PHYSICAL CHEMISTRY OF POLYELECTROLYTES

edited by

Tsetska Radeva

Bulgarian Academy of Sciences
Sofia, Bulgaria

MARCEL DEKKER, INC. NEW YORK · BASEL

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Phase Transitions in Polyelectrolyte Gels

ETSUO KOKUFUTA University of Tsukuba, Tsukuba, Ibaraki, Japan

I. INTRODUCTION

The swelling of gels, such as that observed when rubber is placed in benzene, has long been a well-known phenomenon. As early as 1948, Vermaas and Hermans [1] studied the behavior of lightly cross-linked polymer chain networks with ionic charges, i.e., polyelectrolyte gels. Flory [2] and Katchalsky [3], in collaboration with their colleagues, also made great contributions to theories and experiments in the fields of ionic and neutral gels. In early studies by these pioneers, however, little attention was paid to the existence of a critical endpoint in the phase equilibria, although in 1968 Dusek and Patterson [4] published a theoretical paper on this subject. The earliest report of the phase transition in a gel was in 1978 by Tanaka [5], who discovered a discontinuous volume collapse of poly(acrylamide) (PAAm) gels in acetone–water mixtures when varying the temperature or the composition of the mixture. This phenomenon is now called "volume-phase transition" (or simply "phase transition") of gels and is observed in many gel systems consisting of synthetic and natural polymers. The phase transition is accompanied by reversible, discontinuous (or in some cases, continuous) volume changes, often as large as several hundred times, in response to small variations in the solution conditions surrounding a gel. Variables that trigger the transition include solvent composition [5–11], pH [6], ion concentration [12], temperature [5,10,13], and small electric fields [14,15]. (Related literature published in the 1990s will be cited later as the need arises, since a number of studies focused on stimulus-sensitive polymer gels after the publication of these pioneering works.)

When setting a limit to the phase transitions in polyelectrolyte gels, two studies by Tanaka et al. are of historical importance; these were done with ionic gels of partially hydrolyzed PAAm [6] and copolymer of acrylic acid

(AAc) with *N*-isopropylacrylamide (NIPA) [13]. The former [6] is the earliest paper on ionic gel transition, demonstrating that the introduction of charges into the network chain results in an increase in the gel volume at transition as well as a change in the transition threshold. Further demonstrated in the latter [13] is the ionization effect on the transition temperature; that is, a rise in the temperature leading to a transition when increasing the charge density of NIPA-AAc copolymer gels. In particular in the NIPA-based ionic gel system, a discontinuous volume change was observed with a small variation in temperature, as well as in other solution conditions such as pH and salt concentration. Thus, the polyelectrolyte gel of this sort is called a "thermo-shrinking" or "temperature-sensitive" gel, the properties of which have extensively been studied from both fundamental and technological standpoints (e.g., see Ref. 16).

In the realm of transition theories, as will be seen in Sec. II, all of the descriptions basically contain three terms reflecting the changes in free energies of mixing, elasticity, and osmotic effects. While the expressions of the mixing and elastic contributions to the free energy vary from theory to theory, there is little disagreement on the description of osmotic effects that exist when there is ionic charge in the system. In other words, Donnan equilibria are consistently used in the transition theories for polyelectrolyte gels. Nevertheless, recent and advanced views on molecular grounds have posed the question whether the osmotic effect plays the major role in the ionic gel transition.

Consequently, this chapter will aim to look at the nature of phase transitions in polyelectrolyte gels, so that the theories (Sec. II) as well as the considerations at the molecular level (Sec. III) will be described first. After that, we will discuss in full the molecular mechanism of the ionic gel transition on the basis of experimental results, most of which are taken from the author's publications [17–33].

In this chapter, however, the author does not take up the applications of polyelectrolyte gels that have been appearing in the literature with increasing frequency. We hope that a better understanding of the phase transitions in polyelectrolyte gels can contribute to progress in the technology and engineering of gels.

II. THEORIES

A. Flory's Formula

In order to account for the phase transition of an ionic gel theoretically, it is convenient to imagine that a close analogy exists between swelling equilibrium and osmotic equilibrium. The elastic reaction of the network struc-

ture can be interpreted as a pressure acting on the solution, or swollen gel. In the equilibrium state this pressure is sufficient to increase the chemical potential of the solvent in the solution so that it equals that of the excess solvent surrounding the swollen gel. Thus the network structure performs the multiple role of solute, osmotic membrane, and pressure-generating device.

According to the above considerations, a thermodynamic framework has long existed for interpreting swelling equilibria of ionic as well as nonionic gels in terms of their osmotic pressures. Although our greatest concern for the present should be how to describe theoretically the osmotic pressure (Π) of a gel, let us start with Flory's formula [2] in which Π is written as a sum of three contributions:

$$\Pi = \Pi_{mix} + \Pi_{elas} + \Pi_{ion} \tag{1}$$

Here, Π_{mix} represents the contribution from polymer–solvent mixing, Π_{elas} is the elastic contribution due to deforming the network chains from their reference state, and Π_{ion} is the contribution arising from the difference in mobile ion concentrations. Using the well-known polymer–solution theory of Flory and Huggins (i.e., mean field theory), Π_{mix} can be described as

$$\Pi_{mix} = -\frac{RT}{v_s}[\varphi + \ln(1 - \varphi) + \chi\varphi^2] \tag{2}$$

where R is the gas constant, T is the absolute temperature, v_s is the molar volume of the solvent, φ is the volume fraction of the network chains, and χ is the polymer-solvent interaction parameter. For Π_{elas}, Flory's description (the earliest theory [2]) can be given by

$$\Pi_{elas} = RT\left(\frac{\nu_e}{V_0}\right)\left[\frac{V_0}{2V} - \left(\frac{V_0}{V}\right)^{1/3}\right] \tag{3}$$

where ν_e represents the mole number of effective chains in the network, V_0 is the volume of the "unswollen" polymer, and V is the volume of the swollen gel. It should be noted that the following assumptions are made for Eq. 3: (1) The network is at first formed via cross-linking of the unswollen polymer at volume V_0. (2) Subsequently, it isotropically swells to a volume V with a diluent. (3) This swelling occurs without an appreciable change in the total volume of the system (polymer plus solvent). As a result, the term V_0/V in Eq. 3 should be equivalent with φ in Eq. 2; i.e., $\varphi \sim V_0/V$.

If the polymer chains making up the network do not contain ionizable groups, the phase transition may be accounted for by a combination of Eqs. 2 and 3. For ionic gels, however, we must consider the concentration of "mobile" ions, which would always be greater in the gel than the outside because of the attractive power of the fixed charges. Consequently, the os-

motic pressure of the solution inside could exceed that of the external solution. Then the expansive force may be equal to this difference in osmotic pressures for the two solutions. For a cationic gel, Flory described Π_{ion} as

$$\Pi_{ion} = RT\left[\frac{iC_p}{Z_-} - \nu_{\pm}(C_s^* - C_s)\right] \tag{4}$$

where i denotes the number of electronic charges per polymer unit in a polyelectrolyte gel, Z_- is the valency of anion, C_p is the molar concentration of polymer units, $\nu_{\pm}$ is the number of total ions, and C_s^* and C_s are the molar concentration of salts within a gel and in the surrounding medium, respectively. It is to be emphasized that Eq. 4 holds under conditions where the gel system is sufficiently diluted with the solvent.

B. Modifications of Flory's Formula by Tanaka

Tanaka and his coworkers have used Flory's formula with several modifications to understand a discrete phase transition in ionic gels. First, the term V_0/V in Eq. 3 was replaced by the term φ/φ_0 (but not by φ). Here, φ_0 was defined as the volume fraction of the network on condition that the constituent polymer chains have random-walk configurations [5]. Flory assumed that the "dry" gel (in other words, the network formed by cross-linking of the unswollen polymer at volume V_0) satisfies the condition of no polymer interactions; i.e., $\varphi_0 \sim 1$. However, Tanaka discovered a collapse of covalently cross-linked PAAm gels in an acetone–water mixture; therefore he claimed that the elastic term is generally not a function simply of V_0/V $(=\varphi)$ as was given by Flory, but of φ/φ_0. The reason is that for a gel with $\varphi_0 \sim 1$ there is no possibility for volume collapse.

Tanaka also modified Eq. 4 by assuming that $(c_s^* - c_s) \sim 0$ (see Ref. 6):

$$\Pi_{ion} = \nu fkT\left(\frac{\varphi}{\varphi_0}\right) \tag{4'}$$

Here, f is the number of counterions per effective chain in the network, N_A is Avogadro's number, and ν $(\sim \nu_e N_A/V_0)$ is the number of effective chains per unit volume at $\varphi = \varphi_0$. In addition, χ in Eq. 2 was replaced by $\Delta F/kT$, where ΔF is the free-energy decrease associated with the formation of a contact between polymer segments. As a result, Tanaka et al. obtained Eq. 5 for an ionic gel:

$$\Pi = -\frac{N_A kT}{v_s}\left[\varphi + \ln(1-\varphi) + \frac{\Delta F}{2kT}\varphi^2\right] + \nu kT\left[\frac{\varphi}{2\varphi_0} - \left(\frac{\varphi}{\varphi_0}\right)^{1/3}\right] + \nu fkT\left(\frac{\varphi}{\varphi_0}\right) \tag{5}$$

The osmotic pressure of a gel must be zero for the gel to be in equilibrium

with the surrounding solvent. Zero osmotic pressure is also necessary for the free energy of the gel (F_g) to be minimized, since $\Pi = -\partial F_g/\partial V$, where V is the volume of the gel and $V \propto \varphi_0/\varphi$. Using Eq. 5, such conditions may be expressed as

$$\tau \equiv 1 - \frac{\Delta F}{kT} = \frac{\nu v_s}{N_A \varphi^2}\left[(2f+1)\left(\frac{\varphi}{\varphi_0}\right) - 2\left(\frac{\varphi}{\varphi_0}\right)^{1/3}\right] + 1 + \frac{\varphi}{2} + \frac{2\ln(1-\varphi)}{\varphi^2} \tag{6}$$

where the parameter τ (i.e., $1 - \Delta F/kT$) is called the reduced temperature, which changes with temperature and solvent composition. The equation then determines the equilibrium network concentration as a function of τ. For certain values of τ, however, Eq. 6 is satisfied by three values of φ, corresponding to two minima and one maximum of the free energy. The value of φ corresponding to the lower minimum represents the equilibrium value. A discrete volume transition occurs when the two free-energy minima have the same value.

Figure 1 shows typical swelling curves calculated for an ionic gel as a function of f. In calculations of the equilibrium swelling ratio (φ/φ_0) by Eq. 6, Tanaka et al. used $\varphi_0 = 0.5$ and $\nu v_s/N_A\varphi_0^3 \sim 10$ (i.e., $\nu v_s = 7.5 \times 10^{24}$) [5]. The former value was obtained by assuming that monomers and cross-linkers would be polymerized during gelation in a random walk fashion to form a network, while the latter was chosen so that the theoretical curves agree with the experimental data. As can be seen from Figure 1, an increase in f causes a drastic change in the collapse size at the transition. Therefore it can be predicted that ionic gels undergo a phase transition. As will be mentioned in the latter section, at present there are many experiments demonstrating the phase transitions of ionic gels.

C. Arguments Against Flory's Formula and Other Descriptions for the Osmotic Pressures

After the publications by Tanaka et al. [5,6] concerning the phase transitions in neutral and ionic gels, uses of Eqs. 2–4 to describe Π of Eq. 1 have been criticized by several authors. Before looking at these criticisms, however, it must be kept in mind that there is an argument about the description of Π as a sum of Π_{mix}, Π_{elas} and Π_{ion}. For this treatment, one must assume that the various contributions to the free energy of swelling are additive; in other words, the partition function for swelling can be factored into independent contributions. While this assumption has been questioned [34,35], there exists (as yet) no tractable alternative for describing swelling equilibria.

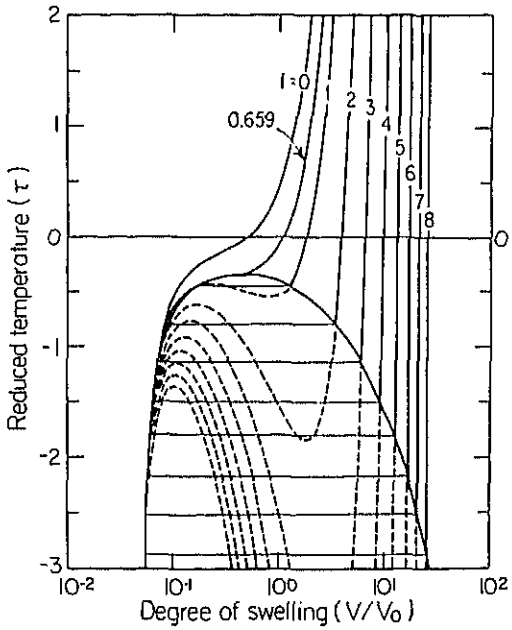


FIG. 1 Relationship between equilibrium degree of swelling (V/V_0; i.e., $-\varphi_0/\varphi$) and reduced temperature at various numbers of ionized groups per chain. Equation 6 with $\varphi_0 = 0.5$ and $\nu v_s/N_A\varphi_0^3 \sim 10$ was used for the calculation as made by Tanaka et al. [6]. (From Ref. 6 with several modifications.)

Table 1 summarizes the essential points of the criticism. First, the use of Flory–Huggins theory becomes the focus of criticism because this is based on a random-mixing lattice model, in which the lattice is assumed to have no holes; thus it is incompressible. Second, the earliest Flory (or Flory–Rehner) theory [2] for rubber elasticity does not hold when the gel is swollen, because the theory unrealistically assumes that the distributions of chains are Gaussian. Furthermore, the model does not account for the chains being finite or taking up space. Third, a simple assumption for osmotic pressure arising from counterions is not realistic, because electrostatic interactions between the fixed charges are neglected. Also neglected is counterion condensation.

Prausnitz and coworkers [36] have developed a theory based on hydrogen bonds in a lattice that permits holes and thus compressibility. This overcomes the deficiencies of Flory–Huggins theory; however, Guassian chains are still assumed, and therefore it is difficult to fit experimental results with a single set of parameters over the entire range of swelling. However, the theory

TABLE 1 Typical Examples for Criticisms to Three Terms of Flory's Formula and Alternative Proposals

Terms	Criticized point	Alternative proposal	Author
Mixing term (Π_{mix})	random-mixing lattice model (Flory–Huggins theory)	quasi-chemical lattice model	Prausnitz et al. [36]
		virial-type expression (for thermoshrinking gels)	Saito et al. [42]
		lattice-fluid model (by Sanchez and Lacombe)	Cussler et al. [40]
Elastic term (Π_{elas})	the earliest elasticity mode based on Gaussian chain distributions (Flory–Rehner and Flory theories)	improved elasticity model based on "constrained junction" theory	Prausnitz et al. [36]
		an elastic expression that accounts for the limits of elongation	Saito et al. [42]
Osmotic term (Π_{ion})	neglecting of charge–charge interaction as well as counterion condensation	Debye–Hückel model (Hasa–Ilavsky–Dusek theory)	Dusek et al. [44]

does correctly predict discontinuous transitions for nonionic gels. In a subsequent paper [37,38] where they discussed results with charged gels, the Prausnitz research group introduced an improved elasticity term based on constrained junctions. This theory actually predicts ionized gels to have discontinuous transitions as well; this is in accord with the Tanaka group's experiments, but not with the Prausnitz group's own observations [39].

Cussler and coresearchers [40] overcame the deficiency due to the use of a lattice-based mixing term; instead of an equation of state their approach applied also permits compressibility. They derived an interaction energy from the various cohesive energy densities in the system that fits the experimental results. In addition, they noted that neither Tanaka's [12] nor Prausnitz's [36] approach will predict pressure dependencies of gel swelling as they have experimentally observed [41]. But their own model, although sensitive to the fact that gels swell under pressure in an attempt to increase entropy, overpredicts this effect. They suggest they can compensate for this result by introducing specific hydrogen bonding interactions into their system.

By focusing on the thermal collapse of NIPA gels, containing as well as not containing ionic charges, Saito and coworkers [42] attempted to develop a phase transition theory. They ignored most of the work so far cited and assumed that the mixing term is a viral volume interaction. An elastic expression that accounts for the limits of elongation was also incorporated. However, in sharp contrast to the works above, Saito et al. incorporated the specific term due to hydrophobic interaction into Eq. 1. Then they assumed that hydrophobic interaction gives rise to physical cross-linking points in the chains that comprise the gel. From the Nemēthy–Sheraga study [43] on the temperature dependence of the hydrophobic interaction between molecules in water, the free energy change ($\Delta G_{\text{hydrophobic}}$) is given by

$$\Delta G_{\text{hydrophobic}} = C_a + C_b T + C_c T^2 \tag{7}$$

where C_a, C_b and C_c are system-dependent parameters. Taking this into account, Saito's group obtained the free energy equation for "thermo-shrinking" gels. This predicts continuous transitions that become discontinuous upon ionization, yet calling for several adjustable parameters.

D. Descriptions for the Fixed Charge Interaction

In the early 1950s, Katchalsky and his coworkers [3] studied the swelling behavior of polyelectrolyte gels consisting of cross-linked poly(methacrylic acid) (PMAAc) in several aqueous salt solutions as a function of the neutralization degree. Then they argued that the Donnan distribution could not give even a rough approximation and proposed a theory based on the random coil model in which the charge interaction along a chain was calculated by

Debye–Hückel theory. This was taken over by Hasa–Ilavsky–Dusek (HID) theory [44] in which a modification of the elastic term was made by considering the influence of charges on the deformation of the network. Although HID theory has not yet been applied to account for the phase transition in ionic gels, Ilavsky et al. [45–48] as well as Konak and Bansil [49] performed several experiments to examine this theory in comparison with the swelling and elastic data for PMAAc gels and related copolymer gels.

Recently, Tong and Liu [50] also attempted to examine carefully the HID theory with their swelling experiments for copolymer gels of *N*,*N*-dimethylacrylamide (DMAAm) and 2-acrylamide-2-methylpropanesulfonic acid (AMPS). They used Eqs. 8 and 9 for the Π of Eq. 1, which was obtained according to the HID theory:

$$\Pi = -\frac{RT}{v_s}[\ln(1-\varphi)+\varphi+\chi\varphi^2] - RT\varphi_0\left[\varphi^{1/3}-\frac{\varphi}{2}+\frac{3}{5n\varphi^{1/3}}+\frac{99}{175n^2\varphi^{1/3}}+\frac{513}{875n^3\varphi^{5/3}}\right] + \frac{RTf_m\rho\varphi}{M_0} - \frac{N_A\nu Z^2e^2f_m^2}{3D\varphi_0\langle R_0^2\rangle^{1/2}\varphi^{4/3}}\left[\frac{2.5A}{1+A}-\ln(1-A)\right] \tag{8}$$

and

$$A = \left[\frac{9DkTM_0}{\pi N_A e^2\langle R_0^2\rangle f_m\rho}\right]^{1/2}\varphi^{-5/6} \tag{9}$$

Here, f_m is the mole fraction of ionic monomer unit (i.e., AMPS), ρ the density of the dry gel, Z the degree of polymerization of the chain in the network, e the electronic charge, D the dielectric constant of solvent, $\langle R_0^2\rangle$ the mean-square end-to-end distance, and M_0 the average molecular weight of copolymer unit (i.e., $M_0 \sim f_m M_{ANPS} + (1-f_m)M_{DMAAm}$, where M_{ANPS} and M_{DMAAm} are the molecular weight of AMPS and DMAAm, respectively). It is clear that Eq. 8 includes the term due to the electrostatic interaction between the fixed charges, which was ignored in Eq. 5 (Flory's equation). In addition, the elastic term in Eq. 5 was modified. Therefore, one may expect that the prediction of swelling degree ($1/\varphi$) as a function of f_m from the HID theory would be better than that from the Flory theory. However, it was concluded that neither the Flory nor the HID theory can provide a reasonable approach for predicting the swelling degree for the polyelectrolyte gel of this sort.

