Macromolecules **1999,** *32,* 4619−4624

Dielectric Properties of Collapsing Hydrogels

Shigeo Sasaki,* Shogo Koga, and H. Maeda

Department of Chemistry and Physics of Condensed Matter, Graduated School of Science, Kyushu University, 33 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received January 27, 1999; Revised Manuscript Received May 4, 1999

ABSTRACT: Dielectric spectra were measured for the polymer gel of *N*-isopropylacrylamide (NIPA) and copolymer gels of *N*-isopropylacrylamide and sodium styrenesulfonate (NIPA−SS) in the swollen and collapsing states in the frequency range from 100 kHz to 2 MHz. Dispersions were observed for the NIPA gel in the collapsing state and NIPA−SS gels in both the collapsing and swollen states. The characteristics of dispersions in the collapsing gels were different from the characteristics in the swollen gels, while the former characteristics are very similar in NIPA and NIPA−SS. The similarity between dispersions observed for NIPA and NIPA−SS gels indicates that counterions of NIAP−SS gels bind tightly to the ionized groups and cannot move freely in the collapsing gels. The analysis of the dispersions reveals that water molecules inside the collapsing gels are surrounded by the gel chains and form electrically disconnected clusters.

1. Introduction

N-Isopropylacrylamide gel (NIPA gel) is well-known to exhibit a discrete volume phase transition with a change in temperature[1] and/or concentration of added salts[2−3] and has been intensively investigated during this decade. Our recent studies[4−5] have shown that the discrete volume reduction of hydrated gel is induced by the coupling effect of the highly cooperative dehydration of gel chains and the large increase in entropy of shrunken chains. The water molecules dissociate from the chains to the bulk when the chemical potential (free energy) of the water molecule in the bulk is lower than that of the polymer associated water molecule.[4] The dehydrated chains have a very poor affinity for water, and the chains shrink. Hydrophobic chains are considered to surround water molecules in the collapsing gel, when the volume fraction of gel chains in the collapsing gel is more than 0.5. Properties of clusters of the water molecules in this situation are considered to be very different from that in ordinary bulk water. Our interest here is in the dielectric dispersion of the collapsing gel which reflect the dynamical properties of the water clusters. It is well-known that ordinary water exhibits the high dielectric constant of 80 at frequencies lower than 1 GHz and a dielectric dispersion at about 30 GHz. However, little is known about the dielectric properties of the collapsing gel. The temperature dependence of the dielectric dispersion of NIPA gel was investigated in the present study.

It has been shown that an introduction of charged groups into NIPA gel chains makes the discontinuous volume change with temperature continuous.[6−9] The alteration of volume change behavior is caused by an addition of the Donnan osmotic swelling pressure to the gel. The volume reduction with rising temperature is due to the dehydration effect of gel chains, and the collapsing state is obtained when the NIPA gel carries a small amount of charged groups.[6−9] In the collapsing state, the movement of counterion may be restricted, and the Donnan osmotic pressure could be reduced. However, little is known about the degree of this restriction. It is the purpose of the present study to clarify the extent of the restriction of the counterion movement in the collapsing gel. For this purpose, the dielectric dispersions of partly ionized NIPA gels and copolymer gels of NIPA with sodium styrenesulfonate were studied.

2. Experiment

NIPA gels were prepared by radical copolymerization in aqueous solutions of *N*-isopropylacrylamide (700 mM) and *N*,*N*′-methylenebis(acrylamide) (3.5 mM). The polymerization was initiated by ammonium persulfate and accelerated by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. Slab gels of 1 mm thickness were synthesized by polymerizing the pregelation solution at 5 °C for 24h in a cavity between two glass plates with a Teflon sheet as a spacer, and spherical gels were synthesized by polymerizing a small volume (ca. 100 mm^3) of the solution floating in the paraffin oil flowing upward at 20 °C for 6 h. The partly ionized NIPA slab gels (NIPA−SS$_X$) were prepared by radical copolymerization in aqueous solutions of *N*-isopropylacrylamide (0.7(1000 − x) mM), sodium styrenesulfonate (0.7x mM) and *N*,*N*′-methylenebis(acrylamide) (3.5 mM) at 5 °C for 24 h. The polymerization was initiated by ammonium persulfate and accelerated by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. The gels were rinsed thoroughly with distilled water and dried in air under vacuum.

The swelling behavior of gel was evaluated from a ratio of the gel weight to that of the dried gel, r_G. To obtain r_G, the slab gel equilibrating with water at a given temperature for longer than 24 h was taken out and weighted after removing surface water carefully. A volume fraction of the gel chain, Φ was estimated from the observed $r_G$value by using the relation

$$r_G = 1 + \frac{1 - \Phi}{\Phi}\frac{\rho_{H_2O}}{\rho_{dry}} \qquad (1)$$

where ρ_{H_2O} is assumed to be 1 g cm^{-3}. The densities of dry gels used in the present experiment, ρ_{dry} were 1.2 ± 0.1 g cm^{-3}, determined from the ratio of its weight to the volume increment of *n*-hexane when immersing the dry gel into it.

