

Effects of continuous water flow on the swelling properties of polyelectrolyte hydrogels

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Abstract. We report the swelling behavior of a polyelectrolyte copolymer gel in water, which consists of poly(*N*-isopropylacrylamide) and sodium acrylate. The diameter of the cylindrical gels was measured at room temperature under a continuous flow of solvent water (equivalent to an infinite amount of water; open system). After a sufficient water flow, the diameter of the gel in the limited amount of water (closed system) was measured as a function of the temperature. The gel in the open system was found to shrink as a result of the continuous flow of water, and the gel in the closed system began to swell again at the phase-transition point by increasing the temperature. The effects of the degree of initial ion exchange by the water flow on the macroscopic swelling behavior were discussed in terms of the exchange of counter ions (the ion dissociation of carboxyl groups) and of the creation and destruction of intermolecular forces (hydrogen bonding). It was concluded that the amount of solvent water determines the environmental variables, such as the pH and ion concentration, which affects the swelling properties of polyelectrolyte hydrogels; intermediate re-swollen states can be observed in a closed system.

Keywords: Polyelectrolyte hydrogels; Hydrogen-bonding; Phase transition

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1 Introduction

Polymer gels are known to have unique properties, particularly with respect to volume phase transition and critical behavior [1-4]. One fundamental technique to observe the phase transition of phase-transition gels, frequently used in experimental studies, is to measure their changes in volume. The observed volume should be reflected by the average network structure, and the macroscopic volume change should be determined by the interactions between the monomers; the phase transition can exaggerate the microscopic conformation changes at the molecular level.

Among phase-transition gels, it has been well established that the swelling behavior of poly(*N*-isopropylacrylamide) (NIPA) gel undergoes a discontinuous phase transition in response to a very small temperature change [5]. When it is slightly ionized by acrylic acid (AA) or sodium acrylate (SA), the phase transition is strongly affected not only by the temperature but also by the specific difference in the ion concentration of the solvent [6]. With increasing the degree of ionization, the swelling ratio increases, and the transition temperature also increases. However, almost all of the reported results on the temperature dependence of the swelling ratio of this system [6-12] have been conducted in a closed system; the gel is sealed in a container (usually glass capillary) with a limited amount of solvent. Generally, the gels are put in pure water to wash away residual chemicals used for gelation, such as unreacted monomers, oligomers, crosslinker, accelerator, and initiator, from the polymer networks, after the gelation is completed. In the case of ionized gels, however, the initial ion exchange that occurs at the ionized groups as the gels are washed has not been considered until now; the effects of the amount of the solvent on the swelling behavior have not been thoroughly studied.

In this paper, the interest is focused on the effects of the amount of the solvent on the phase-transition behavior of polyelectrolyte hydrogels. This is a report of the swelling properties of the polyelectrolyte copolymer gel, which consists of NIPA and SA; poly(*N*-isopropylacrylamide-co-

sodium acrylate) gel (designated here as NIPA-SA gel). The swelling behavior and the phase transition of NIPA-SA gels were investigated not only in a closed system (limited amount of water solvent) but also in an open system (infinite amount of water solvent as water is flushed). The diameter was found to depend heavily on the solvent flow: the diameter of the as-prepared gel decreases by flushing water in an open system, and the gel exhibits unexpected behavior during the phase transition in a closed system. The present findings are discussed on the basis of the roles of counter ions and the creation and destruction of hydrogen bonding in the gels.

2 Experimental procedure

The NIPA-SA gels were synthesized by a free radical polymerization reaction in glass microcapillary tubes (0.5 μ l) with an inner diameter of 141.5 μ m [12]. In this synthesis, the sum of NIPA and SA monomer concentration was fixed to 700 mM, and the amount of SA was changed in the range of 0 to 300 mM. The respective gels are designated here as NIPA- x SA, where x denotes the amount of SA monomer (mM). The base solution is a mixture of the following reagents: purified NIPA (main constituent, Kohjin), SA (ionizable monomer, Wako), 133 mg of *N,N'*-methylene-bis-acrylamide (BIS, crosslinker, Wako), and 240 μ l of *N,N,N',N'*-tetramethylethylenediamine (TEMED, accelerator, Wako) dissolved in 100 g water. The solution was fully saturated with nitrogen by bubbling, and the gelation, which was initiated by adding 40 mg of ammonium persulfate (APS, initiator, Wako) to the mixture, was carried out at ice temperature for more than 12 hours. After the gelation had been completed, the cylindrical gels were removed from the glass microcapillaries and subsequently washed in distilled deionized water (pure water). As is shown in the schematic illustration of the cell in Fig. 1, the cylindrical gel was placed in a quartz capillary whose diameter was about ten times larger than that of the gel. The capillary was encapsulated in a transparent square glass. Within the cell,

water was circulated to control the temperature with an accuracy of ± 0.05 °C. By using this cell, the solvent water can be sealed in the quartz capillary (with limited amount of water solvent), or the solvent water can continuously flow from a reservoir of pure water (with an infinite amount of water solvent). Distilled deionized water was used. It was kept in the reservoir under an N_2 atmosphere to prevent the CO_2 in the air from affecting the pH. The diameter was measured using an optical microscope apparatus equipped with a calibrated Charge Coupled Device (CCD) camera and with a video processor.

