

## Electrical Conductance of Polyelectrolyte Gels

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*Received: October 4, 1996; In Final Form: November 13, 1996*<sup>®</sup>

An attempt to establish a systematic method to precisely evaluate the electrical conductivity of highly water-swollen polyelectrolyte gels was made. It was found that the electrical conductivity and the activation energy of fully ionized polyelectrolyte gel such as cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid) gels with various counterions are almost identical with those of linear polymer in a wide range of swelling, indicating that the conduction of an ionic gel is essentially performed by the “free” counterions of Manning’s condensation theory.

### Introduction

A polyelectrolyte gel consists of a charged network and a fluid filling the interstitial space of the network. It is able to absorb a significant fraction (~3000 times its dry weight) of water within its structure to give swelling but is not able to dissolve in water.

Because specific features of their structure, polyelectrolyte gels are able to exhibit various unique electrical responses. For example, a repetitive current oscillation occurs when a dc voltage is applied to a water-swollen polyelectrolyte gel.<sup>1,2</sup> The amplitude and frequency of the oscillation are strongly associated with the degree of cross-linking, charge density on the network, and temperature.

Some kinds of weak polyelectrolyte gels such as cross-linked polyacrylic acid show the piezoelectric property and produce an electrical potential as large as a few millivolts.<sup>3</sup> A mechanical deformation was supposed to induce a spontaneous ionization of carboxylic acids at a local level.

We have reported in earlier papers<sup>4</sup> that when a water-swollen polyelectrolyte gel is interposed between a pair of electrodes and a dc current is applied, it undergoes electrically induced chemomechanical contraction and concomitant water exudation in the air. The electrically induced contraction of the gel is associated with the electrokinetic transportation of hydrated ions and water in the network, and a one-dimensional electrokinetic model for the contractile phenomenon was postulated.<sup>5,6</sup>

Despite these unique electrochemical observations, however, there is little knowledge on the transportation process of highly swollen charged networks under an electrical field. As far as we know, there has been made no attempts to precisely measure the electrical conductivity of a polyelectrolyte gel, presumably due to experimental as well as theoretical difficulties of the analysis.

Some effects of cross-linkage on the conductive behaviors can be easily expected. One is a decreased contribution of ion transportation from the “giga” macromolecular network. The macroions also make a contribution to the electrical conduction of polymer solution;<sup>7,8</sup> this contribution is expected to be depressed in the case of networked gel. The other is an enhanced counterion “binding” which should increase with increase in the cross-linking density.<sup>9–11</sup> We have previously calculated the electrostatic potential distribution of a polyelectrolyte network using a two-dimensional stacking model.<sup>12</sup> The simulational result revealed that besides potential energy valleys

around the polymer chains, there exist deep electrostatic potential energy wells at every cross-linking point. The potential wells located at the cross-linking point should strongly localize or “condense” counterions through strong electrostatic interactions and should affect the conductive behaviors of the gel.

On the base of these assumptions, we have attempted to establish a methodology to measure the electrical conductance of water-swollen polyelectrolyte gels. This will serve to clarify specific features of transport processes of charged networks.

### Experimental Section

**Sample Preparation.** Alkali-metal salts of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) were obtained by neutralizing AMPS solution with a prescribed amount of hydroxide solution in ethanol.

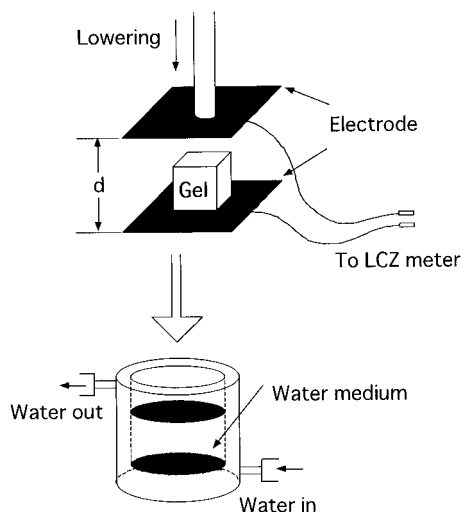
A poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) gel and its alkali-metal salts with various cross-linking density were prepared by radical polymerization of 3.0 M solutions of corresponding monomers using 0.1 mol % potassium persulfate as a radical initiator in the presence of 1–8 mol % of *N,N'*-methylenebisacrylamide (MBAA) used as a cross-linking agent. Polymerization was carried out at 50 °C under a N<sub>2</sub> atm for more than 12 h in a test tube 5 mm in diameter and 100 mm long. To remove any unreacted monomer and initiator, gels were immersed in a large amount of purified water at least for 1 week until they reached to their equilibrium states. Gels showed an extended swelling in water. Solvated linear PAMPS and its corresponding alkali-metal salts were obtained by a similar procedure but in the absence of the cross-linking agent MBAA. Purification of polymers was carried out by pouring the methanol polymer solution into ethyl acetate.

