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Multiple-phase behavior and its microscopic implication for 4-acrylamidosalicylic acid gel

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Poly(4-acrylamidosalicylic acid) gels exhibited multiple-phase behavior depending on their histories in the parameter space of *p*H and temperature. Four different phases, denoted as phase091 (as-prepared), phase244 (swollen at high *p*H), phase064 (heat-treated), and phase233 (swollen at high *p*H after heat treatment) were clearly resolved, where the three digits denote their linear swelling ratios in percentage with respect to their sizes at preparation. Each phase was stable and did not change its swelling ratio with *p*H or temperature as long as the values of *p*H or temperature were within limited ranges. Transitions among different phases were discrete with hysteresis loops. The structure factors corresponding to these four phases were obtained by small-angle neutron scattering, which indicated the presence of characteristic structures depending on *p*H and temperature, particularly in the shrunken state (i.e., phase064). [DOI: 10.1063/1.1357201]

I. INTRODUCTION

Polymer gels are known to have two phases: swollen and collapsed phases. Volume phase transition occurs between the two phases either continuously or discontinuously.[1–3] Recently, more than two phases were found in copolymer gels consisting of copolymers with randomly distributed positively and negatively charged groups. These phases were characterized by different degrees of swelling at a given *p*H: the gel can take different degrees of swelling depending on the route taken in the *p*H–temperature coordinate system. The number of multiple phases appearing in the coordinate system depends on the monomer composition and *p*H.[4–6]

By studying gels that exhibit such a multiple-phase behavior, the criterion for a gel to show the multiple-phase behavior is considered. It is deduced that polymer molecules interact with each other through randomly distributed repulsive and attractive interactions. The latter should be hydrogen bonding plus either hydrophobic or electrostatic interactions. Among these interactions, it has been demonstrated experimentally and theoretically that hydrogen bonding plays an essential role in inducing a multiple-phase behavior. In this study, we will show that such a condition, so far demonstrated only in copolymer gels,[4–6] can also be achieved in homopolymers as in the case of poly(4-acrylamidosalicylic acid) gels (PASA gels) examined in this work.

The multiple-phase behavior in polymer gels has so far been studied by simple swelling ratio measurements as a function of *p*H, temperature, solvent quality, and so on. Although these studies demonstrated essential roles of the fundamental interactions for triggering volume phase transitions in gels, they have not disclosed any microscopic view of the structure of these kinds of gels. In this paper, we will investigate the microscopic structure of PASA gel by means of

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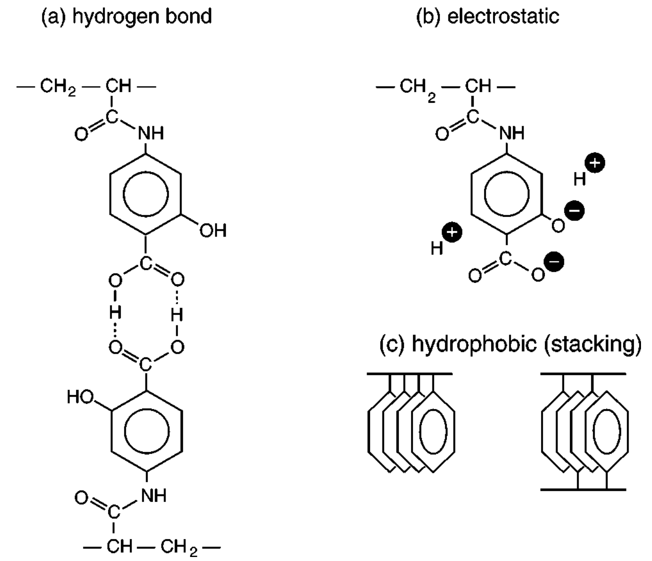

FIG. 1. Chemical structure of poly(4-acrylamidosalicylic acid) (PASA) gel. The molecules can interact with each other through (a) hydrogen bonding; (b) ionic repulsive interaction; and/or (c) hydrophobic stacking between benzene rings. Temperature influences the hydrogen bonding and hydrophobic interaction, whereas *p*H affects the degree of ionization and thus the electrostatic interaction. The monomer undergoes ionization via two steps: one for the carboxyl group and the other for the hydroxyl group.

small-angle neutron scattering (SANS) in order to elucidate the nature of the multiple phases.

