeping them in a desiccator for 12 h and in a vacuum oven at 60 °C for 6 h.

3. Stability of Poly(DMAPAA-Q)/PBDT Complexes in the Aqueous Solutions with Different C_Q. Poly(DMAPAA-Q) was prepared by the radical polymerization of a 1 M aqueous solution of DMAPAA-Q monomer in the presence of 1 mol % potassium persulfate (Tokyo Kasei). M_w and M_w/M_n of polymerized poly(DMAPAA-Q) were 408 000 and 2.3, respectively, which were measured by gel permeation chromatography (GPC). The synthetic polycation solution was directly used for experiments. Then, aqueous solutions with 1 wt % PBDT and different cationic monomer concentrations, C_Q, were prepared, and they were transparent. A certain amount of poly(DMAPAA-Q), calculated from the prescribed charge ratios of polycation/PBDT was added to the PBDT−cationic monomer solutions and mixed sufficiently. The states of the mixtures, precipitate, floccule, and transparent solution, were judged by the naked eye.

Results and Discussion

1. Effects of C_Q and C_{PBDT} on the Microstructure of Gels. We first investigate the effects of C_Q and C_{PBDT} while keeping other factors (C_{MBAA} and C_{Init}) at a constant concentration. We studied the effects of C_Q and C_{PBDT} on phase separation by judging the absorbance of as-prepared gels, QP-C_Q-C_{PBDT}-2-0.15. All precursor solutions are transparent and optically isotropic when C_{PBDT} is lower than C_{LC}* of 2.2 wt %. However, the gels synthesized with relatively low C_Q (C_Q < 1.5 M) are turbid; they become transparent at a relatively high C_Q ($C_Q \geq 2$ M) (Figure 1a). Actually, the turbidity increases to a maximum and then decreases to absolutely transparent with the increase in C_Q. The C_Q-C_{PBDT} diagram for the appearance and microstructure of as-prepared gels is shown in Figure 1b, and the corresponding representative micrographs are shown in Figure 1c. There is a sharp boundary of $C_Q \approx 1.5$ M on the turbid and transparent gels, although it slightly moves to the high C_Q as C_{PBDT} increases, indicating that the occurrence of phase separation is mainly affected by C_Q.

The gels synthesized with relatively high C_{PBDT} (C_{PBDT} > 0.5 wt %), both the turbid and the transparent, show birefringence and characteristic structure. The turbid gels (C_Q < 1.5 M) exhibit weak birefringence but possess a unique well-ordered network-like structure of micrometer size observed under parallel polarizers (images A and B in Figure 1c). The transparent gels (C_Q > 1.5 M) show strong birefringence ($\Delta n > 1.0 \times 10^{-5}$) with anisotropic domains of 1−3 mm in size (image D and E in Figure 1c). These results