Dielectric dispersions of the slab gels were measured by using a LCR meter (4285A Precision LCR meter, Hewlett-Packard Co. Ltd.) equipped with the disk electrode system (16451B Dielectric Test Fixture, Hewlett-Packard Co. Ltd.), which was partly remodeled as shown in Figure 1 to avoid drying the gel during measurements. The electrode system was put in an earthed chamber whose temperature was regulated within 0.1 °C. Before the measurement, the gels were immersed into water of the same temperature as the chamber

10.1021/ma990121n CCC: $18.00

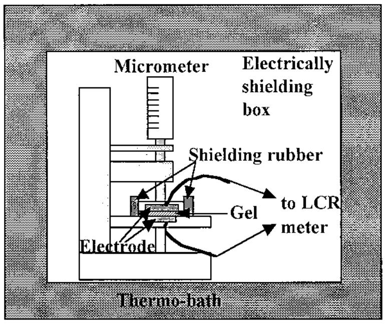

Figure 1. Schematic figure of the apparatus for the measurement of dielectric dispersion of a gel. A cylinder made of rubber surrounding the electrode is vertically slid downward to shield the gel from drying after setting it on the electrode. Silicone grease is used to plug up the gap between the electrode and the rubber.

for longer than 12 h and taken out and placed on the disk electrode. A distance between the electrodes was gradually shortened to electrically connect the gel with the electrodes. To ensure the connection between the electrode and the gel, the distance was shortened further by about 20 μm. Measurements were made about 30 min after placing the gel on the electrode. Just after the measurement, the thickness of slab gel, d (typically 200−800 μm) was measured by using the micrometer equipped with the electrode. The micrometer was calibrated beforehand. The relative dielectric constant, ϵ, and the electric conductivity, κ, of the gel were obtained from the measured capacitance, C (Farad), and conductance, G (Siemens), by using the relations

$$\epsilon = \frac{d}{S\epsilon_0}C \tag{2}$$

$$\kappa = \frac{d}{S}G \tag{3}$$

where S and ϵ_0, respectively, are the area of the electrode ($=1.964 \times 10^{-5}$ m^2) and the dielectric constant of vacuum ($=8.854 \times 10^{-12}$ F/m).

Diffusion of KNO_3 molecules was determined by measurements of the concentration change with time due to transport of the molecules from the inside of spherical gels into the outside solution. Experimental details are described elsewhere.[10] The spherical gel was immersed into a KNO_3 solution at a given temperature and left for longer than 3 days to obtain a homogeneous distribution of KNO_3 in the gel. The gel was then put into the optical cell after carefully removing the solution attached to the surface. The gel was suspended in the plastic net above the optical path, and the solution in the cell was thoroughly stirred. Measurement of the optical absorbance at the wavelength of 230 nm was carried out by using a Ubest-50 Japan Spectroscopic Co., Ltd. spectrophotometer. The relative absorbance (Ab(t) − Ab(0), where Ab(t) is the absorbance at time t) was proportional to the concentration of the solute.

3. Results

Changes of swelling ratios, r_G, with temperature are discrete for the NIPA and NIPA−SS$_1$ gels at about 34 °C but not for NIPA−SS$_5$ gels as shown in Figure 2. As reported previously,[7−9] the introduction of ionized groups into NIPA gel makes the discrete volume change with temperature continuous. The present result is consistent with the previous experimental result[7] that the volume changes of NIPA−SS$_4$ and NIPA−SS$_{10}$, respectively, are discrete and continuous.

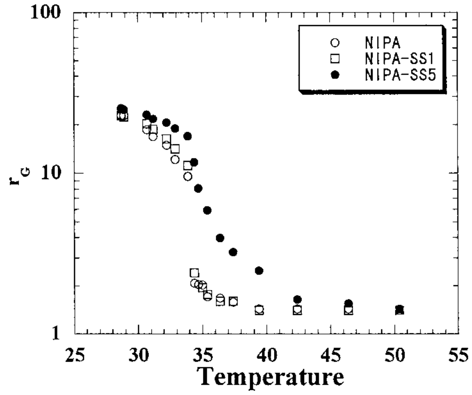

Figure 2. Volume changes with temperature. r_G is the weight ratio of the wet gel to the dry gel. Open circles (NIPA gel) and open squares (NIPA−SS$_1$ gel) show discrete volume changes with temperature, with volume phase transitions at 34 °C. Closed circles (NIPA−SS$_5$ gel) show continuous volume change with temperature.

Observed values of ϵ and κ for the NIPA gels at temperatures lower than a volume phase transition temperature, 34 °C, were essentially constants in the frequency range from 100 kHz to 2 MHz as shown in Figure 3a with $\epsilon = 80$. This indicates that a polarization effect of the electrodes is negligibly small in the present experiment. However, for the NIPA gels at temperatures above 34 °C, ϵ decreased and κ increased with increasing frequency as shown in Figure 3a. An imaginary part of the complex dielectric constant, ϵ' is given by the equation

$$\epsilon' = \frac{\kappa - \kappa_l}{2\pi f \epsilon_0} \tag{4}$$

where κ_l and f, respectively, are a limiting conductivity at low frequencies and a frequency. In the present experiment, κ_l was tentatively assumed to be κ at $f =$ 75 kHz. The frequency dependence of ϵ and ϵ' at temperature above 34 °C indicates that the dispersion frequencies of dielectric constants are about 1 MHz, as shown in Figure 3b. It should be noted that the ϵ' values at f above 300 kHz changed little when using a κ_l value lower than κ at $f = 75$ kHz. Figure 3c shows Cole−Cole plots that describe the relations