II. EXPERIMENT

A. Sample preparation

4-acrylamidosalicylic acid (Fig. 1) was synthesized from acryloyl chloride and sodium 4-aminosalicylate.[7] Sodium 4-aminosalicylate (40 g, 0.24 mol) was dissolved in distilled water (250 ml) and stirred for 1 h. Acryloyl chloride (total 0.37 mol) was added twice, once at the beginning (20 ml, 0.25 mol), and then after the solution was stirred for 1 h (10 ml, 0.12 mol). Acidification to *p*H 4.0 with 10 N hydrochloric acid solution yielded a gray precipitate which was filtered off and washed with distilled water (500 ml) to give 4-acrylamidosalicylic acid (27 g, yield 57%).

PASA gels were prepared by radical polymerization: 1.04 g of 4-acrylamidosalicylic acid, 0.0773 g of N,N′-methylenebisacrylamide (cross linker), and 8.0 mg of azobisisobutyronitrile (initiator) were dissolved in 5.0 ml of dimethyl sulfoxide. The solution was polymerized at 70 °C for 8 h. Two types of gels were prepared, one for swelling measurement and the other for SANS. In the case of the former, a cylindrical gel was prepared in a capillary with an inner diameter 140 μm ($=d_0$). After completion of gelation, the cylindrical gel was removed from the capillary mold and was washed with distilled water. On the other hand, gels for SANS were prepared in petri dishes and then passed through a sieve. The sieved gel was immersed in a large amount of dimethyl sulfoxide to remove unreacted chemicals, and then in water. Water in the gel was replaced by heavy water by keeping its swelling equilibrium. This was done by repeatedly exchanging the water surrounding the gel with heavy water.

B. Determination of phase diagram

The cylindrical gel was placed in a glass cell whose temperature was controlled within ±0.1 °C. The gel was continuously flushed with water of controlled *p*H from a reservoir. *p*H was controlled by adding aqueous HCl solution (to lower *p*H) or water (to increase *p*H) below *p*H 7. Aqueous NaOH solution was used above *p*H 7. Gel diameter at swelling equilibrium, *d*, was measured under a microscope. To avoid the effect of carbon dioxide in the air, all experiments were carried out under nitrogen gas atmosphere. The temperature of the gel was controlled to within ±0.1 °C by circulating water from a Lauda RM-6B, a temperature-controlled water circulation system.

C. Small-angle neutron scattering

Small-angle neutron scattering (SANS) experiments were carried out using the research reactor, SANS-U, of the Institute for Solid State Physics, the University of Tokyo, which is located at the Japan Atomic Energy Research Institute, Tokai, Japan. Cold neutrons from the reactor, monochromatized with a velocity selector to a flux of neutrons with a wavelength of $\lambda=7$ Å and a wavelength distribution of $\Delta\lambda/\lambda=0.1$, were used as the incident beam. Sample gels were introduced into a quartz cell having an optical length of 4 mm. The observed scattering intensity was corrected for cell and solvent scattering, incoherent scattering, and transmission, and then rescaled to the absolute intensity. Incoherent scattering from a Lupolen standard sample was used for intensity calibration. SANS experiments were also performed with a 12-m SANS camera installed at Oak Ridge National Laboratory (ORNL). The incident neutron wavelength was collimated to be $\lambda=4.75$ Å with a graphite crystal. An area detector was located 5.8 m from the sample. The detected intensity was corrected for transmission, sample thickness, measuring time, and background, and was then circularly averaged.

III. RESULTS AND DISCUSSION

A. Phase diagram

When *p*H or temperature was varied, PASA gel changed its volume discontinuously. As shown in Fig. 2(a), the as-prepared gel took phase091 ($d/d_0=0.91$), where d/d_0 is the linear swelling ratio expressed as the gel diameter, *d*, normalized by the original diameter d_0. At low *p*H, the gel was in a shrunken state (phase091). Here, the three digits following the term ''phase'' denote the linear swelling ratio in percentage with respect to the size at preparation. The gel in phase091 swelled discontinuously at *p*H 7.6 to phase244. As the *p*H was lowered from 7.6, it shrank back to phase091 at *p*H 5.8. This process had good reproducibility. The hysteresis indicates that the transition is of the first order.