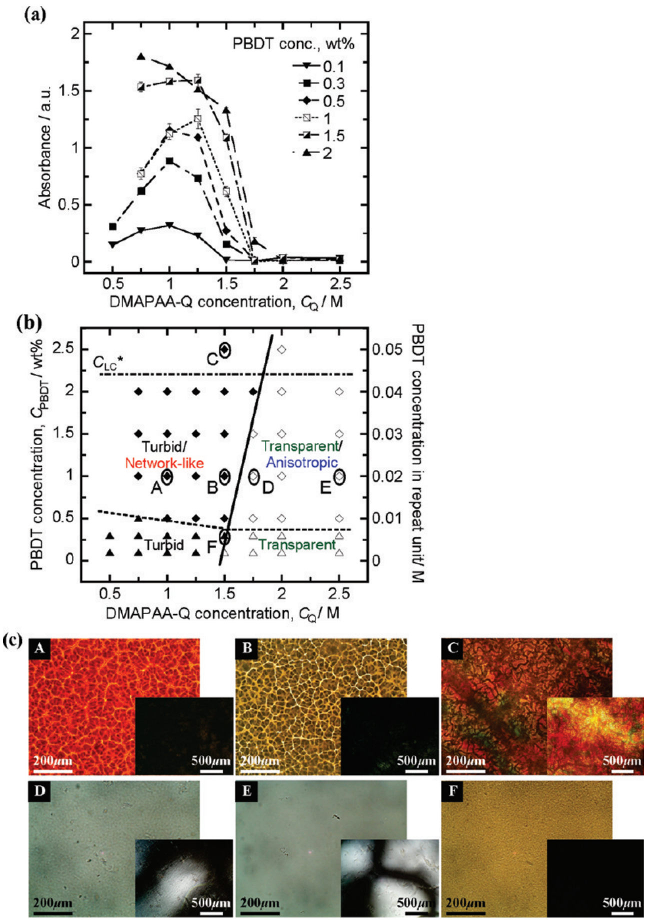


Figure 1. (a) Absorbance at wavelength 550 nm of as-prepared gels QP-C_Q-C_{PBDT}-2-0.15. (b) C_Q-C_{PBDT} diagram for appearance and microstructure pattern of the as-prepared gels. Four types of gel appearances appear in different regions of C_Q and C_{PBDT}. (c) Representative micrographs of as-prepared gels (corresponding to points A–F in part b) observed under microscope with parallel polarizers. Inset micrographs are observed under crossed polarizers.

are in agreement with our previous results.[14,18,19] The gels synthesized with C_{PBDT} higher than the liquid crystalline concentration ($C_{PBDT} > C_{LC}^* = 2.2$ wt %), showed similar structures as those of $0.5 < C_{PBDT} < 2.2$ wt %.

The gels synthesized with relatively low C_{PBDT} ($C_{PBDT} <$ 0.5 wt %), both the turbid and the transparent, have no birefringence and characteristic structure (image F in Figure 1c). Therefore, C_{PBDT} of 0.5 wt % is the critical concentration to induce self-activated orientation of PBDT during the polymerization. Because the crossover concentration of PBDT, C^*, is ~0.2 wt %, this critical $C_{PBDT} = 0.5$ wt % is related to the dramatic increase in the viscosity of the precursor solution due to the entanglement of PBDT.[21,22]

2. Effects of Ionic Strength on the Microstructure of Gels. Why do the gels become transparent at $C_Q > 1.5$ M? Why does phase separation occur in solutions with relatively low C_Q rather than high C_Q? High C_Q should bring about several effects, such as a relatively high ionic strength, a large amount of polycations produced during the polymerization, as well as fast polymerization and gelation kinetics. The disappearance of phase separation at high C_Q therefore might be related to these effects through the following possible mechanisms: (a) polyion complex becomes soluble in the solution with high ionic strength, (b) charge inversion of the polyion complex occurs when polycation is in excess over PBDT, and (c) phase separation is fully suppressed by the fast gelation process.

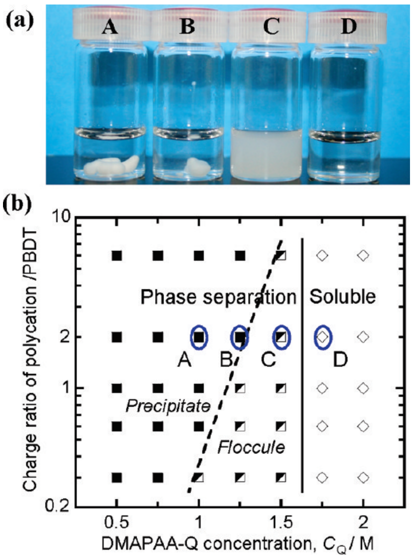


Figure 2. (a) Appearances of the poly(DMAPAA-Q)/PBDT polyion complexes in aqueous solutions of DMAPAA-Q monomer: precipitate (A–B), floccules (C), and transparent (D); corresponding positions are shown in part b. (b) Diagram of polyion complexes (1 wt % PBDT) with different charge ratios of polycation to PBDT in aqueous solutions of cationic monomer with different C_Q.