$$\epsilon = \epsilon_h + \frac{a\Delta\epsilon}{a^2 + b^2};\quad \epsilon' = \frac{b\Delta\epsilon}{a^2 + b^2};$$
$$a = 1 + \left(\frac{f}{f_R}\right)^{1-\alpha}\sin\left(\frac{\alpha\pi}{2}\right);\quad b = \left(\frac{f}{f_R}\right)^{1-\alpha}\cos\left(\frac{\alpha\pi}{2}\right) \tag{5}$$

where ϵ_h, $\Delta\epsilon$, α, and f_R, respectively, are the limiting value of ϵ at high frequencies, the dielectric increment, the Cole parameter, and the relaxation frequency of the dispersion. The dispersions are not of a Debye type and the α values obtained by the analysis are about 0.4, much larger than 0. It should be mentioned that the α values might become larger than 0.4 when κ_l values lower than the tentative ones were used in the analysis. The high α values suggest the multi mode of dielectric dispersion, which might be caused by the inhomgeneity of the collapsing gel. Dielectric dispersions of NIPA−SS$_1$ and NIPA−SS$_5$ gels were found in both the swelling and collapsing states as shown in Figures 4 and 5. It is interesting to find that the dispersion frequencies, f_R for the swollen gels are much lower than those for the collapsing gels. The former is about 200 kHz and the latter is about 1 MHz. The former f_R might be smaller if lower κ_l values than the tentative ones were used in

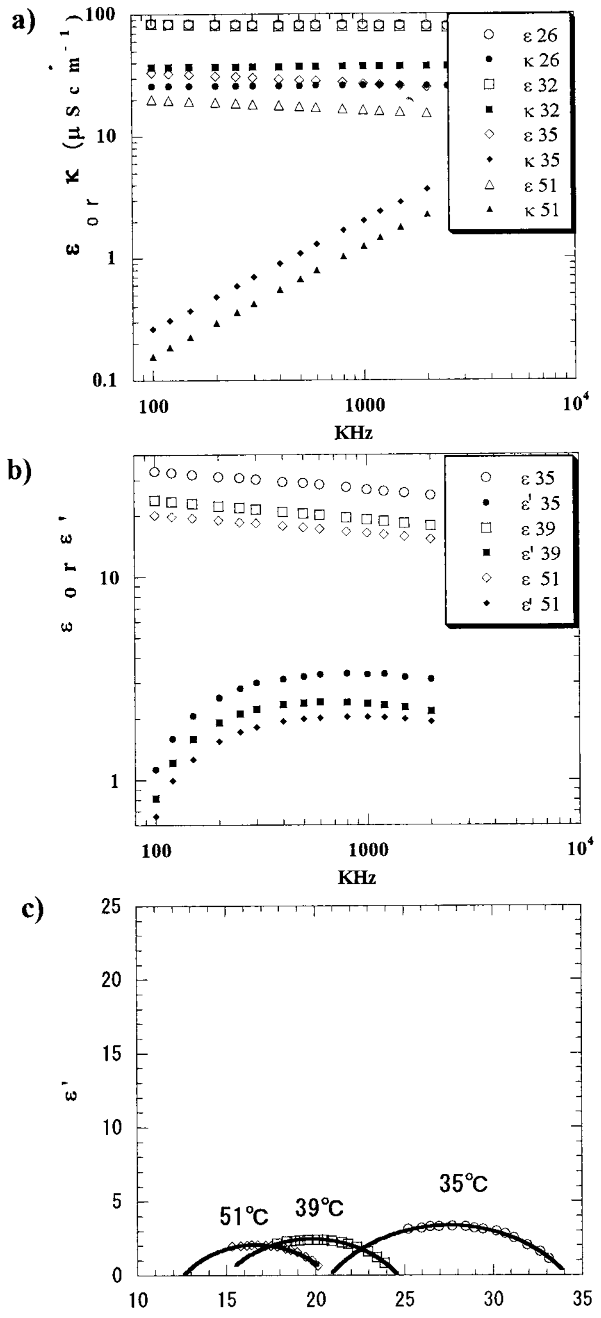

Figure 3. Temperature dependence of the dielectric dispersion spectra of the NIPA gel. Dielectric constant (open symbols) and conductance (closed symbols) as the functions of frequency (a), real (open symbols) and imaginary (closed symbols) parts of complex dielectric constants as the functions of frequency (b), and Cole–Cole plots (c) of dielectric dispersion spectra are shown.