In conclusion, it appears clear that a theoretical explanation of the phase transition of gels, whether as nonionic gels or as polyelectrolyte gels, is far from complete. Better experimental characterization of the networks needs to be done so more realistic elastic effects can be fitted. Mixing terms that

account for nonrandom distributions of molecules need to be applied. As for the nature of the specific interaction, the general concept of hydrogen bonding versus what exactly are hydrophobic interactions is still being debated. We may hope that data from experiments covering a wide range can aid in resolving the debate.

III. UNDERSTANDINGS ON MOLECULAR GROUNDS

We have seen in the previous section that there is much debate about a theoretical explanation of the phase transition of gels. In experiments with a variety of gel systems including ionic gels, on the other hand, a large number of data have been accumulated. Thus it would be interesting to draw a generalized perspective about the phase transition from experimental data. This may be achieved through classification, as well as through explanation on molecular grounds, of experimental swelling curves. Taking this into account, we have tried to present a "unified" model of gel transitions, with an addition of an experimental result from which one may see the role of hydrogen bonding in the phase transition [17]. Then we accounted for the phase transition by hypothesizing a balance between the repulsive and attractive forces within the cross-linked polymers in the networks, which arise from a combination of four intermolecular forces: ionic, hydrophobic, van der Waals, and hydrogen bonding. When a repulsive force, usually electrostatic in nature, overcomes an attractive force such as hydrogen bonding or the hydrophobic interaction between the network chains, gel volume should increase discontinuously in some cases and continuously in others. The variables triggering the transition influence these intermolecular forces and thereby the balanced state of the attractive and repulsive forces.

Because our paper (Ref. 17) included several mistakes in citing references as well as in giving an example for a gel system in which the van der Waals force becomes dominant as the attractive force, Schild [16] criticized the proposed model itself as too idealistic. As we will learn in the following sections, however, this model serves as a good guide for discussing what is the main factor to swell or to collapse a gel. This section discusses the phase transition in ionic gels at the molecular level. For this purpose, the previously proposed diagram has been corrected (see Figure 2). In this correction, the following are taken into consideration: (1) Three diagrams deal with polyelectrolyte gel systems but not with all the gel systems. (2) The variable is thus restricted to factors (conditions surrounding the gel) leading to a change in the volume of ionic gels. (3) No attention is paid to whether the gel undergoes discontinuous or continuous transition (the model makes no mention of this subject).

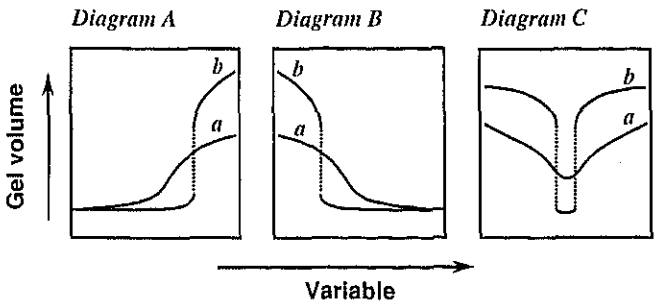


FIG. 2 Universal classification of polyelectrolyte gel transitions. Pictured in expectations upon intermolecular interaction mechanism are changes in the volume of slightly ionized (a) and highly ionized gels (b) with an optional variable such as pH, temperature, and fraction of either water or other solvent in their mixtures.

Let us discuss each of the attractive forces that maintain a gel in a collapsed state. In general, the energy (E) of the intermolecular attractive forces varies as the inverse of the first to sixth power of the intermolecular distance (r); $E \propto (1/r^n)$. For the Coulomb force, E is given by $-e^2/Dr$ (e, the electronic charge; D, the dielectric constant) so that $n \sim 6$. When $n \sim 6$, the intermolecular force is frequently called the van der Waals force. Although there is a difference of several angstroms between the maximum and the minimum distance, the equilibrium ranges from 3 to 5 Å with $E \sim 2$ to 10 kcal/mol.

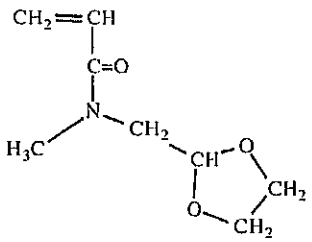
The hydrogen bond can be considered electrostatic or ionic in character, since the classical concepts of chemical bonding allow hydrogen to form only one covalent bond. This model does not, however, account for all the properties of the hydrogen bond; it is appealing to consider the bond covalent in some cases. For example, the distance of a hydrogen bond such as —H—O···O— (1 Å for O—H and 1.8 Å for H···O) is smaller than the van der Waals radius (2.6 Å) between H and O atoms.

The hydrophobic interaction between nonpolar molecules in water or aqueous solvents must be defined in a different category from the other three intermolecular attractive forces. When organic compounds containing nonpolar residues are introduced into an aqueous solution, large positive deviations from ideality are observed. However, whereas poor solvent properties are normally caused by an unfavorable heat of mixing, the solutions of materials such as aliphatic hydrocarbons in water have frequently been found to be exothermic. We are then left with the conclusion that the poor solubility of nonpolar solutions in water is a consequence of large negative excess entropy of mixing. A detailed consideration of these findings was first undertaken in a pioneering investigation of Frank and Evans [51]. They pointed

out that the negative ΔH and the negative ΔS may be rationalized by assuming that an ice-like structure is stabilized in the neighborhood of nonpolar solutes—thus the heat evolved may be thought of as due to the latent heat of freezing of "icebergs" which represent regions of crystalline order and whose formation, therefore, leads to a loss of entropy. The tendency of nonpolar solutes to aggregate in aqueous media reduces the number of water molecules in their immediate vicinity and leads to "icebergs melting." This provides the driving force towards such aggregation and has been referred to as the "hydrophocib bond" by Kauzmann [52].

Now we will return to Figure 2 and try to account for gel volume transitions. When choosing pH as a variable, we may assign Figs. 2A and 2B to polyelectrolyte gels whose ionizable groups are weakly acidic and basic, respectively. Assigned to Fig. 2C is a polyampholite gel with both weak acid and weak base as the ionizable groups. The pH-induced deprotonation (e.g., $\sim COOH \rightarrow \sim COO^-$) and protonation (e.g., $\sim NH_2 \rightarrow \sim NH_3^+$) may strengthen Coulomb repulsion forces between the fixed charges; thus, we may observe the gel swelling with increasing pH for acidic gels but with decreasing pH for basic gels. In order to understand the gel collapse accompanying with the release of a large amount of solvents, however, it is convenient for us to assume the attractive force(s). Then we may assign as an attractive force the Coulomb force in the collapse of an ampholite gel (e.g., curve a in Fig. 2C); the gel collapse would become more dramatic when incorporating another attractive force such as the hydrogen bonding and hydrophobic interaction (curve b in Fig. 2C). In cases of other polyelectrolyte gels having charges of the same sign, we also have to consider the role of attractive forces in the gel collapse. For example, NIPA-based hydrogels with COOH or NH_2 groups shrink gradually through the elimination of charges with pH but do not undergo a collapse transition such as curve b in Figs. 2A and 2B at temperatures at which hydrophobic interaction does not become dominant (see Sec. V).

When temperature is a variable, we may clearly observe a transition in the existence of attractive forces. For such cases, seeing the hydrophobic interaction as the attractive force makes it possible for us to interpret the volume collapse with increasing temperature. If the hydrogen bonding is assumed to be an attractive force, an increase in temperature would result in the swelling. A good example for supporting this has recently observed in a neutral (but not ionic) gel [29]; *N*-(1,3-dioxolan-2-ylmethyl)-*N*-methylacrylamide (DIOMMA) gels that swell in alcohols but shrink in pure water by heating. This opposite trend in the thermal properties in water and alcohols was discussed in terms of polymer–polymer, polymer–solvent, and solvent–solvent interactions. More details of Fig. 2 will be discussed in Sec. V through a comparison with experimental results.



DIOMMA

IV. EXPERIMENTAL METHODS

Before discussing the swelling curves of several polyelectrolyte gels in connection with the phase transition, it would be convenient to provide information about the methods for preparing and characterizing the gels. This section aims at giving a general outline of experimental methods used in Sec. V.

A. Preparation of Gels

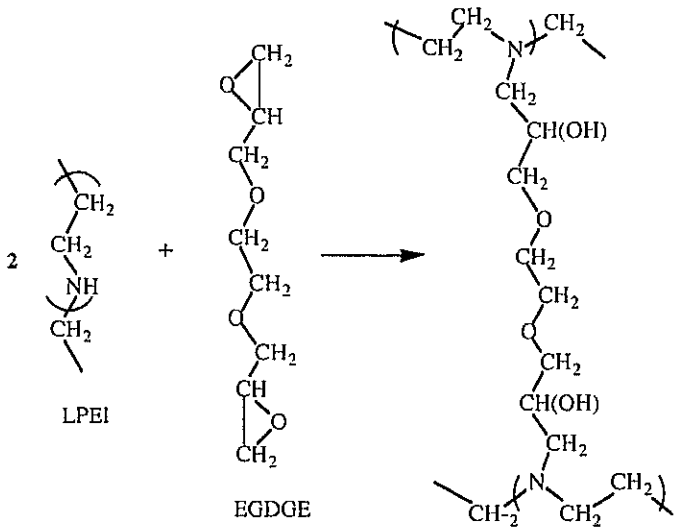
There are two ways of preparing gels: the polymerization of monomers in the presence of a suitable cross-linking agent, and the chemical or physical cross-linking of polymers. The former is more common than the latter; thus, a number of studies have prepared gels using polymerization methods with monomers, among which an aqueous redox polymerization system initiated by a pair of ammonium persulfate (APS) and *N,N,N′,N′*-tetramethylethylenediamin (TMED) has been frequently employed. For forming gels from polyelectrolytes (i.e., polymers), a few instances have been reported; for example, the cross-linking of linear poly(ethyleneimine) (LPEI) with ethylene glycol diglycidyl ether (EGDGE) [27], as well as of copolymers of acrylic acid (AAc) and *N*-substituted alkylacrylamide in water by γ-rays from a ^{60}Co source [22,28].

Other than the above two ways, we may employ chemical and physical techniques for converting a neutral gel into an ionic gel. For example, a neutral gel consisting of PAAm chains crosslinked with *N,N′*-methylenebis(acrylamide) (MBA) converts into an ionic gel with COOH groups via alkaline hydrolysis of the AAm residues [6]. As a physical converting technique, the binding of ionic surfactants [20,24,26,30] to neutral gels such as NIPA gel is useful. However, these techniques are limited to special cases; thus we will look about for the essential point in the preparations of LPEI gels [27] as well as NIPA gels [28] with randomly copolymerized AAc residues or with polymer chains of AAc (PAAc), both of which were obtained by cross-linking of the polymers. Also mentioned for this purpose is

the preparation of submicrometer-sized polyelectrolyte gel particles based on aqueous redox polymerization [32].

1. Cross-Linking of LPEI with EGDGE

The cross-linking reaction can be written as



Thus we may control the degree of cross-linking by means of the molar ratio of the epoxy group to the imino group. The gelation can be performed by incubation of aqueous polymer solutions under suitable conditions; for example, at pH 8 and at 60°C.

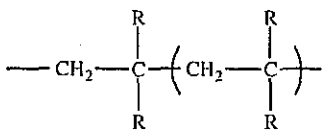
When the preparation was carried out using a reaction vessel (e.g., a test tube) into which glass capillaries with tiny inner diameters (0.1–1 mm) had previously been inserted, two types of gel samples were available from the same preparation: very fine cylindrical gels and powdered gels. The former was then obtained from a fine gel rod that can be taken out of the capillary and cut into cylinders several millimeters in length. The latter was from the gel mass taken out of the vessel together with the capillaries, by grinding and passing through a screen with a fine mesh size. Such fine gel samples (especially cylindrical gels) provide accurate measurements of the swelling degree because of a rapid attainment of swelling equilibrium (the rate for changes in gel volume is inversely proportional to the square of the smallest dimension of the gel [53]).

Purification of gel samples is easier than that of polymers, and it can be performed by repeated swelling and shrinking procedures using appropriate solvents. It is to be emphasized that we must confirm to fully eliminate

impurities due to unreacted cross-linkers as well as un-cross-linked polymers. A combination of total organic carbon (TOC) analysis and conductivity measurement are effective not only for the present case but also for many polyelectrolyte gels.

2. Cross-linking of Polymers in Water by γ-Rays

This method is based on the direct and indirect formations of polymer radicals during γ-ray irradiation. The indirect formation of polymer radicals is mainly due to the $^{\cdot}H$ and $^{\cdot}OH$ radicals arising from water molecules; thus the irradiation method cannot be applied to the polymers when unstable and degrading polymer radicals would be formed. For vinyl polymers whose structure is shown as



it is generally believed that the cross-linking would take place when one of the two R groups in the repeating unit is hydrogen, while polymers such as poly(methacrylic acid) with two R groups other than hydrogen are degraded during irradiation.

For copolymers of AAc with NIPA, therefore, γ-ray irradiation was successfully employed in preparing polyelectrolyte gels. Using an aqueous solution containing the homopolymer of AAc (PAAc) as well as of NIPA (PNIPA), we also succeeded in forming an ionic gel with the network in which the COOH groups are localized along a PAAc chain, but their content is the same as that of the gel from the random copolymer of AAc and NIPA. Typical preparation procedures of the ionic gel with an inhomogeneous distribution of the COOH groups are as follows: (1) PNIPA (0.791 g) and PAAc (50.4 mg) were dissolved in 10 mL of distilled water; (2) the aqueous polymer solution was transferred into a test tube in which glass capillaries had previously been inserted; (3) the test tube was sealed after degassing the solution under a vacuum, and finally (4) the irradiation was performed at ca. 1°C for 12.8 h at a dose rate of 0.156 Mrad/h using γ-rays from a ^{60}Co source.

3. Preparation of Submicron Gel Particles

Ionic microgel particles play an important part in studies of the phase transition, as we will learn in Sec. V. In cases of NIPA-based polymerization systems, submicron-sized polyelectrolyte gel particles can easily be prepared using the usual synthetic technique of aqueous redox polymerization. Different polymerization media were then employed: surfactant-containing wa-

ter [54,63,64] surfactant-free water [55–59,62], and water suspended in oils [53,60,61]. Usually, APS and potassium persulfate (KPS) were employed as initiators and MBA as the cross-linker. In general, the diameters of the gel particles (<1 μm) prepared in the presence of surfactants were smaller than those (>1 μm) obtained from surfactant-free systems. All of the preparations were found to swell or deswell with changes in temperature; such temperature-sensitive swelling–deswelling characteristics were similar to those of bulk NIPA gels in cylindrical, cubic, and other forms.

In order to incorporate ionic groups to the NIPA-based microgels, there are three methods. Hirose et al. [61] have demonstrated a suitable method in which neutral gel beads consisting of MBA-crosslinked NIPA and *N*-(acryloxy)succinimide (AOSI) chains were initially prepared using a water medium suspended in hexane, and subsequently converted into a polyelectrolyte gel with COONa by alkaline hydrolysis. The second method for preparing ionic NIPA latexes was reported by Pelton et al. [54,55]. They conducted an aqueous redox polymerization of NIPA and MBA without ionic monomers in the absence and the presence of surfactant using KPS or azobis(isobuthylamidine) hydrochloride (AIBA·HCl) as an initiator. Since the ionizable groups originating from the initiator may covalently bind to many of the end groups of the NIPA chains within the network during the polymerization, they succeeded in preparing anionic and cationic latexes by use of the KPS and the AIBA·HCl initiator, respectively. Aqueous redox copolymerizations (third method) of NIPA with ionic monomers such as MAAc in the presence of surfactant were also employed by Tenhu and Lowe [63] and Chu and Zhou [64]. While the choice of method depends on the purpose for which the polyelectrolyte gel particles will be used, the inverse suspension polymerization employed by Hirose et al. [61] generally requires great skill to obtain particles with good reproducibilities regarding size and distribution. In Pelton and Chibante's method [55] it is difficult to introduce a large amount of charges into the gel beads from the initiator; this problem has already been pointed out by Pelton in another publication [54]. Thus, Ito et al. [32] have used the third method to prepare submicron microgel particles composed of MBA-cross-linked NIPA network into which different amounts of AAc or 1-vinylimidazole (VI) were incorporated. They were able to control the AAc and VI contents of aqueous monomer solutions (pregel solutions) within 0 to 30 mol%; therefore the particles obtained exhibit very large diameter changes in response not only to temperature but also to the treatment with acid and base.

B. Swelling Measurements

The swelling ratio for a gel can be determined on the basis of either size or weight of the gel. At a glance, one does not feel difficulty in performing

these measurements. However, the data include a serious error which is more than 10% in some cases, especially in the measurements based on gel weight. In our experience this seems to be mainly due to a slow attainment of swelling equilibrium (a cylindrical gel with 1 mm diameter and 3 mm length needs more than a week to attain a swelling equilibrium at transition). As mentioned above, use of fine gel samples could facilitate an accurate measurement of equilibrated volume or size of the gel.

Figure 3 shows our own setup used in the measurements of the swelling ratio under different pH conditions as well as concentrations and kinds of ionic compounds such as salts and surfactants. The instrument consists of four different parts: an aqueous phase supply system (APSS) equipped with a pH meter, a conductivity meter, a TOC sampling port, and an inlet of salts or surfactants; a microscope with a CCD camera and an image-analyzer; a water-jacketed separable measuring cell with glass meshes; and a temperature control system (TCS). A fine gel sample was inserted into the glass cell, and an aqueous solution with the desired pH and salt (or surfactant) concentration was continuously supplied around the gel sample from the APSS with the Ar gas pressure. The salt or surfactant concentration was accurately regulated by means of conductmetric measurements or TOC analyses (at high surfactant concentration ranges). Calibration curves showing the

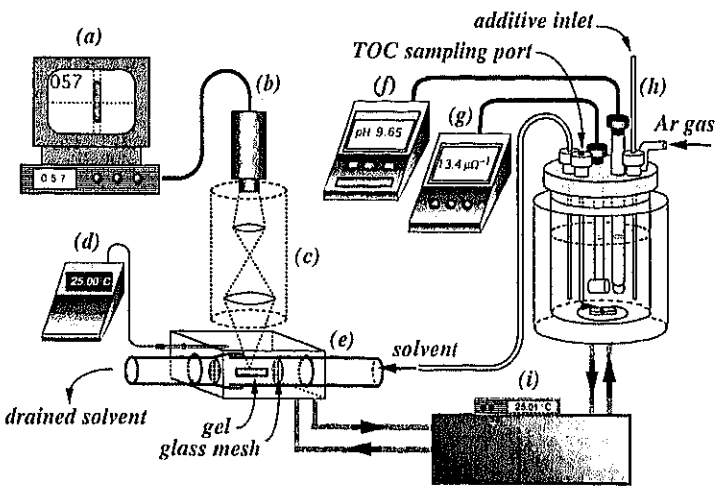


FIG. 3 Setup for the measurements of the swelling ratio: (a) image analyzer; (b) CCD camera; (c) microscope; (d) thermometer; (e) measuring cell; (f) pH meter; (g) conductivity meter; (h) aqueous phase supply system (APSS); (i) temperature control system (TCS). (From Ref. 27.)

changes in conductivity with pH and salt or surfactant concentration as well as the changes in TOC with surfactant concentration were used. The attainment of an equilibrated gel diameter was evaluated by careful measurements in which the pH and/or conductivity was made to fluctuate several times ±3% around a setting used for determining the diameter of the gel sample. The temperature was controlled to within a range of ±0.1°C using TCS with water circulating around both the APSS and the measuring cell.