All of the measurement of the electrical conduction of gels were made at the equilibrium swelling state. The degree of swelling (*q*) was calculated using  $q = (\text{swollen sample weight})/(\text{dry sample weight})$ .

Dry gel was obtained by evacuating until it reached a constant weight. The monomeric concentration *C*(M) of a gel in equilibrium swelling state was obtained using the relation of  $C = 1000/qM_w$ , where *M<sub>w</sub>* is the monomeric molecular weight of the AMPS or its alkali metal salts.

**Measurements.** An apparatus used for the conductivity measurement of gels is shown in Figure 1. The gel was cut in cubic 10 mm in length using a laboratory-made cutter equipped with two razors facing each other 1 cm apart in parallel. The cubic gel was sandwiched between a pair of platinized platinum

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, January 1, 1997.



**Figure 1.** Apparatus for the measurement of electrical conductance of polymer gels.

electrodes and was immersed in water media. This cell was kept in a thermal static water bath composed of two cylindrical cylinders.

The complex impedances  $Z^*$  of the samples were measured by an LCZ meter (HP 2330A), in a range of frequencies  $f$  of 50–10<sup>5</sup> Hz, and the conductance  $G$  and capacitance  $C_e$  were calculated from  $Z^*$ . We supposed that the equivalent circuits of both the sample and the electrode–sample interfaces are expressed as a parallel connection of a condensor and a resistance, and the total impedance is a series connection of the two equivalent circuits. With the assumption that phase displacement due to the alternating current polarization at the electrodes equals  $-45^\circ$ , the extrapolated value of  $R \sim \omega^{-1/2}$  plot at an infinite frequency  $\omega$  was used as the true conductance of the gel, where  $R$  is the resistance and  $\omega$  is the angular frequency.<sup>13</sup>

Conductivities of monomer and polymer solutions were measured by the same method except using a standard cell. The cell was calibrated beforehand using KCl solutions to determine the cell constant.

The equivalent(molar) conductivity  $\Lambda$  (S cm<sup>2</sup> mol<sup>-1</sup>) was calculated from the conductivity  $\kappa$  and the monomeric concentration of the sample  $C$  by the relation

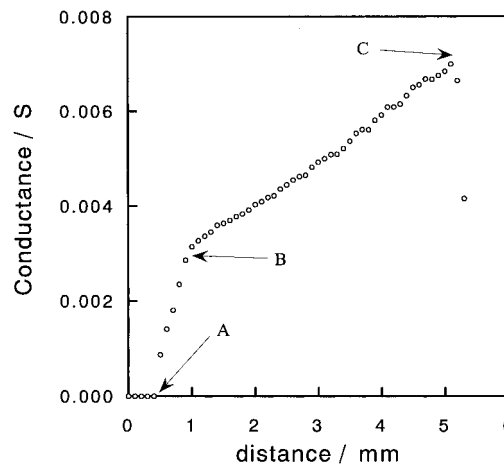
$$\Lambda = 1000\kappa/C$$

The detailed experimental setup and the procedure of measurement are described in the following section.

## Results and Discussion

It must first be recognized that there exist several fundamental difficulties in carrying out the measurement of conductance of water-swollen gels: First, to establish a perfect contact of the electrodes with the sample surfaces. Second, to set up proper electrodes and their arrangement to minimize unnecessary electrochemical reactions and concomitant contamination. Third, to choose a proper frequency range where undesirable dielectric dispersion due to relaxation of macroions and counterions may not occur. Followings are the procedures attempted to solve these problems.

