Elastic Relaxation of Collapsed Poly(alkylacrylamide) Gels and Their Complexes with Phenol

Shogo Koga,† Tatsuya Kawashima, and Shigeo Sasaki*

Department of Chemistry, Faculty of Science, Kyushu University, 33 Hakozaki, Higashiku, Fukuoka 812, Japan

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The effects of phenol-binding (Ph-binding) and temperature on the Young's moduli, the volumes, and the nanostructures of *N*-isopropylacrylamide (NIPA) and *N*, *N*-diethylacrylamide (DEA) hydrogels were investigated. The modulus and volume of the NIPA gel varied discontinuously with respect to the Ph concentration of solution outside the gel and temperature, while those of the DEA gel varied discontinuously with respect to the Ph concentration, but continuously with respect to temperature. The large relaxation of the modulus observed only in the case of the shrunken gels could be described by a power function of time elapsed after stretching the gel. The small-angle X-ray scattering spectra obtained for the Ph-binding NIPA and DEA gels exhibited the broad peaks indicating the regular distribution of the electron-rich entity with the periodic length about 1.2 nm. The shrunken NIPA and DEA gels were found to reswell and decrease their moduli at Ph concentrations much higher than the critical transition concentration. These results demonstrate the attractive interaction between the phenol molecules and the amide group of NIPA or DEA gel that induces the volume phase transition and condenses the phenol in the chain networks.

1. Introduction

Polymer gels responsive to variations in physical conditions such as temperature and solvent composition are applicable to actuators, drug delivery systems, and other chemical switches.[1−3] The *N*-isopropylacrylamide (NIPA) hydrogel is known to exhibit a temperature-induced volume phase transition and has been intensively investigated in the last few decades.[4−7] The volume transition behavior of NIPA hydrogels can be explained by the coupling of the cooperative hydration-dehydration with the entropy force of the polymer chains.[8] The volume phase transition temperature of the NIPA gel is reduced by the addition of inorganic salts,[9] saccharide,[10] alcohol, and several hydrophobes[11−16] to the ambient solution. Our recent studies[8,10,17] on the transition of NIPA gels in inorganic salt- and saccharide-added systems have revealed that the chemical potential of water molecules at the transition points are essentially identical. This shows that the volume phase transition occurs when the chemical potential of water molecules in the bulk drops below that of the water molecules attached to the gel chain. The raise in the temperature and the addition of inorganic salts or saccharides have the effect of reducing the chemical potential of water molecules in the bulk, thus lowering the transition temperature. A significant decrease in the transition temperature was also observed in the case of the low-concentration hydrophobe solution, where the chemical potential of water molecules is substantially the same as that of the hydrophobe-free solution. In this respect, the hydrophobe-induced volume phase transition should occur via a different mechanism than the volume transition induced by the addition of inorganic salts. It has been reported[16] that the transition temperature is lowered by the addition of benzoic acid and phenol (Ph), and that the amount of decrease correlates with the degree of binding of the hydrophobes to the gel chains. The infrared spectra for shrunken NIPA gel with Ph demonstrated that Ph molecules bind to the NIPA gel chain via hydrogen bonding between the amide groups of NIPA and the hydroxyl groups of Ph. These results have led us to conclude that the binding of hydrophobes, accompanied by the dehydration of the gel chains, lowers the volume phase transition temperature with respect to the ordinary NIPA gel. Such materials can be used as adsorbents for hydrophobic molecules, such as nonylphenol, which has received great attention due to the its endocrine disrupting effect.[18]

The tensile force on the shrunken NIPA gel following uniaxial elongation has recently been found to decay according to a power function of time.[19] This same relaxation behavior has been observed in elastomers. Curro and Pincus[20] have attributed the slow relaxation to the liberation of dangling chains from the topological constraint in the cross-linked network. The relaxation of Young's modulus observed in the shrunken NIPA gel has also been explained by the stress relaxation of the deformed dangling chains which reptate in the cross-linked network to liberate the stress.[19] The Young's modulus of the gel was found to increase with temperature and change discontinuously at the volume phase transition point. The increase in Young's modulus reflects the increase in the degree of dehydration of the gel chain.

The binding of Ph molecules to the gel chains is expected to alter the chains' conformation and hence the gel's elastic properties by inducing dehydration of chain segments. The purpose of this study is to elucidate the effects that the binding of Ph molecules has on the gels' volume change behavior and elastic properties, and nanostructures of the complex of gel chain with Ph as the result of the binding. The binding isotherms of Ph, tensile force measurements, and the small-angle X-ray scattering (SAXS) experiments of NIPA and *N*, *N*-diethylacrylamide (DEA) gels in aqueous Ph solutions are presented.

2. Experimental Procedure

Gel Synthesis. The NIPA or DEA gel was prepared by radical copolymerization in a solution containing the NIPA or DEA

* E-mail address: s-sskscc@mbox.nc.kyushu-u.ac.co.jp.
† Present address: Mitsubishi Chemical Group Science and Technology Research Center, Inc. 1, Toho-cho, Yokkaichi, Mie 510-8530, Japan.

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monomers (1 M) and the cross-linker *N*, *N*′-methylenebisacrylamide (5 mM). The copolymerization was initiated by adding ammonium persulfate (5 mM). *N*, *N*, *N*′, *N*′-tetramethylethylendiamine (0.016 mM) was added as an accelerator. The gels were synthesized in glass tubes with an inner diameter of 0.3 mm, and in containers having two glass plates separated by a 1-mm-thick spacer for 24 h at 5 °C. The synthesized gels were taken out, thoroughly rinsed with water, cut into small pieces (about 10 mm square and about 50 mm length), and dried under vacuum. The NIPA monomer was purified by recrystallization using a mixture of *n*-hexane and toluene.