C. Several Characterization Methods

Most experiments on the phase transition of ionic gels were performed in order to learn how swelling degree varies with variables such as pH and salt concentration; however, the gel sample should be fully characterized before the swelling measurements. The following are important techniques for characterizing the polyelectrolyte gels used in Sec. V.

1. Degree of Cross-linking

A number of studies have reported gel transitions without determination of the degree of cross-linking. In other words, the cross-linking degree was estimated from the amount of cross-linking agents by assuming a complete gelation reaction; however, this is not realistic in many cases.

Elemental analysis, though it is classical, serves as an excellent tool for determining the degree of cross-linking when there are a few differences in the chemical compositions around the cross-linking point in the network. For example, this can be seen from the chemical structure of the LPEI network cross-linked with EGDGE (see Sec. IV.A.1). Taking into account 100 monomer units of the EGDGE-cross-linked LPEI chains (base form), the contents (in w/w%) of nitrogen (C_N) and carbon (C_C) can be expressed as functions of the number of cross-linking points per 100 monomer units (x) by the equations

$$C_N = \frac{100m_N}{M_1(100 - x) + M_2x} \times 100 \tag{10}$$

$$C_C = \frac{[2(100 - x) + 6x]m_C}{M_1(100 - x) + M_2x} \times 100 \tag{11}$$

Here, m_N (14.01) and m_C (12.01), respectively, denote the atomic masses of nitrogen and carbon; M_1 (43.97 for C_2H_5N) and M_2 (138.17 for $C_6H_{12}O_2N$), respectively, are the molar masses of un-cross-linked and cross-linked monomer units of the polymers in the network. Since the elemental analysis for the dry gel gave $C_N = 25.91\%$ and $C_C = 54.71\%$ [27], we can estimate $x \sim 12$ for the gel sample. This value was a third the value estimated from the amount of EGDEG used in gelation.

For gel samples such as NIPA-AAc copolymer gels cross-linked by MBA and γ-rays, however, there is little difference in the chemical composition around the cross-linking point. Therefore the elemental analysis is not helpful. In such a case, one may recall the Flory–Rehner theory. Indeed, several studies have attempted to estimate the effective number of chains in a network (ν_e; see Sec. II.B) or the molecular weight between cross-links ($\bar{M}_c$) through equilibrium swelling experiments. For example, Bray and Merrill [65] made a modification of the Flory–Rehner equation by considering that the cross-links are introduced between polymer chains of number-average molecular weight ($\bar{M}_n$) as the polymer existed in a solution and its volume fraction is φ_r. They obtained

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{\dfrac{\bar{v}}{v_s}[\ln(1-\varphi_s) + \varphi_s + \chi\varphi_s^2]}{\varphi_r\left[\left(\dfrac{\varphi_s}{\varphi_r}\right)^{1/3} - \dfrac{1}{2}\left(\dfrac{\varphi_s}{\varphi_r}\right)\right]} \tag{12}$$

where $\bar{v}$ denotes the specific volume of polymer, and v_s is the molar volume of solvent. In addition, φ_s (volume fraction of swollen gel) and φ_r (volume fraction of relaxed gel) were given by $\varphi_s = V_p/V_{g,s}$ and $\varphi_r = V_p/V_{g,r}$, where V_p, $V_{g,s}$, and $V_{g,r}$ are the volume of the dry polymer, the swollen gel, and the relaxed gel, respectively. For the cross-linking density (ρ_x in mol/cm^3), we may thus obtain

$$\rho_x = \frac{\nu_e}{V_p} = \frac{1}{\bar{v}}\left(\frac{1}{\bar{M}_c} - \frac{2}{\bar{M}_n}\right) = \frac{\dfrac{1}{v_s}[\ln(1-\varphi_s) + \varphi_s + \chi\varphi_s^2]}{\varphi_r\left[\dfrac{1}{2}\left(\dfrac{\varphi_s}{\varphi_r}\right) - \left(\dfrac{\varphi_s}{\varphi_r}\right)^{1/3}\right]} \tag{13}$$

In experiments, V_p, $V_{g,r}$, and $V_{g,s}$ can be determined from the weight of gel samples under dry, relaxed, and swollen states. For this purpose, Peppas et al. [66] have utilized the following relations: $V_{g,r} = (w_{a,r} - w_{h,r})/\rho_h$, $V_{g,s} = (w_{a,s} - w_{h,s})/\rho_h$, and $V_p = \bar{v}w_{a,d}$, where $w_{a,r}$ is weight in air after gelation, $w_{h,r}$ is weight in n-heptane after gelation, $w_{a,s}$ is weight in air after swelling, $w_{h,s}$ is weight in n-heptane after swelling, and $w_{a,d}$ is weight in air after drying.

For determining the cross-linking degree by Eq. 12 or 13, the χ must be known for the polymer. Even if χ is determined for a polymer system, Flory–Rehner theory has been questioned due to the assumption of a Gaussian chain distribution (see Sec. II.C). Thus Peppas et al. [66] have made a modification by introducing the terms $\{1 - (\varphi_s/\varphi_r)^{2/3}/N\}^3$ and $\{1 + (\varphi_s/\varphi_r)^{1/3}/N\}^2$ (where $N = 2M_c/M_0$, and M_0 is the molecular weight of poly-

mer-repeating unit) into the numerator and denominator of Eq. 12, respectively, when they attempted to determine ρ_x for nonionic hydrogels of 2-hydroxyethyl methacrylate (HEMA) cross-linked with ethylene glycol dimethacrylate (EGDMA). Nevertheless, the Flory–Huggins theory based on a random-mixing lattice model, from which χ has been determined, is also questioned, as was mentioned in Sec. II.C.

Through measurements of the modules of elasticity for a gel, the cross-linking degree may be determined, but this is also based on a theoretical model. Thus it appears that chemical analyses such as elemental analysis of the dry LPEI gel would be a good way, from which the cross-linking density (in mol/cm^3) can be determined by $\rho_x = x/(100\bar{v}M_0)$. We may hope that polyelectrolyte gels whose cross-linking degree can be determined by chemical analysis would be used in the study of gel transitions, in particular in a quantitative comparison of experimental results with a theoretical prediction.

2. Acid–Base Equilibrium

The ionization process of polyacids with a base as well as of polybases with an acid can be studied by means of potentiometric titration. For polyelectrolyte gels, however, there is a rather difficult problem; for example, how to estimate the "real" acid–base equilibrium within the gel phase from the pH measurements of the outer solution. Thus no study has so far dealt with the potentiometric titration of polyelectrolyte gels, except for ion exchangers; i.e., a highly cross-linked polyelectrolyte gel. Nevertheless, we have demonstrated that the potentiometric titration is available for the investigation of ionization characteristics of acid or basic groups bound to a network [33]. We employed submicron gel particles with 70 mol% NIPA and 30 mol% AAc. Also employed were the bulk NIPA-AAc gel of a fine grind and the NIPA-AAc copolymer, both of which contain 30 mol% AAc. One might expect that use of the microgel would help to eliminate a general problem in the pH titration for gels; that is, the great difficulty in judging whether the H^+ and OH^- concentrations within the gel phase come to equilibrium with those in the aqueous bulk phase at different stages of the titration. The titration can be performed using a burette and a pH-meter equipped with a combination pH electrode.

Figure 4 shows typical titration curves with 0.1 M NaOH for two kinds of the NIPA-AAc gels as well as the corresponding copolymer in the absence and the presence of 0.1 M NaCl. The titration curves for the gels were obtained by plotting the pH of the outer medium against the titrant volume (V_t). A very clear end point was observed in each titration curve; thus the overall content of COOH was easily determined from V_t at the end point. There was little difference in the COOH content between the gels, as well

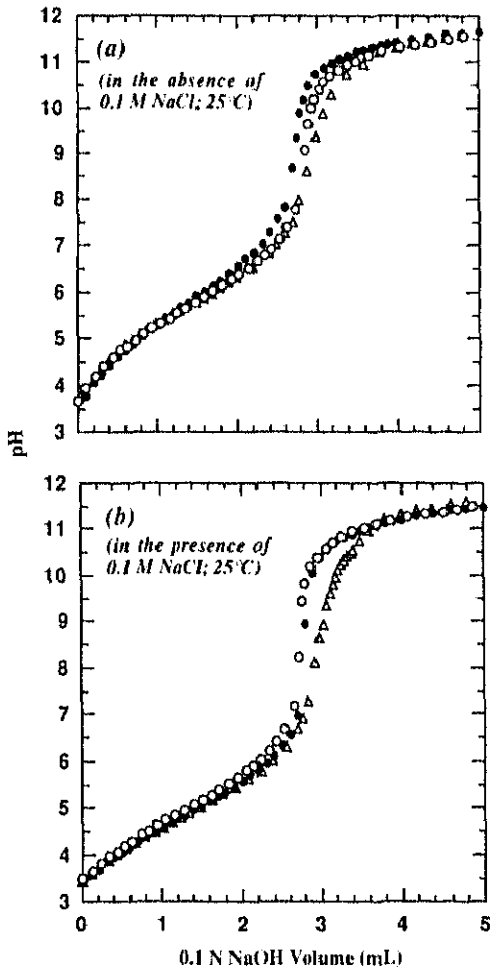


FIG. 4 Potentiometric titration curves with 0.1 M NaOH in the absence (a) and the presence (b) of 0.1 M NaCl for the copolymer (closed circles), the bulk gel (open triangles), and the microgel (open circles) at 25°C. (From Ref. 33.)

as between the gel and the copolymer. The same result was also obtained when titration was carried out at 35°C, the temperature of which is slightly higher than the phase transition temperature (T_v; ~33°C) of neutral NIPA gels or the lower critical solution temperature (LCST; ~31°C) of NIPA polymer (see Ref. 33).

Another piece of important information from Figure 4 is that the titration curves of the gels show a striking resemblance to that of the copolymer. From this, we may suggest that the dissociation of protons from the COOH groups bound to the linear polymer chain and the cross-linked polymer network is essentially the same. However, one might doubt whether the pH between the gel phase and the bulk solution with suspended gels was equilibrated or not. Taking this into account, we performed a back titration with HCl after the bulk or the microgel in the acid form was titrated with NaOH beyond the V_t at the end point. As can be seen from Figure 5, there was little difference in the results between the front and the back titration not only for the microgel but also for the bulk gel. This indicates that our titration data for both the gels do not include serious errors relating to a pH difference between the gel and the bulk phase.

3. Surfactant Uptake

We can convert neutral NIPA gels into a polyelectrolyte gel through the binding of surfactant molecules such as sodium dodecylbenzene sulfonate (NaDBS) and sodium dodecyl sulfate (SDS) [20]. As will be seen in Sec. V.B, the polyelectrolyte gel of this sort provides us with important infor-

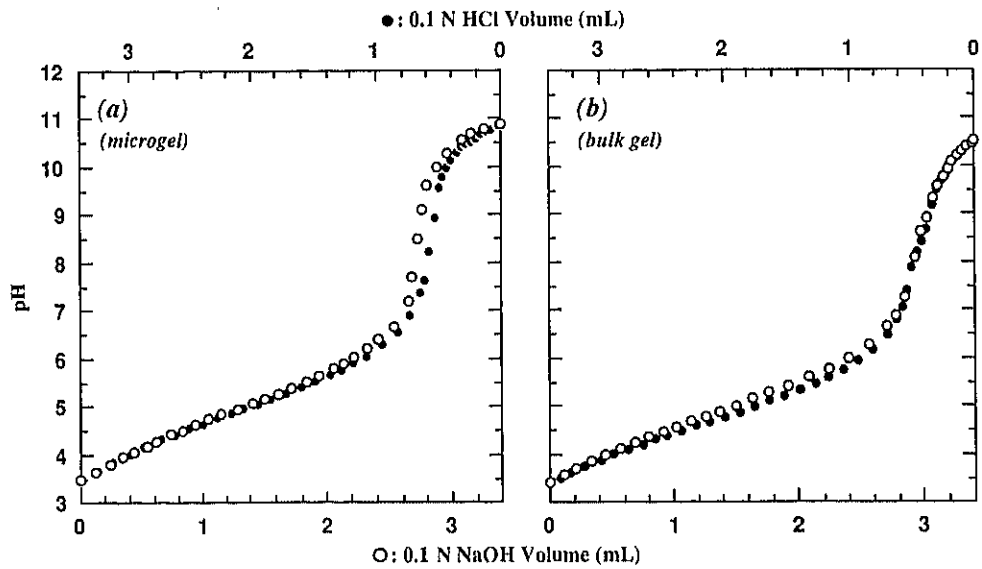


FIG. 5 Changes in pH during titrations of the microgel (a) and the bulk gel (b) with 0.1 M NaOH (open circles) followed by back-titration with 0.1 M HCl (closed circles); ionic strength = 0.1 (NaCl), 25°C. (From Ref. 33.)

mation about the main factor that swells the gel. Thus the gel should be characterized in terms of the overall charge density and charge distribution.

To determine the overall charge density, two experiments were carried out using cubic gels as well as cylindrical gels with different sizes. The surfactant uptake by the former was first measured in aqueous solutions containing different amounts of SDS or NaDBS as follows: the lyophilized cubic gels were introduced into a measuring flask and then allowed to swell with a small amount of distilled water. After adding the required amount of SDS or NaDBS solution to the flask, the volume of the aqueous phase containing the gels was precisely adjusted to 50 mL with distilled water. The flask was slowly shaken for more than one week (e.g., 10 days) at 25°C. The SDS concentration of the supernatant liquid after the incubation was determined by TOC analysis. In addition to this, we applied the spectrophotometric method using a calibration curve showing the relationship between NaDBS concentration and absorbance at 220 nm. There was a good agreement between both analytical methods (within ±3%) [24].

To study the effects of gel size on the surfactant binding [26], we used lyophilized cylindrical gels that had been prepared in glass capillaries with different inner diameters (d_0) of 3, 5, and 10 mm and cut into lengths of 10 mm. Two types of gel samples were employed in the measurements, "wet" and "dry" gels. To prepare the wet gel, one lyophilized sample was accurately weighed and allowed to swell with pure water whose volume was double the gel volume in a small volumetric vial, prior to the addition of 0.1 mM NaDBS solution. In the case of the dry gel, the lyophilized sample was directly immersed in the NaDBS solution without the swelling with pure water. The volume ratio of the gel and the NaDBS solution was fixed to 1:10 throughout all the experiments. The incubation was allowed to continue at 25°C for 25 h as described above. The NaDBS concentration was determined at suitable time intervals with the spectrophotometric method.

4. Distribution of Bound Surfactant Molecules in Gels

A position-dependent change in the concentration of bound NaDBS molecules within the gel can be monitored directly by microscopic spectroscopy [26]. The wet and dry samples were obtained from lyophilized cylindrical gels (d_0 = 2, 3, and 4 mm and a length of 1 mm) with and without their swelling in pure water, respectively. The incubation was performed in an aqueous 10 mM NaDBS solution at 25°C for 10 days. After that, the gels with the adsorbed surfactant were cut with a microtome into disks with a thickness of ca. 0.2 μm. NaDBS is an appropriate surfactant for our purpose because it carries a phenyl group, which exhibits an absorption band in the UV range. In order to measure the position dependence of transmittance (PDT) for the sample gel disks with bound NaDBS, scanning at 261 nm

was performed from the right-hand to the left-hand end of each gel disk. The size of the beam going through the gel disks was fixed to 30 μm, which corresponds to about 1% of the diameters of the disks. We may also measure the PDT at 400 nm as control, because NaDBS has no absorption at 400 nm and therefore the transmittance at this wavelength varies depending on the sample thickness.

V. FINDINGS THROUGH EXPERIMENTS

A. Effect of Charge Density

Almost all the studies on the transition of polyelectrolyte gels have paid much attention to the effect of charge density. Historically, a pioneering paper [6] that referred to this effect was published by Tanaka and his coworkers. Since Tanaka [5] already reported his findings about an abrupt volume collapse of neutral MBA-cross-linked PAAm gels in acetone–water mixtures (see Sec. II), the gel of the same sort was again used as a starting material, to which the ionizable groups were introduced via partial hydrolysis of the amide groups with a base (BOH):

$$\sim CONH_2 + BOH \rightarrow \sim COO^-B^+ + NH_3$$

The swelling ratio of the gel at different stages of the hydrolysis was measured as a function of acetone concentration in acetone–water mixtures. The important findings from this experiment may be summarized as follows: (1) For short hydrolysis times of 0 to 1 day, the equilibrated gel volume changes continuously with the acetone concentration. (2) When the gel was hydrolyzed for 2 days, the swelling curve has a zero slope inflection point. (3) For longer hydrolysis times, the gel undergoes discrete transitions. (4) Volume change at the transition becomes larger, and the acetone concentration bringing about the transition becomes higher. By comparing these results with the theoretical prediction using Eq. 6 (see Figure 1 in Sec. II.A), Tanaka et al. claimed that an increase in the counterion concentration with increasing charge density raises the osmotic pressure of a gel and thereby the volume change at the transition becomes larger. Also claimed by them was that such an increase in the osmotic pressure lowers the reduced temperature (τ) in Eq. 6.

The above provides an explanation for a role of ionic charges bound to the polymer network in the gel transition, i.e., how the charge density affects the volume of an ionic gel at a transition as well as the transition threshold. However, the partially ionized PAAm gel is not a very good sample for discussing the effect of charge density on the reduced temperature as the transition threshold. Acetone acts as a "poor" solvent for PAAm or its hy-

drolysate; thus addition of acetone to a water solution of the polymer leads to a phase separation. Such a phase separation is, however, not observed in the water solution, even when lowering temperature to the freezing point of water. On molecular grounds, therefore, one may not say that the transition temperature falls with increasing charge density, even though an increase in the charge density lowers τ at the transition point. The temperature-induced transition in the neutral PAAm gel in a 40% acetone–water mixture, as previously reported by Tanaka [5], can be understood at the molecular level in terms of temperature effects on the interactions of polymer–water, polymer–acetone, and water–acetone. (To the best of the author's knowledge, the only ionic gel [17] with an interpenetrating polymer network consisting of PAAm and PAAc undergoes a temperature-induced transition in pure water; the transition temperature falls with increasing ionization degree.)

A polyelectrolyte gel system from which we may discuss the phase transition in terms of charge density as well as temperature has also been published by Tanaka et al. [13]. Then they used NIPA instead of AAm and synthesized the gels via aqueous redox copolymerization of NIPA with AAc (as sodium salt) in the presence of MBA as the cross-linker. As can be seen from Figure 6, the gel of this sort exhibited a clear effect of charge density on both the transition temperature and the gel volume at the transition; with

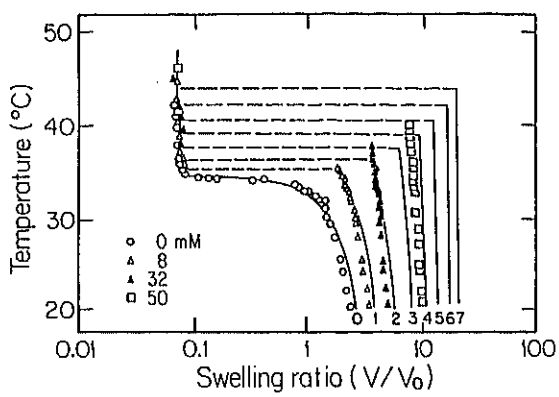


FIG. 6 Temperature dependence of swelling ratio for ionic NIPA gels with different amounts of COONa groups. Numbers in the figure denote the f value, the number of counterions per chain. The curve calculated with $f = 0$ was obtained so as to fit the calculation to the experimental data (circles) through choosing freely the parameters in Eq. 15, the values of which were then used in the calculation of the other curves ($f \geq 1$). Plots with different symbols are experimental results. (From Ref. 13 with a modification.)

increasing charge density, a marked increase was observed in the volume change at a transition as well as the transition temperature. (For neutral NIPA gels, it should be noted that Tanaka et al. mentioned in Ref. 13 a continuous volume change, although their previous paper [10] had reported a discontinuous transition; it is still unclear whether the neutral NIPA gel in pure water undergoes a continuous or a discontinuous volume change.)