**Establishment of Methodology.** The most fundamental but serious problem in carrying out the precise measurement of the conductance of a polymer gel is how to lead electrodes from a gel. For the case of electrolyte solutions, a pair of parallel plate electrodes with a certain area are usually placed in the fluid



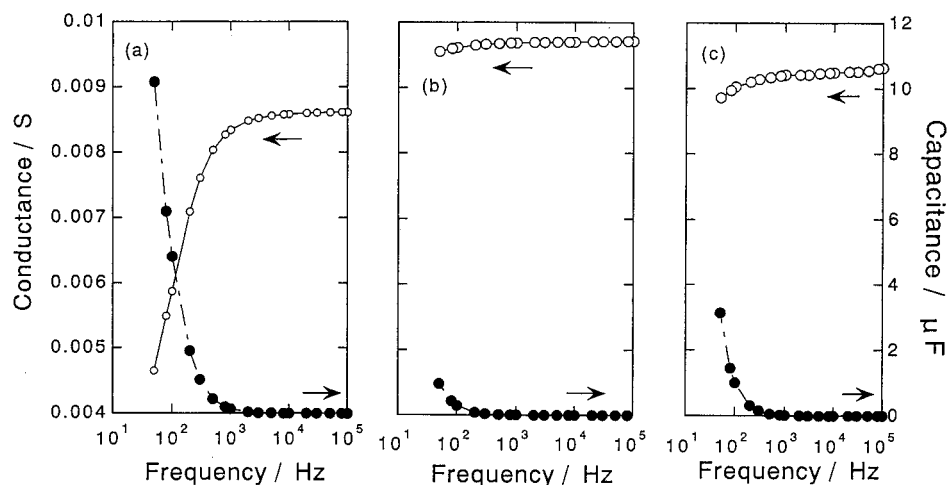
**Figure 2.** Change in the conductance on the contact condition between electrodes and the PAMPS gel measured by 2Pt–Pt method.

with a prescribed distance between them. By measurement of the cell constant using a standard KCl solution, the conductance of a solution can be obtained. For the solid materials, metals are usually placed or deposited to give sandwich or coplanar type electrodes. However, methods used for solution and solid are no longer appropriate for a gel. A water-swollen gel is a soft and wet material. It contains a large amount of water which does not flow like a liquid but gradually evaporates and changes its size and concentration. A gel keeps a certain shape but is deformable or easily broken. Unnecessary pressure of electrodes on the gel may lead to a break or a change not only of the distance between the two electrodes but also of the nature of the gel. Taking into account these characteristics of the gel, we used the following method to make a reproducible and optimal contact of the electrode with the gel.

The two platinized platinum electrodes 20 mm × 20 mm in size were placed in parallel in the vertical direction, and the distance between the electrodes  $d$  was measured using a micrometer (Figure 1). The gel was placed on the lower electrode, and the upper electrode was gradually lowered down toward the gel making the conductance measurement simultaneously.

The conductance was zero until the upper electrode started to contact with the gel, but it increased rapidly with an increase in the contact area between the gel and the upper electrode; after the whole surface of the gel was supposed to have completely contacted with the electrode, the conductance increased rather modestly presumably due to the deformation of the gel under the pressure (Figure 2). The inflection points A, B, and C were considered to correspond to initiation of contact, total contact, and breakup by excess stress, respectively. Measurements were carried out at the point B, which could be easily determined from graphs as shown in Figure 2.

Air is a thermal insulator and interferes with temperature homogeneity. Besides, the gel evaporates water in the air, which brings about change of the water content of the gel. We have attempted to perform measurements in water and in organic solvents immiscible with water like toluene. Since the conductance of the ionized gel is approximately of order 10<sup>-3</sup> S/cm, which is several orders of magnitude higher than that of water (10<sup>-6</sup>–10<sup>-7</sup> S/cm), water is sufficient as an electrical insulator and thermal conductor. Indeed, the preliminary measurement of the conductance of a piece of PAMPS gel showed 4.08 × 10<sup>-3</sup> S mol<sup>-1</sup> in water, 4.06 × 10<sup>-3</sup> S mol<sup>-1</sup> in toluene, and 4.08 × 10<sup>-3</sup> S mol<sup>-1</sup> in air. Although both water and toluene showed almost the same value and indicated they are good media for the measurement, we decided to use water as a



**Figure 3.** Frequency dependencies of the conductance (○) and the capacitance (●) of a PAMPS gel measured by (a) the two-terminal method with platinum electrodes (2Pt); (b) the two-terminal method with platinized platinum electrodes (2Pt–Pt); and (c) the four-terminal method with platinized platinum electrodes (4Pt–Pt).