Modulus. Details of the apparatus for tensile force measurement of rod gels have been described elsewhere.[19] A rod gel was inserted into two platinum rings, each connecting to a strain gauge (AE801, SensoNor, Norway) and a translational stage. To embed the gel between the rings, stoppers were prepared of silk strings and carefully wound around the gel at its ends. The radius of the rod gel, r, in equilibrium with the solution at a given temperature and Ph concentration C_{out}, and the tensile force $F(t)$ generated by elongating the gel in the solution were monitored with a computer-aided instrument. The force was found to decay to a final value, Fe, in about 500 s after elongation. The natural length of the gel, l, was obtained from the inflection point in the plot of Fe against the distance between the rings. The gel was elongated by a given distance (typically a few hundred μm) within 0.2 s. The initial Young's modulus, Yi, and the modulus at mechanical equilibrium after elongation, Ye, are given by:

$$Yi = \frac{Fi \cdot l}{\pi r^2 (l^* - l)} \tag{1}$$

and

$$Ye = \frac{Fe \cdot l}{\pi r^2 (l^* - l)} \tag{2}$$

where l^* is the length of the elongated gel. The ratio of l^* to l was typically about 1.1. The solution temperature was controlled within 0.1 °C. The C_{out} was changed by replacing the solution in which the gel was immersed.

Binding Isotherm. The isotherm of Ph-binding to gel chains was carried out as follows. The weight of a dried plate gel w_{dgel}, the weight of the solution w_{sol}, and the initial concentration of Ph in the solution $C^0{}_{out}$ were measured. The gel was immersed in a solution of a given Ph concentration at 35 °C. The temperature was slowly (0.1 °C/min) changed from 35 °C to 25 °C. It took more than two weeks for the gel to attain binding equilibrium with the solution. The Ph concentration at equilibrium, C_{out}, was evaluated based on the optical absorbance at λ = 269.6 nm, as measured by a spectrophotometer (U-best50, Jasco, Japan). The number of Ph molecules bound to one monomeric unit of NIPA or DEA gel chain, β, is given by

$$\beta = \frac{M_{am}}{w_{dgel}} w_{sol} (C^0_{out} - C_{out}) \tag{3}$$

where M_{am} is the molecular weight of the alkylacrylamide monomer. It should be noted that the Ph concentration in the solution phase of the gel was assumed to be equal to C_{out}. To ensure the accuracy of β, the amount of adsorbed Ph, $w_{sol}(C^0_{out} - C_{out})$ was compared with the amount of Ph discharged into *N*,*N*′-dimethylformammide (DMF), as evaluated from the absorbance of the DMF solution at λ = 279.4 nm. The difference between the discharged and differentiated amount was within 10% of the latter.

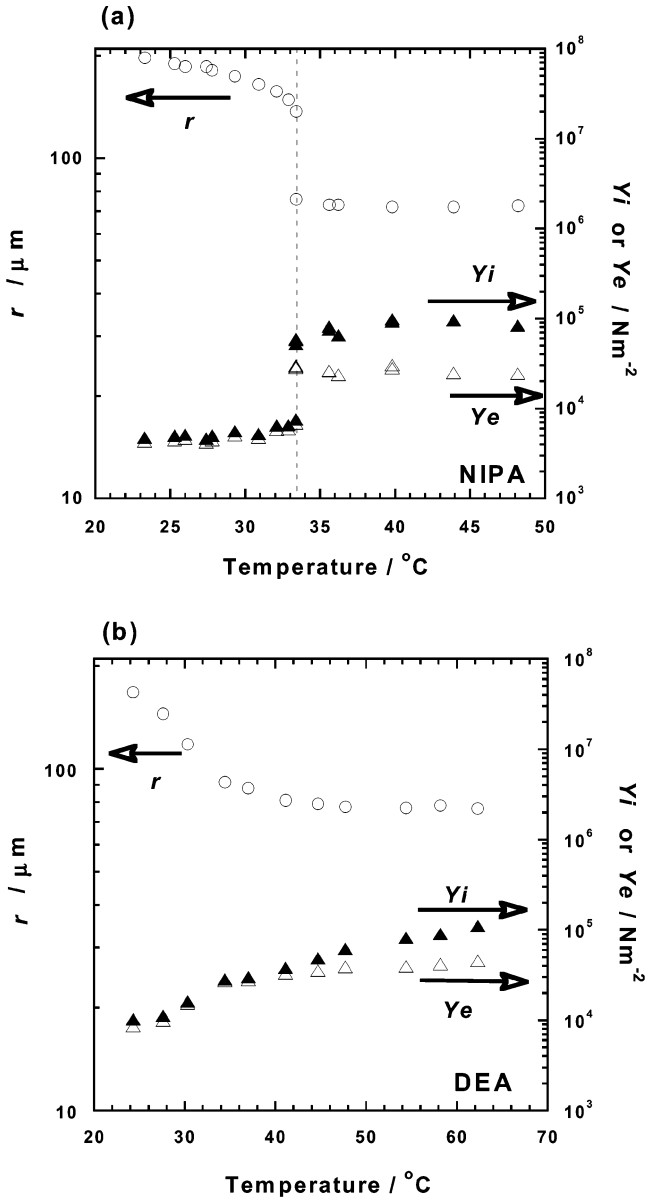

Figure 1. Young's moduli and radii of the NIPA (a) and DEA (b) gels as functions of temperature. Open circles represent the radii r. Closed and open triangles represent the initial modulus Yi, and the modulus at mechanical equilibrium Ye, respectively. Dotted lines represent the volume phase transition points.