We assume that (c) should not be the case because the phase separation induced by the poor solubility of the polyion complexes should occur in the early stage of polymerization, whereas the cross-linking process occurs in the late stage.

To check (a) and (b), we study the stability of the aqueous solutions of poly(DMAPAA-Q)/PBDT polyion complexes with various charge ratios in the presence of DMAPAA-Q monomer (Figure 2). The aqueous solutions, containing a constant amount of PBDT ($C_{PBDT} = 1$ wt %) and different C_Q of DMAPAA-Q monomer (different ionic strength, I), are transparent and optically isotropic.[21,22,24] When a prescribed amount of poly(DMAPAA-Q) is added dropwise to these solutions and mixed sufficiently, they exhibit slight birefringence, indicating that the oppositely charged polymers do form complex. The poly(DMAPAA-Q)/PBDT solution with different C_Q changes from a compact precipitate ($C_Q \leq 1$ M) to a loose floccules ($C_Q = 1.25$ to 1.5 M), and then to an absolutely transparent state ($C_Q \geq 1.75$ M), which matches well with the absorbance change of as-prepared gels in Figure 1a. The critical C_Q for the maximum absorbance of as-prepared gels (Figure 1a), as well as the transition from precipitate to floccules of the poly(DMAPAA-Q)/PBDT solution (Figure 2b), is approximately 1 to 1.25 M. These results indicate that the polyion complexes form aggregates and phase separation occurs in the solutions with relatively low ionic strength ($C_Q \leq 1.5$ M), whereas they are stable and soluble, forming a transparent solution with high ionic strength ($C_Q > 1.75$ M) (Figure 2). Furthermore, the occurrence of phase separation has no dependence on the charge ratio of polyion complex. Therefore, the disappearance of the VPS at high C_Q in Figure 1b results from the relatively high ionic strength that screens the electrostatic interaction between polyions (mechanism (a)), rather than the charge inversion (mechanism (b)). It is interesting to note that the anisotropic association (aggregate) observed in the solution with high ionic strength ($C_Q > 1.5$ M) indicates that although strong phase separation is suppressed, interaction between polycation and polyanion still exists. The critical $C_Q = 1.5$ M corresponds to a Debye length $\kappa^{-1} = 2.58$ Å; below this

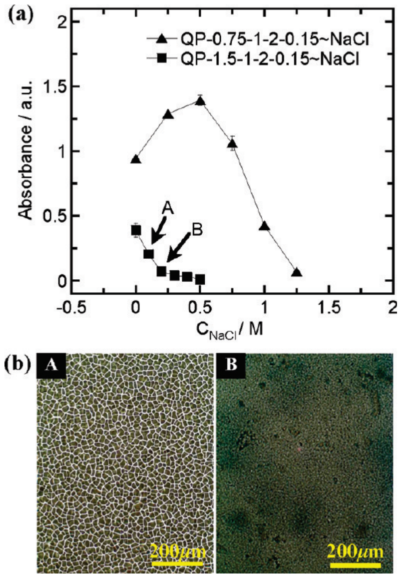


Figure 3. Effect of monovalent salt on phase separation during the synthesis of gels. (a) Absorbance of as-prepared gel QP-1.5-1-2-0.15 and QP-0.75-1-2-0.15 synthesized in the presence of salt, NaCl. (b) Optical micrographs under parallel polarizers of as-prepared gel QP-1.5-1-2-0.15 synthesized in the presence of different C_{NaCl}: (A) 0.1 and (B) 0.2 M.