3 Results and discussion

3.1 Effects of SA concentration

Figure 2(a) shows the time course of the diameter of as-prepared NIPA- x SA ($x = 0, 4, 60$, and 150) gels at 25 °C when the pure water continuously flows in the quartz capillary from the pure water reservoir. The diameter decreases as a function of time, or depending on the amount of flowing water, and it ultimately becomes constant. This is mainly due to the exchange of Na^+ counter ions for H^+ . The initial and the final diameters at 25 °C strongly depend on the SA concentration of the gel, which is shown in Fig. 2(b). The initial diameter increases with increasing the SA concentration, since the ionization can make the swelling ratio larger in the swollen state due to the osmotic pressure created by the counter ions trapped within a Donnan potential [13,14]. The initial diameter increases steeply when the SA concentration exceeds 100 mM (dense concentration). On the other hand, although the final diameter increases slightly with increasing the SA concentration below 10 mM (dilute concentration), it becomes thoroughly constant when the SA concentration exceeds 20 mM. It should be noted that the final diameters are only slightly larger than the diameter of the neutral NIPA gel. As

is reported in the literature [11], the carboxyl groups ($-\text{COOH}$) in the gel are largely dissociated COO^- even when the pH of the solvent water decreases to 5.6. Since the final pH of the surrounding solvent water was obtained at around 5.7 after sufficient water exchange, the carboxyl groups ($-\text{COOH}$) in the gel might be dissociated $-\text{COO}^-$ plus H^+ to some extent, even if the pH of the inner solvent water is slightly smaller than that of the surrounding one. Therefore, the saturation in the larger SA concentration after a sufficient flow of water could not be explained by the exchange of counter ions alone (see later discussion).

3.2 Phase transitions in open and closed systems

After the gel reached a constant diameter at 25 °C, the temperature was increased under continuous water flow (open system). An example is shown in Fig. 3 for the NIPA-60SA gel. The gel can be observed to shrink with increasing temperature and to exhibit a shrinking phase transition at 33.5 °C. The diameter was also measured with decreasing temperature, and the phase transition has heating and cooling hystereses lower than 0.1 °C. This behavior is similar to the phase transition of neutral NIPA gels [5] but not to the results reported on slightly ionized NIPA-SA gels [6].

In a closed system, on the other hand, the phase transition is quite different from that in the open system, which is shown in Fig. 4. After the diameter of the NIPA-60SA gel became constant (open circles in Fig. 4(a)), the water flow was stopped, and the quartz capillary was sealed, resulting in the creation of a system of the gel in a finite amount of solvent (closed system) at 25 °C. The diameter does not change with time, as shown in Fig. 4(b), indicating that the equilibrium of the gel can be maintained with a sufficient flow of water in a closed system. In other words, the ion exchange (in the process of seeking equilibrium in the closed system) is too small to affect the macroscopic volume of the gel. If the water flow is stopped and the quartz capillary is sealed before the gel reaches

the equilibrium state, the diameter decreases and approaches a constant with time in the closed system, as shown in Figs. 4(a) and (b) (open triangles). In this insufficient water flow, the ion exchange in the closed system is large enough to decrease the macroscopic volume of the gel. It has been reported that the environment variables of the solvent, such as the pH and ion concentration, are very important to determine the swelling properties of ionized gels [10]. The present observation of the decrease in diameter caused by the continuous water flow suggests that the amount of solvent water determines the environmental variables, which affect the swelling ratio of polyelectrolyte hydrogels. Although it is technically impossible to measure the environmental variables in the present apparatus, both the pH and ion concentration decrease and finally become constant after a sufficient water flow. These results have been confirmed in another experiment for similar polyelectrolyte hydrogels, which will be published elsewhere. In order to avoid these problems in the following measurements for closed systems, the swelling properties were examined for gels that were completely flushed by pure water at 25 °C. Moreover, the amount of water in the closed system was adjusted in proportion to the gel volume so that the effects of the ratio of the gel to the volume of water in the capillary could be avoided.

After the gel became equilibrium by a sufficient water flow, the diameter of the gel in the closed system was measured while gradually increasing the temperature (Fig. 4(c)). When the gel was heated on the heating process, it became completely swollen at 33.8 °C. When the temperature was increased at a minimum increment of 0.1 °C from 33.8 to 33.9 °C, both ends of the cylindrical gel eventually collapsed, and the collapsed portion developed with time. This behavior is similar to that of the phase transition of a gel under a water flow, which is shown in Fig. 3(b). The diameter of the swollen portion increased with the development of the collapsed portion. However, the development became slower and slower with time, and, finally, it stopped. From this point on, the swollen portion started

to recover, while the swollen diameter continued to increase. Finally, the gel reached a completely swollen phase at 33.9 °C with a much larger diameter (135 μm) than that at 33.8 °C (115 μm). The results showed that the gel exhibited the swelling phase transition when the temperature was changed from 33.8 to 33.9 °C. While the temperature was increased step by step with a minimum increment of 0.1 °C, these "*re-swelling phenomena*" (the schematic conformation change is shown in Fig. 5), that is, the development, stopping, and re-swelling of the collapsed portion to the different states, were repeated (five times in total). After the diameter reached the final state after the re-swelling phenomena (181 μm at 34.4 °C), it decreased with increasing the temperature, and the gel collapsed discontinuously when the temperature was increased from 36.8 to 36.9 °C. Above this temperature, the gel stayed in a completely collapsed state. The gel took four intermediate swollen states (from 1 to 4 in Fig. 4(c)) between two swollen states at 33.8 °C and at 34.4 °C. On the cooling process, the gel returned to the swollen state at 36.0 °C and assumed a diameter that was nearly equivalent to that of the re-swollen state at 36.0 °C on the heating process. As the cooling continued, the diameter reached about 200 μm at 25 °C, which was almost identical to the diameter before the water flow. After the gel returned to the initial state, the phase transition was reversible in the closed system for further temperature cycling across the transition temperature; the gel could transform into the completely collapsed state through one step transition at about 36.5 °C with about 1 °C hysteresis.