SAXS Experiment. The SAXS experiments were carried out for the plate gels at 25 °C with a SAXS spectrometer of BL45XU-A (RIKEN Beamline I) installed at SPring8 of Japan Synchrotron Radiation Research Institute, Hyogo, Japan. The β-values of the gels were determined by the experiments of the binding isotherm beforehand. The observed scattering vectors, $q = (4\pi/\lambda)\sin\theta/2$, where λ and θ, respectively, are a wavelength of the beam and the scattering angle, were ranged from 0.1 to 6 nm^{-1}.

3. Results

Figure 1 shows the temperature dependence of Yi, Ye, and r for NIPA and DEA gels in Ph-free solution. Yi, and Ye increase with temperature, while r decreases with temperature. Discrete changes in the Yi and Ye of the NIPA gel are observed at about 34 °C, where r also changes discontinuously. No discontinuous change in Yi, Ye, or r is observed in the case of the DEA gel.

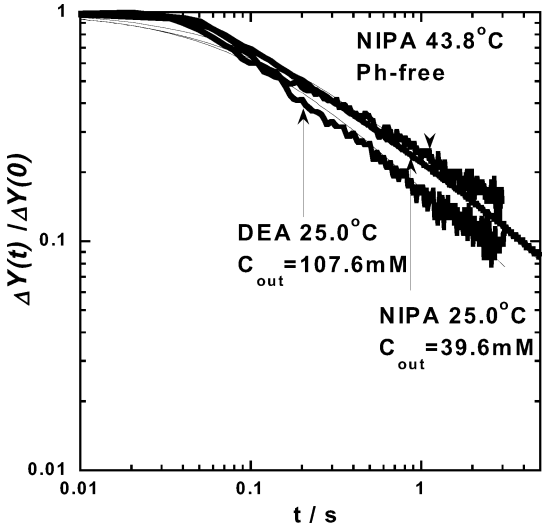

Figure 2. Relaxation behavior of the Young's moduli of shrunken NIPA and DEA gels. The ordinate is the normalized relaxation modulus, $\Delta Y(t)/\Delta Y(0)$, where $\Delta Y(t) = Y(t) - Ye$. Solid lines represent the best-fitting curves.

Figure 2 shows the log−log plot of the normalized relaxation modulus $\Delta Y(t)/\Delta Y(0)$, where $\Delta Y(t) = Y(t) - Ye$, for the shrunken NIPA gel in Ph-free solution at 43.8 °C. As reported elsewhere,[19] the observed $\Delta Y(t)/\Delta Y(0)$ is attributable to the stress relaxation of dangling chains under topological constraints.[20] The $\Delta Y(t)/\Delta Y(0)$ of the shrunken gel can be described by the following power function of time, t, elapsed after stretching the gel:

$$\Delta Y(t)/\Delta Y(0) = (1 + t/\tau_1)^{-\gamma} \tag{4}$$

where, τ_1 and γ are the primary reptation time of entangled chains and a constant related to the mesh density of the cross-linked polymer network, respectively. The best-fit τ_1 and γ values for the NIPA gel at 43.8 °C are 0.048 ± 0.03 s and 0.45 ± 0.1, respectively, and those for the shrunken DEA gel at 58.2 °C are 0.046 ± 0.03 s and 0.48 ±0.1, respectively. These values are very close to those reported in a previous publication[19] for the shrunken, Ph-free NIPA gel ($\tau_1 = 0.04$ s, $\gamma = 0.45$).

Figure 3 shows the C_{out} dependence of Yi, Ye, and r for NIPA and DEA gels at 25 °C. The r values of NIPA and DEA gels change discontinuously at $C_{out} = 25$ mM and 7.5 mM, where abrupt changes in Yi and Ye are observed. The $\Delta Y(t)/\Delta Y(0)$ observed for shrunken gels at C_{out} values below 200 mM are also describable as power functions of t, as shown in Figure 2. The differences in the τ_1 and γ between the NIPA gel in 39.6 mM aqueous Ph solution ($\tau_1 = 0.108 \pm 0.03$ s and $\gamma = 0.64 \pm 0.1$), the DEA gel in 107.6 mM aqueous Ph solution ($\tau_1 = 0.069 \pm 0.03$ s, $\gamma = 0.63 \pm 0.1$) and their shrunken counterparts in Ph-free solution are within experimental error. To detect any real differences, more accurate measurements will be needed. The r of the NIPA and DEA gels increase with C_{out} for $C_{out} >$ 200 mM, where the $\Delta Y(0)$ of the gels decreases significantly and $\Delta Y(t)/\Delta Y(0)$ can no longer be fitted by eq 4.

Figure 4 shows the weights of NIPA and DEA gels per mole of monomeric unit, W_g, and the degree of binding, β, as a function of C_{out} at 25 °C. Discontinuous changes in W_g are observed at $C_{out} = 25$ mM and 7.5 mM for NIPA and DEA, respectively, where the β values change discretely. The significant increase in W_g of both gels with increasing C_{out}, particularly above 200 mM, demonstrates that Ph molecules cause the gels to reswell.