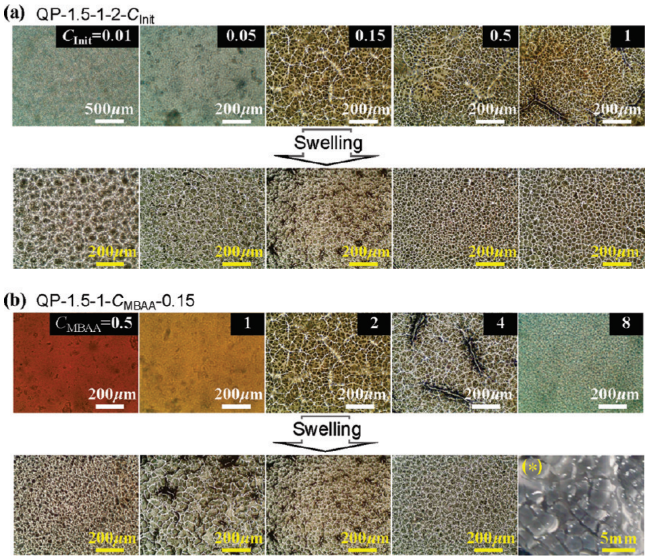


Figure 4. Optical micrographs under parallel polarizers of as-prepared and swollen gels, synthesized with different concentrations of (a) initiator (QP-1.5−1−2-C_{Init}) and (b) chemical cross-linker (QP-1.5−1-C_{MBAA}-0.15). The unit for the numbers in the Figure is mol % in relative to monomer concentration. The image marked with (*) is the fracture appearance of swollen gel QP-1.5-1-8-0.15, which is taken by a digital camera.

Debye length, the electrostatic interaction becomes weak and the polyion complexes are stable with a maximized number to gain translational entropy, as studied by Hayashi, Wong, and their coworkers.[25,26]

This ionic strength-induced effect is further verified by synthesizing the gels in the presence of NaCl with different concentrations, C_{NaCl}. The turbidity of the as-prepared gel QP-1.5-1-2-0.15 decreases with an increase in C_{NaCl}, and the gel becomes transparent when C_{NaCl} reaches 0.5 M (Figure 3a). Simultaneously, the network-like structure changes from clear to obscure and disappears at high C_{NaCl} (Figure 3b). Even for the gel QP-0.75-1-2-0.15 with a much lower C_Q, the polymeric gel becomes transparent when synthesized in the presence of 1.25 M NaCl (Figure 3a). Moreover, the turbidity first increases to a maximum and then decreases to transparent with the addition of NaCl; the tendency and rhythm are identical to that of salt-free gels QP-C_Q-1-2-0.15 in Figure 1a. Therefore, the ionic strength I of the precursor solutions, directly affected by C_Q (in the presence of NaCl, $I = C_Q + C_{NaCl}$), determines the occurrence of phase separation during the polymerization.

3. Effects of C_{Init} and C_{MBAA} on Dual Network Gels. To elucidate the effect of polymerization and cross-linking kinetics on the dual network structure formation, we synthesized gels with different C_{Init} and C_{MBAA}, keeping C_Q of 1.5 M and C_{PBDT} of 1 wt % (in turbid region). All as-prepared and swollen gels shown in Figure 4 are turbid and with micrometer-scaled network-like structures, despite having different turbidity degrees. The turbidity degree increases with an increase in C_{Init} or a decrease in C_{MBAA}, corresponding to different quench depths of the phase separation. For example, higher C_{Init} results in a larger amount of polycations that interact with PBDT and render a faster self-assembly and a deeper quench of the phase separation. A higher C_{MBAA} results in a faster cross-linking reaction that prevent deeper quench of the VPS.

To characterize the network morphology quantitatively, characteristic wavelengths are extracted from 2D images by Fourier transformation with the software of Image J.[27] Figure 5a,b shows a micrograph of the swollen gel QP-1.5-1-2-0.01 and its typical intensity curve after fast Fourier transformation, respectively. The characteristic lengths calculated from the pixel of peaks are 77.9 and 8.6 μm, corresponding to the mesh size and thread thickness of the network-like structure, respectively. The images of as-prepared and swollen gels QP-1.5-1-2-C_{Init} are selectively analyzed using this method. The results show that these two characteristic lengths are about 20−80 and 8−15 μm, as shown in Figure 5c,d.