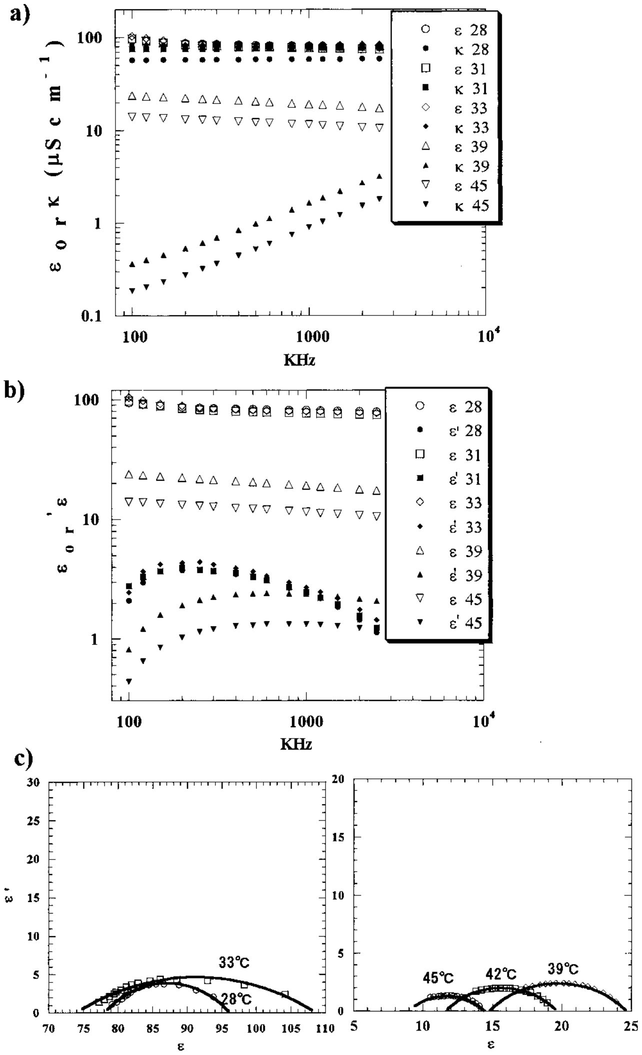

Figure 4. Temperature dependence of the dielectric dispersion spectra of the NIPA–SS$_1$ gel. Dielectric constant (open symbols) and conductance (closed symbols) as the functions of frequency (a), real (open symbols) and imaginary (closed symbols) parts of complex dielectric constants as the functions of frequency (b), and Cole–Cole plots (c) of dielectric dispersion spectra are shown.

the analysis. The f_R for the latter is very close to the f_R for the collapsing NIPA gels. The temperature dependence of ϵ_h, $\Delta\epsilon$, f_R, κ_l, α, and Φ for NIPA, NIPA–SS$_1$, and NIPA–SS$_5$ gels is tabulated in Table 1. It should be noted that the conductivity, κ_l, of the collapsing gel is 2 orders of magnitude lower than that of the swollen gels and that α values of all dispersions are observed ranging from 0.3 to 0.6.

Diffusion coefficients of KNO$_3$ molecules in the gels were evaluated from time evolutions of the concentration due to transport of KNO$_3$ molecules from the inside of spherical gels to the outside. According to theory,[10] the concentration outside the gel at time t, $C(t)$ changes according to

$$\frac{C(t=\infty)-C(t)}{C(t=\infty)-C(t=0)}=\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-D\left(\frac{n\pi}{a}\right)^2 t\right\} \qquad (6)$$

where D and a, respectively, are the diffusion coefficient and the radius of the gel. At a longer time, eq 6 is reduced to

$$\frac{C(t=\infty)-C(t)}{C(t=\infty)-C(t=0)}\propto \exp\left\{-D\left(\frac{\pi}{a}\right)^2 t\right\} \qquad (7)$$

In the present experiment, $C(t)$ was determined by the optical absorbance, Ab(t). The D values were obtained from the following relationship at longer t.

$$\ln\left\{\frac{\mathrm{Ab}(t=\infty)-\mathrm{Ab}(t)}{\mathrm{Ab}(t=\infty)-\mathrm{Ab}(t=0)}\right\}\propto\left\{-D\left(\frac{\pi}{a}\right)^2 t\right\} \qquad (8)$$