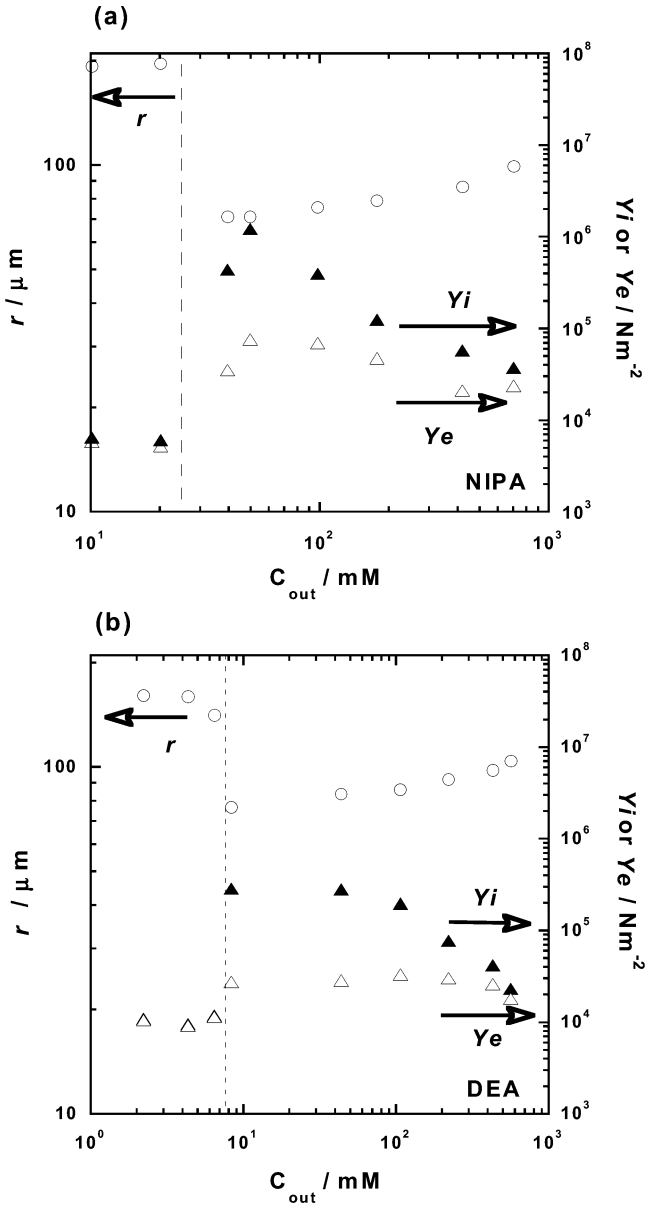

Figure 3. Young's moduli and radii of the NIPA (a) and DEA (b) gels as functions of phenol concentration. Open circles represent the radii r. Closed and open triangles represent the initial Young's modulus Yi, and the modulus at mechanical equilibrium Ye, respectively. Dotted lines represent the volume phase transition points.

Figure 5 shows the C_{out} dependence of the number of Ph, N_{Ph}, and water molecules, N_{H2O} per monomeric unit of the NIPA and DEA gel chains. N_{Ph} and N_{H2O} were estimated by using the following equations:

$$N_{Ph} = \frac{M_{am}}{w_{dgel}}(w_{sgel} - w_{dgel})C_{out} + \beta \tag{5}$$

$$N_{H_2O} = \frac{1}{18}\left\{\frac{M_{am}}{w_{dgel}}(w_{sgel} - w_{dgel}) - 94N_{Ph}\right\} \tag{6}$$

where w_{sgel} is the weight of the gel in equilibrium with the solution. N_{Ph} and N_{H_2O} values both change discretely at $C_{out} =$ 25 mM and 7.5 mM for the NIPA and DEA gels, respectively, where the transitional changes in r are observed (Figure 3). Interestingly enough, the N_{H_2O} of both gels decreases with C_{out} below 100 mM, but increases above 200 mM, where reswelling of the gels occurs as shown in Figure 3.