After the loop, the temperature of the gel in phase091 immersed in deionized water was raised from 25 to 60 °C. The gel shrank to phase064 ($d/d_0=0.64$) at 50 °C, as shown in Fig. 2(b). This phase remained unchanged even if the temperature was lowered back to 25 °C. This temperature scan was followed by another experiment at 25 °C by vary-

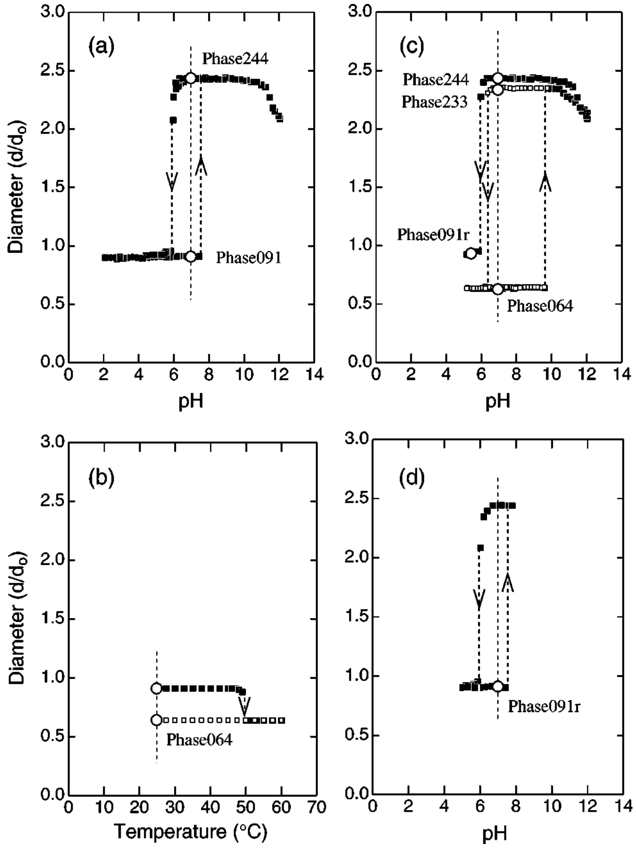

FIG. 2. Diameter, d, of the PASA gel normalized by the mold size, d_0, as a function of *p*H and temperature. Measurements were carried out on a single gel under a microscope. The time course of the variation of d was carefully monitored whenever *p*H or temperature was changed in order to ensure that equilibrium was reached at each measurement. The sequence of each set of measurements is given in alphabetical order (a) to (d). The starting point of each diagram is the last point of the previous diagram. The detailed description of the paths is given in the text. Open circles in the phase diagram indicate the phases of the samples used for SANS experiment.

ing *p*H, the results of which are shown in Fig. 2(c). The gel underwent another phase transition from phase064 to a new phase, i.e., phase233 ($d/d_0=2.33$). This cycle also had good reproducibility.

When *p*H was further increased to 12 and then decreased, the gel went back to its original swollen phase (phase244), as shown by solid squares in Fig. 2(c). This experiment was followed by another *p*H-loop experiment for $4<p\mathrm{H}<8$, the results of which are shown in Fig. 2(d). It is shown that the transitions at *p*H 7.5 and *p*H 5.8 are the same as that observed in the first loop in Fig. 2(a). Therefore, this series of d/d_0 measurements discloses the following features of the gel: (1) As the starting point, the gel is in phase091. (2) It swells to phase244 at higher *p*H (i.e., $8<p\mathrm{H}<10$). (3) A temperature-induced transition from phase091 to phase064 takes place at 50 °C. (4) However, the memory of phase064 can be erased by immersing the gel in a reservoir of *p*H 12. (5) In all of these transitions, there exists a clear hysteresis loop.

Although PASA gel is a homopolymer gel consisting of a single kind of monomer, it exhibits a multiple-phase behavior with four discrete phases. This multiple-phase behavior is a result of its unique chemical structure. PASA has both hydrogen bond donor and acceptor in the monomer unit and undergoes two-step ionization. As a result, due to a combination of hydrogen bonding [Fig. 1(a)], electrostatic interaction [Fig. 1(b)], and hydrophobic interaction [Fig. 1(c)], PASA gels can have several different phases depending on the route of *p*H and/or temperature conditioning. Temperature influences the hydrophobic interaction, whereas changes in the degree of ionization the gel by *p*H variation affect the electrostatic interaction. The ionization process of the monomer units consists of two steps: one for the carboxyl group and the other for the hydroxyl group at higher *p*H. Hydrogen bonding, on the other hand, is governed by both temperature and *p*H. Hence, the unique phase behavior of PASA gel is deduced to result from its unique chemical structure.