The observed values of the left-hand side in eq 8 are

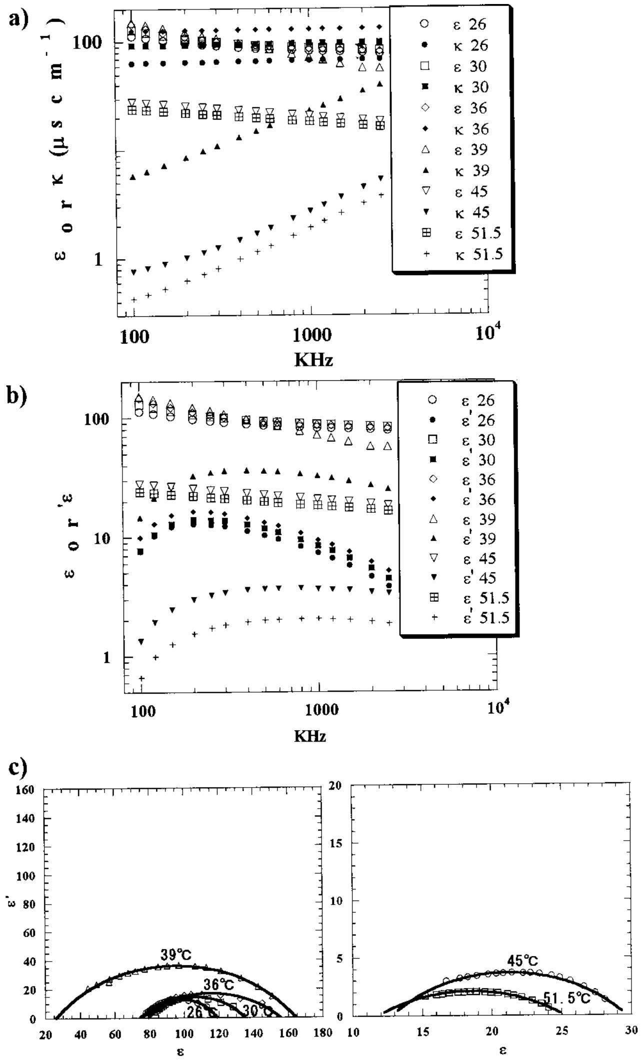

Figure 5. Temperature dependence of the dielectric dispersion spectra of the NIPA$-$SS$_5$ gel. Dielectric constant (open symbols) and conductance (closed symbols) as the functions of frequency (a), real (open symbols) and imaginary (closed symbols) parts of complex dielectric constants as the functions of frequency (b), and Cole$-$Cole plots (c) of dielectric dispersion spectra are shown.

Table 1. Characteristics of Dielectric Dispersion Spectrum of NIPA Gel

T/°C	ϵ_h	$\Delta\epsilon$	f_R/kHz	κ_l/μS cm^{-1}	α	Φ
26	81.8			25.75		0.03
29	82.3			28.01		0.04
31	80.8			29.99		0.05
35	20.8	13.3	800 ± 100	0.204	0.40	0.49
39	14.9	9.7	700 ± 100	0.32	0.41	0.66
51	12.6	8.1	900 ± 100	0.12	0.40	0.67

plotted against t, which are shown in parts a and b of Figure 6. The D values obtained for the NIPA gels at 25 and 40 °C, respectively, were 1.6×10^{-5} and 6.9×10^{-8} cm^2 s^{-1}. The former value is about four-fifths of the diffusion coefficient of KNO$_3$ in aqueous solution at 25 °C ($D = 1.9 \times 10^{-5}$ cm^2 s^{-1}). This is consistent with the previous experimental result[10] that the diffusion coefficients of small molecules in the acrylamide gels are about four-fifths the size of their diffusion coefficients in bulk solution. It is noteworthy that the diffusion coefficient in the collapsing gel is four thousandths of that in the swollen gel.

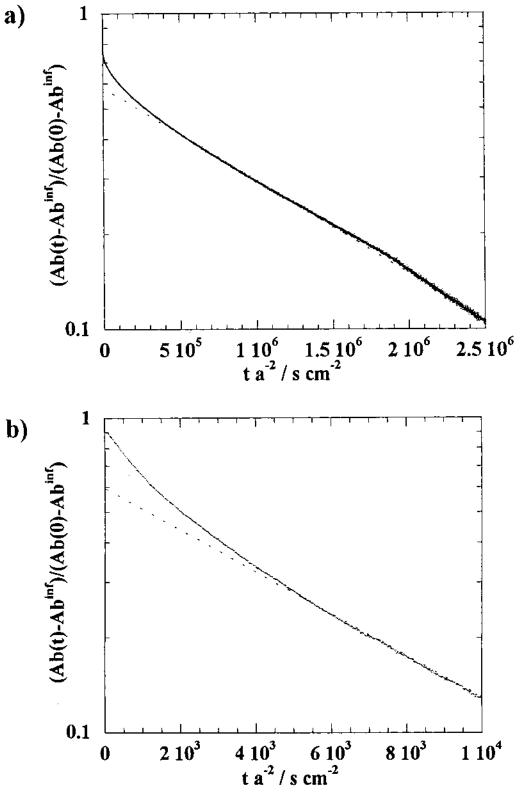

Figure 6. Time evolutions of KNO$_3$ concentrations outside the gels in the swollen (a) and collapsing (b) states. The ordinate, $F(t)$ is $(\mathrm{Ab}^{\mathrm{inf}} - \mathrm{Ab}(t))/(\mathrm{Ab}^{\mathrm{inf}} - \mathrm{Ab}(t = 0))$ where Ab$^{\mathrm{inf}}$ denotes the absorbance at $t = \infty$.

Table 2. Characteristics of Dielectric Dispersion Spectrum of NIPA$-$SS$_1$ Gel

T/°C	ϵ_h	$\Delta\epsilon$	f_R/kHz	κ_l/μS cm^{-1}	α	Φ
28	78	9.1	175 ± 10	57	0.49	0.03
29	76	12.9	175 ± 10	70	0.61	0.04
31	71.5	15.6	175 ± 10	75	0.66	0.04
33	73.9	17.4	175 ± 10	83	0.66	0.06
39	14.8	4.9	700 ± 100	0.32	0.42	0.67
42	11.6	4.0	700 ± 100	0.27	0.41	0.67
45	9.0	2.7	800 ± 100	0.16	0.43	0.67

Table 3. Characteristics of Dielectric Dispersion Spectrum of NIPA$-$SS$_5$ Gel

T/°C	ϵ_h	$\Delta\epsilon$	f_R/kHz	κ_l/μS cm^{-1}	α	Φ
26	75.7	21.7	180 ± 10	63	0.32	0.03
27	80.1	25.0	180 ± 10	77	0.36	0.03
30	78.9	28.1	180 ± 10	91	0.40	0.04
33	77.2	29.7	180 ± 10	96	0.41	0.04
36	74	41	175 ± 10	124	0.50	0.22
39	25.7	69.4	450 ± 100	5.0	0.39	0.36
45	12.7	8.5	900 ± 100	0.69	0.47	0.60
52	11.7	6.8	900 ± 100	0.37	0.38	0.66