Successively, the gel was placed again under a second water flow at 25 °C. Figure 4(d) shows that the diameter decreases and approaches a constant (identical to that in the first flow). The water flow was again stopped, and the temperature was changed. Figure 4(e) shows the equilibrium diameter as a function of the temperature on the heating and cooling processes. In this second treatment, the gel exhibited the phase transition at 33.8 °C through a one-step transition with a

hysteresis of less than 0.1 °C, which is similar to the phase transition under a continuous water flow (Fig. 3).

The same experiments with different amounts of SA proved that the re-swelling phenomena at the phase-transition point (after the diameter decrement under the continuous water flow) were reproducibly observed, which indicates that this is a universal property in this system. An example is shown in Fig. 6 for the NIPA-200SA gel. The qualitative behavior in this figure is the same as that of NIPA-60SA gels (as is shown in Fig. 4), although the details are quite different. For a much larger SA concentration (200 mM), the gel may take three intermediate states (numbered from 1 to 3 in Fig. 6(b)). The respective intermediate state is stable in the larger temperature range, and the final transition temperature to the complete collapsed state is much larger. However, the gel recovers almost the same diameter at 25 °C before the water flow and can shrink as a result of successive water flow at 25 °C (Fig. 6(c)). In the following temperature increase in the closed system, re-swelling phenomena were observed with much smaller temperature widths. In successive treatments (the water flow in an open system and the successive temperature change in a closed system), the width became smaller and smaller, and, after several treatments, the gel finally exhibited a phase transition through a one-step transition in a closed system.

3.3 Roles of ion exchange and hydrogen bonding

Two interesting features appeared that should be noted in the observation of the macroscopic change in size of the gels in open and closed systems. First, the diameter of as-prepared gels with an SA concentration (larger than 20 mM) decreases in an open system, approaching a constant diameter (slightly larger than that of the neutral NIPA gels) that does not depend on the SA concentration. Second, when the temperature is raised in a closed system, the gel exhibits re-swelling behavior,

resulting in a discontinuous swelling transition at the phase-transition temperature. Below is an explanation of these features using a qualitative model based on the ion exchange and the creation and destruction of hydrogen bonding.

In the infinite water solvent (under a water flow), the original counter ion Na^+ in the carboxyl groups, which are fully dissociated COO^- plus Na^+ , could be exchanged for the hydrogen ion H^+ . After a sufficient water flow, the carboxyl groups are largely neutral COOH . Only dissociated COO^- plus H^+ contributes to the internal osmotic pressure (swelling force). As is mentioned in the former section, the neutral COOH in this system is largely dissociated COO^- plus H^+ after the sufficient water flow [11], which increases the osmotic pressure due to ionization. Therefore, it is very difficult to explain that the final diameter of the largely ionized NIPA gel can take a diameter that is only slightly larger than that of the neutral NIPA gel. It could be assumed that an attractive force between polymer networks would be created by the water flow, which can compensate for the positive osmotic pressure due to ionization. Since the final diameter is constant in the wide range of SA concentrations between 20 and 300 mM, the attractive force could result from the same origin of the positive pressure, that is, the carboxyl groups, which should produce and balance both the positive and negative osmotic pressure in the gel. The most possible force is the hydrogen bonding between the associated carboxyl groups ($-\text{COOH}$) from SA and the carbonyl groups ($-\text{CO}$) from NIPA, which tends to collapse the network. The incorporation of SA has two effects: positive osmotic pressure due to ionization in one case and negative osmotic pressure due to the attractive force of the hydrogen bonding in the other.

From these considerations, we anticipate that the origin of the re-swelling phenomena is found in the closed system for the following reasons. First of all, it is necessary to consider the competition of the hydrophobic interaction and the hydrogen bonding; when the temperature is increased, the

former becomes larger, while the latter becomes smaller. Secondly, it is important to take into account the residual Na^+ counter ions even after a sufficient water flow. This is because the ion exchange is a diffusion process, and we could not completely remove Na^+ from the gel within a finite time. With increasing the temperature in the closed system, the phase transition due to the hydrophobic interaction can start at both edges of the sample [12], which changes the balance of the distribution of Na^+ in the transient phase coexistence of the gel. Since the Na^+ concentration decreases in the collapsed phase due to the hydrophobic atmosphere in the collapsed phase, the excess Na^+ should diffuse into the swollen phase. Therefore, the equilibrium state of the swollen phase shifts away from the neutral state (the pH in the gel should increase slightly). The perturbation from the equilibrium state could accelerate the destruction of hydrogen bonding, and the neutral carboxyl groups are dissociated to ionic groups, COO^- and H^+ , which contributes to the internal osmotic pressure. The development of the collapsed portion finally stops when the hydrophobic interaction in the collapsed phase balances with the osmotic pressure in the swollen phase. The two-phase state, however, is not equilibrium but transient, since the free-energy gain by the decrement of hydrogen bonding exceeds the elastic energy loss by the deformation at the boundary of the two phases. The diameter of the swollen phase continues to increase until the two-phase boundary disappears. We assume that the respective intermediate state could correspond to the different degrees of the strength of the hydrogen bonding, which results from the hierarchical structure of polymer networks [15,16]. In the final stage of the re-swelling phenomena, the gel can take a stable swollen state without the excess hydrogen bonding formed by the water flow.