Figure 2 also shows that the swelling properties of PASA gel depend on its past history: the phase behavior of the gel depends on whether the gel had experienced the most swollen phase (phase244) or the most collapsed phase (phase064) in the past. When a *p*H loop is started from phase091, the gel remains in a hysteresis loop, as shown in Fig. 2(a). On the other hand, once the gel experiences phase064, the phase transition loop is changed to a different loop, as shown in Fig. 2(c). The most collapsed state (i.e., phase064) is formed by hydrophobic interaction, followed by interlocking with hydrogen bonding [see Fig. 1(a)]. The memory can be easily erased by high *p*H conditioning [see Fig. 2(c)]. Therefore, information about its history, i.e., whether the gel has experienced the most swollen or the most shrunken state, can be stored as the degree of swelling.

These results strongly suggest that the most collapsed phase is interlocked with another kind of physical interaction that is created when the gel is in phase064. Recent studies have shown that the incorporation of a hydrophobic moiety into polyelectrolytes leads to a decrease in acidity or basicity. This decrease in acidity or basicity is related to the dielectric constant surrounding ionizable groups.[8–10] In the case of PASA gel, since benzene rings are less polar than water, the dielectric constant surrounding the charges of carboxyl groups and hydroxyl groups is considered to be lowered with an increase in temperature. This will lower the value of pK_a and is expected to lead to the formation of hydrogen bonds. Therefore, hydrogen bonding may be a reasonable interpretation of the observed interaction.

The swelling behavior of the most collapsed gel (phase064) was examined as a function of urea concentration at 25 °C to confirm the effect of hydrogen bonds. As shown in Fig. 3(a), the gel swelled discontinuously at the urea concentration of 0.75 mol/L to phase233. As the urea concentration was reduced from 6 mol/L to pure water (0 mol/L), the gel shrank gradually and finally went back to its original shrunken phase (phase091). After that, the phase transition loop remained in the loop shown in Fig. 2(a) [Fig. 3(b)]. Urea is a protein denaturant and is considered to break protein hydrogen bonds. From these facts, it is most likely that the multiple-phase behavior and the memory effect will appear when hydrogen-bonding interlocking effects are significant.

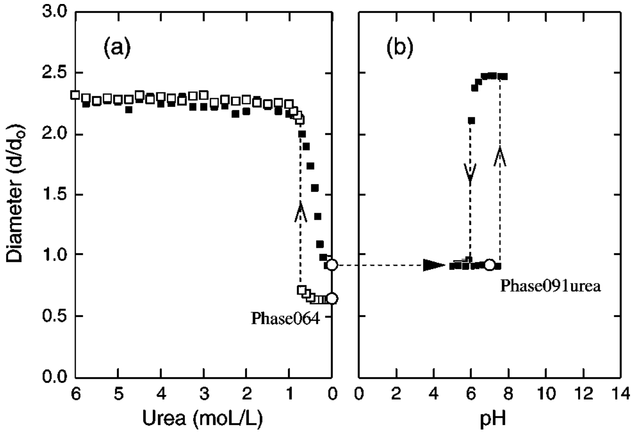

FIG. 3. Diameter of PASA gel as a function of concentration of aqueous urea solution. Open squares indicate the process of increasing concentration of urea. Solid squares indicate the process of decreasing concentration of urea (a). Equilibrium swelling degree d/d_0 of the PASA gel in water as a function of pH at 25 °C (b). The starting point of the diagram is the last point of (a). Temperature was fixed at 25 °C and was controlled to within ±0.1 °C by circulating water from LAUDA RC-3 during the measurement. Open circles in the phase diagram indicate the phases of the samples used for SANS experiment.

B. Theoretical consideration

According to the mean-field theory, the swelling behavior of a gel is described by the following equation:[2,3,11]

$$\tau \equiv 1-\frac{\Delta F}{kT}=\frac{2v\nu_0}{N_A\phi_0^2}\left[\left(\frac{\phi}{\phi_0}\right)^{-5/3}-\left(f-\frac{1}{2}\right)\left(\frac{\phi}{\phi_0}\right)^{-1}\right]+1+\frac{2}{\phi}+\frac{2\ln(1-\phi)}{\phi^2}, \quad (1)$$

