

High-frequency dielectric relaxation of polyelectrolyte gels

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The dielectric relaxation of polyelectrolyte gels (PEG) in the high-frequency region 10 kHz–1 GHz has been experimentally investigated by analogy with the high-frequency relaxation of semidilute polyelectrolyte solutions (PES). It is found from the dependence of the relaxation time on the concentrations of crosslinks and added salts that the relaxation mechanism is, similarly to PES, ascribable to the diffusion process of the counterions bound to the local Coulombic potential around the charged network as a backbone of gel. Furthermore, the dielectric relaxation spectroscopy has revealed the details of the Coulombic field in PEG. First, the Coulombic potential difference between the inside and outside of the gel is saturated to an almost constant value with adding salt. Second, the number of counterions bound to the local Coulombic potential around the network is independent of salt concentration, similarly to the counterion condensation phenomena in PES. [S1063-651X(97)09106-X]

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I. INTRODUCTION

It is well known that the volume change of polymer gels due to the change of external parameters becomes discontinuous by introducing charged groups into a polymer network as a backbone of gel [1]. This implies that the Coulombic interactions in such polyelectrolyte gels (PEG) play a significant role in the conspicuous volume change (volume phase transition). However, there have been few experimental studies to clarify the details of Coulombic interactions.

In the present paper, we apply to PEG the dielectric relaxation spectroscopy in the high-frequency region 10 kHz–1 GHz. The spectroscopy has been found to be a powerful tool for investigating the local profile of the Coulombic field in semidilute polyelectrolyte solutions (PES) [2–6], which are analogous to PEG in that polyions in both systems are entangled with each other, though the polyions in PEG are not uniformly dispersed, unlike those in PES, but are localized in the solution due to fixed crosslinks. Hence the dielectric relaxation spectroscopy is expected to reveal the unknown properties of the Coulombic field in PEG.

In the semidilute PES, some of counterions are bound to the Coulombic potential produced by highly charged polyions and contribute to the electric polarization induced by the external electric field [2]. The high-frequency dielectric relaxation of PES has been ascribed to the diffusion process of such counterions bound to the Coulombic potential around polyions [2–6]. In this case, the relaxation time τ is given as

$$\tau \cong \frac{l^2}{2D} \quad (1)$$

by using the diffusion constant D of counterions and the diffusion distance l , which directly reflects the width of the Coulombic potential valley. In the case of no added salt, we have found that l is of the same order as the correlation length ξ in the semidilute solutions [4–6].

On the other hand, the highly charged network in PEG produces not only a strong Coulombic field around the backbone network, but also a Coulombic field at the gel bound-

ary, in other words, a Coulombic potential difference ψ between the inside and outside of the gel due to the localization of polyions constituting the gel, which is schematically depicted in Fig. 1. Then we expect two kinds of dielectric