Tanaka in collaboration with Hirotsu has attempted to compare the results in Figure 6 with theoretical swelling curves, the calculation of which was performed through a modification of Eq. 6 by considering that the temperature dependence of the term $\Delta F/kT$ (i.e., χ parameter) can be rewritten as

$$\chi = \frac{\Delta F}{2kT} = \frac{\Delta H - T\Delta S}{2kT} \tag{14}$$

Thus Eq. 6 becomes

$$\frac{1}{T} = \frac{\Delta S}{\Delta H} + \frac{k}{\Delta H}\left\{\frac{\nu v_s}{N_A \varphi^2}\left[(2f+1)\left(\frac{\varphi}{\varphi_0}\right) - 2\left(\frac{\varphi}{\varphi_0}\right)^{1/3}\right] + 1 + \frac{\varphi}{2} + \frac{2\ln(1-\varphi)}{\varphi^2}\right\} \tag{15}$$

In calculating the swelling ratio with a relation of $V/V_0 = \varphi_0/\varphi = (d/d_0)^3$, where d is equilibrium gel diameter and d_0 (1.35 mm) is a gel diameter at the preparation, each parameter in Eq. 15 was estimated as follows: (1) φ_0 (~0.07) from the experimental asymptotic value of V/V_0 at high temperatures; (2) ν (1×10^{23} L^{-1}) from the amount of MBA in the gel preparation; (3) ΔH (-8.7×10^{-14} erg) from the literature (Bulletin of Research Institute for Polymers and Textiles, in Japanese, No. 114, 1984). (It should be noted that neutral NIPA gels in pure water exhibit an endothermic shrinking upon heating, $\Delta H > 0$, but exothermic swelling upon cooling, $\Delta H < 0$ [67]; therefore, Tanaka's calculation focuses on the swelling transition.) In addition to these, it was assumed that since the transition temperature is determined principally by the ratio $\Delta H/\Delta S$, ΔS is approximately equal to $\Delta H/T$, and the curvature of a swelling curve is mainly determined by the value of ΔH. Taking these into account, the theoretical swelling curve was first obtained for the neutral gel; however, the estimated theoretical fit was rather poor. For example, the calculated curve predicts much smoother change than the measured curve near the transition region. Thus, as the second approach, an attempt was made to estimate the parameters from the experimental data for the neutral gel by a curve fitting technique. The results of the best fit gave the following values: $\Delta H = -5.4 \times 10^{-11}$ erg, $\Delta S = -1.8 \times 10^{-13}$ erg·K^{-1}, $\nu = 1.2 \times 10^{24} L^{-1}$, and $\varphi_0 = 0.07$. Using these parameters, the swelling curves for ionic NIPA gels with COONa (8 to 50 mM in preparation) were

calculated (see the solid curves in Figure 6). The calculated curves well reproduced the experimental data for the ionic gels; however, the values obtained from the two-parameter fit for ΔH and ν were significantly greater than the values estimated from independent measurements. For this discrepancy, the following reasons were pointed out: In modeling, it did not consider the effects of loops, free branches, non-Gaussian properties of chains (due to self-avoiding random walk, and stretching limit due to finite length of the chains), polydispersity of chains, etc. For the particular case of ionic gels, it also neglected the charge–charge interaction and counterion condensation, which may affect the actual value of osmotic pressure by counterions.

Prior to discussing the disagreement between prediction and observation in connection with the above factors, we have to answer the question why ionic gels collapse with rising temperature. As can be predicted from Eq. 4, the osmotic pressure should be strengthened not only by concentration of counterions but also by temperature. In order to resolve this conflict, several studies (e.g., see Ref. 42) have assumed "hydrophobic interaction" as a force being in competition with the osmotic pressure arising from counterions. Nevertheless, it is preferable to verify experimentally whether the concept of osmotic pressure is adequate. This subject will be discussed in the following section.

B. Effects of Charge Distributions Observed in Ionic Surfactant–Bound NIPA Gels

1. Historical Backgrounds

Since the earliest report by Eliassaf [68] on the interactions of the NIPA polymer with sodium dodecyl sulfate (SDS), various studies have focused on this subject. In the case of NIPA gels, however, only a few studies [20,24,69–71] have dealt with surfactant interactions in aqueous media. These studies demonstrated that ionic surfactants such as SDS tend to raise the transition temperature (T_v), bringing about a discontinuous volume change, and to increase the gel volume over a wide temperature range $<T_v$. A similar result has also been obtained from the study on the interaction of surfactants with NIPA microgel latexes as a function of temperature [58]. These results were explained by assuming that the surfactant molecules bind to the polymer network of NIPA, converting the gel into a polyelectrolyte gel. A qualitative discussion was given in terms of the Flory theory with modifications to account for the free energy of association of the surfactant molecules with the gel network and surfactant self-association [20]. The micellar formation of surfactants within the gel phase was then considered, because the micellization had been suggested by Zhang et al. [70] based on results from small-angle neutron scattering (SANS) for a SDS-NIPA gel

system. (It should be noted that the original work of the binding of surfactant micelles to a polymer of NIPA was carried out by Schild and Tirrell [72], although Zhang et al. did not cite it in their paper [70].) In these previous works [20,69–71], however, little attention was paid to investigating the amount of surfactant binding to the gels. In other words, the conclusions were drawn mainly from swelling measurements, although several studies employed additional experimental techniques such as SANS [70] and thermal analysis [69,71] using a differential scanning calorimeter (DSC).

Kokufuta et al. [24] have presented highly accurate quantitative measurements of the uptake (or adsorption) of an ionic surfactant, sodium dodecylbenzene sulfonate (NaDBS), by NIPA gels. NaDBS was used because it has UV adsorption at ca. 220 nm, which allows an accurate determination of the surfactant uptake by the gels. Detailed analyses of the experimental data suggest that NaDBS molecules are bound only to the region in the near vicinity of the gel surface but fail to penetrate into the core of the gel phase. Such an ionic gel with "locally" bound surfactant seems to be considerably different from the usual polyelectrolyte gels with regard to the phase transition. Therefore, the gel of this sort would provide a key to learning the role of ionic charges in the gel transition on the molecular level.

2. Swelling Characteristics of NIPA Gels in SDS and NaDBS Solutions

There seems to be a similarity between the surfactant effects on the volume phase transition of NIPA gels and the LCST-type phase separation of NIPA polymers. In the case of the polymers, it is known that the binding of surfactant micelles to the polymer causes an elevation of the LCST as a result of electrostatic repulsion between the charges of polymer-bound micelles. The concentration at which such a surfactant binding takes place has been referred to as the critical aggregation concentration (CAC). The CAC (0.79 mM) for SDS in the NIPA polymer solution was determined by Schild and Tirrell using the fluorescence probe method [72]. Saito et al. reported the observation of the CAC for SDS in the NIPA gel system [71], although they did not mention the CAC in Ref. 69 dealing with the same system. Saito et al. applied the DSC method for monitoring the changes in T_v for the gel and in LCST for the polymer and obtained a relatively broad curve of T_v or LCST against SDS concentration. Based solely on these results, it is rather difficult to judge whether the CAC in the polymer agrees with that in the gel system. In addition, it is questionable whether the CAC can be defined for the gel system because the surfactant binding mechanism remains unclear at the present stage. Thus the effects of SDS and NaDBS on the volume phase transition of NIPA gels were studied over a wide range (0–40 mM) of surfactant concentration without considering the CAC.

Figures 7 and 8 show the changes in T_v and swelling ratio (V/V_c) with initial surfactant concentrations (C_i), respectively. SDS and NaDBS affect the thermally induced phase transition of the NIPA gel; both T_v and V/V_c increase remarkably with increasing C_i, as reported in previous studies [20,24,69–71]. The observed effects can be understood by assuming that both SDS and NaDBS bind to the polymer network within the gel phase through hydrophobic interaction, subsequently converting an otherwise neutral NIPA gel into a polyelectrolyte gel. These acquired network charges and counterions associated with the charges exert an extraosmotic pressure on the network, so that both the transition temperature and the gel volume increase. (Although this explanation has been widely accepted, this chapter has raised questions with regard to the assumption of osmotic pressure.)

Now we will focus on why a difference due to the type of surfactant appeared in the swelling ratio (Figure 8) but not in the transition temperature (Figure 7). We first studied the SDS and NaDBS uptake by the gel as a function of C_i. The results obtained are shown in Figure 9. We found that the saturated amount of surfactant uptake at $C_i > 10$ mM was larger for SDS than for NaDBS. However, we cannot simply relate this result to the observed difference in V/V_c between SDS and NaDBS, because an increase in the charge density for polyelectrolyte gels, such as NIPA-NaAAc gels, brings about simultaneous increases in both transition temperature and gel volume.

To demonstrate this point more definitely, we compared the present results with those for the NIPA-NaAAc gels with different NaAAc contents. The

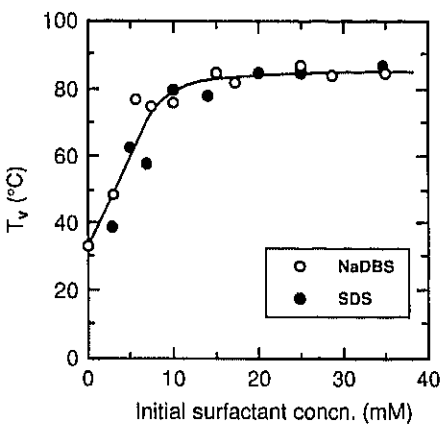


FIG. 7 Dependence of volume phase transition temperature (T_v) of NIPA gel (cylindrically shaped wet sample with $d_0 = 0.7$ mm) on initial surfactant concentration. (From Ref. 26.)

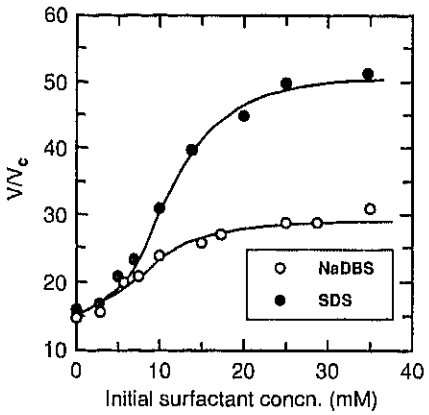


FIG. 8 Changes in the swelling ratio (V/V_c) of the cylindrically shaped wet NIPA gel (d_0 = 0.7 mm) with initial surfactant concentration at 25°C. V_c denotes the gel volume in the fully collapsed state determined for each sample in pure water at 50°C. (From Ref. 26.)

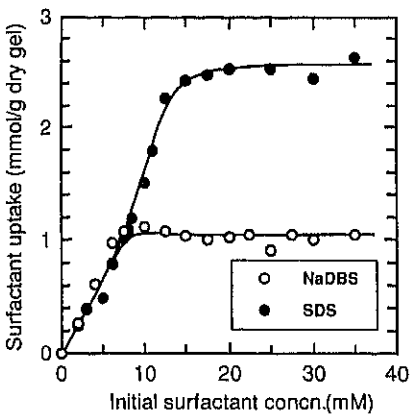


FIG. 9 Changes in surfactant uptake with initial surfactant concentration at 25°C. We used a cubic gel with sides of 2 ± 0.5 mm. It should be noted that these uptake data can be compared with the swelling data (T_v and V/V_c) in a qualitative but not in a quantitative way because the size of the gel samples can be regarded as the primary factor affecting the uptake amount. (From Ref. 26.)

"overall" charge density expressed in moles of bound surfactant per one mole of monomer unit in the gel may be calculated from the saturated amount of surfactant binding at $C_i > 10$ mM; i.e., 0.29 for the gel with SDS and 0.12 for the gel with NaDBS. This means that the NaDBS and SDS-bound gels apparently correspond to polyelectrolyte gels with 10 and 30 mol% ionic groups, respectively. Matsuo and Tanaka [53] measured the temperature dependence of the swelling degree for spherical copolymer gels consisting of NIPA (100 to 82 mol%) and NaAAc (0 to 18 mol%) in pure water. They reported that T_v increased from 34 to 60°C (shrinking process) when the NaAAc content was increased from 0 to 18 mol%. This increase in the NaAAc content simultaneously changed V/V_c from 16 to 510 at 25°C. It should be noted that there are large discrepancies in T_v and V/V_c between the NaAAc-copolymerized and surfactant-bound NIPA gels. For example, T_v (60°C) for a NIPA/NaAAc gel with 18 mol% of NaAAc is lower than that (85°C) for a NIPA gel with 10 mol% NaDBS, although the charge density for the former is larger than that for the latter. In contrast, V/V_c (510) for the same 18 mol% NaAAc-containing gel is much larger than that (51) for a NIPA gel with 30 mol% SDS. The same discrepancy can be found by comparing the results for the surfactant-bound gels with those for cylindrical NIPA–NaAAc gels reported by Hirotsu et al. [13] (see Figure 6).

In the above discussion, we have not considered how surfactant molecules adsorbed on or penetrated into the gels. It has been suggested that NaDBS molecules are bound only to the region in the near vicinity of the gel surface but fail to penetrate into its core [24]. This naturally implies that the charges due to the bound surfactants are spread unevenly over the NIPA polymer network. In the case of NIPA–NaAAc gels, on the other hand, we can expect the COONa groups to be uniformly distributed over the polymer networks. Therefore it is not surprising that we cannot explain all aspects of the behavior of surfactant-bound NIPA gels based only on the analogy to those of NIPA gels with copolymerized NaAAc.

3. Size Dependence of NaDBS Uptake

Gels that are usually employed in studies of surfactant uptake are previously saturated with the same solvent as that of surfactant solutions. When such gels are immersed in a surfactant solution, the binding should take place through the gel surface. The size and shape of the gel are then regarded as the primary factor directly affecting the uptake amount because it depends on the available surface area of the gel.

Taking the above into account, kinetic studies of NaDBS uptake were performed using cylindrical gels with 3, 5, and 10 mm in diameter (d_0) and 10 mm in length (l). We employed a dry gel free of water, in addition to the usual wet gel. The results are shown in Figure 10a for the wet gel and

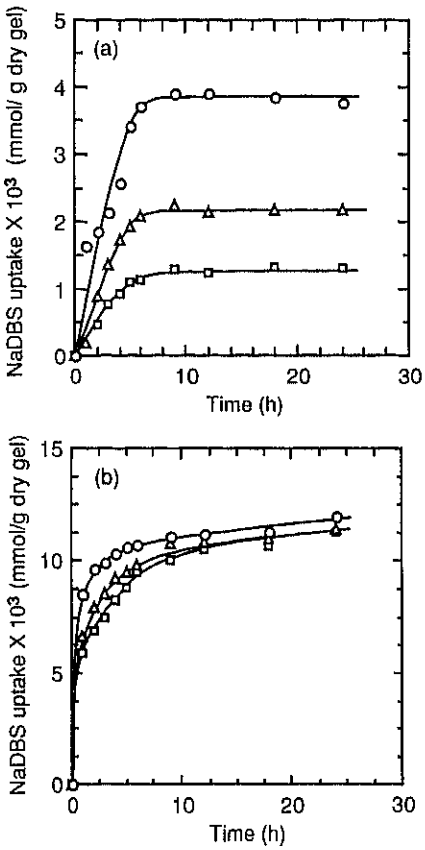


FIG. 10 Time courses of NaDBS uptake by various cylindrically shaped wet and dry gels. Circles denote d_0 = 3 mm, triangles 5 mm, and squares 10 mm, with a fixed 10 mm length. (a) Wet gels for which surfactant uptake was given in dry weight base; (b) dry gels for which surfactant uptake was given in dry weight base; (c) wet gels for which surfactant uptake was given in surface area. (From Ref. 26.)

in Figure 10b for the dry gel. A marked difference between both types of gels was observed in the size dependence of NaDBS uptake when its amount was expressed in moles per unit of dry mass: a large change in the uptake amount appeared in the wet gel while the change was negligibly small in the dry gel. This difference may be attributed to where the binding of the surfactant molecules takes place within the gel phase. In the case of the dry gel, the absorption sets in as soon as it is immersed in the surfactant solution, which causes the scattering of surfactant molecules all over the gel phase.

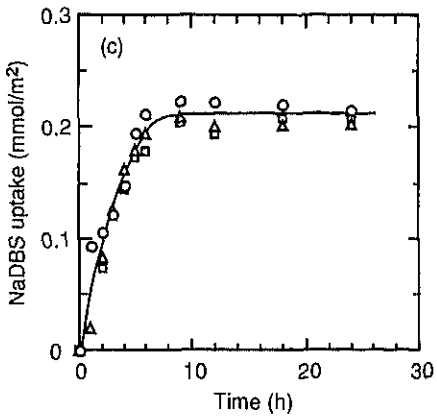


FIG. 10 *Continued.*

This makes it possible for the surfactant molecules to bind to the polymer network throughout the gel phase. In the wet gel system, however, the surfactant binding begins at the surface of the gel because it already contains a saturated amount of water as the solvent. Even after a certain amount of surfactant molecules have penetrated into the gel, the binding will continue through its surface. This means that in the wet gel system the effect of size on the uptake amount can be eliminated if we express it by the number of moles per unit surface area. As shown in Figure 10c, this is actually the case. The surface area (S) was then calculated by $S = \pi d_0(l + d_0/2)$: 108, 196, and 471 mm^2 for the gels with d_0 = 3, 5, and 10 mm, respectively.

A detailed comparison of the surfactant uptake by the wet and dry gels provides a possible interpretation for the difference between SDS and NaDBS observed in the surfactant-induced changes in the transition temperature and swelling ratio of the NIPA gels (see Figures 7 and 8). The amount of NaDBS uptake by the wet and dry gels with the same d_0 reached certain saturation levels after 6 hours, but the level for the former was substantially lower than that for the latter. This implies that the NaDBS concentration within the wet gel is not even throughout its entire volume. From the above discussion, it is reasonable to assume that the NaDBS concentration is high in the vicinity of the gel surface. This situation has been schematically represented in Figure 11, in which a horizontal sectional view of a cylindrical gel after attainment of a saturated level of surfactant uptake is illustrated together with a concentration profile of bound surfactant. Also included in this figure is the temperature dependence of the swelling ratio

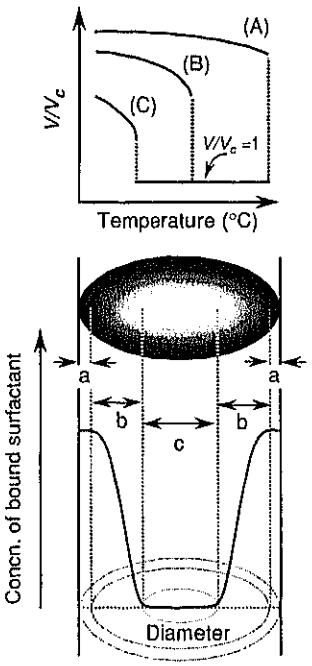


FIG. 11 Schematic representation for a cylindrical gel with inhomogeneously bound surfactant molecules. Swelling curve A corresponds to region a with a saturated level of bound surfactant; curve B represents a limited section of region b in which the surfactant concentration gradually decreases towards the center; curve C is for region c in which there is no bound surfactant (i.e., corresponding to neutral gel). (From Ref. 26.)

for three typical regions with different levels of surfactant binding. When considering Figure 11, it seems that a NIPA gel with bound surfactant resembles a sort of "composite" polyelectrolyte gel consisting of cross-linked polymer chains with different amounts of ionizable groups. Since the T_v of nonionic NIPA gels is lower than that of ionic NIPA gels, region c, free of bound surfactant molecules, should collapse first with rising temperature, while regions a and b should remain in the swollen state. We defined as T_v the temperature at which a gel discontinuously and completely collapses; therefore the experimentally determined T_v is primarily governed by the degree of ionization due to the surfactant binding in region a but not in regions b and c. Since region a is saturated by surfactant molecules, its ionization degree is independent of the kind of surfactant. As a result, little

difference was observed in the curves of T_v vs. C_i for SDS and NaDBS (Figure 7). However, the swelling ratios at temperatures $<T_v$ are strongly affected by changes in the degree of ionization in region b. Even if region a is maintained at the same level of ionization in both the SDS and NaDBS-bound gels, the level in region b for the former is higher than that for the latter. This is evident from Figure 9, which indicates that NIPA gels tend to bind SDS rather than NaDBS. Thus the SDS-bound gel exhibited a high swelling degree compared with the NaDBS-bound gel (see Figure 8).