where N_A is Avogadro's number, k the Boltzmann constant, T the temperature, v the molar volume of the solvent, ϕ the volume fraction of the polymer network, ϕ_0 the volume fraction of the polymer network at the reference state, ΔF the excess free energy for the association between polymer segment and solvent, ν_0 the number of elastically active chains per unit volume at ϕ_0, and f the number of dissociated counterions per effective chain. The equation of state of a gel uniquely determines the equilibrium swelling degree of the gel, $V/V_0=\phi_0/\phi$ at a given value of the reduced temperature. Three values of ϕ, which correspond to two minima and one maximum value of the free energy, satisfy Eq. (1) for a certain value of τ. Equation (1), however, does not predict the experimental results shown in Figs. 2 and 3 because these equations apply to only non-hydrogen-bonded networks. These results suggest that a new, attractive, and short-range interaction arises in the polymer network of PASA gel after the gel experiences the most collapsed phase. In the case of PASA gel, carboxylic acid groups can lead to the formation of both ionic and hydrogen bonds. When a hydrogen bond is formed, it influences the equation of state: it adds a new cross linking between polymers and effectively shortens the polymer chain length, and the energy is lowered due to hydrogen bonding. Therefore, we obtain the equation of state of a gel by considering hydrogen bonds that form a new cross linking under the following three assumptions:[12,13]

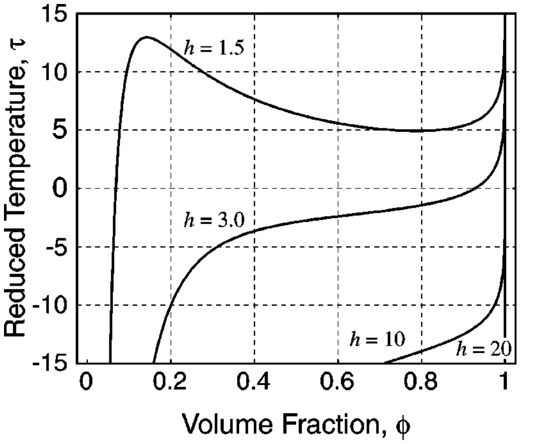

FIG. 4. Swelling curves of the gel for various values of h, the number of hydrogen bonds on an active chain, calculated using Eq. (2), $2v\nu_0/N_A=0.25$, $\phi_0=0.1$, $\Delta F_{HB}/kT=10$, and $fN=10$.

(1) Hydrogen bonding gives rise to additional physical cross-linking points in the chains comprising the gel. The formation of these cross-linking points divides a chain into short, connected chains of equal length. The number of elastically active chains per unit volume at ϕ_0 changes to $(h+1)\nu_0$ due to the formation of h cross-linking points.
(2) Physical cross-linking points are randomly distributed in the network, and no cooperative interactions are considered.
(3) Solvent molecules and monomers composing the gel system have the same molar volume.

$$\tau \equiv 1-\frac{\Delta F}{kT}=\frac{2v\nu_0}{N_A\phi_0^2}\Bigg[(h+1)^{1/2}\left(\frac{\phi}{\phi_0}\right)^{1/3}-(h+1)^{-3/2} \times\left\{\frac{(1-h/f)}{h+1}f+\frac{1}{2}\right\}\left(\frac{\phi}{\phi_0}\right)^{-1}\Bigg] +\frac{2v\nu_0}{N_A}\frac{h}{2}\frac{\Delta F_{HB}}{kT}+1+\frac{2}{\phi}+\frac{2\ln(1-\phi)}{\phi^2}, \quad (2)$$

where ΔF_{HB} is the free-energy change of the system due to the formation of hydrogen bonds in an active chain.

It is worthy to note that Eq. (2) coincides with the equation of state for a non-hydrogen-bonded network (1) when $h=0$. In the case of hydrogen-bonded networks, Eq. (2) determines the equilibrium volume fraction of the polymer network, ϕ, as a function of the reduced temperature and the number of hydrogen bonds h. Thus, a set of swelling curves corresponding to different numbers of hydrogen bonds is obtained. The calculated results are shown in Fig. 4. Phase behaviors of the PASA gel shown in Fig. 2(b) are considered to correspond to the hydrogen-bonded network. The discrete volume phase transition temperature of the gel decreases as the number of hydrogen bonds in the gel increases, and then it disappears at a critical value of h, i.e., $h=h_c$. The volume change at the phase transition temperature becomes smaller as the value of h is increased. The swelling curves of the gel become monotonic above h_c. The swelling ratio of the gel in the swollen state becomes smaller as the number of hydrogen

TABLE I. Sample characteristics.