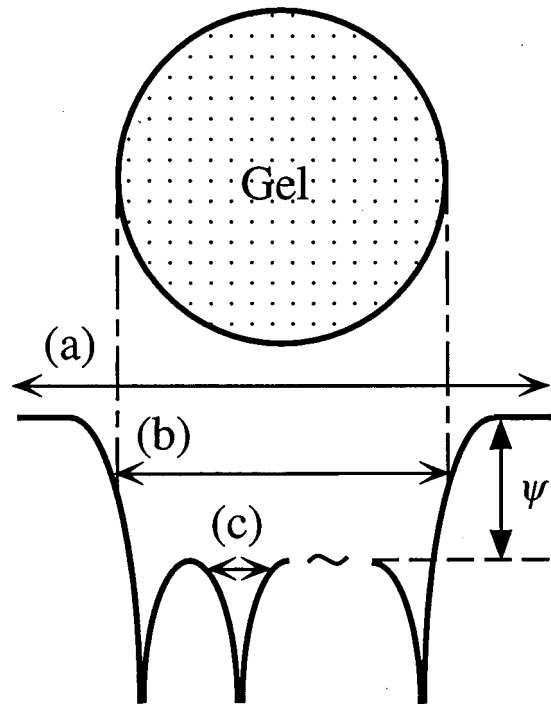


FIG. 1. Profile of the Coulombic potential in a highly charged polyelectrolyte gel, which elucidates that counterions dissociated from the backbone network are classified into three categories: (a) counterions that are freely mobile over the entire solution, (b) counterions that are confined to the gel but mobile inside it, and (c) counterions that are locally bound to the Coulombic potential around highly charged network. In the present frequency region 10 kHz–1 GHz, (a) counterions contribute to σ_{out} , (b) counterions to σ_{in} , and (c) counterions contribute to the dielectric relaxation.

TABLE I. Number fractions of crosslinks and charged groups to the total number of monomers, which are denoted by n_{cr} and n_{CG} , respectively, for the samples used in the present study. $G1-G4$ correspond to SA gels and $G5-G7$ to NIPA-SA gels.

Sample	$n_{cr} (\times 10^{-2})$	n_{CG}
G1	0.25	0.75
G2	0.6	0.75
G3	1.0	0.75
G4	1.5	0.75
G5	0.25	0.5
G6	0.25	0.375
G7	0.25	0.25

relaxation processes in PEG. One process is due to the presence of a gel boundary that prevents counterions subject to the external electric field from passing through the gel. The counterions that are confined to the gel but mobile inside the gel contribute to the electric polarization. In this case, the relaxation time τ would be determined by the diffusion time of counterions spreading over the inside of gel and estimated as $\tau \cong L^2/2D$, where L is the linear dimension of gel. If we use 1.0 cm as a typical value of L , we obtain a value of more than 1.0×10 h for τ , which is too slow to detect experimentally. The other process is due to the Coulombic field around the charged network and is expected to be observed in the high-frequency range, similarly to PES, as will be treated below.

II. EXPERIMENT

As typical samples of PEG we used sodium acrylate (SA) gels and *N*-isopropyl acrylamide (NIPA)-SA copolymer gels, which are listed in Table I. The complex dielectric constants $\epsilon^* = \epsilon' - i\epsilon''$ of these samples were obtained from the multifrequency simultaneous measurement of sample admittance in the range 10 kHz–500 kHz and the reflectivity coefficient measurement with the impedance analyzer (Hewlett-Packard 4191A) in the range 1 MHz–1 GHz. The sample cell used in both frequency ranges was a coaxial type of cylindrical condenser with platinum-plated stainless-steel electrodes.

As a typical example of the results, Fig. 2 shows $\epsilon^* = \epsilon' - i\epsilon''$ of the sample G1 of SA gel, where a continuous line represents the best-fitting curve using the semi-empirical formula of extended Cole-Cole type [7]:

$$\epsilon^* = \frac{\Delta\epsilon}{1 + (i\omega\tau)^\beta} + \epsilon_s - i \frac{\sigma}{\omega\epsilon_0}. \quad (2)$$

In Eq. (2), $\Delta\epsilon$ is the dielectric increment, $\omega = 2\pi f$ the angular frequency of applied electric field (f is the frequency), τ the average relaxation time, β a parameter representing the broadness of distribution of relaxation times, ϵ_s the dielectric constant of solvent, ϵ_0 the vacuum permittivity, and σ the solution ac conductivity, which is independent of frequency above 10 kHz. The results show $\beta \geq 0.8$ for all the gels used, which indicates that the distribution of relaxation times is rather sharp.