The surfaces of the gels QP-1.5-1-2-C_{Init} are rough, as observed by differential interference contrast microscope, whereas those without phase separation are quite smooth. (The images are omitted here.) The roughness of the swollen gel is greater than that of as-prepared gel, and both of them decrease as C_{Init} increases (Figure 6). The size of bulged domains is approximately several tens of micrometers, the same as the characteristic length of mesh size shown in Figure 5. All of these phenomena indicate that inner stress exists in both the as-prepared and swollen gels, and the increase in roughness after swelling should result from the different expansion ratios (osmotic pressure) of two different phases. Specifically, the swollen gel QP-1.5-1-8-0.15 is fractured into small fragments, as shown in Figure 4 marked with (*); this is also caused by the existence of too great inner stress due to the mismatching of the osmotic swelling pressure.

The network structure of micrometer order is much larger than the conventional network of gels. For a homogeneous and amorphous polyelectrolyte gel, it has a network structure with a mesh size ξ of nanometer order calculated from the scaling theory for polyelectrolyte hydrogel $\xi \approx bq^{5/9}$, where b is in the order of the monomeric length and q is the swelling ratio of the gel.[28,29] For poly(DMAPAA-Q) gels synthesized with or without PBDT, q is in the range of 10−100, corresponding to ξ of 1−3 nm (using b = 0.2 nm). Therefore, the hydrogels we obtained have dual well-defined networks of 10 000 different spatial scales. The micrometer-scaled network-like structure consists of a PBDT-rich

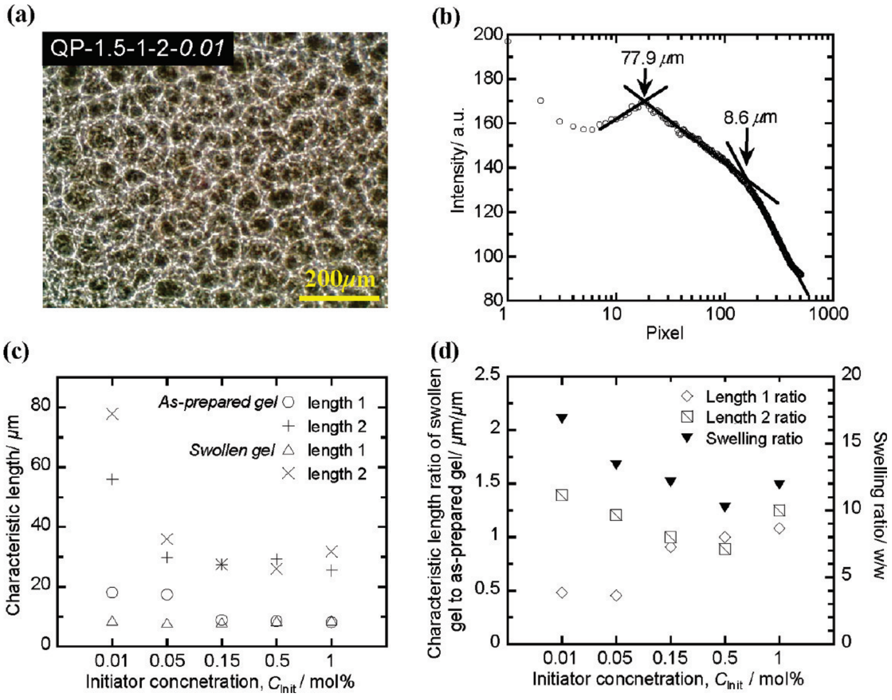


Figure 5. Characteristic lengths extracted from 2D images by Fourier Transformation. (a) Micrograph of swollen gel QP-1.5-1-2-0.01 observed under microscope with parallel polarizers (b) Typical characteristic intensity curve of image (a) after fast Fourier transformation. The characteristic lengths calculated from the pixel of the peaks are noted in this Figure (c,d) Characteristic lengths of as-prepared (c) and swollen (d) gels with various C_{Init}, QP-1.5-1-2-C_{Init}. Swelling ratios relative to the as-prepared state are also shown in part d.