4. Determination of Special Distribution of NaDBS Concentration in Gels

The measurement of the special distribution of surfactant concentration within the gel phase should provide direct evidence for the local surfactant binding expected in the previous sections. The position dependence of transmittance (PDT) for the sample gel disks with bound NaDBS is shown in Figure 12, in which PDTs a, b, and c were obtained using wet gels with d_0 = 4, 3, and 2 mm, respectively; they had fully swollen in pure water prior to contact with the NaDBS solution. A dry gel with d_0 = 2 mm, which had been directly treated with the surfactant solution without swelling procedure, was used for the measurement of PDT d.

In PDTs a to c, a rapid decrease in transmittance at both ends of each sample was observed when using the wavelength 261 nm. However, the transmittance increased gradually and became constant when the scanning point approached the central core of the gel disk. On the other hand, the transmittance at 400 nm was almost constant, independent of the position. Therefore it is evident that the surfactant molecules bond strongly only around the gel walls. This conclusion can be supported by PDT d for the dry gel, in which we did not observe specific position-dependent changes in transmittance at 261 nm. In the case of the dry gel, the surfactant solution permeated throughout the gel phase, allowing the surfactant molecules to bind to the network without distribution. This brought about a marked difference in the diameters of the surfactant-bound wet and dry gels; i.e., the distance between the right- and left-hand ends of the dry gel was larger than that of the wet gel, both of which were 2 mm before the surfactant binding.

The observed inhomogeneous binding of NaDBS within the wet gel can be understood by taking into account the generation of a Donnan potential due to the surfactant bond. When the wet gel comes in contact with the surfactant solution, the NaDBS molecules bind in the near vicinity of the gel surface. Through such binding, the surface carries the negative charges, resulting in a high Donnan potential, which makes further diffusion of the NaDBS anions more difficult.

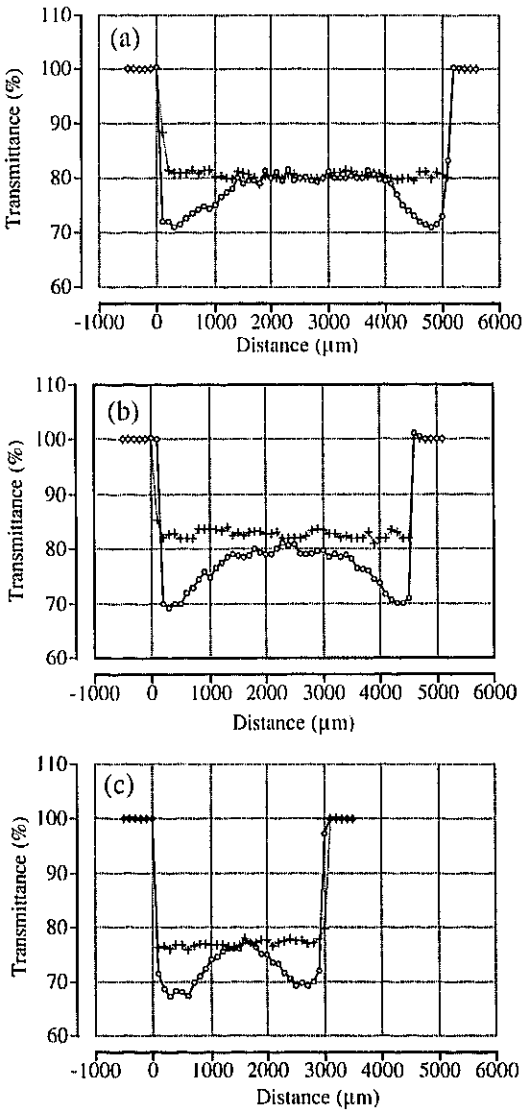


FIG. 12 Position dependence of transmittance (PDT) for cylindrical wet gel disks with diameters d_0 = 4 mm (a), 3 mm (b), and 2 mm (c), and for a cylindrical dry gel disk with d_0 = 2 mm (d). Circles and plus signs, respectively, denote 261 and 400 nm. (From Ref. 26.)

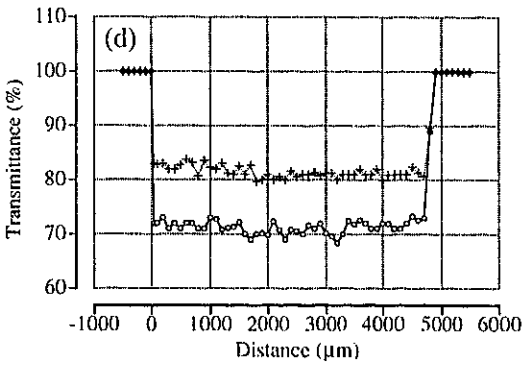


FIG. 12 *Continued.*

Another important finding in PDTs a to c is that the magnitude of the characteristic change in transmittance around both ends of the gel disk is independent of its size. This means that the surfactant binding occurs within specific domains of the gel phase. In other words, the concentration distribution of bound surfactant as illustrated in Figure 11 is uniquely determined by the affinity of the surfactant toward the polymer as the constituent of the gel. If hydrophobic interaction between the surfactant and the NIPA polymer is the primary factor determining the surfactant binding, NaDBS rather than SDS would exhibit a high affinity toward the polymer. This leads to the formation of a densely packed surfactant layer within region b in Figure 11. It is reasonable to consider that such a layer of NaDBS generates a Donnan potential higher than that of SDS. As a result, we observed that the uptake amount of NaDBS by NIPA gels was smaller than that of SDS.

5. Behavior of the Surfactant-Bound NIPA Gel as a Polyelectrolyte Gel

As mentioned above, the NIPA gel with bound SDS or NaDBS behaved as a polyelectrolyte gel. However, the volume phase transition was obviously affected by the inhomogeneously distributed charges. If the osmotic pressure due to mobile counterions plays an important role in the volume phase transition of polyelectrolyte gels, one would expect that there is little influence of the inhomogeneity of charge distributions within the gel. Thus the present results may provide a key to determine whether the volume phase transition of polyelectrolyte gels is governed by osmotic pressure. The same conclusion has been obtained from the study of the surfactant binding to the NIPA polymer networks within a very narrow domain, such as a submicron-sized gel particle [30].

C. Effect of AAc Distribution in NIPA Networks

We have demonstrated that an inhomogeneous binding of surfactants brings about a different swelling behavior from that of the usual ionic gels prepared via random copolymerization of NIPA and acrylic acid (AAc). It is thus interesting to examine the effect of the charge distribution (i.e., the distribution of AAc residues in the network) on the swelling behavior of NIPA–AAc gels. If the concept of osmotic pressure is correct, one might not observe any difference in the swelling curves between the two kinds of ionic NIPA–AAc gels into which the AAc residues were homogeneously or inhomogeneously introduced. The reason for this is that counterions to the ionized groups should move freely within the gel phase surrounded by the Donnan potential barrier and thereby increase the osmotic pressure acting to swell the gel (see Sec. II.A). The object of this section is to examine the swelling behavior of NIPA–AAc gels with the same amount but a different distribution of AAc; through this examination we can discuss the validity of the concept of osmotic pressure on the molecular level.

1. Design of NIPA–AAc Gels with Different Charge Distributions

For the present purpose, we designed four ionic gels (Gel I–IV) composed of NIPA and AAc residues. The AAc distributions within the polymer network of these gel samples may be classified into three schemes as shown in Figure 13. The preparation methods considered are as follows: (1) for Gel I, the redox polymerization of an aqueous solution containing NIPA, AAc, and MBA (cross-linker), which can be initiated by a pair of APS and TMED; (2) for Gel II, the physical entrapment of PAAc by an MBA-cross-linked NIPA gel, the performance of which is based on the same method employed in (1) except for the use of PAAc instead of the AAc monomer; (3) for Gel III, the gelation of an aqueous solution containing PNIPA and PAAc by γ-rays from ^{60}Co under conditions where no complexation occurs between

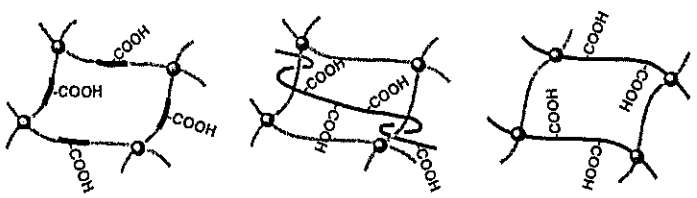


FIG. 13 Schematic illustration of four polyelectrolyte gels consisting of NIPA and AAc residues. (From Ref. 28.)

PNIPA and PAAc; (4) for Gel IV, whose AAc distribution may be expected to be similar to that of Gel I, the γ-ray irradiation of an aqueous solution of a copolymer of NIPA and AAc, i.e., copoly(NIPA, AAc).

2. Swelling Curves for Gels I–IV

Figure 14 shows the temperature dependence of the normalized equilibrium diameters (d/d_0) at pHs 3 and 10 for Gels I to IV. The normalization of each

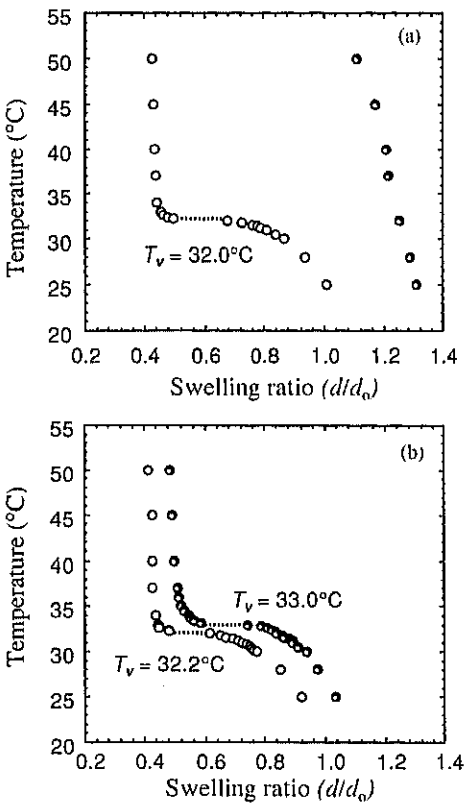


FIG. 14 Temperature dependence of normalized equilibrium diameters (d/d_0) at pHs 3 (open circles) and 10 (shadowed circles) for four polyelectrolyte gels consisting of NIPA and AAc residues: (a) Gel I; (b) Gel II; (c) Gel III; (d) Gel IV. PAAc with $\bar{M}_w = 4.5 \times 10^5$ was used for the preparation of Gels II and III. Dashed line indicates a discontinuous volume phase transition at a temperature (T_v) at which we observed a transient pattern in both swelling and shrinking processes and thereby were not able to measure d. Such a transient pattern was not observed in the measurements for Gel III at pH 3, suggesting a continuous transition. (From Ref. 28.)

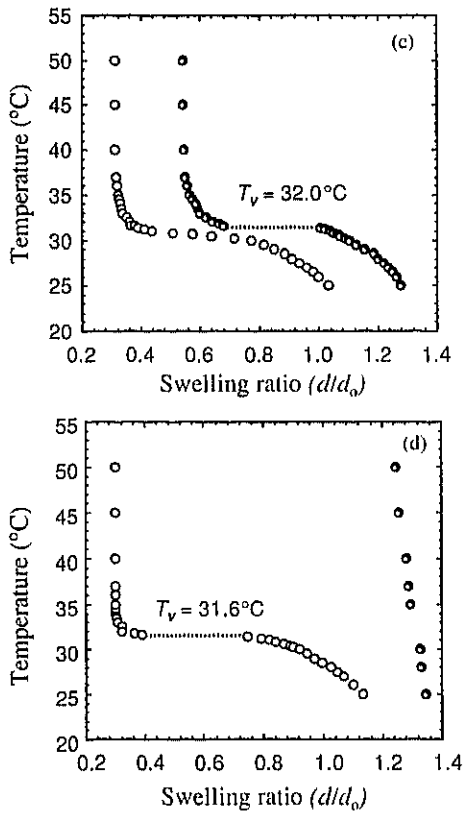


FIG. 14 *Continued.*

observed equilibrium diameter (d) was performed using the inner diameter (d_0) of the capillary utilized in the gel preparation. It was found that Gels I and IV, with a random distribution of the AAc residues, exhibited a similar volume phase transition when varying the temperature at pHs 3 and 10. A similarity was also observed in Gels II and III with the locally distributed AAc residues. Therefore the volume phase transitions for Gels I to IV are divided into two different classes when taking into account the distribution of the AAc residues. In particular, at pH 10 at which the COOH groups bound to the AAc residues are ionized ($COOH \rightarrow COO^- + H^+$), there is a marked difference due to the AAc distribution; the localized COO^- ions are not effective in preventing the thermally induced gel collapse at temperatures above the volume phase transition temperature (T_v). This indicates an effect

of the "charge distribution" in the network on the phase transition of ionic gels.

The phase separation of PNIPA in pure water at the lower critical solution temperature (LCST) was generally understood by considering both hydrogen bonding and hydrophobic effects [16]. Since there was little disagreement between the T_v for the usual nonionic NIPA gels and the LCST for PNIPA when the measurements were performed in the same solvent, Schild has surmised a similar molecular mechanism for the phase separation and the volume transition (see page 211 of Ref. 16). For Gels II and III composed of 90% (in unit mole base) of MBA-cross-linked "pure" NIPA chains, it is predictable that their phase transition behaviors are not so different from those of nonionic NIPA gels or PNIPA, even at pH 10 where the incorporated PAAc chains (10% in unit mole base) are ionized. Indeed, at pH 10 Gels II and III underwent a volume phase transition at temperatures near to the T_v for nonionic NIPA gels or the LCST for PNIPA.

A more detailed interpretation could be made when taking into account the mechanism of microphase separation of weakly charged polyelectrolytes in poor solvents that has been proposed by Borue and Erukhimovich [73] as well as by Dormidontova et al. [74]. According to this, it appears that microphase separation takes place at T_v; i.e., the NIPA chains within Gels II and III collapse to form hydrophobic "micromicellelike" aggregates surrounded by water-rich domains including both the ionized PAAc chains and their corresponding counterions (NH_4^+) at pH 10. The microphase separation mechanism also makes it possible for us to understand the results of Gels I and IV. For both gels, the NIPA and AAc monomer residues should be intermixed in the network; therefore the dissociation of the COOH groups at pH 10 strongly hinders the formation of hydrophobic aggregates not only through an increase in the hydrophilicity due to the COO^- plus NH_4^+ ions but also through the Coulomb repulsion between the COO^- ions. A similar molecular mechanism may be applied to explain the fact that at pH 10 copoly(NIPA, AAc) does not undergo phase separation, even at 50°C. Consequently, these discussions lead us to conclude that the volume transition of ionic gels, at least in our gels, is no longer explainable in terms of the concept of osmotic pressure.

Nevertheless, one more aspect to be taken into account when analyzing the present results is the Manning-type condensation of counterions, which has been neglected in previous theories (see Sec. II) as pointed out by Grosberg and Khokhlov [75]. For Gels II and III at pH 10, many of the counterions are condensed around the charged PAAc ions, and hence the osmotic pressure may not be generated to swell the gel. However, for Gels I and IV, in which the charged AAc residues are randomly distributed, many of the counterions are free from condensation and mobile at pH 10. Therefore,

their substantial contribution to the osmotic pressure should allow the gel to swell over a wide temperature range; in other words, we can again conclude that the osmotic pressure plays an important role in the volume phase transition of ionic gels.

The above discussions have led to conflicting conclusions. When carefully examining the swelling curves in Figure 14, however, one should not forget that the swelling curves at pH 10 for Gels II and III are shifted to the right-hand side (i.e., high degree of swelling) over all the temperatures measured. This suggests the existence of a microphase within which the NIPA chains around the charged PAAc fail to form hydrophobic aggregates via the collapse transition at temperatures $>T_v$. Thus our attention will be focused on the effect of the charged or uncharged PAAc chains incorporated into the NIPA gel on its volume transition.

3. Effect of the Molecular Weight of Entrapped PAAc within Gel II

If the osmotic pressure due to mobile counterions plays an important role in the volume phase transition of NIPA–AAc gels, one would expect to observe either one of the following: (1) little change in the gel volume caused by the molecular weight of the PAAc ions entrapped within the cross-linked NIPA chains; or (2) an increase in the molecular weight leading to the tendency for the gel to collapse due to a decrease in the entropy of the counterions. Consequently, the study of the swelling behavior of Gel II with entrapped PAAc of different molecular weights may provide a key to determining whether the volume phase transition of NIPA–AAc gels is governed by microphase separation or by osmotic pressure.

Figure 15 shows changes in the swelling curves of Gel II at pHs 3 and 10 caused by the molecular weights of the entrapped PAAc chains. It can be seen that the increase in the molecular weight at pH 10 brought about an increase in the gel volume over the temperature range of 25°C to 50°C. This result evidently suggests little contribution of the osmotic pressure to the swelling of a polyelectrolyte gel consisting of the NIPA–AAc system. In other words, the observed results may be understood in connection with the microphase separation mechanism rather than the contribution of osmotic pressure; the increase in the molecular weight of the entrapped PAAc ions leads to the formation of larger water-rich regions due to the COO^- ions around the water-unfriendly hydrophobic aggregates of the NIPA chains, and therefore the swelling of the gel with high-molecular-weight PAAc ions should increase.