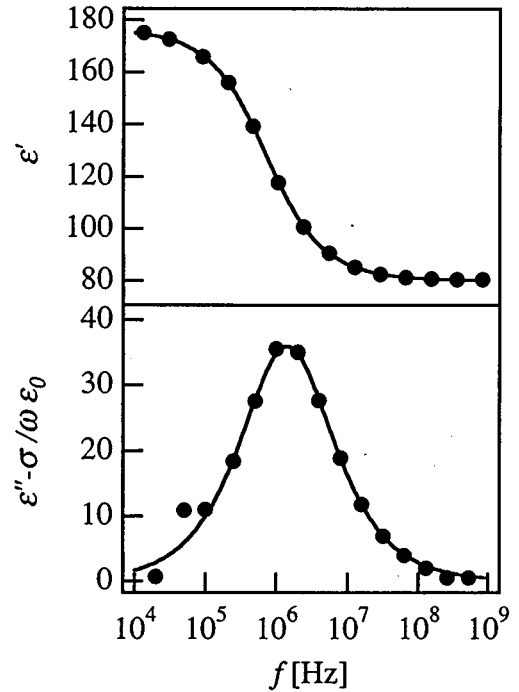


FIG. 2. Real part ϵ' and imaginary part $\epsilon'' - \sigma/\omega\epsilon_0$ subtracting the conductivity contribution of the complex dielectric constant ϵ^* for the sample G1. The filled circles represent the observed data points and the continuous curves are the best-fitting ones by Eq. (2).

III. RESULTS AND DISCUSSION

In Fig. 3 the diffusion distance l in PEG with no added salt is compared with the average distance between crosslinks, or mesh size, which is identified with the correlation length ξ in PEG. Here l has been calculated from the experimental value of τ as $l = (2D\tau)^{1/2}$ by using Eq. (1), while ξ has been estimated from the relation $C_c \xi^3 \cong 1$ in terms of the concentration C_c of crosslinks, which was obtained by dividing the total amount of crosslinker in prepa-

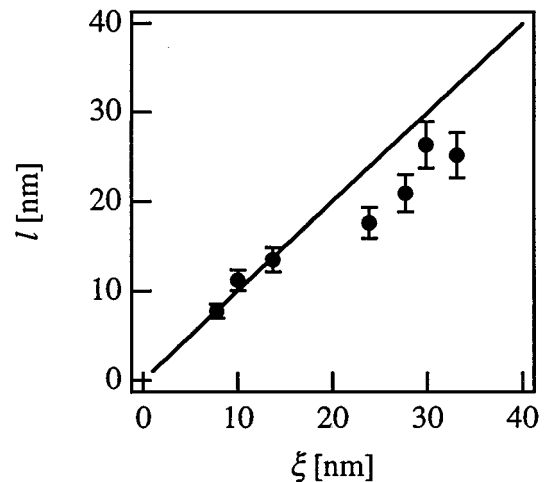


FIG. 3. l plotted against ξ for all the samples G1–G7. The continuous straight line represents $l = \xi$.

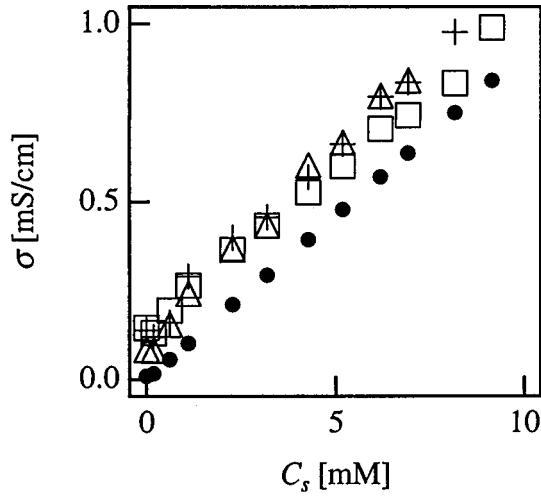


FIG. 4. Change of σ with the increase of C_s . Each symbol represents the sample difference: +, G1; Δ , G2; \square , G5; \bullet , σ_{out} .

ration by the gel volume in aqueous solutions with no added salt. Here the volume was measured by weighing the gels absorbing water.

According to a recent calculation based on the Poisson-Boltzmann equation to investigate the Coulombic field in the highly charged gel [8], the mesh size ξ is nearly equal to the width of the potential valley around the charged backbone network of the gel in the case of no added salt. Figure 3, on the other hand, shows that l is of the order of ξ . Then we have the conclusion that the diffusion distance l is of the order of the width of the potential valley around the network. This indicates that the high-frequency dielectric relaxation of PEG is ascribable to the diffusion process of counterions bound to the local Coulombic potential as predicted in Sec. I.