4. Discussion

The increments of dielectric constants, $\Delta\epsilon$, of swollen gels increase with increases in the introduced charge amount, as shown in Tables 1$-$3. Essentially no $\Delta\epsilon$ values are observed for the swollen NIPA gel in the frequency range from 100 kHz to 2 MHz. Dipole moments inducing $\Delta\epsilon$ of the swollen and ionized gels are caused by the asymmetric distribution of counterions around the ionized sites of the chain. A simple theory for the mechanism to induce the $\Delta\epsilon$ is described in the Appendix. The greater $\Delta\epsilon$ of NIPA$-$SS$_5$ compared to that of NIPA$-$SS$_1$ reflects the greater amount of the counterion of the former. The $\Delta\epsilon$-values of NIPA$-$SS in the swollen state increase with increases in the counterion concentration ($\propto \Phi$), as shown in Tables 2 and 3. These experimental results are consistent with the theoretical conjecture (see eq A4). The relaxation frequency of the dipole, which corresponds to the frequency of dielectric dispersion, is theoretically written as

$$f_R = \frac{D_C {q_C}^2}{2\pi} \tag{9}$$

where D_C and q_C, respectively, are the diffusion coefficient of the counterion and the inverse of correlation length of counterion distribution in the gel. The fact that the dispersion frequencies are about 200 kHz suggests that $q_C^{-1} \sim 28$ nm on the assumption that $D_C = 1 \times 10^{-5}$ cm^2 s^{-1}. As demonstrated in the Appendix, q_C^{-1} should be close to $\lambda_D = (4\pi e_0^2 C_C/DkT)^{-1/2}$, where C_C is the counterion concentration in the gel. This holds in the cases of NIPA−SS$_1$ ($\lambda_D = 22$ nm; $C_C = 0.39$ mM) and NIPA−SS$_5$ ($\lambda_D = 10$ nm; $C_C = 1.8$ mM).

In the collapsing state, the dielectric increments are observed even for the nonionic NIPA gel as shown in Table 1. The applied electric field produces a dipole moment at the interface between mediums of different dielectric properties. The collapsing NIPA gel is composed of approximately equal amounts of the chain and water, the polarizabilities of which are very different from each other. The dielectric increment is induced by the dipole moment at the interface between the chain and water. It is noticeable that the characteristics of dielectric dispersions are very similar for NIPA at a temperature, T, higher than 35 °C, NIPA−SS$_1$ at T higher than 39 °C, and NIPA−SS$_5$ at T higher than 45 °C. This indicates that the counterions of NIPA−SS$_1$ and NIPA−SS$_5$ in the collapsing state cannot move in response to the applied electric field. The counterions and ionized groups are considered to bind tightly to each other and to form ion pairs. The fact that the dielectric increments of NIPA, NIPA−SS$_1$, and NIPA−SS$_5$ are approximately the same indicates that the contribution of the ion pairs to the dipole moments is negligibly small. It is noticeable that the characteristics of dielectric dispersion of NIPA−SS$_5$ at $T = 39$ °C shown in Table 2 reflect the intermediate state, partly collapsing, and the partly swollen state of the gel chains. That is, some of the counterions form ion pairs with the ionized groups and others are moving freely to contribute to the conductivity which is relatively high compared with those at T higher than 45 °C, as shown in Table 2.

There exists no theory to describe well the dielectric dispersions of the collapsing gel network composed of comparable amounts of the chain and water. The observed dielectric dispersion indicates that the movement of ion in the collapsing gel medium does not follow freely the oscillating electric field at the frequencies used in the present experiment. Usually, ions such as H$^+$ and OH$^-$ in ordinary water follow the electric field. In this sense we can say that the water in the collapsing gel is not ordinary. For a semiquantitative description, we adopt the Wagner theory,[12] which regards the collapsing gel as the suspension of particles in a medium with different dielectric properties. According to the theory,[12] the suspension in which particles having conductivity, κ_P, and dielectric constant, ϵ_P are distributed in a conducting medium, κ_m and dielectric constant, ϵ_m, shows the dielectric properties described as

$$\epsilon_h = \frac{2(1-\phi)\epsilon_m + (1+2\phi)\epsilon_P}{(2+\phi)\epsilon_m + (1-\phi)\epsilon_P}\epsilon_m \tag{10}$$

$$\kappa_l = \frac{2(1-\phi)\kappa_m + (1+2\phi)\kappa_P}{(2+\phi)\kappa_m + (1-\phi)\kappa_P}\kappa_m \tag{11}$$

$$\epsilon_l \equiv \epsilon_h + \Delta\epsilon = \frac{2(1-\phi)\kappa_m + (1+2\phi)\kappa_P}{(2+\phi)\kappa_m + (1-\phi)\kappa_P}\epsilon_m + \frac{9(\epsilon_P\kappa_m - \epsilon_m\kappa_P)\kappa_m\phi}{\{(2+\phi)\kappa_m + (1-\phi)\kappa_P\}^2} \tag{12}$$