Another important feature of Figure 15 is that, at pH 3 and at temperatures $<T_v$, the gel volume decreased with increasing molecular weight of the en-

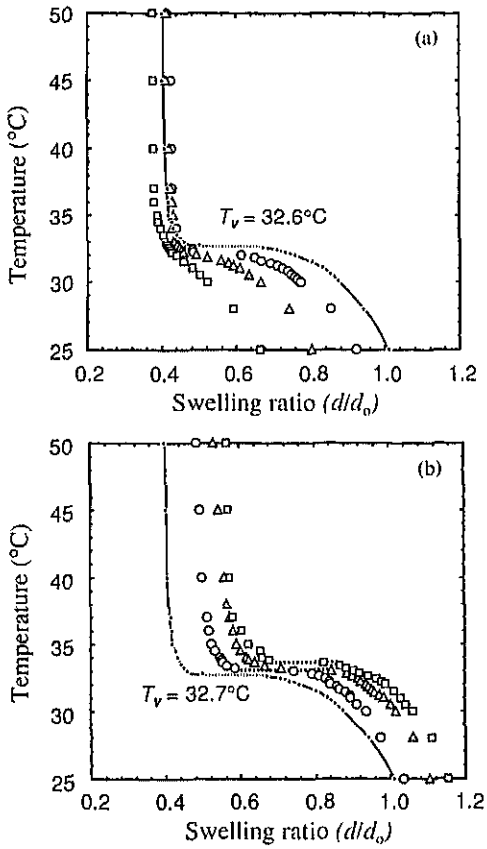


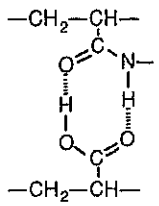
FIG. 15 Effect of the molecular weight of the entrapped PAAc on the normalized equilibrium diameters (d/d_0) for Gel II at pHs 3 (a) and 10 (b). $\bar{M}_w$: (○) 9×10^4; (△) 4.5×10^5; (□) 1.25×10^6. Swelling curves (small solid circles) for the neutral NIPA gel (T_v = 32.6°C at pH 3 and 32.7°C at pH 10) are shown in Fig. 15a and b as the standard. The increase in the molecular weight alters the transition at pH 3 from a discontinuous to a continuous type accompanying a decrease in T_v, whereas at pH 10 it leads to a discontinuous transition with an increase in T_v. (From Ref. 28.)

trapped PAAc with the nonionized COOH groups. A possible interpretation of this result is the increase in the cross-linking points by the formation of hydrogen bonds between the NIPA and AAc residues. In order to confirm this assumption, we attempted to examine the temperature-induced swelling changes for Gels I and III in the presence and absence of 4 M urea at pH

3. However, we found that urea shifts both the LCST of aqueous NIPA solutions and the T_v of NIPA gels to a low-temperature range. We therefore discontinued this experiment and tried to find another approach to study the formation of hydrogen bonds between the NIPA and AAc chains (see below).

4. Complexation of PNIPA and PAAc at pH 3

Our preliminary experiments showed that a mixed solution of PNIPA and PAAc was transparent under alkaline pH conditions but became turbid under acidic conditions, where most of the PAAc-bound COO^- groups are protonated. Moreover, the acidic mixture turned from opaque to transparent by the addition of 4 M urea and upon cooling, while such a change did not take place in the absence of urea. These results suggest the complexation of PNIPA with PAAc via hydrogen bonding between —COOH and —CONH—groups; for example,



We thus assumed that dynamic light scattering (DLS) would be an appropriate approach in order to carry out a quantitative study on this kind of complexation.

As mentioned above, however, a decrease in the LCST was observed when urea was added to an aqueous PNIPA solution. We thus tried to determine the LCSTs of both the PNIPA solution and the PNIPA-PAAc mixture in the presence of 4 M urea (Table 2). It is generally believed that urea breaks up the hydrogen bonds between solute molecules and also disrupts the cluster structure of water molecules ("structure breaking effect"). The latter brings about a weakening of the hydrophobic interaction between solute molecules (e.g., see Ref. 76). In the case of an aqueous PNIPA system, however, the addition of urea shifted the LCST to a low-temperature range. Therefore we cannot simply state that hydrophobic interaction between NIPA residues is weakened by the addition of urea.

Taking the above into account, we initially examined the effect of 4 M urea on the size distributions of PNIPA and PAAc at pHs 3 and 10 (Figure 16). It was found that there was little influence of urea on the size distributions of PNIPA and PAAc. Thus urea can be used in order to break the hydrogen bonds between PNIPA and PAAc. Figure 17 shows the size dis-

TABLE 2 Effects of pH and 4 M Urea on the LCST for Aqueous 0.1 M NaCl Solutions Containing PNIPA or PNIPA–PAAc Mixture

Sample[a,b]	pH	4 M urea	LCST[c]
PNIPA	3	absence	31.3 ± 0.2
PNIPA	3	presence	26.1 ± 0.3
PNIPA	10	absence	31.4 ± 0.3
PNIPA	10	presence	25.9 ± 0.3
PNIPA–PAAc mixture	3	absence	—[d]
PNIPA–PAAc mixture	3	presence	26.2 ± 0.3
PNIPA–PAAc mixture	10	absence	31.1 ± 0.2
PNIPA–PAAc mixture	10	presence	26.4 ± 0.3

[a]Concentrations of PNIPA ($\bar{M}_w$ = 7.6 × 10^5) and PAAc ($\bar{M}_w$ = 4.5 × 10^5) in the sample solutions were adjusted to 0.5 g/dL and 0.16 g/dL, respectively.
[b]The same volumes (10 mL each) of the PNIPA and PAAc solutions were mixed; thus, the ratio of PNIPA:PAAc in the mixed sample was 2:1 by unit mole base and the total polymer concentration was 0.33 g/dL.
[c]Denotes the average of five measurements.
[d]The measurement could not be performed because the solution was turbid even at 1°C.

tributions in the presence and absence of urea for the 2:1 (unit mole base) mixtures of PNIPA and PAAc at pHs 3 and 10. At pH 10, at which PAAc is completely ionized, no urea effect was observed. In contrast, the results at pH 3 revealed that a large PNIPA–PAAc complex was formed in the absence but not in the presence of urea. It should be noted that the size distribution of PNIPA or PAAc observed in the mixture containing 4 M urea is the same as the distribution of each original polymer (see Figure 16). As a result, we can say that the formation of hydrogen bonds between the NIPA and AAc residues plays an important role in the volume collapse of Gels II and III at pH 3.

The effect of the distribution of the NIPA residues on the swelling of terpolymer gels consisting of NIPA, AAc, and 2-hydroxyethyl methacrylate (HEMA) has been studied by Vakkalanka and Peppas [77]. They prepared two sorts of terpolymer gels; (1) a gel with cross-linked random terpolymer chains, and (2) a gel with cross-linked chains consisting of blocks of NIPA (continuous NIPA segments) in a random copolymer of AAc and HEMA. It was demonstrated that there is a marked difference in swelling behaviors between the block and random terpolymer gels when temperature was varied at a constant pH. This appears to be another evidence supporting the validity of our discussion mentioned above.

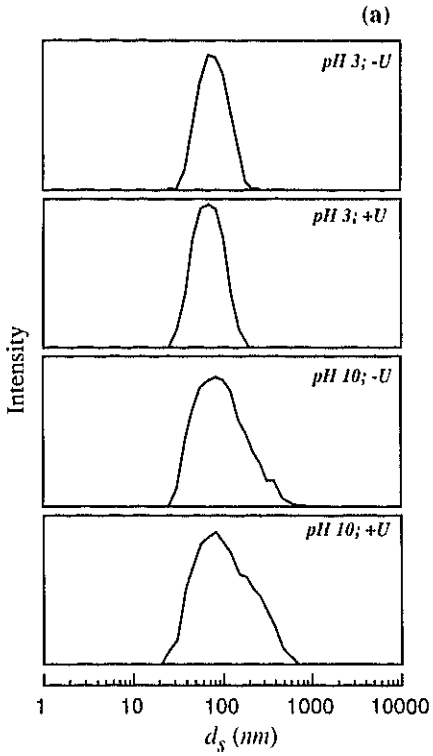


FIG. 16 Effects of pH and 4 M urea on the size distribution of PAAc (a) and PNIPA (b) examined by DLS at 15°C. The samples were the same as those in Table 2. +U and −U represent the presence and absence of 4 M urea, respectively. (From Ref. 28.)

D. Role of Hydrogen Bonding and Hydrophobic Interaction in Gel Collapse

We have discussed the role of hydrogen bonding and hydrophobic interaction in the volume collapse of NIPA–AAc gels. However, one may claim that the gel system examined would be a special kind of polyelectrolyte gel. Thus we have tired further to examine the effects of both intermolecular forces on the gel transition with another polyelectrolyte gel.

Poly(ethyleneimine) (PEI) is a representative polybase with either a linear or a branched polymer structure; the former is more often abbreviated as LPEI and the latter as BPEI. The acid hydrolysis of poly(ethyloxazoline)

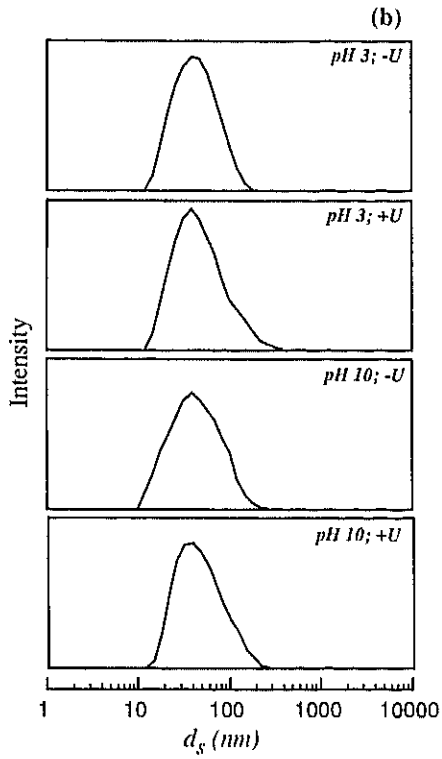


FIG. 16 *Continued.*

(PEOX) gives rise to LPEI [78–79], while BPEI can be obtained through the ring-opening polymerization of ethyleneimine [80]. In this study, we selected LPEI in the preparation of the polyelectrolyte gel because of the following advantages: (1) The deprotonation was fully studied as a function of pH by means of potentiometric [81,82] and calorimetric titrations with strong bases such as NaOH [83]; (2) the polymer precipitates to form crystalline hydrates from alkaline solutions (pH > 9) through hydrogen bonding between the —NH— groups and water molecules [82,84]; (3) x-ray structure analysis [84] has demonstrated that such hydrates consist of alternately stacked layers of polymers and water molecules in the crystallized state; (4) in addition, our preliminary experiments revealed that a gel of LPEI can be obtained without difficulty via cross-linking with ethylene glycol diglycidyl ether (EGDGE).

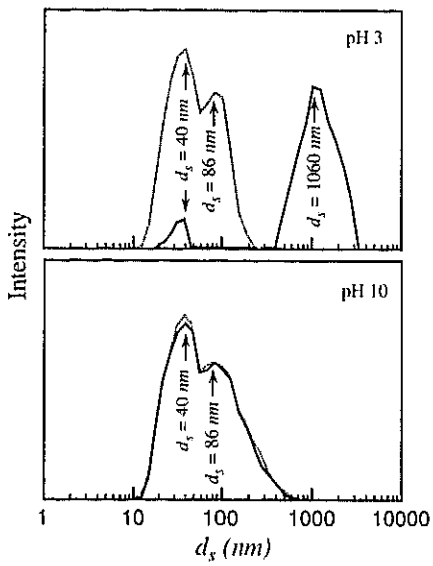


FIG. 17 Effects of pH and 4 M urea on the size distribution of the PAAc–PNIPA mixture examined by DLS at 15°C. Full lines and dashed lines respectively denote the absence and presence of 4 M urea. From the results of Figure 16, we can assign the peak appearing at $d_s \sim 40$ nm to PNIPA and the peak at $d_s \sim 86$ nm to PAAc. A complex with the average Stokes diameter ~1060 nm was observed in the PNIPA–PAAc mixture at pH 3 in the absence of urea. (From Ref. 28.)

1. Effects of pH and NaCl Concentration on the Swelling Degree

The gel sample was inserted into a glass cell together with 0.001 M HCl. After this, the outer medium which was maintained at 20 ± 0.1°C and adjusted to a desired pH within the range of 3 to 12 using various concentrations of HCl (pH < 6.7) or carbonate-free NaOH (pH > 6.7), was made to flow slowly through the cell until the diameter of the gel reached equilibrium under the given conditions. Figure 18 shows pH-dependent changes in the normalized equilibrium gel diameter (d/d_0). The normalization of each observed equilibrium diameter (d) was then performed with the inner diameter (d_0) of the capillary used in the gel preparation. During a pH change cycle (3 to 12 followed by 12 to 3), the gel underwent a discontinuous volume phase transition near pH 10.7 (collapse) and pH 5.9 (swelling); thus a large hysteresis appeared in the swelling curve.

The effect of NaCl concentration on the gel diameter was studied at pH 3, at which the gel was in a fully swollen state. As can be seen from Figure

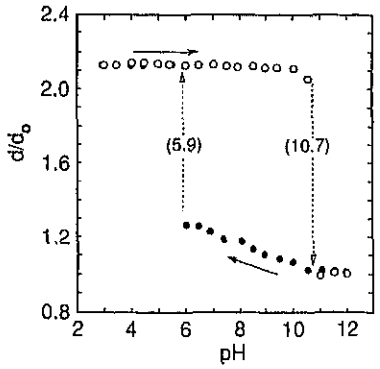


FIG. 18 Normalized equilibrium diameters (d/d_0) of the LPEI gel in aqueous solution at 20°C as a function of pH. Open symbols denote an increase in pH from 3 to 12, whereas closed symbols show a decrease in pH from 12 to 3. The values in the parentheses indicate the pH at the phase transition point. (From Ref. 27.)

19, an increase in the NaCl concentration brought about a monotonic gel collapse without transition. The gel diameter at 0.1 M NaCl concentration was almost half that in an NaCl-free solution at pH 3; this value was close to the fully collapsed diameter in Figure 18 (i.e., pH > 10.7). No hysteresis appeared in a concentration change cycle of NaCl.

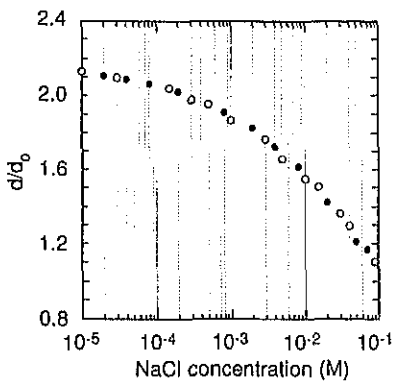


FIG. 19 The change in the normalized equilibrium gel diameters (d/d_0) with NaCl concentration at pH 3 and at 20°C. Open symbols denote an increase in the concentration from 0 to 0.1 M, whereas closed symbols show a decrease in the concentration from 0.1 to 0 M. (From Ref. 27.)

It is true that pH and NaCl concentration influence the ionization state of polyions. If we assume that these factors affect the state of ionization of the network in a polyelectrolyte gel and thereby its swelling degree is altered, the ionization state of a PEI gel in a 0.1 M NaCl solution and that in a salt-free solution at pH ~ 10.7 seem to be almost the same, because there is little difference between the d/d_0 ratios determined in both solutions. However, a large difference was observed in the deswelling of the gel when increasing the pH and NaCl concentration. At present, to our knowledge, there is no theory that fully accounts for this difference on the basis of a mathematical model.

We will now attempt to explain on molecular grounds the observed swelling–deswelling characteristics of the LPEI gel, especially the pH-induced change, in terms of a balance between the repulsive and attractive forces within the cross-linked polymers in the network. Previous studies [81,82] have reported that a highly deprotonated LPEI forms crystalline hydrates in its alkaline solutions (pH > 9). The existence of two distinct hydrates, sesquihydrate with a unit cell containing 8 monomeric units and 12 water molecules, and dihydrate with a unit cell containing 4 monomeric units and 8 water molecules, has been reported on the basis of the x-ray structure analysis. The crystals of both hydrates consist of alternatingly stacked layers of polymers and water molecules arranged parallel to the *bc* plane. As shown in Figure 20, three types of hydrogen bonds (N—H···O, O—H···O, and O—H···N) play a major role in the stabilization of the crystal lattices. In the case of the cross-linked LPEI, i.e. the gel, it should not form such crystalline hydrates, but several parts of the polymer chain segments in the network would form a stable structure like that in Figure 20, at pH > 10.7, at which both the —NH— and —N< groups are highly deprotonated. Therefore it is at this pH that the attractive force overcomes the repulsive electrostatic force. We consider hydrogen bonding to be the attractive force at work and assume that the gels that have collapsed due to hydrogen bonding do not swell again until significant numbers of the —NH— and —N< groups are protonated as the pH decreases; this would account for the large hysteresis in the swelling curves. On the other hand, an increase in NaCl concentration may eliminate the positive charges of the network as the repulsive electrostatic force, but it fails to form such a hydrogen-bond-stabilized structure because of the protonated ionizable groups ($—NH_2^+—$ and $—NH^+<$); therefore the gel collapses monotonically.

2. pH Dependence of Viscosity for the Polymer

Since we expected a similarity between the pH-induced changes in gel volume and polymer conformation, we thus measured the reduced viscosity of LPEI·HCl in salt-free and 0.1 M NaCl solutions as a function of pH. Ko-

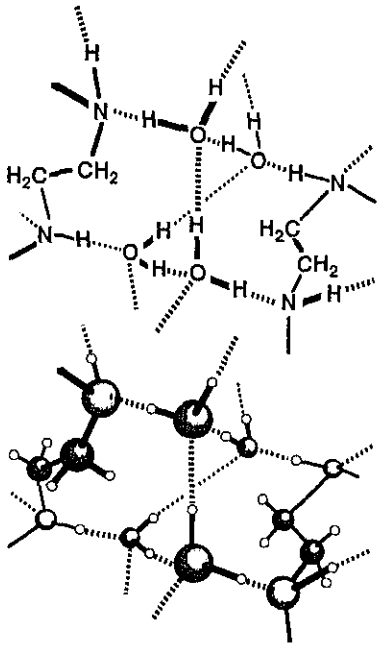


FIG. 20 Schematic illustration for three types of hydrogen bonds in a dihydrate of LPEI. The structural formula (top) and the corresponding atomic arrangement (bottom) are illustrated by reference to Figures 4, 6, and 7 in Ref. 84. Each H_2O oxygen atom is bound to four hydrogen atoms; two of them are covalently bonded and the remaining two are hydrogen bridged from neighboring water molecules or NH groups. Such a hydrogen bond–stabilized structure would form in highly deprotonated LPEI chain segments in the network. (From Ref. 27.)

bayashi et al. [81] have already studied the pH dependence of the reduced viscosity for LPEI in a 1 M KCl solution at 24.5°C and reported that an increase in pH from 2.9 to 8.8 brought about a viscosity fall at pH < 6 but an increase at pH > 8 after passing through a minimum value around pH 6.5. As can be seen from Figure 21, however, our measurements showed a monotonic decrease in the viscosity with increasing pH from 2.9 to 8.8. At pH > 9, it was very difficult to measure the viscosity, especially for the salt-containing system, because more often the sample became turbid due to the formation of hydrates of highly deprotonated LPEI via polymer–polymer association. Kobayashi et al. have considered such an association as one possibility leading to an increase in the viscosity at pH > 8, but they also mentioned that another reason was the stretching of the LPEI chain due to "repulsion" between lone-pair electrons of nitrogen atoms in the polymer

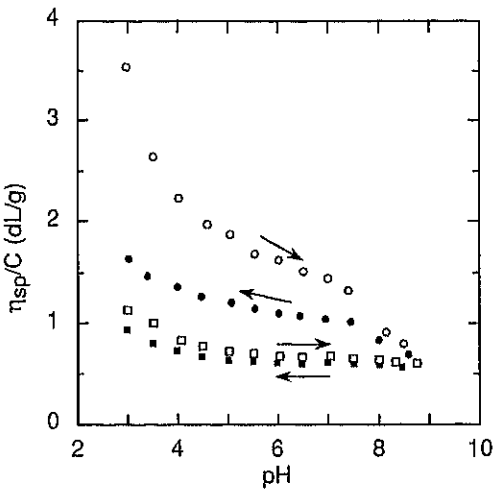


FIG. 21 pH-induced changes in reduced viscosities (η_{sp}/C) of salt-free solution (open and closed circles) and 0.1 M NaCl solution (open and closed squares) of LPEI at 20°C. Open symbols denote an increase in pH, whereas closed symbols denote a decrease in pH. (From Ref. 27.)

and Cl^- and/or OH^- ions in the medium. (Since it is reasonable to consider that lone-pair electrons of nitrogen atoms in the —NH— groups are solvated by coordination to water molecules as the solvent, we cannot understand why such lone-pair electrons serve as the anion.)