Next we treat the effect of NaCl as an added salt on the dielectric relaxation of PEG. In Fig. 4 the solution conductivity σ is compared with the conductivity σ_{out} outside the gel, which has been measured separately. Here σ is written as

$$\sigma = \sigma_{in}\phi + \sigma_{out}(1 - \phi) \quad (3)$$

in terms of the conductivity σ_{in} inside the gel and the volume fraction ϕ of gels in the sample solution. ϕ is given by $\phi = v/V_s$, with use of the solution volume V_s and the gel volume v , of which the C_s dependence has been experimentally obtained as shown in Fig. 5. Figure 4 reveals that σ is larger than σ_{out} . Then we may expect the presence of another dielectric relaxation in the lower-frequency region because σ , which is larger than σ_{out} , should decrease to $\sigma_{out}(1 - \phi)$ at a sufficiently low frequency where σ_{in} becomes zero and is absorbed into the dielectric increment due to the trapping of counterions inside the gel.

The result in Fig. 4 indicates also that σ_{in} is always larger than σ_{out} since Eq. (3) is rewritten as $\sigma - \sigma_{out} = (\sigma_{in} - \sigma_{out})\phi$. This is due to the presence of the Coulombic potential difference ψ between the inside and outside of the gel,

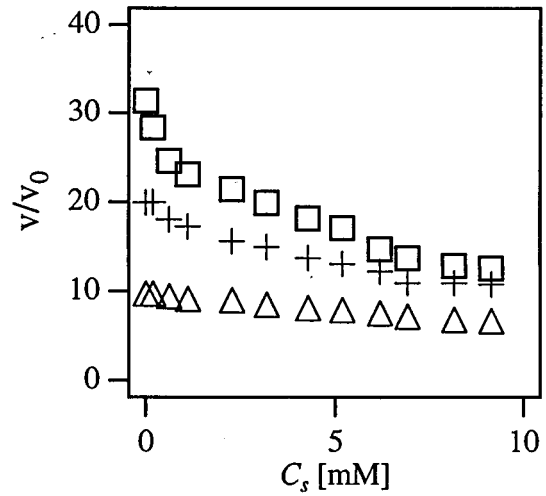


FIG. 5. Change of v/v_0 with the increase of C_s , where v_0 denotes the reference volume. Each symbol represents the sample difference as in Fig. 4.

as found from the following relation. When the mobility of small ions inside the gel is approximately equal to that of the outside, we have

$$f \equiv \frac{\sigma_{in}}{\sigma_{out}} = \frac{\mu_{in}c_{in}}{\mu_{out}c_{out}} \cong \frac{c_{in}}{c_{out}}, \quad (4)$$

where μ is the mobility of small ions and c the concentration of small ions satisfying the Boltzmann distribution such that

$$c_{in} = c_{out} \cosh\left(\frac{e\psi}{kT}\right) \quad (5)$$

(e is the elementary charge). Equations (4) and (5) give

$$f \cong \cosh\left(\frac{e\psi}{kT}\right), \quad (6)$$

which elucidates that f larger than unity, i.e., σ_{in} larger than σ_{out} , arises from ψ .

Conversely, ψ is calculated as

$$\frac{e\psi}{kT} = \ln(f + \sqrt{f^2 - 1}) \quad (7)$$

by using Eq. (6), where f is obtained from Eq. (3) as $f = \phi^{-1}(\sigma/\sigma_{out} - 1 + \phi)$ with use of the observed values of σ , σ_{out} , and ϕ . The results are shown in Fig. 6, which indicates that, with increasing C_s , $e\psi$ is saturated to almost constant values after an initial decrease to about the thermal energy kT commonly for three kinds of gels (i.e., the samples, G1, G2, and G5 in Table I).