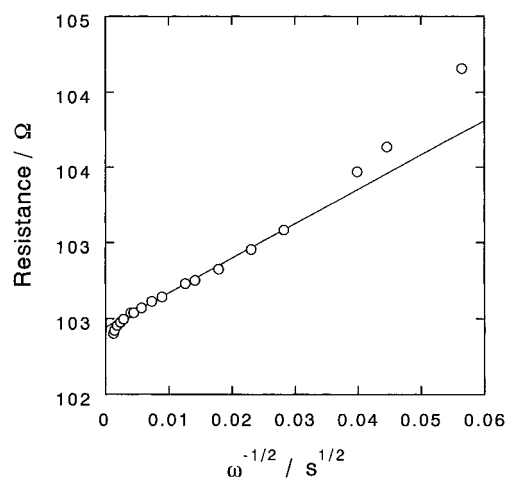
medium for the measurement since we found that a portion of water in the gel immersed in toluene diffuses out through the toluene–gel interface (nearly 10% of water in the gel diffused out after 24 h).

To select an appropriate electrode configuration, three kinds of electrodes were examined and their frequency dependencies studied: a two-terminal method with bare platinum (2Pt) electrodes; a two-terminal method with platinized platinum electrodes (2Pt–Pt); a four-terminal method with platinized platinum electrodes (4Pt–Pt). For the two former cases, the electrode was 20 mm × 20 mm in size, and for the 4Pt–Pt method, platinum wires 0.5 mm in diameter were used as voltage probes. Tips of probes were platinized, and the other portion was covered with a glass. The distance between the two voltage probes was 0.85 mm.

Figure 3a–c shows the frequency dependencies of the conductance  $G$  and the capacitance  $C_e$  obtained by using these three types of electrodes.

For the 2Pt method, the constant values of  $G$  and  $C_e$  were obtained only in the frequency range higher than 10 kHz. When the frequency was below 1 kHz, the value showed a strong frequency dependence, indicating the presence of extensive electrode polarization effect. In contrast, the  $G$  and  $C_e$  values obtained by 2Pt–Pt method were almost constant throughout a wide range of frequency even down to 100 Hz, indicating the effect of increased surface of the platinized platinum electrodes. The 4Pt–Pt method also showed constant  $G$  and  $C_e$  values over a relatively wide range of frequency, while the  $G$  value decreased prominently in the low-frequency range compared with that of the 2Pt–Pt method.

Since  $G$  and  $C_e$  obtained by the 2Pt–Pt method showed the most consistent values at frequencies higher than 1 kHz, we have decided to use the 2Pt–Pt method for conductance measurements of the gel. As shown in Figure 4, the resistance  $R$  obtained by the 2Pt–Pt method showed a linear dependence on  $f^{-1/2}$ , here reduced to angular frequency  $\omega$ , when  $f$  is higher than 100 Hz. The deviation from the linearity at frequencies higher than 10<sup>5</sup> Hz is due to the dielectric relaxation of counterions.<sup>14,15</sup> We took the extrapolated value of  $R-\omega^{-1/2}$  plot at an infinite  $\omega$  as the true resistance of the gel. The difference between the values of conductance calculated from  $R$  thus obtained and that obtained at 1 kHz was within 2%. The resistance measured by the 2Pt–Pt method showed a linear dependence on the distance between the two electrodes, and the resistance became zero by extrapolating it to zero distance.