$$f_R = \frac{(2+\phi)\kappa_m + (1-\phi)\kappa_P}{(2+\phi)\epsilon_m + (1-\phi)\epsilon_P}\frac{1}{2\pi\epsilon_0} \tag{13}$$

where ϕ is the volume fraction of the particle. If $\kappa_m \gg \kappa_P$, eqs 11−13 can be reduced to

$$\kappa_l = 2\frac{1-\phi}{2+\phi}\kappa_m \tag{14}$$

$$\epsilon_l = 2\frac{1-\phi}{2+\phi}\epsilon_m + \frac{9\phi}{(2+\phi)^2}\epsilon_P \tag{15}$$

$$f_R = \frac{2+\phi}{2(1-\phi)\epsilon_m + (1+2\phi)\epsilon_P}\frac{\kappa_m}{2\pi\epsilon_0} \tag{16}$$

If $\kappa_P \gg \kappa_m$, eqs 10−12 can be reduced to

$$\kappa_l = \frac{1+2\phi}{1-\phi}\kappa_m \tag{17}$$

$$\epsilon_l = \frac{1+2\phi}{1-\phi}\epsilon_m \tag{18}$$

$$f_R = \frac{(1-\phi)}{(2+\phi)\epsilon_m + (1-\phi)\epsilon_P}\frac{\kappa_P}{2\pi\epsilon_0} \tag{19}$$

For a suspension of oil in water, $\kappa_m \gg \kappa_P$, and for that of water in oil, $\kappa_P \gg \kappa_m$. Since the relatively apolar gel chains may be regarded as an oil, it can be said that $\phi = \Phi$ in the former case and $\phi = 1 - \Phi$ in the latter case. The values of ϵ_m, ϵ_P, κ_m, and f_R in the former condition are evaluated from the observed ϵ_h, $\Delta\epsilon$, and κ_l by using eqs 10 and 14−16 and were tabulated in Table 4. The values of ϵ_m, ϵ_P, κ_m, and κ_P in the latter case are also evaluated from the observed values of ϵ_h, $\Delta\epsilon$, f_R, and κ_l by using eqs 10 and 17−19 and tabulated in Table 5. It is obvious that ϵ_m and ϵ_P evaluated on the assumption that water is suspended in chains (that is, $\kappa_P \gg \kappa_m$) are more reasonable and that ϵ_m, ϵ_P, and f_R evaluated on the assumption that chains are suspended in water are less realistic. This indicates that water molecules in the collapsing gels are not electrically connected with each other. The percolation of water in the collapsing gels might be incomplete. This is consistent with the fact that the water droplets do not spread spontaneously on the collapsing NIPA gel surface. The collapsing NIPA gels appear to behave as an apolar medium. From the dielectric dispersion spectra, it emerges that water molecules inside the collapsing gels are surrounded by the gel chains and form electrically disconnected clusters.

It should be mentioned that the absolute values shown in Table 5 are not necessarily true ones, since they are model dependent and the conventional Wagner

Table 4. Characteristics of Dielectric Properties Evaluated from the Observed Dielectric Dispersion Spectrum, Assuming That Chains Are Suspended in Water

gel	T/°C	f	ϵ_m(water)	ϵ_P(chain)	κ_m/μS cm^{-1}	f_R/kHz
NIPA	35	0.49	10.6	42	0.50	24
NIPA	39	0.66	5.0	28	1.25	88
NIPA	51	0.67	4.1	23	0.49	41
NIPA−SS$_1$	39	0.67	7.0	21	1.29	114
NIPA−SS$_1$	42	0.67	5.4	17	1.09	122
NIPA−SS$_1$	45	0.67	4.5	13	0.65	96
NIPA−SS$_5$	45	0.60	5.0	25	2.24	180
NIPA−SS$_5$	52	0.66	4.2	21	1.45	136

Table 5. Characteristics of Dielectric Properties Evaluated from the Observed Dielectric Dispersion Spectrum Assuming That Water Molecules Are Suspended in Chains

gel	T/°C	ϕ	ϵ_m(chain)	ϵ_P(water)	κ_m/μS cm^{-1}	κ_P/μS cm^{-1}
NIPA	35	0.51	8.3	56	0.05	44
NIPA	39	0.34	9.7	33	0.13	26
NIPA	51	0.33	8.4	28	0.05	28
NIPA−SS$_1$	39	0.33	8.0	58	0.13	33
NIPA−SS$_1$	42	0.33	6.3	44	0.11	26
NIPA−SS$_1$	45	0.33	4.7	38	0.06	25
NIPA−SS$_5$	45	0.40	7.1	30	0.23	29
NIPA−SS$_5$	52	0.34	7.3	29	0.15	27

model adopted here is not necessarily suitable for the collapsing gel. However, the decreasing tendency of ϵ_P(water) with rising temperature shown in Table 5 is considered to be significant, since our preliminary experiment[12] shows that the ratio of the NaCl concentrations inside and outside the collapsing gel decreases with rising temperature (the ratios are 0.7 at 34 °C and 0.1 at 40 °C).