Code	ϕ	d/d_0	ϕ_0/ϕ
Phase091	0.294	0.91	0.754
Phase244	0.0152	2.44	14.5
Phase064	0.832	0.64	0.262
Phase233	0.0170	2.33	13.0
Phase0.91r	0.294	0.91	0.754
Phase091urea	0.294	0.91	0.754
Dry gel	1.00	⋯	⋯

bonds increases in the gel, while that of the collapsed state is insensitive to the number of hydrogen bonds. Numerical calculation reveals that the critical number of hydrogen bonds h_c is 2.8 under the present conditions. It indicates that the formation of only three hydrogen bonds out of ten acrylic acid units in an intact active chain causes a drastic change in the swelling behavior of the gel. These results imply that the hydrogen bond in the polymer network affects the phase behavior of the gel.

C. SANS

Open circles in Figs. 2 and 3 indicate the phases of the samples used for the SANS experiment. SANS samples are coded as phase091, phase244, etc., according to the results of swelling experiments. Table I lists the characteristics of SANS samples, such as the volume fraction of the polymer, ϕ, d/d_0, and the volume swelling ratio, V/V_0, where V/V_0 was simply obtained by $(V/V_0)\equiv(d/d_0)^3$. The volume fraction ϕ was assumed to be equal to the weight fraction of the polymer because the mass density of heavy water is 1.1 and is close to that of the solute.[14]

Figure 5 shows the SANS intensity functions, $I(q)$, for PASA gels in phases 091, 244, 064, 233, phase091r, and phase091urea, where q is the scattering vector. Numbers in parentheses indicate the order of sample treatment in the *p*H–temperature coordinate system. Phase091r is the revisited phase of phase091 after passing through the loop of phase064–phase233–phase064–phase244. Phase091urea is the revisited phase of phase091 after experiencing the urea aqueous solution. The magnitudes of $I(q)$ for phase091, phase064, and phase091r and phase091urea are much larger than those for phase244 and phase233. This is due to the difference in the polymer concentration in the gel by a factor of approximately 20 (between phase244 and phase091, for example). $I(q)$ for the gel in phase091 seems to be a monotonically decreasing function of q. $I(q)$ of phase064, obtained by heating the gel in phase091, has a scattering maximum around $q=0.02$ Å^{-1}. This scattering maximum indicates the presence of charged groups in a poor solvent moiety whose repeating distance is about 400 Å.

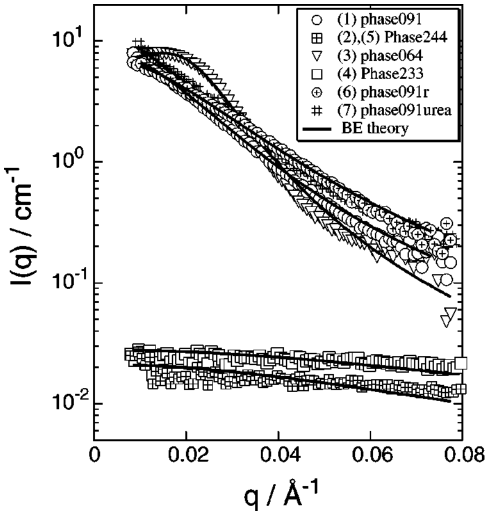

FIG. 5. SANS intensity profiles of PASA gels obtained at 25 °C. Solid lines are fitted curves using Eq. (3).

As predicted by Borue and Erukhimovich,[15] and by Joanny and Leibler,[16] weakly charged polymer solutions (and polymer gels) in a poor solvent undergo microphase separation in order to compromise for a huge penalty of localization of charges caused by collapse in a poor solvent by forming microclusters (or microphase separation). Therefore, this peak is a strong indication that PASA gel is charged.[17–20]

In order to analyze the structure factor of PASA gels more quantitatively, we employed a theory proposed by Borue and Erukhimovich (the BE theory), which deals with the structure factor of weakly charged polymers in a poor solvent. The scattering intensity is given in the form

$$I(q)\sim\frac{x^2+s}{(x^2+t)(x^2+s)+1}, \tag{3}$$

where x and s are the reduced scattering vector and the reduced salt concentration, respectively, as defined by

$$x=r_0q,\quad s\equiv\kappa^2r_0^2. \tag{4}$$

The parameter r_0 is the characteristic length of screening in a salt-free polyelectrolyte solution. κ is the Debye screening length. The variable t is the reduced temperature related to Flory's interaction parameter χ and is defined by