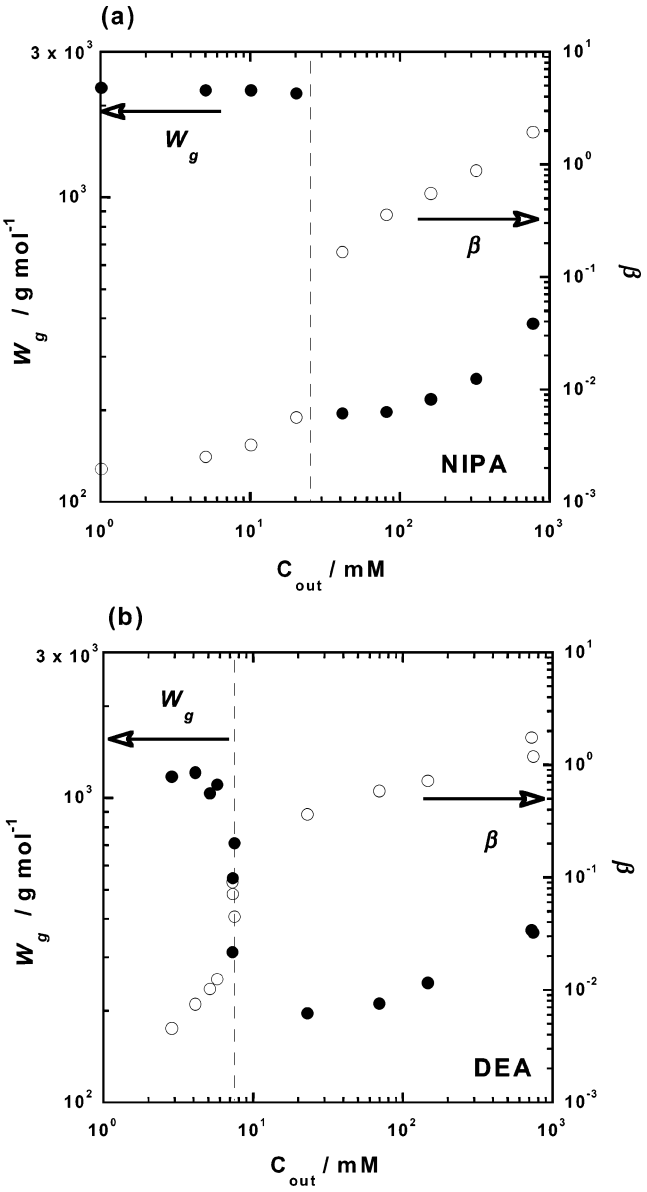

Figure 4. Weight of the gel per mole of alkylacrylamide monomer, W_g, and the degree of binding β of NIPA (a) and DEA (b) gels as functions of phenol concentration. Closed and open symbols represent W_g and β respectively. Dotted lines represent the volume phase transition points.

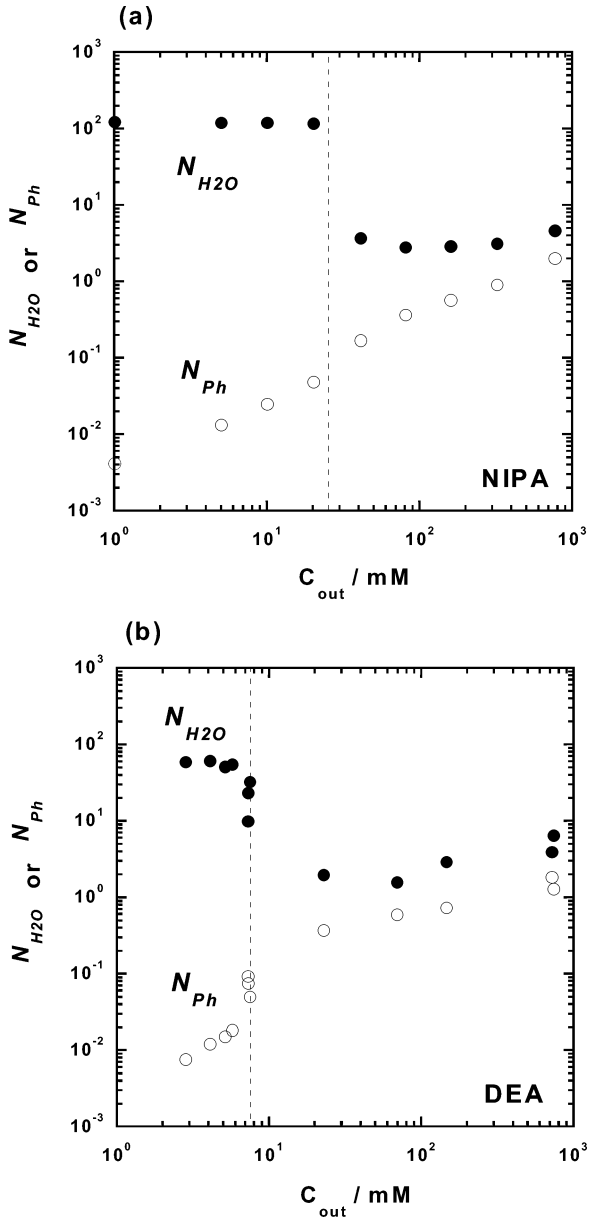

Figure 5. The number of water and phenol molecules per monomeric unit of NIPA (a) and DEA (b) gels. Closed and open symbols represent the number of water and phenol molecules, respectively. Dotted lines represent the volume phase transition points.

Figure 6 shows the SAXS spectra for the Ph binding NIPA and DEA gels. The broad peaks around $q = 5$ nm^{-1} became significant with an increase in β. The single broad peak of the SAXS spectrum indicates the regular distribution of particles. The mean characteristic distances between particles, ξ, defined as $\xi = 2\pi/q_{max}$, where q_{max} is a q-value of the intensity max position of the peak,[21] are about 1.22 nm for the Ph-binding NIPA gel and about 1.24 nm for the Ph-binding DEA gel.

4. Discussion

The r of the DEA gel changes continuously with temperature in Ph-free solution, while that of the NIPA gel changes discontinuously, as shown in Figure 1. The continuous change of the DEA gel with temperature has also been reported elsewhere.[22] The volume phase transition of the NIPA gel is induced by the temperature rise and the addition of inorganic salts, both of which have the effect of reducing the chemical potential of water molecules. Dehydration of the hydrophobic residue of the gel chain occurs when the chemical potential of the water molecules in the bulk is lower than that of the hydrating water molecules. The volume phase transition can be explained by the cooperative hydration-dehydration of the segment of gel chain coupled with a change in conformational free energy. According to the simple theory of volume phase transition of hydrogels described by Sasaki,[8] the volume change at the transition point decreases with a decrease in the cooperativity parameter ζ ($\sim \exp\{(2\epsilon_{hd}^n - \epsilon_{hh}^n - \epsilon_{dd}^n)/2T\}$, where ϵ_{ab}^n is the interaction energy between the neighboring segments in the a and b states. A segment takes a hydrated (h) or dehydrated (d) state.). The continuous change in the r value of the DEA gel indicates that the ζ value of the DEA gel chain is not large enough to cause the volume phase transition. Hydrogen-bonding between the C═O and N−H groups of the dehydrated segments of NIPA gel chains has been confirmed by Fourier transform infrared (FT-IR) spectra of the shrunken NIPA gel.[16,23] DEA gel chain's smaller ζ value compared to that of NIPA is the result of its smaller magnitude of negative ϵ_{dd}^n. This, in