The most striking feature in the viscosity curves is the appearance of a hysteresis during the pH change cycle (from 2.9 to 8.8 and vice versa). Since the hysteresis was also observed even in the presence of 0.1 M NaCl, it is not due to an increase in ionic strength during the pH change cycle. One might assume that a very slow alteration in the polymer conformation under a given pH may cause a hysteresis. Although each of the sample solutions was allowed to stand for one day with mild stirring after the pH adjustment, we cannot conclude that there is no kinetic effect in an infinite period. However, the appearance of the hysteresis in both the viscosity and the swelling curves seems to be due to the same reason as described in the previous section. Even when the solution basicity is not high enough to result in crystalline hydrates of LPEI, the deprotonation of a large portion of the ionizable groups could lead to the collapse of the polymer chain through "intrapolymer" hydrogen bonding with the aid of water molecules (interpolymer hydrogen bonding was not the case, since we did not observe a rise in viscosity under the conditions used here). Therefore the successive

protonation of such a collapsed polymer becomes increasingly difficult; as a result, we observed that the viscosity during the pH decrease is lower than that during the pH increase.

3. Potentiometric Titration Curves

Investigation of the protonation–deprotonation process by means of potentiometric titration could provide a key to understanding the pH-dependent changes in the gel volume and polymer conformation. Three previous studies [81–83] have dealt with the potentiometric titrations of aqueous polymer solutions; the results are outlined as follows: (1) Protons were dissociated from LPEI·HCl with increasing difficulty, in particular at the protonation >50%, due to their strong interaction with neighboring charged ammonium ions; i.e., the nearest neighbor interaction originally proposed by Katchalsky et al. [85]. (2) It was not possible to achieve 100% protonation even at pH ~ 2, but an approx. 70% degree of protonation gave an "apparent end point" of titration. (3) At less than 10% of the protonation the polymer precipitated to form crystalline hydrates. With respect to the formation of crystalline hydrates through hydrogen bonding, Weyts and Goethals [82] reported that aqueous salt-free solutions containing 0.1 M LPEI·HX ($X = Cl^-$, $HCOO^-$ and CH_3COO^-) exhibited an unusual pH change when the titration proceeded until 10% of the protonation (i.e., pH ~ 9.4); that is, the solution pH increased due to the addition of a strong base until 10% protonation, but further addition of a very slight amount of the base brought about a decrease in pH by ca. 0.7 units accompanied by the appearance of solution turbidity. This phenomenon was then interpreted as follows: Once the crystallization starts, the enthalpy of crystallization provides energy to expel more protons of LPEI·HX into the solution; this promotes the formation of crystalline hydrates via interpolymer hydrogen bonding with the aid of water molecules and results in an increase of the fraction of protonated ammonium groups on the LPEI remaining in the solution; therefore these in turn lead to a decrease in the solution pH. For this reason, no previous studies have attempted to carry out a back titration with strong acids after titrating LPEI·HX with strong bases, although it would provide important information in order to understand the hysteresis observed in the viscosity curves.

In the case of the gel, on the other hand, the back titration with an acid for the sample dispersion, which has already been titrated with a base until an equivalent point, should be possible, since precipitation does not need to be taken into consideration. In contrast to the polymer, however, there are several difficulties in the analysis of the titration data; for example, how to estimate the "real" acid–base equilibrium within the gel phase from the pH measurements of the outer solution (see Sec. IV.C.2). So far, no study has dealt with the potentiometric titrations of polyelectrolyte gels. We neverthe-

less employed the potentiometric titration with NaOH for the aqueous dispersion of powdered LPEI·HCl gels, followed by a back titration with HCl; through both titrations we intended to clarify the origin of the hysteresis in the swelling curve.

Figure 22 shows the titration curves in which the pH of the outer medium was plotted against the volumes of NaOH (V_N) and HCl (V_H). Also shown in Figure 22 for the purpose of comparison is the titration curve of the polymer (LPEI·HCl) with NaOH. In the titrations of the gel, the time (t_{eq}) required for the establishment of equilibrium pH calculated on the basis of 1 mL of titrant was measured at each stage of the titration and plotted against V_N and V_H. In all the titration curves, both sample and titrant concentrations were precisely controlled on the basis of the results of the elemental analysis in order to complete the stoichiometric neutralization of all the titratable groups with 1 mL of NaOH or HCl titrant; i.e., 1 mL of NaOH or HCl being equivalent to moles of the $—NH_2^+—$ plus $—NH^+<$ groups or the —NH— plus —N< groups. A comparison of the three titration curves in Figure 22 provides us with some significant information: (1) The pH of the gel dispersion is higher than that of the polymer solution over all the stages of titration with NaOH, especially in the range of $V_N < 0.5$ mL at which, as demonstrated in a previous study [83], the nearest neighbor interaction does not have a strong influence on the deprotonation reaction of LPEI·HX (i.e., $—NH_2^+— \rightarrow —NH— + H^+$). (Even though at the protonation degree <50% there is little influence from the nearest neighbor interaction on the dissociation of protons from the polymer, but there is a strong influence in the case of the gel because cross-linking should facilitate "intramolecular" interactions between the ionizable groups bound to the network; therefore we assumed that the cross-linking of the polymer chains was responsible for this result.) (2) At the onset of the back-titration of the gel with HCl, a very rapid decrease in pH is observed and the curve exhibits an inflection point at $V_H \sim 0.1$ mL. (3) This is not due to the titration with HCl of the remaining NaOH in excess in the system because a very slow attainment of acid–base equilibrium was observed from the t_{eq} vs. V_H curve at $V_H < 0.15$ mL. (4) In the back titration, the initial pH level (2.9) of the original gel dispersion is reaced even at $V_H = 0.71$ mL.

Special attention ought to be paid to results (2) and (4) with regard to our present purpose. Our gel contains two kinds of amines as the ionizable groups, —NH— and —N< in the form of a free base; the contents are 88 mol% for the former and 12 mol% for the latter by means of elemental analysis. It is generally believed that pK_a (i.e., $-\log K_a$) for tertiary alkyl ammonium salts is larger than 10, e.g., $pK_a = 10.64$ for $(CH_3CH_2)_3N \cdot HCl$ at 25°C. Taking this into account, we may predict that the —N< groups in the network are preferentially protonated at $V_H < 0.1$ mL: $—N< + H^+ \rightarrow$

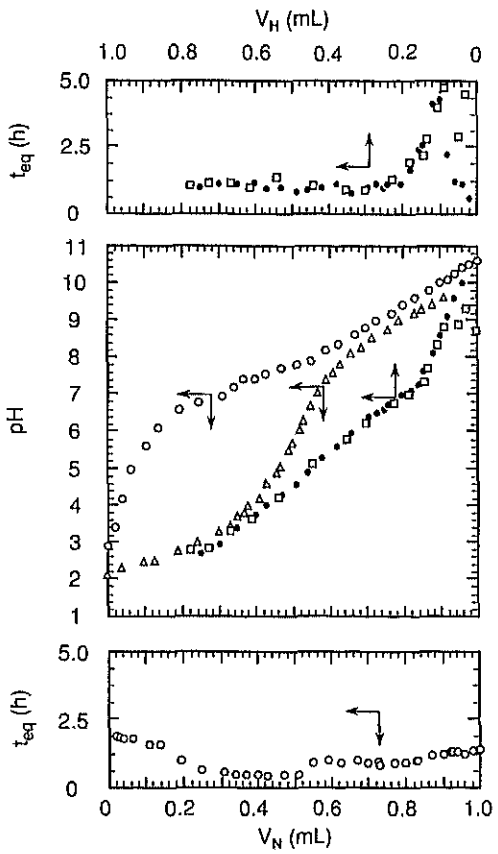


FIG. 22 Change in pH during titration of LPEI·HCl with NaOH (open triangles) as well as pH changes during titration of LPEI·HCl gel with NaOH (open circles) followed by back titration with HCl (closed circles). Also shown in this figure is the titration curve (open squares) with HCl of LPEI gel in the form of free base. The curves of t_{eq} vs. V_N (open circles) and V_H (closed circles and open squares) were given to indicate the time (t_{eq}) required for the establishment of pH equilibrium at each stage of the titration if unit volume of the NaOH or HCl titrant were added into the titration system. Titration conditions: titrant concn., 3 M for each; sample concn., 0.1 M for each (by moles of the —NH_2Cl— groups in the polymer, the —NH_2Cl— plus —NHCl< groups in LPEI·HCl gel, and the —NH— plus —N< groups in LPEI gel); sample size, 30 mL for each; 20°C. (From Ref. 27.)

—$NH^+<$. In fact, the amount of the titrated groups in this range is about 10 mol% of the total ionizable groups in the system, the value of which is very close to the content of the —N< groups.

If the protonation of the —N< groups could be terminated at $V_H \sim 0.1$ mL, the stage of the titration at $V_H > 0.1$ mL may be related to the reaction —NH— + $H^+ \rightarrow$ —NH_2^+—. As mentioned above, however, this reaction appears to go essentially to completion at $V_H \sim 0.7$ mL; this corresponds with the 68% degree of protonation for a total of the —NH— groups because the —NH— content = 88%. Therefore the reaction does not follow a 1:1 stoichiometry. However, this is not surprising when we consider that a highly deprotonated LPEI gel contains a large number of —NH— groups whose nitrogen atoms are stabilized with bound water molecules via hydrogen bonding and resistant to the coordination (protonation) with the protons added. The same interpretation has been applied to the viscosity curves, and even in the gel system a structure as shown in Figure 20 may form within chain segments of the networks. As a result, the potentiometric titration clearly demonstrated that the origin of the hysteresis in the swelling–deswelling process is due to the hysteresis in the deprotonation–protonation process; in other words, a large difficulty in the protonation caused by hydrogen bonding as shown in Figure 20. However, this does not account for the gel discontinuously swelling in the protonation process or discontinuously collapsing in the deprotonation process. We thus have to consider that the gel undergoes a transition when the repulsive force due to the NH_2^+— and —$NH^+<$ groups overcomes the hydrogen bonding as the attractive force or vice versa.

By taking the above into account, we can explain why the —N< groups were preferentially protonated in the titration with HCl, but the preferential deprotonation did not take place in the titration with NaOH. In the protonation process, the —NH— groups behave as a very weak base due to the previously mentioned stabilization effect, while the —N< groups as a strong base preferentially accept protons to form the tertiary alkyl ammonium ions. At the onset of the titration with NaOH, the —NH_2^+— groups may be taken as a strong acid since at $V_N = 0$, pH = 2.1 for LPEI·HCl and 2.9 for LPEI·HCl gel. Thus in the range of $V_N < 0.1$, the dissociation of protons from the —NH_2^+— groups overlaps with that from the —$NH^+<$ groups, leading to a titration curve without an inflection point.

Our titration data have indicated that there was a hysteresis in the deprotonation–protonation process. However, we should consider that the titration was performed in the absence of supporting electrolytes such as NaCl. Consequently, the ionic strength of the system increased during the course of titration; for example, at $V_N = 1.0$ mL the ionic strength became 0.1 M due to NaCl resulting from the reaction —NH_2Cl— + NaOH $\rightarrow$ —NH— +

NaCl + H_2O. Thus a titration which is not accompanied by such a salt formation is desired. Taking this into account, we performed the titration with 3 M HCl of an aqueous dispersion containing the LPEI gel (base form). The result obtained was overplotted in Figure 22 (see open squares). At V_H < 0.03 mL the titration curve for the LPEI gel was different from the back titration curve for the salt-form gel, perhaps due to a difficulty in the protonation of the —N< groups (this may be conceivable when the gel sample in the base form was directly subjected to the titration). At V_H > 0.05 mL, however, there was a good agreement between the titration curves, indicating that NaCl resulted from the titration of the LPEI·HCl gel with NaOH and accumulated in the system little influences the back titration.

4. Effect of Urea on the pH-Induced Volume Transition

Urea has been frequently employed in the biochemical field as a means to identify hydrogen bonds, since it is generally believed that urea can break up intra- or intermolecular hydrogen bonding of proteins in aqueous systems. We thus studied the effects of urea on the pH dependence of the gel diameter (Figure 23) and found that urea facilitates the swelling of the gels at higher pH levels during the protonation process, even at urea concentrations one fourth or one eighth lower than the most commonly employed concentration (8 M) in the denaturation of proteins.

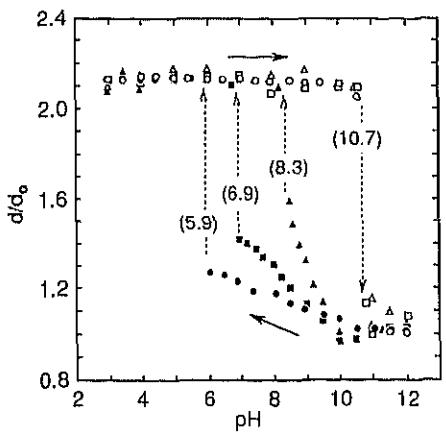


FIG. 23 pH-induced changes of normalized equilibrium gel diameters (d/d_0) at 20°C in aqueous solutions containing different concentrations of urea: 0 M (circles); 1 M (squares); 3 M (triangles). Open symbols denote an increase in pH from 3 to 12, whereas closed symbols show a decrease in pH from 12 to 3. The values in the parentheses indicate the pH at the phase transition point. (From Ref. 27.)

It has long been believed that urea disrupts the cluster structure of water molecules; i.e., "structure breaking effect." (For previous studies showing that urea acts as a water structure breaker, see the introductions of Refs. 86 and 87; however, it should be noted that both articles deal with a molecular dynamics simulation of a dilute aqueous urea solution and report that urea has little effect on water structure under an infinitely low concentration.) Thus it appears that urea may inhibit the formation of a structure (as shown in Figure 20) stabilized through the hydrogen bonds with water molecules. In the presence of urea, therefore, both the acceleration of the protonation (i.e., ionization) and the weakening of the attractive interaction between the cross-linked chains takes place at the same time during the protonation process. As a result, a pH at which the gel swells discontinuously should shift to an alkaline pH side; in other words, a tendency for the hysteresis to disappear can be observed when adding urea.

5. Effects of Anionic Surfactants on the Swelling Degree

Urea, being a water structure breaker, would weaken the hydrophobic interaction between solute molecules as reported in several previous studies (see Ref. 76). It is thus necessary for us to examine the effects of urea on the hydrophobic interaction in the present gel system. However, this is a considerably difficult problem which, to our knowledge, has not yet been dealt with by any researchers in the field of polyelectrolyte gels. The main reason is the lack of information about whether hydrophobic interaction plays a role in the volume collapse of usual polyelectrolyte gels with a lot of hydrophilic ionizable groups, such as the LPEI gels in question. As a novel approach in order to overcome this difficulty, we examined the swelling curves of the LPEI gel as a function of the concentration of anionic surfactants in the presence and absence of urea.

Our previous study [23] demonstrated that the binding of sodium dodecyl sulfate (SDS) anions to the charged ammonium ions of EGDGE-cross-linked branched poly(ethylenime) gels brings about a dramatic volume collapse due not only to the neutralization of the charges but also to hydrophobic interaction. As shown in Figure 24, this is the case in the LPEI gel system. Sodium butyl sulfonate (SBS) without definitive critical micelle concentration (C_{mc}) in aqueous solutions exhibited the same effect on the gel diameter as NaCl (see Figure 19). However, sodium octyl sulfonate (SOS; $C_{mc} \sim 130$ mM) and SDS ($C_{mc} \sim 8.3$ mM) showed remarkable and strong effects on the volume phase transition of the LPEI gel: (1) The concentration at which the transition takes place is lower for SDS than for SOS because the former is stronger than the latter with respect to hydrophobicity. (2) The SDS concentration bringing about the transition was lower at 60°C than at 20°C, the

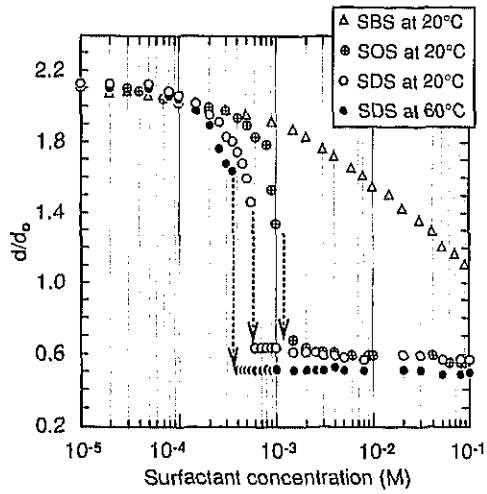


FIG. 24 Changes of normalized equilibrium gel diameters (d/d_0) in aqueous pH 3 solutions containing different surfactants at 20 and 60°C. The kinds of surfactants and the temperatures for the measurements are shown in the figure. (From Ref. 27.)

result of which agrees with the common knowledge that a rise in temperature enhances the hydrophobic interaction. (3) In addition, the gel diameter was reduced to 26% with SOS and SDS at 20°C and to 23% with SDS at 60°C; these values are about half compared to the diameter of a fully deprotonated gel at pH > 10.7, clearly indicating that the hydrophobic interaction may act as an attractive force in the gel collapse.

In a previous study [31] we suggested that the binding of surfactants such as SDS to LPEI gels occurs mainly in the region in the near vicinity of the gel surface but that the molecules fail to penetrate into the core of the gel phase. A Donnan potential, generated due to an excess of surfactant anions around the gel surface, would make further diffusion of the surfactants with anionic charges more difficult. From the results in Figure 24, however, the surfactant-LPEI gel system may be regarded as a well-defined polyelectrolyte gel whose volume collapse takes place via hydrophobic interaction as an attractive force. We thus measured the d/d_0 of the gel samples in aqueous solutions containing different amounts of SDS in the presence and absence of urea; the pH of the solutions was adjusted to 3.0 so as to maintain a completely swollen state for the gels. As can be seen from Figure 25, urea has no influence on the SDS-induced discontinuous volume collapse for the LPEI gel, which indicates that urea does not contribute to weakening the hydrophobic interaction, at least in our model system. Therefore, we may

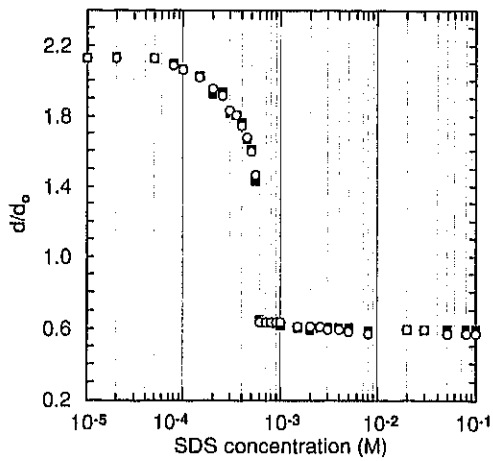


FIG. 25 Effect of urea on SDS-induced changes in normalized equilibrium gel diameters in aqueous pH 3 solutions at 20°C. Closed squares and open circles, respectively, show the curves in the presence and absence of 3 M urea. (From Ref. 27.)

say that the results shown in Figure 23 are due to the breaking up of hydrogen bonds by urea molecules.

E. Ionization Equilibria of COOH Groups Bound to Polymer Network

To understand the nature of the phase transition of ionic gels, it should be necessary to obtain accurate information about the ionization equilibria of acidic or basic groups within the gel. The object of this section is to examine the dissociation behavior of the COOH groups in the NIPA–AAc gels by means of potentiometric titration and to compare it with the results of swelling experiments; through this approach we intend to discuss the swelling mechanism of ionic NIPA gels at the molecular level. In particular, our attention has been paid to the role of mobile counterions, as well as those of hydrophobic interaction and hydrogen bonding. The submicron-sized gel particles with 70 mol% NIPA and 30 mol% AAc, in addition to the bulk gel of a fine grind, were employed in this study, because we have succeeded in preparing such microgel particles [33]. We also employed the NIPA–AAc copolymer with the same AAc content as a control sample. One might expect that use of the microgel would help to eliminate a general problem in the pH titration for gels; that is, a great difficulty in judging whether the H^+ and OH^- concentrations within the gel phase come to equilibrium with those

in the aqueous bulk phase at different stages of the titration. We should note that our microgel has most of the COOH groups located in the interior but not on the hydrodynamic surface of the particle (see Ref. 33).