On the other hand, the electrical neutrality condition inside the gel is written as

$$C_{CG} = 2C_s \sinh\left(\frac{e\psi}{kT}\right), \quad (8)$$

with use of the concentration C_{CG} of charged groups on the network. Since C_{CG} is obtained by dividing the total amount

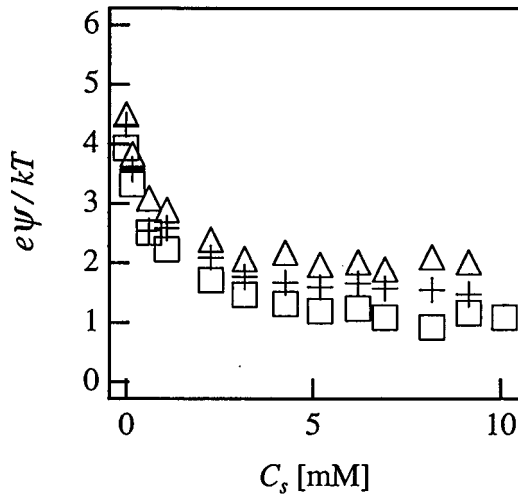


FIG. 6. Change of ψ evaluated from Eq. (7) with the increase of C_s . Each symbol represents the sample difference as in Fig. 4.

of charged groups in preparation by the gel volume v , Eq. (8) also gives the value of ψ as

$$\frac{e\psi}{kT} = \ln(p + \sqrt{p^2 + 1}), \quad (9)$$

where $p \equiv C_{CG}/2C_s$. Figure 7 shows that the C_s dependence of ψ calculated by using Eq. (9) is in qualitative agreement with the results in Fig. 6, though $e\psi$ in Fig. 7 is larger than that in Fig. 6 by the about thermal energy. This difference seems to be ascribable to the approximation in Eq. (4). The mobility is actually smaller inside the gel than outside the gel because the viscosity inside the gel is higher due to the porous structure and the concentration of Na^+ with a smaller mobility than Cl^- is larger than that of Cl^- inside the gel. Then we have the relation $c_{in}/c_{out} = (\mu_{out}/\mu_{in})f > f$, which increases the value of $e\psi$ estimated from Eq. (7) and thus may explain the results in Fig. 7.

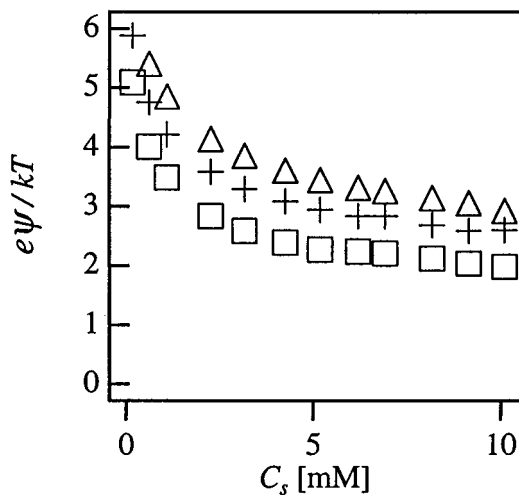


FIG. 7. Change of ψ evaluated from Eq. (9) with the increase of C_s . Each symbol represents the sample difference as in Fig. 4.

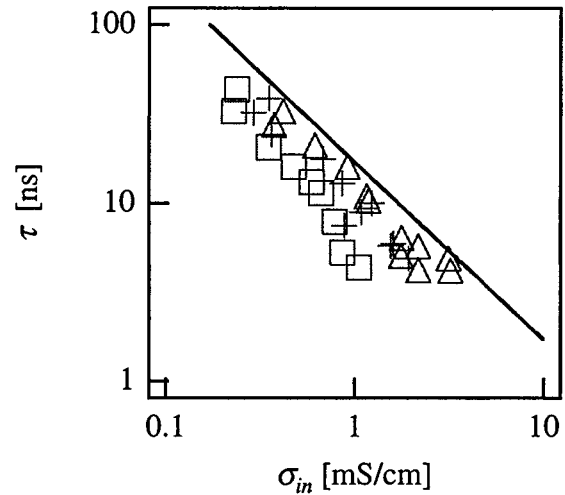


FIG. 8. Doubly logarithmic plot of τ against σ_{in} . Each symbol represents the sample difference as in Fig. 4. The continuous straight line represents τ proportional to σ_{in}^{-1} .