An activation energy might be necessary for small molecules to move between clusters. A high activation energy in diffusion could explain why the diffusion coefficient of KNO_3 in the collapsing gel is four thousandth of that in the swollen gel. The obstacle effect of gel chains reduces D approximately as[13]

$$\frac{D}{D_0} = \left(\frac{1-\Phi}{1+2\Phi}\right)^2 \qquad (20)$$

where D_0 is the diffusion coefficient in the absence of obstacles. Equation 20 gives $0.15D_0$ in the case $\Phi = 0.66$. It is obvious that the observed very low D ($=0.004D_0$) of KNO_3 in the collapsing gel is not due to the obstacle effect of gel chains. The movement of small ions between water clusters in the collapsing gel is much slower than that in the continuous water medium. This is one of the reasons why the conductivity of collapsing gel is of the order of one hundredth of that in the swollen gel as shown in Table 1, since the contribution of the chains to the electrical conductivity is considered to be very low.

Appendix

The concentration change of counterion, δC responding to the externally applied electric field, E is described by

$$\frac{\partial}{\partial t}\delta C = D_C \nabla^2 \delta C + \frac{e_0}{\varsigma} E \nabla \langle C \rangle \qquad (A1)$$

where $\langle C\rangle$, e_0, and ς, respectively, are the concentration in the absence of E, the elementary charge, and the friction constant of the counterion. Here, $\langle C\rangle$ is described by the Boltzmann equation

$$e_0\psi + kT \ln\langle C\rangle = kT \ln\langle C_0\rangle \qquad (A2)$$

where ψ and $\langle C_0\rangle$, respectively, are the electrostatic potential made by the charged groups on the chain and the concentration at $\psi = 0$. Fourier transformation of eq A1) gives the relation

$$\delta C(q,\omega) = \frac{iq\frac{e_0}{\varsigma}E_0}{i\omega + D_C q^2}\langle C(q)\rangle \qquad (A3)$$

where $\delta C = \int \mathrm{e}^{i\omega t}\,\mathrm{d}\omega \int \mathrm{e}^{iqx}\,\mathrm{d}q\,\delta C(q,\omega)$, $\langle C\rangle = \int \mathrm{e}^{iqx}\,\mathrm{d}q\langle C(q)\rangle$, and $E = E_0\mathrm{e}^{i\omega t}$. The dielectric increment, $\Delta\epsilon_C$, which is due to the asymmetric distribution of counterions around the ionized sites of the chain, is approximately given by

$$\Delta\epsilon_C \propto {E_0}^{-1}\int \mathrm{d}x\, e_0 x \delta C = \frac{{e_0}^2}{\varsigma}\int \mathrm{d}q \int \mathrm{d}x\, iqx\mathrm{e}^{iqx}\, \frac{\langle C(q)\rangle}{i\omega + D_C q^2} \qquad (A4)$$

This predicts that $\Delta\epsilon_C$ increases with an increase in the concentration of counterion. When $\langle C(q)\rangle$ is significant only around q_C, f_R is approximately given by

$$f_R = \frac{D_C {q_C}^2}{2\pi} \qquad (9)$$

Equation A2 can be rewritten as $\langle C\rangle = \langle C_0\rangle\{1 - e_0\psi/kT\}$ under the condition that $e_0\psi/kT < 1$ and ψ is approximately of the Debye−Hückel type.[14] The gel system in which the concentration of the charged groups is much less than 10mM satisfies the condition mentioned above. Therefore, it can be inferred that $\langle C(q)\rangle \propto (q^2\xi^2 + 1)^{-1}$ where $\xi \approx 1/\sqrt{8\pi {e_0}^2\langle C_0\rangle/DkT}$. This indicates $q_C \approx (\sqrt{2}\xi)^{-1} = \sqrt{4\pi {e_0}^2\langle C_0\rangle/DkT}$, and the mode of the dielectric dispersion is multiple.

Acknowledgment. This work is supported by a Grant-in Aid for Scientific Research (C) (No. 10640494) from the Ministry of Education, Science, Sports and Culture of Japan.

References and Notes

(1) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
(2) Suzuki, A. *Adv. Polym. Sci.* **1993**, *110*, 199.
(3) Park, T. G.; Hoffman, A. S. *Macromolecules* **1993**, *26*, 50454.
(4) Sasaki, S.; Maeda, H. *Phys. Rev. E* **1996**, 54.
(5) Sasaki, S.; Kawasaki, H.; Maeda, H. *Macromolecules* **1997**, *30*, 1847.
(6) Beltran, S.; Baker, J. P.; Hooper, H. H.; Blanch, H. W.; Prausnitz, J. M. **1991**, *24*, 2476.
(7) Kawasaki, H., Sasaki, S., Maeda, H. *J. Phys. Chem.* **1997**, *101*, 4184.
(8) Sasaki, S.; Maeda, H. *J. Chem. Phys.* **1997**, *107*, 1028.
(9) Kawasaki, H., Sasaki, S., Maeda, H. *J. Phys. Chem.* **1997**, *101*, 5089.
(10) Sasaki, S.; Maeda H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2173.
(11) Wagner, K. W. *Arch. Electrotech.* **1914**, *3*, 83.
(12) Kawasaki, H.; Mito, T.; Sasaki, S.; Maeda, H. Submitted for publication in *Langmuir*.
(13) Mackie, J. S.; Meares P. *Proc. R. Soc. London* **1955**, *A232*, 498.
(14) Debye, P.; Huckel, E. *Phys. Z.* **1923**, *24*, 185.

MA990121N