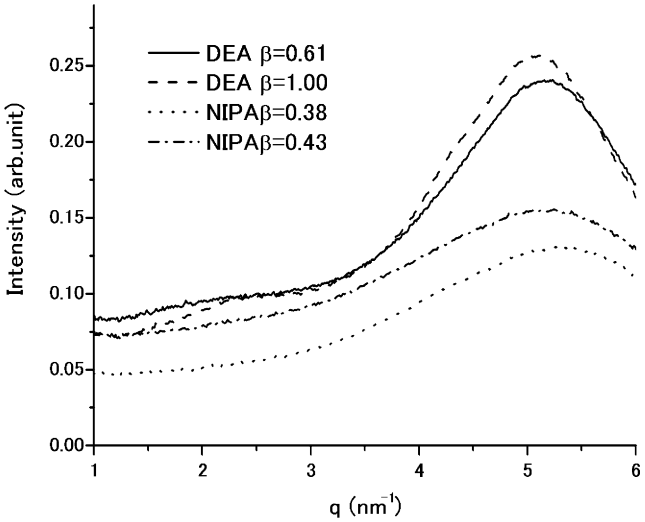

Figure 6. SAXS spectra of the Ph binding NIPA and DEA gels.

turn, results from the fact that hydrogen bonding cannot occur between the dehydrated DEA segments, which contain C═O groups but not N−H groups. The stabilization energy due to the hydrogen bond between C═O and N−H groups increases ζ in the case of NIPA but not so much in the case of DEA.

Ph-binding leads to discontinuities in the r values of NIPA and DEA gels, as shown in Figures 3 and 4. In the shrunken NIPA gel, hydrogen-bonding between NIPA's amide group and Ph's hydroxyl group has been demonstrated by FT-IR spectrum.[16] Hydrogen-bonding probably occurs between the carbonyl groups of dehydrated DEA segments and Ph's hydroxyl groups because the tertiary amide group is known as a powerful hydrogen bond acceptor.[24] The fact that the volume change in the NIPA gel at the volume phase transition point increases with an increase in the β change[16] suggests that hydrogen-bonding between the gel segment and Ph causes the removal from the segment of the water molecules hydrating. The Ph-binding to segments of NIPA and DEA gel chains enhances the hydrophobicities of the segments, which leads to a drop in the interaction energy $\epsilon_{dd}{}^n$ and an increase in $\epsilon_{hd}{}^n$, hence the ζ value, rendering the r curve discontinuous.

The Ph concentration at the volume phase transition point, C_{tr}, for the DEA gel is lower than that for NIPA, as shown in Figure 3. This indicates that the Ph-induced free energy change in the DEA chain segment is greater than that in NIPA. The contribution of hydrogen-bonding to the Ph-induced free energy change is greater in the NIPA gel than in DEA since Ph's O−H group can form the hydrogen-bond with the C═O and N−H groups of NIPA gel chains, but only the C═O group of DEA gel chains. Thus, hydrogen bonding alone cannot account for the result described above. It is inferred that hydrophobic interactions also play a specific role in Ph-binding and that DEA gel chains are more hydrophobic than their NIPA counterparts. This leads to DEA's lower C_{tr} compared to that of NIPA.

Figure 3 shows that the shrunken NIPA and DEA gels reswell significantly with C_{out} for $C_{out} > 200$ mM. Both β and N_{H_2O} increase with C_{out}, as shown in Figures 4 and 5. Ph-binding increases N_{H_2O} for $C_{out} > 200$ mM, but decreases N_{H_2O} for $C_{out} < 100$ mM. The dehydration of segments neighboring the Ph-bound segment occurs at $C_{out} < 100$ mM, which can explain the large decrease in N_{H_2O} (100 for the NIPA gel and 50 for the DEA gel) caused by an increase in β (of 0.15 for either gel) at the transition point. The increase in N_{H_2O} accompanied by the increase in N_{Ph} suggests that the Ph molecules bound to the dehydrated portions of the gel chains are hydrated. There could