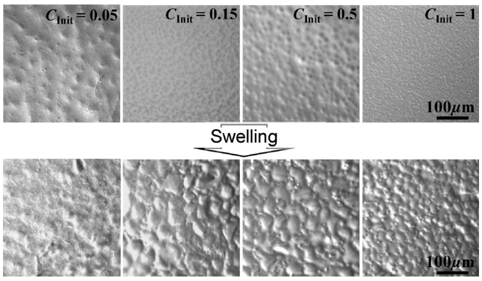


Figure 6. Differential interference contrast microscope images of as-prepared and swollen gels synthesized with various initiator concentrations, QP-1.5−1−2-C_{Init}, The unit for the numbers in the figures is mol % relative to monomer concentration. All images are shown with the same magnification as that of $C_{\mathrm{Int}} = 1$.

phase, as elucidated by the fluorescent micrographs of gels synthesized with labeled PBDT.[14] This mesh size with characteristic length of 20−80 μm is larger than that found in other systems induced by VPS, such as polymer solutions and blends, usually smaller than 10 μm.[15,16,30,31] The differences should come from the different molecular structures of slower dynamic components; PBDT has a significantly high molecular weight and typically semirigid conformation, whereas others do not. The similar mesh size (several tens of micrometers) has been found in a lyotropic liquid crystal solution of triethyleneglycol mono *n*-decyl ether with a concentration of 19.9 wt %.[17]

Regarding the gels synthesized with different C_{MBAA}, QP-1.5-1-C_{MBAA}-0.15, lower C_{MBAA} results in the higher turbidity degree of as-prepared gel. It is because a relatively low cross-linking kinetics renders a more fully developed phase separation. However, the coupling of phase separation and cross-linking reaction becomes worse if the C_{MBAA} is lower than 2 mol %. When no cross-linker is added in the precursor solutions ($C_{\mathrm{MBAA}} = 0$), a soft physical gel with high viscoelasticity is obtained. The physical gel possesses a high degree of turbidity; however, no network-like structure appears. We consider that a certain amount of chemical cross-linker is favorable but not necessary to develop the dual network gels. This is because we have also observed the typical VPS process by letting linear polycations diffuse into a PBDT drop, as we previously described.[14] This result suggests that the primary cross-linking reaction should promote the occurrence of VPS during the polymerization, possibly because it dramatically increases the molecular weight of polycation and viscosity of polyion complexes to enhance dynamic asymmetry near the gelation point.

4. Structure Observation during Polymerization Reaction. To understand the mechanism of structure formation, we have to trace the structure formation during the polymerization process. The morphologic evolution is observed under the microscope with parallel and crossed polarizers during the reaction for QP-1.5-2-2-0.15 (Figure 7). The precursor solution exhibits no birefringence because of the relative low C_{PBDT}. Actually, some preliminary PBDT aggregates with several hundreds of micrometers exist in the precursor solution, as elucidated in previous papers.[21,22] They are similar to other LC macromolecules after mixing with monovalent salt.[32] After polymerization is triggered, the sample becomes turbid within 0.5 h, indicating the occurrence of phase separation. Simultaneously, obvious birefringence emerges. With the polymerization proceeding, network-like structure appears in 90 min, indicating that VPS occurs in this stage. This structure does not change distinctly in the following stage and is trapped by the subsequent cross-linking process.