In the present experiments, the relaxation time for the gel to enter a state of equilibrium as a result of the water flow or of the change in the temperature was extremely large; it took several days to finish the re-swelling transition (by the minimum step of 0.1°C shown in Fig. 5). This relaxation

time is not caused by the network diffusion induced by the temperature change, since a small amount of gel with a submillimeter size would usually swell or collapse at the phase-transition point within minutes or several hours at most [17]. This means that it is the ionization of the individual carboxyl groups and the exchange of the counter ions Na^+ for H^+ that result in the exceptional slow kinetics [12,18,19]. The diffusion processes of H^+ take place over a much longer time because of the binding effect of H^+ to acidic groups, which determines the phase-transition kinetics of the present system. Near the neutral pH, the H^+ concentration is on the order of that of water, and, thus, the kinetics, which is proportional to the ion concentration, can be very slow. This is another reason for the slow kinetics.

The transient intermediate state was reported in a similar system, which has a large relaxation time [20]. Intermediate states characterized by a distinct swelling ratio were also observed in several polyampholytic hydrogels [21-25]. For example, multiple phases can appear in gels consisting of randomly distributed positively and negatively charged groups, in which hydrogen bonding is pointed out to have an important role [21,22]. A theoretical study on the basis of a Flory-type swelling model suggested that multiple phases could be observed when the hydrogen bonding effects were significant [24,25]. Generally, multiple phases can be seen by the pH change of the solvent in an open system, which is reversible and reproducible. A critical difference between the present intermediate states and multiple phases is that the present states can be seen only on the heating process in the closed system after the water flow. This could be attributed to the fact that positively charged groups are not incorporated into the present gel. Because of their stability and reproducibility, however, the present findings are important for understanding the fundamental principle of the intermediate states that are frequently observed in swelling experiments on phase-transition gels.

Finally, washing the polyelectrolyte hydrogels continuously with pure water is equivalent to putting the gel into a reservoir with an infinite amount of water; doing so eliminates the finite size effects as well as the incomplete ion exchange. The swelling and shrinking of the present gels are controlled through the reversible creation and destruction of the hydrogen bonding by a water flow and temperature increase, respectively. Therefore, it is crucially important to understand the re-swelling behavior under well-defined pH and ion strength and to investigate the chemical and physical bases at the microscopic level in the same sample.

4 Conclusion

We have investigated the swelling behavior and phase transition of poly(*N*-isopropylacrylamide-co-sodium acrylate) gel in an open system (gel in an infinite amount of water) as well as in a closed system (gel in a limited amount of water). The present main results are the observations of the decrement of the swollen diameter under a continuous water flow (open system) and the re-swelling phenomena at the phase-transition point (closed system). A phenomenological model was proposed to explain the observations. The model is based on the ion exchange of the counter ions and the formation and destruction of the hydrogen bonding by the water flow.

The results obtained here strongly indicate that the amount of solvent has an important role, in general, in determining the swelling behavior of polyelectrolyte hydrogels. We believe that the present work is of crucial importance not only for understanding the nature of the phase transition of polyelectrolyte hydrogels but also in establishing the foundation for future applications of new technologies. The present results certainly indicate one direction for understanding the intermediate states frequently observed in phase-transition gels. Further investigation through microscopic

techniques is required to qualitatively understand the swelling behavior and the phase transition of polyelectrolyte hydrogels.

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Figure Captions

Fig. 1. Top view schematic of the cell, which is made of glass, bolted plexiglas sides, tubing, rubber seals, and a Teflon stopper. The gel was placed in a quartz capillary with an inner diameter of 2 mm. The capillary was encapsulated in a transparent glass cell, where water from a temperature-controlled water-bath (regulated with an accuracy of ± 0.05 °C) was circulated through the thicker tubing to control the temperature of the gel and the solvent. Through the thinner tubing, the solvent continuously flowed from a reservoir.

Fig. 2. (a) Time course of the diameter of NIPA- x SA gels ($x = 4, 60$, and 200 mM) at 25 °C just after the synthesized gel was placed in the flow of pure water. (b) Initial and final equilibrium diameters of NIPA- x SA gels (x is between 0 to 300 mM) at 25 °C. Lines were added to guide the eye.

Fig. 3. Time course of the diameter of NIP-60SA gel at 25 °C under a continuous water flow, and (b) its successive temperature dependence under a continuous water flow. Lines were added to guide the eye.