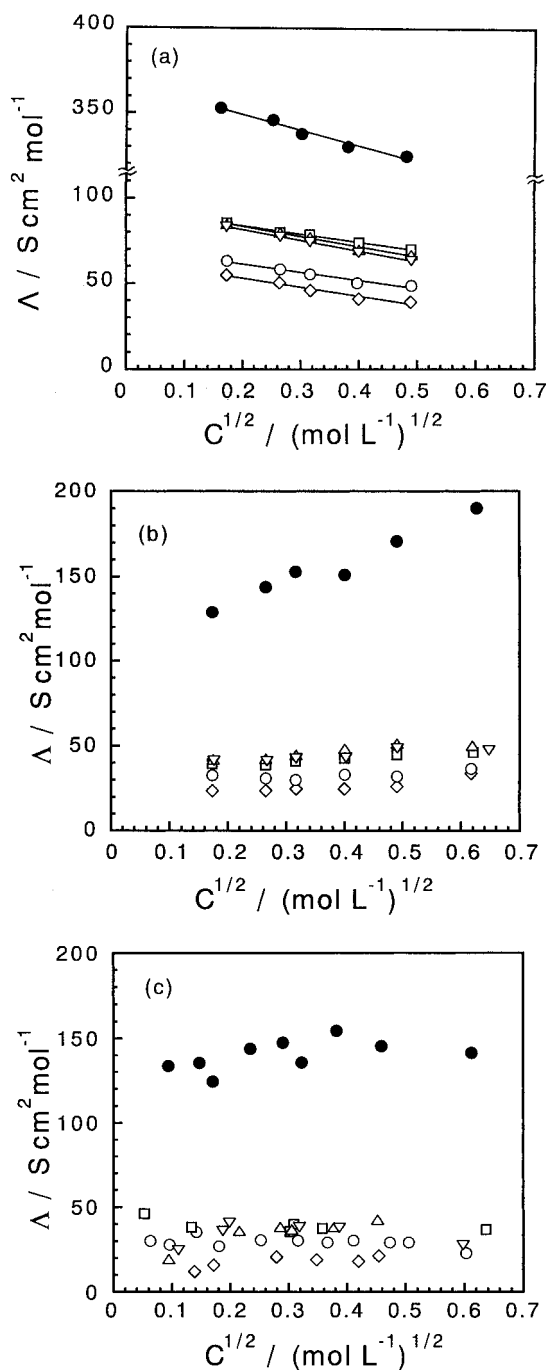


**Figure 4.**  $\omega^{-1/2}$  dependence on the resistance  $R$  of a PAMPS gel measured by the two-terminal method with platinized platinum electrodes (2Pt–Pt).

This confirmed that there is no appreciable resistance at the electrode–gel interfaces.

**Equivalent Conductance.** Under the described experimental setup and conditions, the conductance of the PAMPS gel with various counterions has been measured at different monomeric concentrations  $C$ .  $C$  of a gel is inversely proportional to the degree of swelling and is varied by changing the cross-linking density of the gel. The  $C$  of a gel is usually at a high concentration range even for highly swollen gels. As described before, a water-swollen gel is very soft and fragile, evaporating considerable amounts of water with time. This makes it difficult to accurately measure the degree of swelling, especially when the gel is highly swollen. The error in determining the monomeric concentration  $C$  of the gel at a highly swollen state brought about a large error in the equivalent conductance, especially when  $C$  is less than 0.01 M. The standard deviations of the monomeric concentration  $\Delta C$  and conductivity  $\Delta \kappa$  obtained from the average over 10 samples were within 5% and 2%, respectively, at  $C$  higher than 0.03 M, while they increased up to 18% and 5% when  $C$  was lower than 0.01 M.

Figure 5c shows the concentration dependencies of the equivalent conductance  $\Lambda$  for the PAMPS gels with various counterions. The equivalent conductance of solutions of corresponding monomers (AMPS) and linear polymers (PAMPS) are shown in Figure 5a,b. For all counterion species measured,



**Figure 5.** Equivalent conductance  $\Lambda$  of monomer AMPS solution (a), linear polymer solutions (b), and polymer gel (c) of PAMPS with various counterions at various monomeric concentration.  $T = 25^\circ\text{C}$ . (●):H; (◇):Li; (○):Na; (□):K; (△):Rb; (▽):Cs.

the monomer solution showed a highest equivalent conductance  $\Lambda$  comparing with polymer or gel and decreased with concentration. The good linearity between  $\Lambda$  and the square root of concentration  $C^{1/2}$  indicates that Kohlrausch's law was still holding at such high concentrations. The extrapolated value of the equivalent conductance at zero concentration gives the specific value of the monomer  $\Lambda^0$ .

Linear polymer solutions showed an increasing tendency in  $\Lambda$  with concentration, and this is especially prominent when proton is the counterion. This increasing tendency is the same with the results observed for the salts of polystyrenesulfonic acid when the monomeric concentration is higher than 0.01 M.<sup>16</sup> Considerable coiling of the polymer chain at such high concentrations was considered to be responsible for the decrease-

ing in the fraction of counterions condensed on the polyions, leading to higher values for the counterion mobility and  $\Lambda$ .

The gels showed almost the same  $\Lambda$  values with those of the corresponding linear polymer solutions for all counterion species. However, different from linear polymers, no distinct concentration dependences of  $\Lambda$  were observed for gels. The  $\Lambda$  of the PAMPS gel was explicitly smaller than that of corresponding linear polymer solution when the concentration was higher than 0.25 M. PAMPS gels with alkali metal as counterions also showed somewhat smaller  $\Lambda$  than those of linear polymer solutions at higher concentrations. Since the cross-linking density of gels increases with the concentration, the enhanced depressing of  $\Lambda$  of gels at higher concentrations might be associated with the potential wells located at the cross-linking points which should strongly localize or "condense" counterions through strong electrostatic interactions according to our previous theoretical calculation.<sup>12</sup> This means that the enhanced mobility at higher concentrations due to presumed polymer chain coiling effect may be canceled by the increase of condensation effect due to the increased cross-linking density and may lead to little concentration dependence of  $\Lambda$  of gels.