The results indicate that at the preliminary step, general phase separation concomitant with the self-assembly of semirigid polyion complexes occurs before the formation of network-like structure. The birefringence appears because local concentration and orientation of PBDT increase rapidly through self-assembling, despite being weakened by the turbidity. The preliminary self-assembly process should

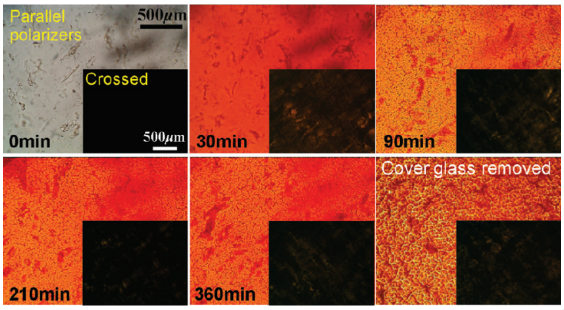


Figure 7. In situ observation of the structure formation during polymerization. Microscopic images of QP-1.5-2-2-0.15 are observed under parallel and crossed polarizers at different times during polymerization process. The last image is taken after removing the cover glass of reaction cell. The images are shown with the same magnification as that at 0 min.

promote the VPS developed from general phase separation because it can enhance the formation of viscoelastic asymmetry due to the high viscosity of polyion complex aggregates.

5. Proposed Mechanism for Structure Formation of Gels. On the basis of these results, we propose a detailed mechanism for the formation of mesoscopic network-like structure, as shown in Figure 8. Before polymerization, the solution of the cationic monomer with a small amount of PBDT ($C_{\mathrm{PBDT}} < C_{\mathrm{LC}}^*$) is optically isotropic and without specific structure, except for some preliminary aggregates due to the spontaneous aggregation of PBDT after mixing with a large amount of monovalent monomers (Figure 8a).[22,32] When polymerization starts, generated polycations interact with oppositely charged PBDT to form polyion complexes. The polyion complexes, due to the semirigid nature of PBDT, self-assemble to form small anisotropic aggregates which show birefringence and dramatically enhance the viscosity (Figure 8b).[21,22] Simultaneously, phase separation occurs when C_Q is low because of the poor solubility of polyion complexes in the solution with low ionic strength.[25] The two separating phases have strong asymmetrical viscosities, and thus the general phase separation quickly develops into the VPS, where the PBDT-rich phase with slow dynamics forms a transient micrometer-scaled network structure (Figure 8c), even if it is the minority in composition.[15−17] Before the network threads relax to form isolated droplets with lower interface energy,[14,33] the transient network-like structure is frozen by the subsequent chemical cross-linking reaction (Figure 8d).

When the reacting solutions have a relatively high C_Q ($C_Q \geq$ 1.5 M in the present case), the electrostatic interaction between the two oppositely charged polymers is largely screened because of the strong ionic strength. Therefore, weak complexes are formed with small structures that are stable and soluble (Figure 8e).[25] Therefore, no severe phase separation occurs. With the polymerization proceeding, the polyion complexes and small aggregates self-assemble further to form large size (1−3 mm) anisotropic domains (Figure 8f), which are immediately frozen by the gelation to result in anisotropic gels (Figure 8g). This is consistent with our previously published results, where anisotropic domain size increases with reaction time, and the birefringence of synthesized gels increases with the decrease in chemical cross-linker concentration.[19]

Apparently, C_Q, directly affecting the ionic strength of reacted solutions, is crucial for the occurrence of phase separation. We summarize the necessary conditions for developing the dual network gel: (i) high PBDT concentration ($C_{\mathrm{PBDT}} > C^*$), (ii) low cationic monomer concentration C_Q (low ionic strength), and (iii) a certain amount of chemical cross-linker.