Fig. 4. Effects of the water flow and the temperature change of the diameter of NIP-60SA gel. (a) Time course at 25 °C under a continuous water flow (0.045 ml min⁻¹, a sufficient water flow, open circles) together with an insufficient water flow (open triangles), (b) aging effect in a limited amount of water (the symbols are the same as those in (a)), (c) temperature dependence in a limited amount of water, (d) time course at 25 °C under a continuous water flow (0.083 ml min⁻¹), and (e) temperature dependence of the diameter in a limited amount of water. Lines were added to guide the eye.

Fig. 5. Schematic changes in the shapes of the gel with time at the shrinking phase-transition temperature when the temperature is increased by the minimum step of 0.1 °C. The re-swelling phenomena were observed at those points where the swollen diameter continued to increase.

Fig. 6. Effects of the water flow and the temperature change of the diameter of NIP-200SA gel. (a) Time course at 25 °C under a continuous water flow (0.05 ml min⁻¹, a sufficient water flow), (b) temperature dependence in a limited amount of water, (c) time course at 25 °C under a continuous water flow (0.05 ml min⁻¹). Lines were added to guide the eye.

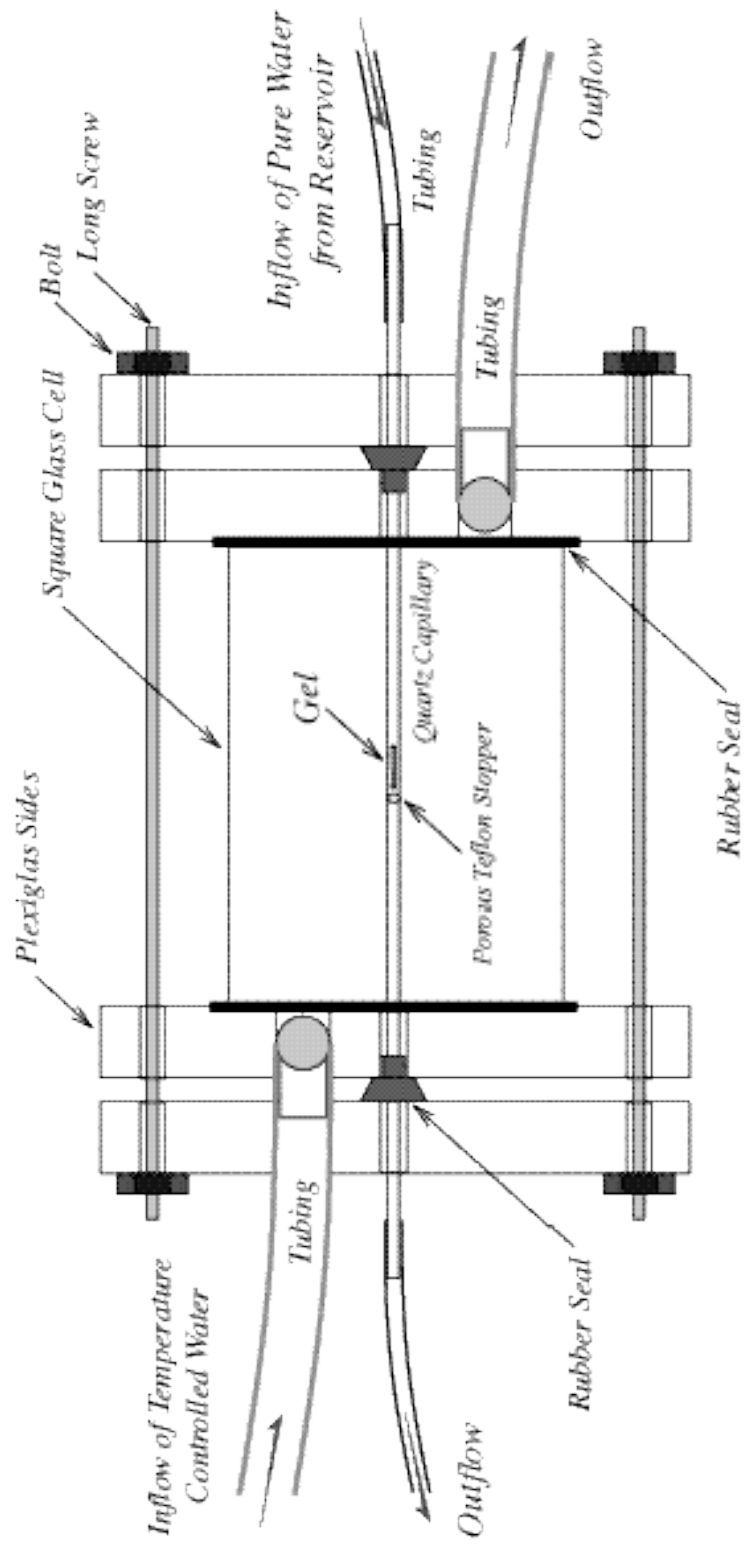


Figure 1. Bai and Suzuki

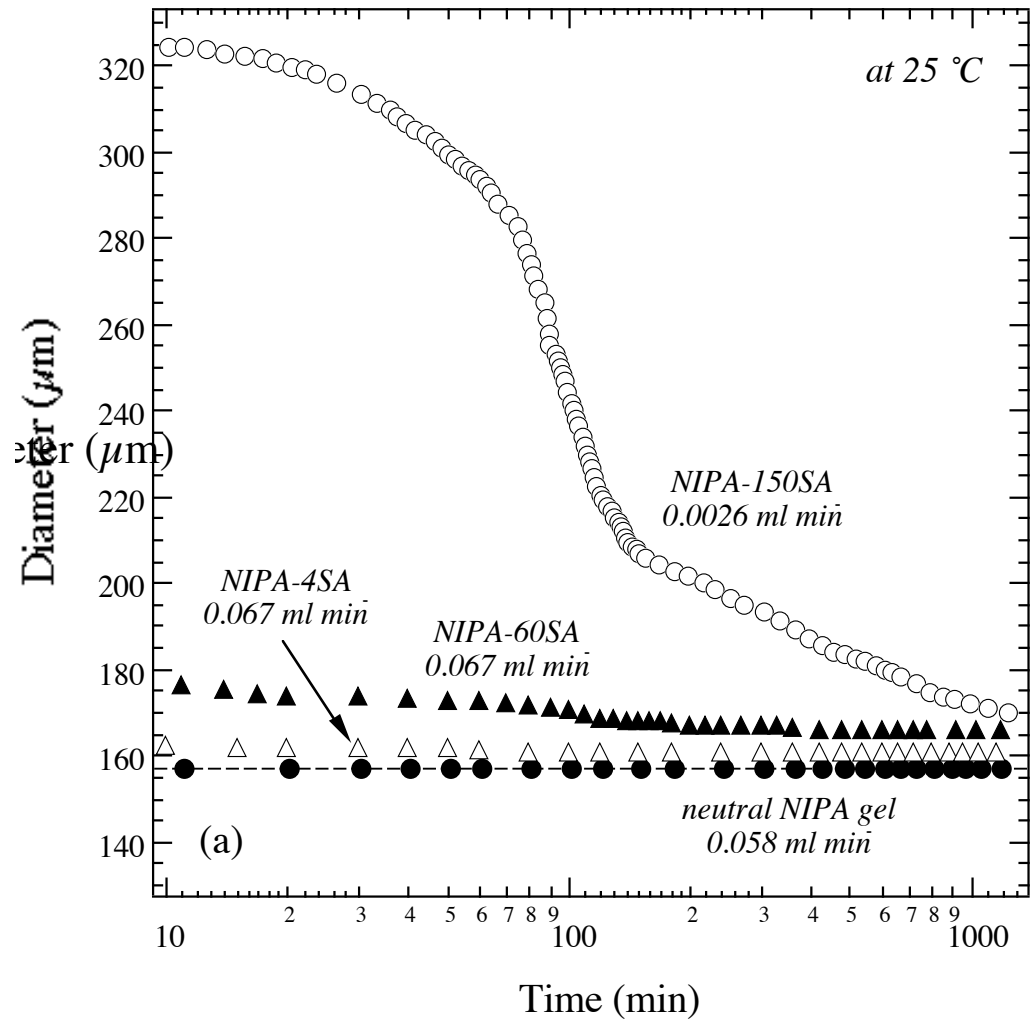


Figure . Bai and Suzuki

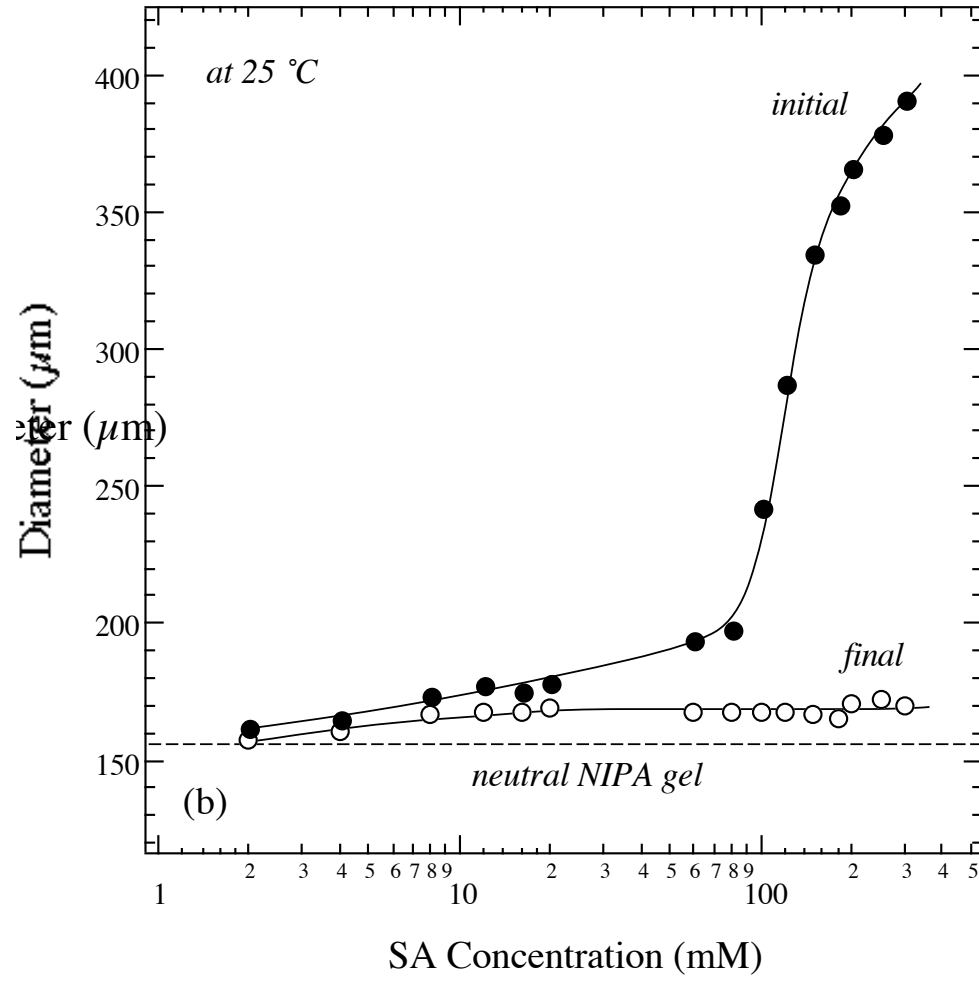


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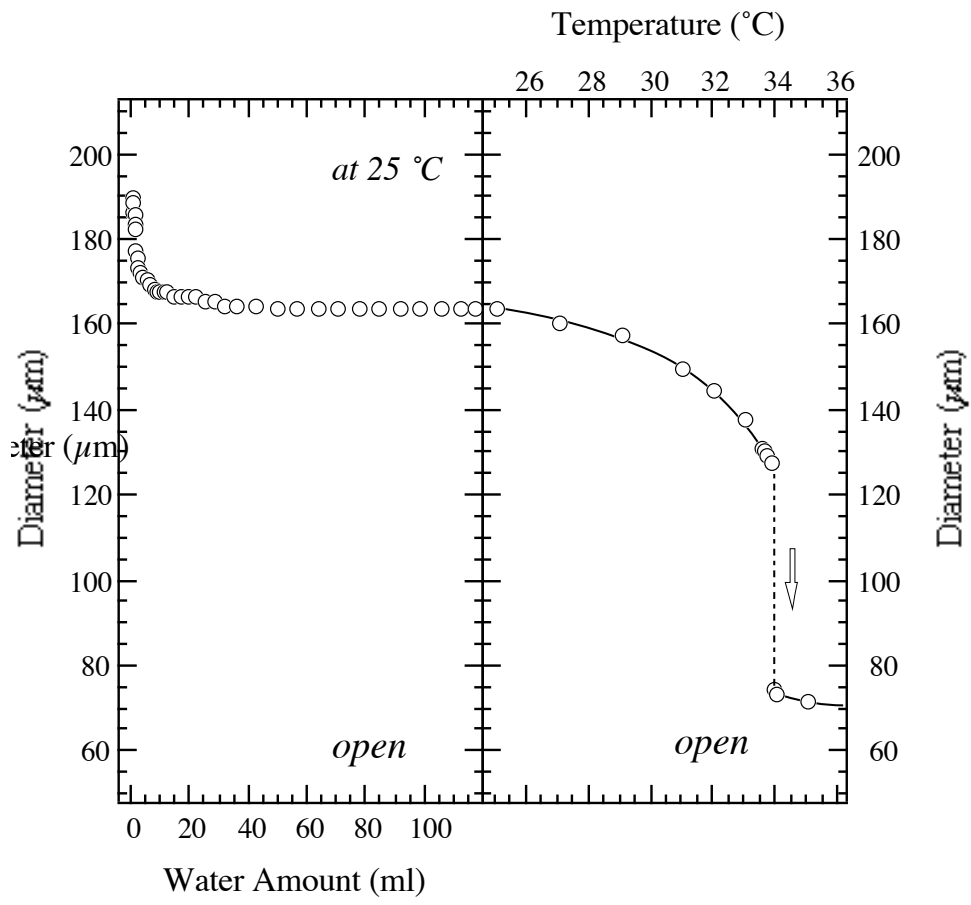


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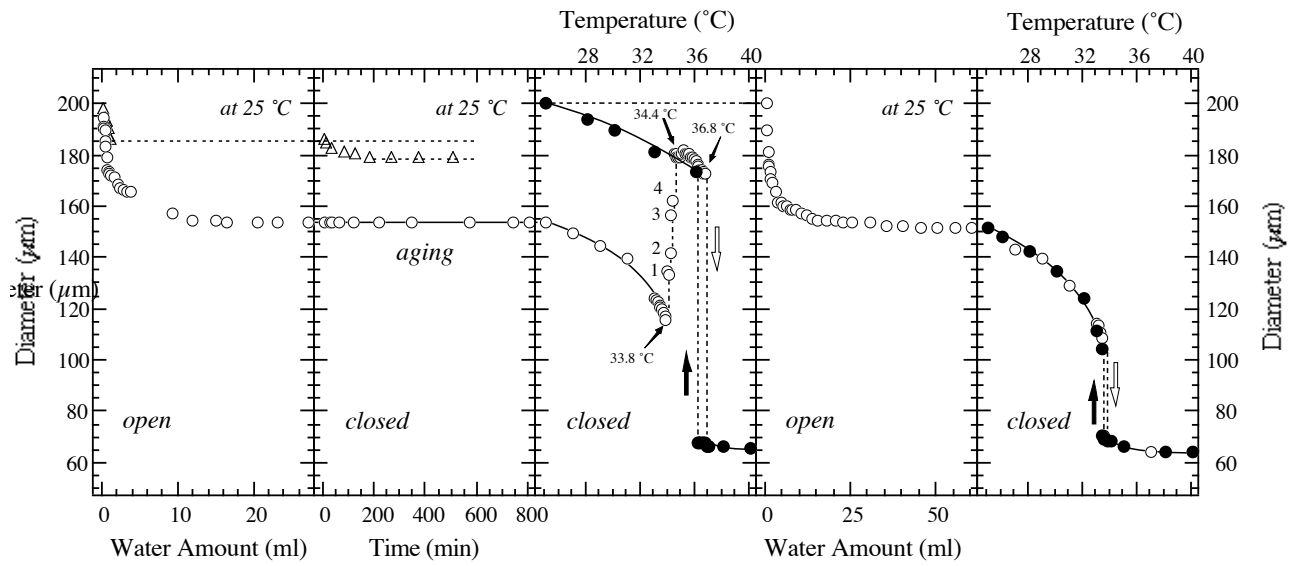