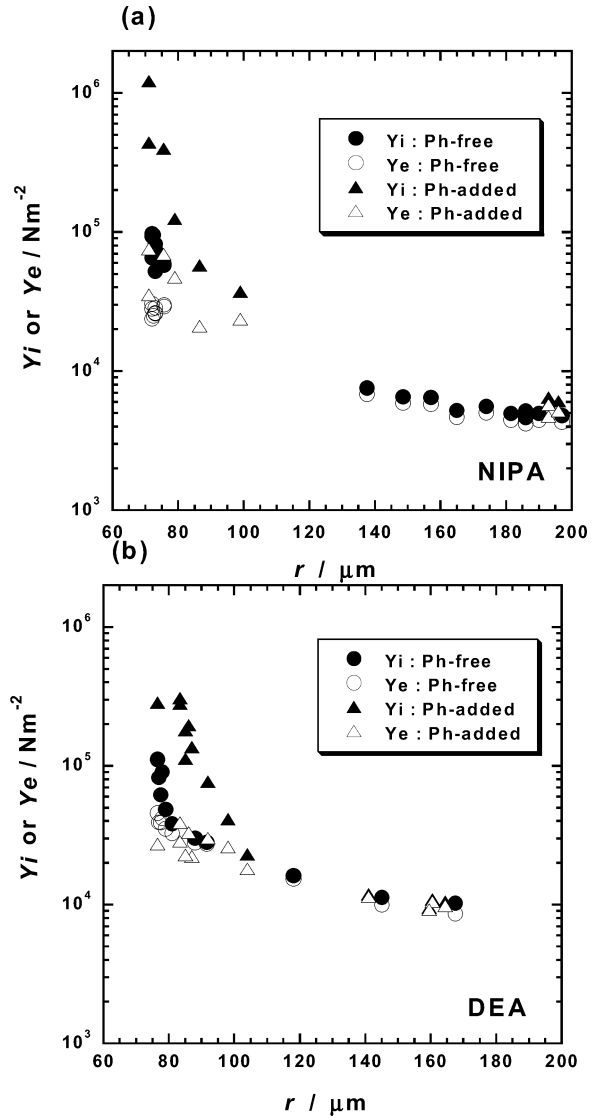

Figure 7. Young's moduli of the NIPA (a) and DEA (b) gels as a function of the radius of the gel with or without phenol. Closed and open symbols represent the initial Young's modulus *Yi*, and the modulus at mechanical equilibrium *Ye*, respectively. Circles and triangles represent the moduli of the gels in a phenol-free solution and aqueous phenol solution, respectively.

be two interactions for inducing the Ph-binding; the hydrogen-bond between the O−H group of Ph and the amide group of chain, and the hydrophobic interaction between the phenyl group of Ph and the alkyl chains or the hydrophobic entity. The contacting group of Ph with the bulk phase is the phenyl group in the former case and the O−H group in the latter case. Thus the former type of the binding causes the hydration water molecules to discharge and the latter type can hydrogen bond to water molecules. The former and the latter types of binding will be called an *A*-type binding and a *B*-type binding for convenience. The *A*-type binding prevails and causes hydration water molecules to be discharged at C_{out} below 100 mM. The *B*-type binding can be induced by the interaction between the phenyl groups of Ph molecules in the binding state and the bulk phase at C_{out} above 100 mM. Therefore, it is possible for β to exceed 1 as seen around $C_{out} = 770$ mM in Figure 4. The increase of N_{H_2O} with increase in N_{Ph} seen in Figure 5 clearly indicates the existence of the *B*-type binding.

The regularly distributing particles indicated by the SAXS spectra shown in Figure 6 are composed of the Ph-binding NIPA

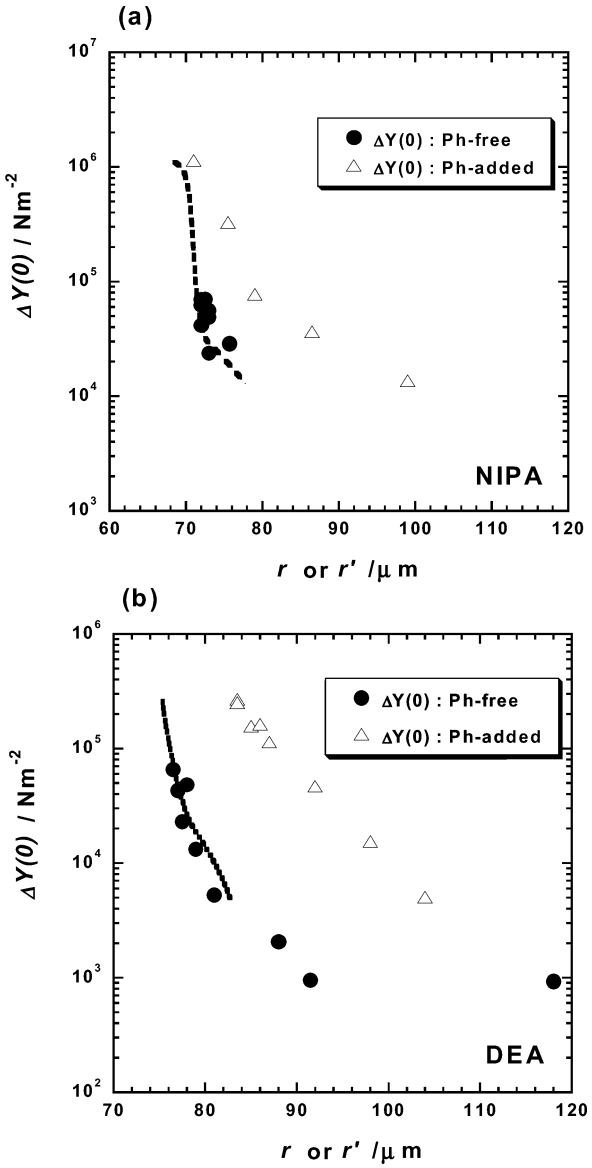

Figure 8. $\Delta Y(0)$ of NIPA (a) and DEA (b) gels as a function of the radii (r and r') of the gel with or without phenol. Open and closed circles represent the $\Delta Y(0)$ of the gel in an aqueous phenol solution and phenol-free solution, respectively. Dotted lines represent the $\Delta Y(0)$ as a function of the calculated r' (see text).

and DEA gel chain segments, since the SAXS spectra narrowing with an increase in β indicates the increase of the domain size occupied by the regularly distributing particles with β. The sizes of particles should be less than ξ, 1.2 nm. This suggests that a few monomeric units bound with the Ph segregate to compose the particle. The binding isotherm experiments shown in Figure 5 suggest that the molar ratios of water to the Ph molecule are about 8 in the NIPA gel at $\beta = 0.4$ and about 2 in the DEA at $\beta = 0.6$. The complex of the Ph molecule with the amide group cannot be mixed with the water molecules and is segregated from the water to form a self-assembled particle. The attractive π/π interaction between the Ph molecules might induce the segregation.[24] The *Ye* increases with β, as shown in Figure 3, since the elastic modulus of the assembled parts of chain is much higher than that of the nonassembled parts.