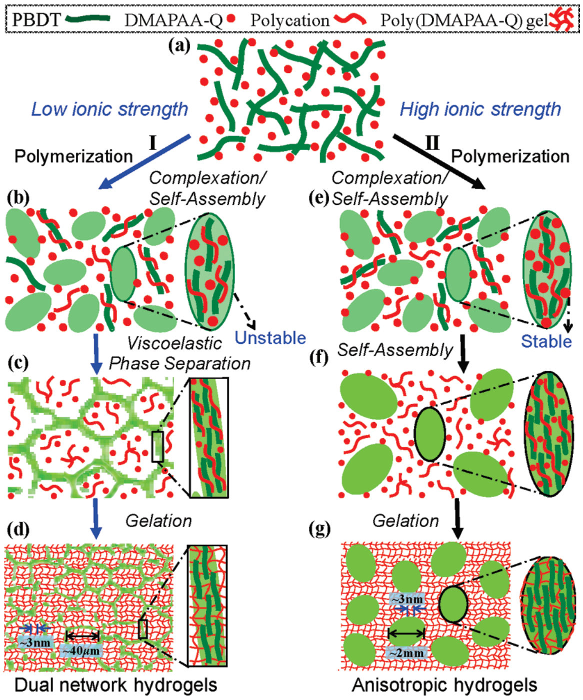


Figure 8. Formation mechanism for the structured hydrogels is proposed. The precursor solution ($C_{\mathrm{PBDT}} < C_{\mathrm{LC}}^*$) is optically isotropic (a). When polymerization starts, the polycation interacts with anionic PBDT to form polyion complex. The polyion complexes, with semirigid nature, self-assemble to form small anisotropic aggregates with high viscosity (b,e). When the ionic strength of the solution is low ($C_Q \leq$ 1.5 M), the polyion complexes are unstable in the solution, and phase separation occurs. The phase separation rapidly develops into VPS, forming a network-like structure of ~40 μm in size (c), which is permanently frozen by the following chemical cross-linking reaction (d). If the reacted solution has strong ionic strength $C_Q \geq 2$ M), then no phase separation occurs. The small polyion complex aggregates self-assemble further to form macroscopically anisotropic domains of 1−3 mm in size (f) that are frozen by the subsequent gelation to form anisotropic hydrogels (g).

Conclusions

We have systematically studied the hydrogels with dual networks of 10^4 different mesh sizes that are developed by polymerization of a cationic monomer in the presence of semirigid polyanion as dopant. These gels, developed by the competition of self-assembly and VPS of semirigid polyion complex, can be obtained in a large range of component concentrations ($C_Q \leq$ 1.5 M, $C_{\mathrm{PBDT}} \geq 0.5$ wt %). We elucidate further that the ionic strength of the solution is crucial for the stability of polyion complex and the occurrence of phase separation. Moreover, the effects of reaction kinetics on VPS and microstructure of synthesized gels are studied by changing C_{Init} and C_{MBAA}. High C_{Init} promotes the phase separation to a deep quench by producing a large amount of polycations and thus makes the gels with a high degree of turbidity and small mesh size. High C_{MBAA} corresponds to a fast gelation process that traps the VPS in an early stage, decreasing the degree of turbidity. When $C_{\mathrm{MBAA}} < 2$ mol %, the coupling of phase separation and chemical cross-linking reaction becomes worse; the gel synthesized with no cross-linker ($C_{\mathrm{MBAA}} = 0$) has no network-like structure.

In summary, a formation mechanism for the structured hydrogels is proposed. The precursor solution ($C_{\mathrm{PBDT}} < C_{\mathrm{LC}}^*$) is optically isotropic. When polymerization starts, the polycation interacts with anionic PBDT to form polyion complex. The polyion complexes, with semirigid nature, self-assemble to form small anisotropic aggregates with high viscosity. When the ionic strength of the solution is low ($C_Q \leq 1.5$ M), the polyion complexes are unstable in the solution, and phase separation occurs. The phase separation rapidly develops into VPS, forming a network-like structure of ~40 μm in size, which is permanently frozen by the following chemical cross-linking reaction. If the reacted solution has strong ionic strength ($C_Q \geq 2$ M), then no phase separation occurs. The small polyion complex aggregates self-assemble further to form macroscopically anisotropic domains of 1−3 mm in size that are frozen by the subsequent gelation to form anisotropic hydrogels. This work will merit designing novel structured hydrogels and understanding the mechanism of mesoscopic structures formation process in living organisms.

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