1. Relation Between Dissociation Constant and Degree of Dissociation

A complete titration curve can be given by plotting apparent dissociation constant (pK_a) against the degree of dissociation (α_d). We may determine pK_a from the titration data using the following relations:

$$pK_a = pH - \log\left(\frac{\alpha_d}{1 - \alpha_d}\right) \tag{16}$$

$$\alpha_d = \alpha_n + \frac{C_{H^+} - C_{OH^-}}{C_p} \tag{17}$$

Here, α_n is the degree of neutralization, and C_{H^+} and C_{OH^-} are the molar concentrations of H^+ and OH^- ions, respectively. Writing the required electrostatic free energy for the removal of an equivalent of protons at a given α_d as $\Delta G^i_{el}(\alpha_d)$, its relation to pK_a may be given as (for example, see Ref. 88)

$$pK_a = pK^0 + 0.43\,\frac{\Delta G^i_{el}(\alpha_d)}{RT} \tag{18}$$

where pK^0 is characteristic of the ionizing group under conditions where electrostatic interactions with other ionizing groups are absent.

The NIPA–AAc gel undergoes a volume phase transition in response not only to pH and ionic strength but also to temperature; thus, it would be interesting to examine the dependence of pK_a upon α_d as a function of ionic strength and temperature. We studied the effect of ionic strength on the α_d dependence of pK_a at 25 and 35°C (Figures 26 and 27). The latter temperature is slightly higher than the T_v of NIPA gel and the LCST of NIPA polymer. Since our copolymer and gels in the acid form may be taken as a neutral NIPA, the phase separation and the volume phase transition should take place during the titration at 35°C. Thus it would be interesting to see how these effects appear in the dependence of pK_a on α_d. However, we did not perform the titration of the bulk gel at 35°C because (1) the characteristic times of swelling and deswelling for NIPA gels are proportional to the square of a linear dimension of the gel and (2) the transition becomes very slow when temperature comes close to T_v [53].

The titration curves in Figures 26 and 27 provide us with some significant information: (1) On the whole, pK_a increases with increasing α_d but decreases with addition of NaCl. (2) There is little difference in pK_a between

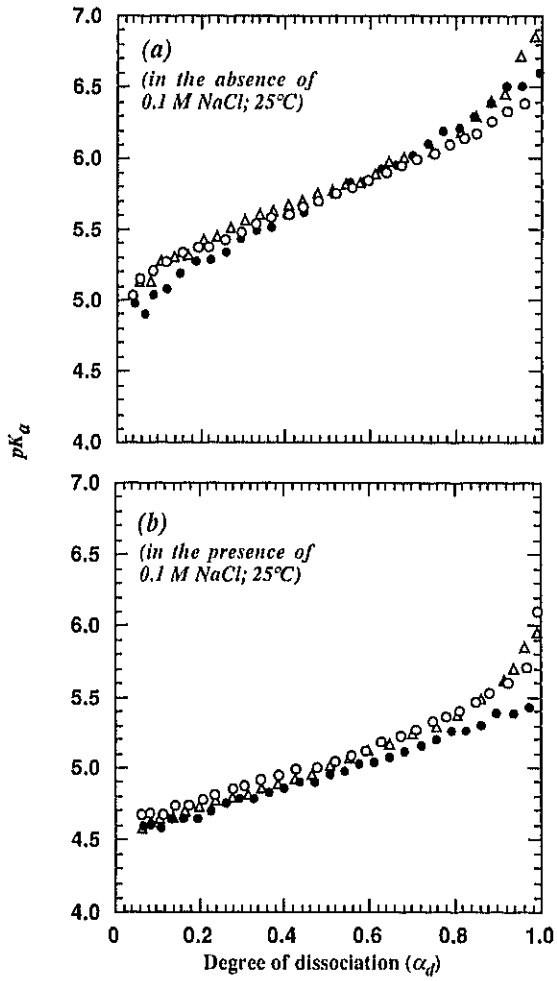


FIG. 26 Changes in apparent dissociation constant (pK_a) with the degree of dissociation (α_d) for the copolymer (closed circles), the bulk gel (open triangles), and the microgel (open circles) in the absence (a) and the presence (b) of 0.1 M NaCl at 25°C. A very slight initial fall in pK_a was observed in the salt-free system with the copolymer. This was reproducible and not an experimental error; thus it seems that in the case of the copolymer the interaction (being discussed in the text) appears not only at 35°C but also at 25°C. (From Ref. 33.)

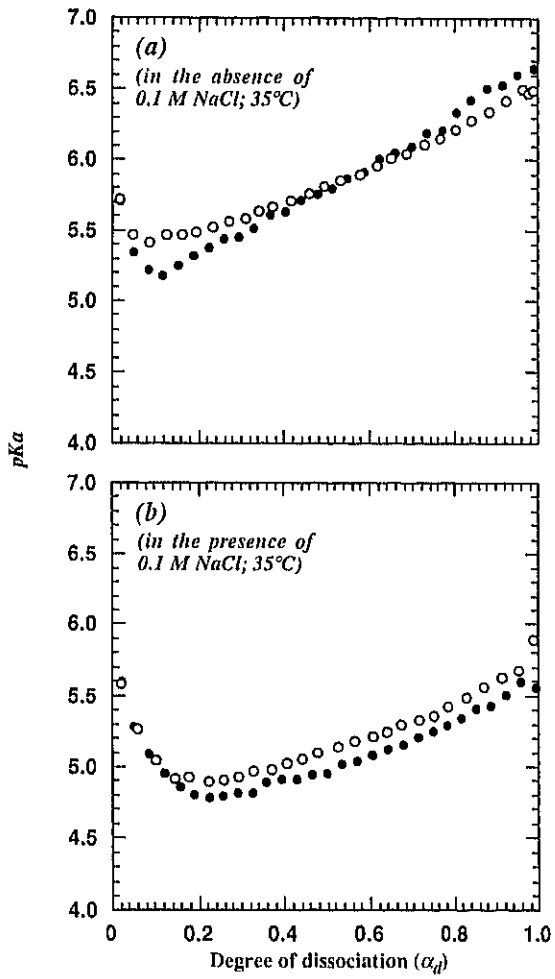


FIG. 27 Changes in apparent dissociation constant (pK_a) with the degree of dissociation (α_d) for the copolymer (closed circles) and the microgel (open circles) in the absence (a) and the presence (b) of 0.1 M NaCl at 35°C. (From Ref. 33.)

the gels, as well as between the gel and the copolymer. (3) At 35°C and at $\alpha_d < 0.15$ (see Figure 27), however, an increase in α_d leads to a distinct fall in pK_a for both gel and copolymer; their pK_a values at 35°C are larger than those at 25°C.

Result (1) is the general aspect that appeared in the titrations of polymeric acids, such as PAAc, in the absence and the presence of added salt (e.g.,

see Refs. 88 and 89). From an increase in pK_a with α_d, meaning that the removal of H^+ from the polymeric acid becomes increasingly difficult as the titration proceeds, we may learn an increase in $\Delta G^i_{el}(\alpha_d)$ due to the electrostatic attraction between H^+ ions and polyanions. Since the counterions from added salts contribute to weakening this attraction through the elimination of polyion charges, $\Delta G^i_{el}(\alpha_d)$ should decrease over a wide α_d range. Then we may see a decrease in pK_a displaying that the dissociation of H^+ from the polymer becomes easy. Therefore, result (2) indicates that the ionization mechanism for the gels is essentially the same as that for the polymer solution.

Taking the above into account, result (3) may be explained as follows. At the initial stage of the titration ($\alpha_d \sim 0$) and at 35°C, both copolymer and cross-linked copolymer network should be in a collapse state due to hydrophobic interaction. This shortens the distance of a COOH group from the surrounding functional groups; thus interactions of this COOH with the neighboring groups would become strong (i.e., "nearest neighbor interaction" originally proposed by Katchalsky et al. [85]). Actually, PNIPA and PAAc give forth a water-insoluble complex under conditions where the COOH groups are fully protonated (see Sec. V.C.4). If this is the case, the removal of the H^+ from the COOH should be impeded. Consequently, pK_a at 35°C became larger than that at 25°C. By ionizing a few COOH groups with NaOH, however, a mutual repulsion among the resulting COO^- ions weakens by degrees the nearest neighbor interaction. This should facilitate the dissociation of other COOH groups (a decrease in pK_a with α_d). Indeed, a turbidity appeared both in the salt-free and the salt-containing solution of the copolymer at 35°C, but the solution became transparent as the titration proceeded ($\alpha_d > 0.1$ for the salt-free system; $\alpha_d > 0.16$ for the salt-containing system).

In the case of the microgel system at 35°C, a turbidity was also observed in the presence of NaCl ($\alpha_d < 0.1$) but not in pure water. This provides a key to supporting the above interpretation (see the following section).

2. Effects of pH, Ionic Strength, and Temperature on the Size of Microgel

It would be interesting to learn how the size (or the swelling degree) of the NIPA–AAc microgel particle varies depending on the ionization of the COOH groups as well as on temperature. For this purpose, we measured apparent Stokes diameters (d_s) by means of dynamic light scattering (DLS) and plotted d_s against α_n as a function of temperature (see Figures 28 and 29). The results obtained in pure water (Figure 28) and in 0.1 M NaCl solution (Figure 29) were then reported separately, because there was a large difference in the magnitude of size changes caused by the absence and the

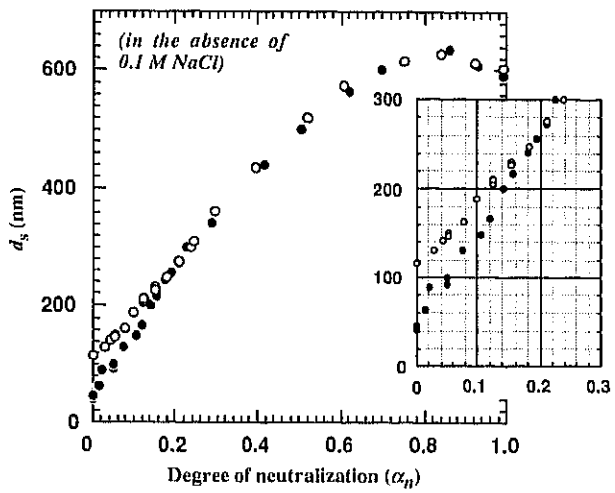


FIG. 28 Changes in apparent Stokes diameter (d_s) of the microgel with the degree of neutralization (α_n) in the absence of NaCl at 25°C (open circles) and 35°C (closed circles). (From Ref. 33.)

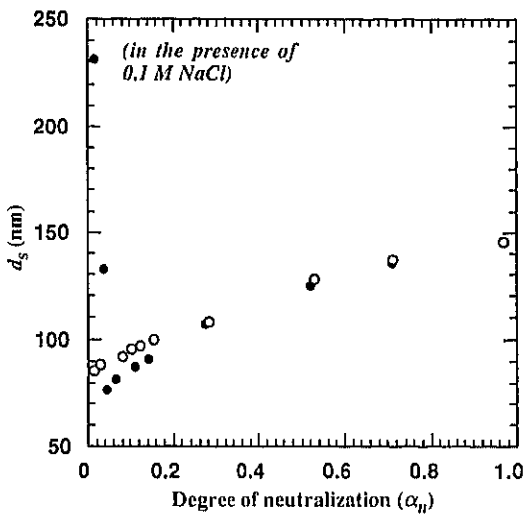


FIG. 29 Changes in apparent Stokes diameter (d_s) of the microgel with the degree of neutralization (α_n) in the presence of 0.1 M NaCl at 25°C (open circles) and 35°C (closed circles). (From Ref. 33.)

presence of the salt. With ionizing the COOH groups, the particle size linearly increased at $\alpha_n < 0.6$ and then leveled off at $\alpha_n > 0.6$; this feature was remarkable in the salt-free system rather than in the NaCl-containing system. With screening the charge of COO^- ions with the counterions from NaCl added, the size decreased over a wide α_n range, except for the result in the salt solution at 35°C and at $\alpha_n < 0.1$ (see Figure 29). These aspects are quite analogous to the changes in the end-to-end extension of PAAc ions in aqueous solutions. Kokufuta [89] has performed the viscometric and electrophoretic studies with aqueous PAAc solutions and obtained the following results (both viscosity and mobility data have been reported in Ref. 89 as a function of pH; however, these can be converted into a relation with α_n [or α_d], because the reference includes the titration curves by pH vs. α_d as well as pK_n vs. α_d): (1) An increase in ionic strength results in a marked decrease in the viscosity as an indication of the end-to-end extension of a polymer chain. (2) The viscosity increases with increasing α_n at $\alpha_n < 0.6$ and levels off at $\alpha_n > 0.6$. (3) These viscosity changes correspond to the mobility changes, because the mobility may be considered as an indication of the net charge density of a polyion when it behaves as a free draining coil in electrophoresis. Among results (1) to (3), we draw particular attention to the fact that the charge density scarcely increases at $\alpha_n > 0.6$. In general, this phenomenon is known as the "counterion binding effect," a strong experimental evidence for which has been reported by Wall et al. [90]. From their transference experiments using radioactive sodium (^{22}Na) in salt-free aqueous solutions containing PAAc partially neutralized with NaOH, we may learn the following important two features: (1) The binding degree of Na^+ ions linearly increases at $\alpha_n < 0.6$ and levels off at $\alpha_n > 0.6$; and (2) the concentration of mobile Na^+ ions increases linearly at $\alpha_n < 0.2$, gradually at $0.3 < \alpha_n < 0.7$, and rapidly again at $\alpha_n > 0.8$. By comparing these results with those of potentiometric titrations in the previous section, let us consider the role of Na^+ ions in our gel system. Then we may assume that at $\alpha_n > 0.6$, at which the gel swells little, the concentration of mobile Na^+ ions still increases. According to the Flory theory for polyelectrolyte gels, a very slight increase in the concentration of mobile counterions within the gel phase brings about a dramatic increase in the swelling degree (e.g., see Sec. II.A). Therefore our results in Figures 28 and 29 may not be understood by assuming that an increase in α_n raises osmotic pressure arising from mobile counterions within the "overall" gel phase. Otherwise, by considering that at $\alpha_n > 0.6$ the "net" charge density of the gel increases little but levels off due to the counterion binding, the dependence of the swelling degree upon α_n may favorably be accounted for. As a result, we may see the strong resemblance between the α_n changes in the swelling degree for the NIPA–AAc gel and in the end-to-end extension for PAAc in solutions.

We examined in detail the effect of temperature on the size of the microgel in pure water at $\alpha_n < 0.3$ (see inset in Figure 28). At $\alpha_n < 0.15$, the particle size at 35°C was smaller than that at 25°C because $T_v \sim 33$°C for neutral NIPA gels. However, this difference disappeared at $\alpha_n \sim 0.15$ at which the gel has 4.5 mol% "COONa" plus 25.5 mol% COOH. These mean that our microgel undergoes "thermal" swelling transitions at $\alpha_d < 0.15$ when lowering temperature from 35°C to 25°C (see Figure 6 in Sec. V.A). We have discussed in the previous section why the initial fall in pK_a, as well as the solution turbidity, appears both in the salt-free and the salt-containing system not only with the copolymer but also with the microgel, under conditions at 35°C and at $\alpha_d < 0.15$. For the copolymer, these phenomena were satisfactorily accounted for in terms of the nearest neighbor interaction, in which hydrogen bonding and hydrophobic interaction play an important role. Although the turbidity did not appear in the salt-free microgel system, the results in the window of Figure 28 clearly indicate that the microgel particles are in a collapse state at $\alpha_d < 0.15$ and at 35°C. Under such a situation, we may reasonably assume the nearest neighbor interaction mechanism to account for the initial fall of pK_a in the microgel system. As a result, the swelling behavior of our polyelectrolyte gel may be understood, without relying on models based upon the Flory theory, through detailed considerations of the mechanism for the dissociation of COOH at the molecular level, even when a slight amount of NaOH was added in the gel system to ionize the COOH groups.

We must discuss separately the α_n change of d_s for the microgel in the salt-containing system, because the turbidity has been observed at 35°C and at $\alpha_n < 0.1$, while the turbid suspension became transparent at $\alpha_n > 0.1$. From this turbidity change, an abrupt decrease in d_s at the initial stage of the neutralization ($\alpha_n < 0.05$; see Figure 29) may be attributed to the disaggregation of microgel particles. It appears that in the salt-free system the microgel surfaces are considerably hydrated by water molecules even at 35°C, while the cross-linked polymers in the particle interior are in a collapse state due to hydrophobic interaction. When adding NaCl into the system, the dehydration due to Na^+ and Cl^- ions seems to favor the aggregation of the particles. This would enhance an "interparticle" interaction, in other words, interactions of the surface functional groups of a particle with those of other particles. If this is the case, the ionization of a few surface COOH groups with NaOH should cause an electrostatic repulsion among the microgel particles to weaken the interparticle interaction. Consequently, we have observed at the same time the initial fall in pK_a as well as in d_s relating to both the intra- and the interparticle interaction. Indeed the initial fall in pK_a was more clear in 0.1 M NaCl solution than in pure water (see Figure

27). Hydrogen bonding as well as hydrophobic interaction would also be conceivable in both the intra- and the interparticle interaction.

VI. CONCLUSIONS AND FUTURE PROSPECTS

We have viewed the phase transitions in polyelectrolyte gels from both sides, theory and experiment. The initial impetus for research on this subject came from work done on a transition observed by Tanaka with nonionic polyacrylamide gels. Thus later work on ionic gels evolved rather independently from that on single polyion chains. In the field of gel transition theories, many studies focused exclusively on modifications of Flory's theory, although several critical studies have claimed this is not realistic because an "incompressible" random-mixing lattice model as well as Guassian chain distributions are assumed. Prior to such physical arguments, on the other hand, several experiments mentioned in Section V have questioned the validity of the concept of osmotic pressure arising from mobile counterions, which has long been assumed as the chief driving force for the swelling of ionic gels. Another important finding through experiments has addressed the issue of "counterion condensation" in ionized gels, which is central to research on solution properties of polyelectrolytes. Then, it is natural to mention that the behavior of ionic gels, including the gel transitions, should be understood in terms of the analogy with those of polyions in solutions.

In respect to applications of polyelectrolyte gels, to which this chapter did not refer, a considerable number of researches have focused on regulation of the phase transitions in ionic gels by externally applied appropriate stimuli. Almost all the researches were performed in the 1990s without relying on the above transition theories, but with simple models in which polymer–polymer interactions are taken into account at the molecular level. For example, we have attempted to establish a simple molecular model [17] for interpreting the phase transition of gels in studies on the construction of "biochemo-mechanical systems" [18,19,21,25,91–95], which convert the energy arising from biochemical changes (such as enzyme reactions) into mechanical work through a swelling–deswelling transition of the gel with immobilized biocatalysts. In this regard, we accounted for the gel transitions by hypothesizing a balance between the repulsion and attraction among functional groups attached to the cross-linked polymers which arise from a combination of four intermolecular forces (see Sec. II). Then, one took a critical attitude to this model due to the general assumption that a simple concept cannot be used to explain complex systems such as gels. Nevertheless, almost all of the experimental swelling curves can be understood in terms of this concept (see Secs. II and V). Consequently, it would be expected that the simple concept should be helpful to develop one of the most promising

physical models, which provides a better explanation not only of the phase transition but also of the swelling behavior of ionic gels.

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