The elastic moduli *Yi* and *Ye* increase with the decrease in r, as shown Figures 1 and 3. The *Yi* and the *Ye* of the NIPA and the DEA gels as functions of the r are shown in Figure 7. It is interesting that the *Ye* can typically be described by a function of r irrespective of the presence or absence of Ph. The

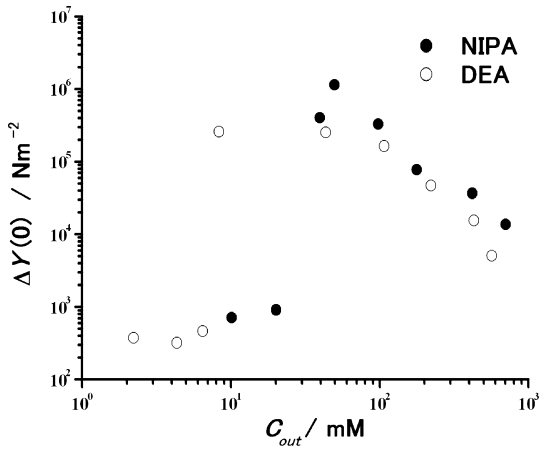

Figure 9. $\Delta Y(0)$ of NIPA and DEA gels as functions of C_{out}. Open and closed circles represent the $\Delta Y(0)$ of the DEA and NIPA gels, respectively.

constraining forces to change r in the cases of the presence and the absence of Ph are different from each other. Nevertheless, Ph has little effect on the r-dependence of *Ye*. This indicates that the conformation entropy of the gel chain, which is an origin to yield the *Ye*, is independent of the type of constrained force and given as a function of r.

It is seen in Figure 7 that the Ph-binding greatly influences the r dependence of *Yi* in the region of r less than 100 μm, where the elastic relaxation modulus, $\Delta Y(t)$ is describable as the power function of t. The $\Delta Y(0)$-values of the NIPA and the DEA gels in the solution with and without Ph are plotted against r as shown in Figure 8. The $\Delta Y(0)$-values of both gels are rather large for $r < 100$ μm and very small for $r > 100$ μm. In the range of $r < 100$ μm, $\Delta Y(t)$ is proportional to the constraint force exerting on the deformed dangling chains, which increases with a decrease in the room for the dangling chains to freely move. Therefore the $\Delta Y(0)$-values of the Ph-containing gel are considered to approximate that of a Ph-free gel having a volume equal to the difference between the volume of the Ph-bound gel and the volume of bound Ph and water molecules hydrated to the B-type bound Ph. As such, the $\Delta Y(0)$ of the Ph-containing gel as a function of the radius corresponding to the hypothetical volume mentioned above, $r' = r[\{ W_g - 94\beta - 18(N_{H_2O} - N^0_{H_2O})\}/W_g]^{1/3}$, should be the same as the $\Delta Y(0)$ of the Ph-free gel as a function of r. Here, $N^0_{H_2O}$ is the minimum value of N_{H_2O} shown in Figure 5 ($N^0_{H_2O} = 2.8$ for NIPA and 1.5 for DEA), and the densities of the gel chains and the bound Ph are assumed to be 1 for simplicity. The $\Delta Y(0)$ of both gels as a function of V' closely matches the $\Delta Y(0)$ of the Ph-free gel as a function of r for $r < 100$ μm, as shown in Figure 8. This could corroborate that $\Delta Y(0)$ is the modulus of dangling chains in the space constrained by the bound Ph, hydrophobic hydration water of Ph, and the cross-linked chains of the gel network.

The decrease in $\Delta Y(0)$ with r as mentioned above might be related to β or N_{H_2O}, which cannot be measured for the gel set in the apparatus for the tensile force measurement. The β and N_{H_2O} values are obtained as functions of C_{out} as shown in Figures 4 and 5. The relation between $\Delta Y(0)$ and C_{out} instead of β and N_{H_2O} is examined in the present study. The $\Delta Y(0)$-values plotted against C_{out} are shown in Figure 9. The decrease in $\Delta Y(0)$-values for both of the NIPA and DEA gels starts at C_{out} of about 100 mM, where the N_{H_2O} values start to increase with C_{out} as shown in Figure 5. The β-values, however, increase monotonically with C_{out} at C_{out} above C_{tr} as shown in Figure 4. These facts indicate that the free water molecules in the collapsed gel act as a lubricant between dangling and cross-link chains.

5. Conclusions

The effects of phenol-binding (Ph-binding) on the Young's moduli and volumes of *N*-isopropylacrylamide (NIPA) and *N*, *N*-diethylacrylamide (DEA) hydrogels were investigated. The Ph-binding affects the behavior of volume change, the relaxation moduli, and the nanostructures of NIPA and DEA gels as follows;

1) Ph-binding induces discontinuous changes in the volumes and moduli of NIPA and DEA gels.

2) Ph-binding causes reswelling of NIPA and DEA gels.

3) The relaxation moduli of shrunken gels can be described by a power function of time.

4) The magnitude of the relaxation moduli can be described as a function of the volume that is not occupied by bound Ph or hydrated water in the gel.

5) A few monomeric units that are bound by the Ph are segregated and form the particle as indicated by the SAXS spectrum.

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References and Notes

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