$$t\cong12\left(\frac{r_0}{a}\right)^2(1-2\chi), \tag{5}$$

where a is the segment length of the chain molecules. Solid lines in Fig. 5 are the results of curve fitting with Eq. (3), where the parameters, x, s, and t were floated. The theoretical curves reasonably reproduce the observed scattering intensity functions. Since the essential parameters are s and x, an s-t phase diagram is constructed in Fig. 6. This phase diagram shown is divided into eight regimes (denoted by Roman numerals) depending on the values of s and t. The borders of these regimes are given by simple relations, such as $t=s+2$ and $st=1$, as denoted in the figure. The classification of these regions and their characteristics are described in the original paper[15] and elsewhere;[18–20] thus, we focus on the case of PASA gels studied here. The gels in phase091, phase091r, and phase091urea are located very close to the spinodal line with $t<0$ and $s>1$ ($s=1.062$ and $t=-0.936$ for phase091, $s=1.078$ and $t=-0.921$ for phase091r, and $s=1.097$ and $t=-0.908$ for phase091urea). However, because of $t>-1/s$, phase091, phase091r, and phase091urea are in regime V, where Coulomb interactions are practically

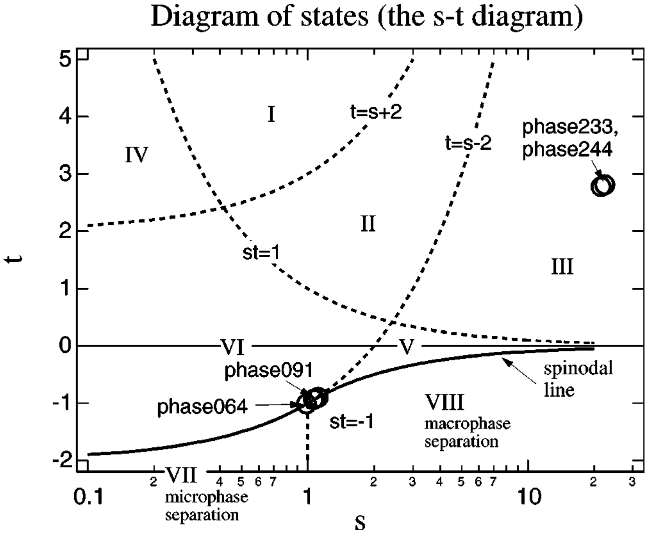

FIG. 6. Phase diagram showing the states of weakly charged polymer gels. t and s are the reduced temperature and the reduced salt concentration, respectively. The thick solid curve indicates the spinodal line. Dashed lines and the spinodal line divide different regimes coded by I to VIII. The states of PASA gels are indicated by open circles in the diagram.

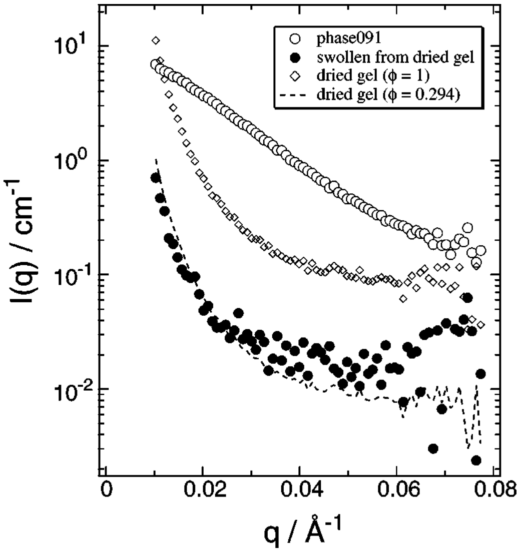

FIG. 7. Comparison of scattering intensity functions among phase091 (open circles), bulk PASA gel ($\phi=1$; open diamonds), and the gel with $\phi=0.294$ prepared by swelling from dried PASA gel (solid circles). The dashed curve is obtained by multiplying $\phi=0.294$ with $I(q)$ of the dried gel.

neglected. This is why $I(q)$ values for phase091, phase091r, and phase091urea are monotonically decreasing functions, as is often observed for neutral polymer solutions in the semidilute regime. On the other hand, phase064 is classified under regime VI since $t>-1/s$ ($s=0.987$ and $t=-1.012$), where Coulomb interactions are practically neglected but microscopic fluctuations are amplified. Note that at $st=-1$, $I(q=0)$ diverges (macrophase transition) for $s>1$ and $I(q\neq 0)$ diverges (microphase transition) for $s<1$. Hence, $I(q)$ for phase064 starts to exhibit a scattering maximum near its spinodal line. According to the above discussion, it can be deduced that phase064 and phase091 are very close to microphase separation transition and macrophase transition, respectively. Phase244 and phase233, on the other hand, are located in regime III, where the excluded volume effects dominate over Coulomb interactions. In this regime, a gel behaves like a neutral polymer solution in the semidilute regime. It should be noted here that s becomes indeterminant for phase244 and phase233 and the evaluated values of s do not have any strong physical meaning. The essential feature to be noted here is that the states of PASA gel differ quite significantly in the s-t phase diagram due not only to pH or temperature but also to the history of sample treatment.