In Fig. 8 the dielectric relaxation time τ of PEG with added salt is plotted against σ_{in} , which has been calculated from Eq. (3) as $\sigma_{in} = \phi^{-1}\{\sigma - \sigma_{out}(1 - \phi)\}$ by using the experimental values of σ , σ_{out} , and ϕ . Figure 8 shows the relation $\tau \sim \sigma_{in}^{-1}$, which is equivalent to $\tau \sim \kappa^{-2}$ because σ_{in} is proportional to the ionic strength c_{in} inside the gel and related to the screening length κ^{-1} in the gel as $\kappa^2 = e^2 c_{in} / \epsilon_0 \epsilon_s kT \propto \sigma_{in}$. Comparing $\tau \sim \kappa^{-2}$ with Eq. (1), we can see that l is proportional to κ^{-1} , which is different from the result $l \sim \xi$ for PEG with no added salt (see Fig. 3). This result also confirms the above relaxation mechanism due to bound counterions because κ^{-1} is the characteristic length as a measure for the spread of the potential valley around the charged network of PEG with added salt.

Finally, we investigate the C_s dependence of the dielectric increment $\Delta\epsilon$, which is expressed as

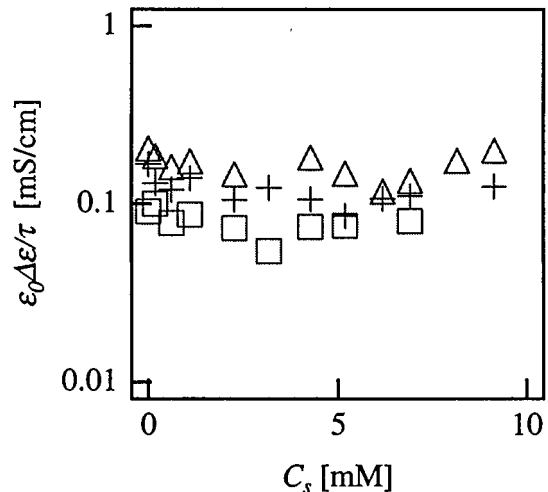


FIG. 9. Change of $\epsilon_0 \Delta\epsilon / \tau$ with the increase of C_s . Each symbol represents the sample difference as in Fig. 4.

$$\varepsilon_0 \Delta \varepsilon = \alpha_e \frac{N_b}{V_s}. \quad (10)$$

Here N_b is the total number of bound counterions in the sample solution and α_e is the electrical polarizability due to a bound counterion given by

$$\alpha_e \sim \frac{e^2 l^2}{kT}. \quad (11)$$

From Eqs. (1), (10), and (11) we get

$$\frac{\varepsilon_0 \Delta \varepsilon}{\tau} \propto N_b. \quad (12)$$

Figure 9 shows that $\varepsilon_0 \Delta \varepsilon / \tau$ calculated from the observed values of $\Delta \varepsilon$ and τ is independent of C_s . This result, combined with Eq. (12), indicates that N_b is independent of C_s , which implies that counterions bound to the highly charged network have a similar property to the counterion condensation in PES [2].

IV. SUMMARY

In the present paper we have found that the high-frequency dielectric relaxation observed in PEG is ascribable to the diffusion process of counterions bound to a highly charged network of PEG. Furthermore, the dielectric relaxation spectroscopy has revealed the following two properties of the Coulombic field in PEG. First, with increasing the salt concentration C_s , the Coulombic potential difference between the inside and outside of the gel estimated from the conductivity is saturated to an almost constant value after the initial sharp decrease, which is consistent with the result evaluated from the electrical neutrality condition inside the gel. Second, the C_s dependence of the relaxation time and the dielectric increment indicate that the number of counterions bound to the local Coulombic potential around the network is independent of C_s , similarly to the counterion condensation phenomena in PES.

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