Figure 4. Bai and Suzuki

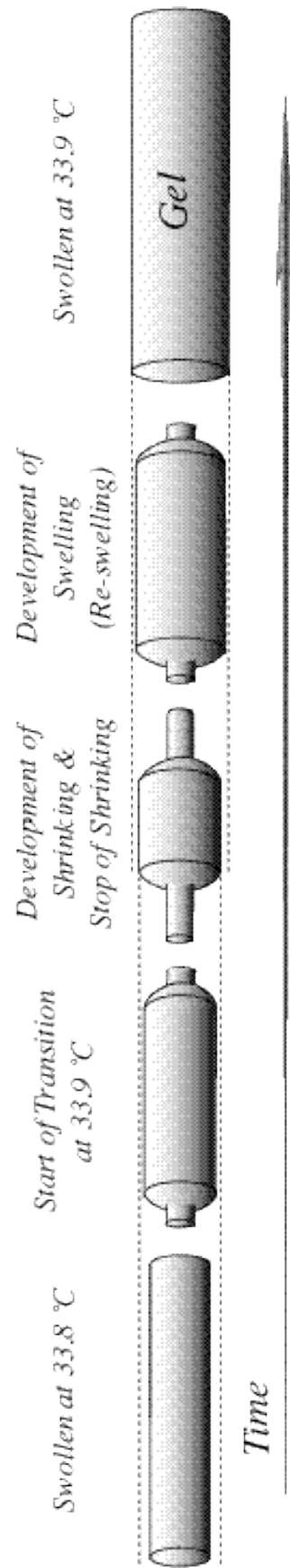


Figure 5. Bai and Suzuki

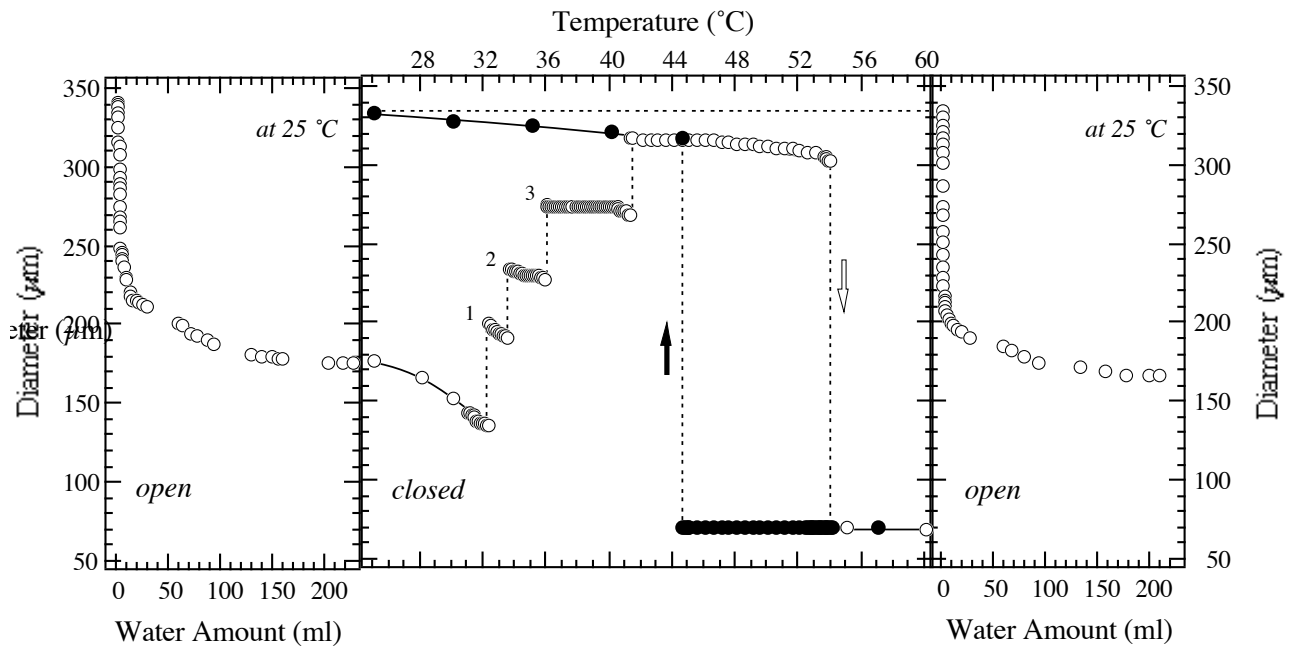


Figure 6. Bai and Suzuki