Now, we discuss why PASA gels can be found in many regimes in the s-t diagram even though pH and T are fixed. One possibility is that the gel in phase064 is strongly interlocked via hydrogen bonds. This possibility is deduced from the fact that phase064 is stable with temperature change [see Fig. 2(b)] and the chain molecules are packed compactly ($\phi=0.89$). In order to break hydrogen bonds, an aqueous medium with high pH (>10) is required, which leads to strong ionization of the gel and breaking of hydrogen bonds. This is why the gel undergoes swelling transition from phase064 to phase233. Note that (1) phase233 is different from phase244 [see Fig. 2(c)] and (2) phase233 does not go to phase091 but to phase064 upon lowering pH. Unfortunately, any difference in the structure factor between phase244 and phase233 could not be resolved by SANS because the scattering intensity functions for these phases were very weak and highly scattered. Phase233 went back to phase244 by increasing pH to 12. The resultant phase244 could finally go back to phase091r, whose scattering intensity is shown in Fig. 5. Although $I(q)$ values for phase091r and phase091urea are somewhat larger than that for phase091, they are roughly the same. Therefore, it can be concluded that not only macroscopically but also microscopically, PASA gels return to their original state by traveling along the pH-temperature loop applied here.

Figure 7 shows a comparison of $I(q)$ values among phase091 (open circles; $\phi=0.294$), dried PASA gel ($\phi=1$; open diamonds), and the gel with $\phi=0.294$ prepared by swelling from dried bulk PASA gel (solid circles). Note that bulk PASA gel is porous and $I(q)$ originates from void scattering. This comparison allows us to judge the difference in structure between as-prepared gel in phase091 (open circles) and the gel having a history being completely dried (filled circles). As is clearly shown here, $I(q)$ for the gel prepared from the dry state (solid circles) is quite different from that for the gel in phase091 (open circles). The dashed curve obtained by multiplying $\phi=0.294$ with $I(q)$ of the dried gel (open diamonds) nicely superimposes on the results for the gel prepared by swelling from the dry state (filled circles). Therefore, the microscopic structure of the gel prepared by swelling from the dry state is similar to the dried gel itself. This indicates that the structure of the gel changes irreversibly by complete drying, probably due to the formation of strong hydrogen bonds.

This transformation reminds us of the denaturation of protein by heat and or acid/base treatment.[21] It is well-known that most proteins can fold spontaneously into their desired shapes. Proteins can be unfolded, i.e., denatured, by treatment with certain solvents, to form flexible polypeptide chains. When the denaturing solvent is removed, the proteins usually refold into their original conformations. In the case of PASA gel, however, the ‘‘denatured’’ gel can revert back to its original conformation (or size) by treatment with a high *p*H aqueous solution. Hence, PASA gel can be used as a model system for studying the processes of denaturation and renaturation of proteins. It should be noted that Takata *et al*. recently observed the temperature-induced denaturation process of a globular protein.[22] A scattering maximum in the SANS intensity profile for β-lactoglobulin aqueous solution was detected, which is very similar to that observed in PASA gel. This observation supports the hypothesis on the analogy between the denaturation of proteins and the multiple-phase behavior of polymer gels.

IV. CONCLUSION

PASA gel exhibits multiple phases that are characterized by different degrees of swelling; the gel can take one of four different values of the degree of swelling, but none of the intermediate values. The gel exhibited a marked memory capability: its phase behavior depends on whether it has experienced the most swollen phase or the most collapsed phase in the immediate past. The information is stored during a *p*H-*T* cycle, and can be easily erased by high- *p*H or urea treatment.

The structure factors obtained by small-angle neutron scattering also indicate the presence of characteristic structures corresponding to the four phases, particularly the shrunken state (i.e., phase064). The structure factors also indicate that PASA gel reverts to its original state not only macroscopically but also microscopically via the *p*H–temperature loop or urea treatment applied here. It is also found that the microscopic structure of the gel prepared by swelling from the dry state is similar to that of the dried gel itself.

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