The gels with alkali metal counterions showed much lower  $\Lambda$  values than that of PAMPS gel. It is well-known that protons have a high mobility compared with other alkali-metal ions, and this is explained by Grothuss's so-called "proton jump" mechanism in which the proton conduction is performed not only by the drift of ions but also by the hydrogen-bond transfer under the electric field.

The equivalent conductance of PAMPS gels with alkali-metal counterions increased in the order of  $\text{Cs}^+ \approx \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$  which is the same order of the increase of the equivalent conductance of the alkali ions at the infinite concentration and associated with their Stokes radius. These results indicate that similar to that of linear polymer solution, the conductivity of a gel is largely dominated by the microions of the gel.

According to condensation theory,<sup>9-11</sup> the electrical conduction of a polyelectrolyte solution is made by the electrical drift of a fraction ( $f$ ) of counterions which are located in a Debye-Hückel atmosphere. The remaining  $(1 - f)$  fraction of counterions are considered to be "bound" to the macroions and do not make contribution the conduction. For monovalent ions, the fraction  $f$  is determined by

$$f = 0.866\xi^{-1}$$

where  $\xi$  is a parameter related to the charge density of polyion and is defined as

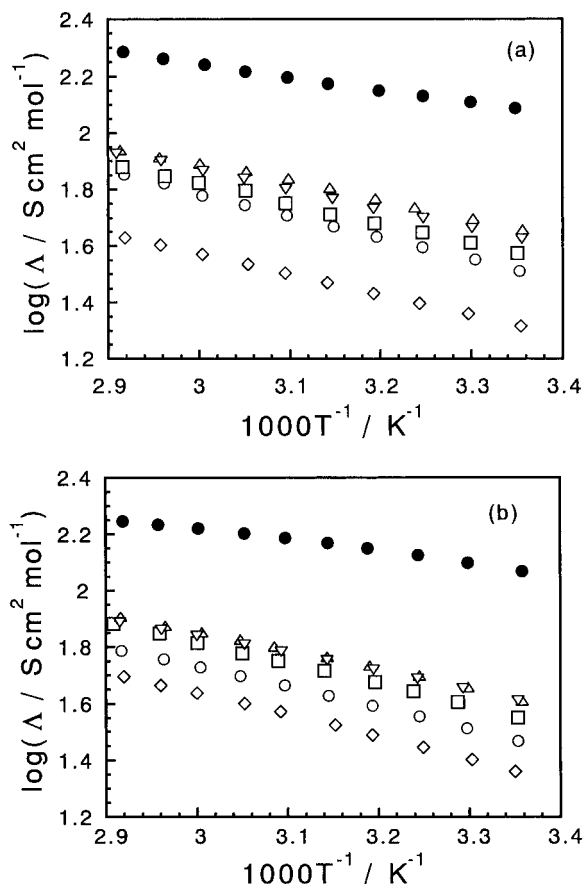
$$\xi = \frac{e^2}{4\pi\epsilon kTb}$$

Here  $e$  is the elementary charge,  $\epsilon$  the bulk dielectric constant,  $k$  Boltzmann's constant,  $T$  the absolute temperature, and  $b$  the spacing between charged groups taken along the axis of the polyion chain. This theory suggests that the conductance of the "free" counterions of polymers should behave as that of simple salt ions.

The equivalent conductance  $\Lambda$  of a polyelectrolyte solution is the sum of  $\lambda_p$  and  $\lambda_c$ , where the former is the equivalent conductance of polyions and the latter is that of counterions in the solution. In the absence of simple salt,  $\Lambda$  can be expressed as

$$\Lambda = \lambda_c + \lambda_p = f(\lambda_c^0 + \lambda_p)$$

where  $\lambda_c^0$  is the equivalent conductance of the counterion in pure solvent. Measurements of aqueous solutions of polysty-



**Figure 6.** Arrhenius plot of equivalent conductance of linear polymer solutions (a) and gels (b) of PAMPS with various counterions at a monomeric concentration of 0.1 M. (●):H; (◇):Li; (○):Na; (□):K; (△):Rb; (▽):Cs.

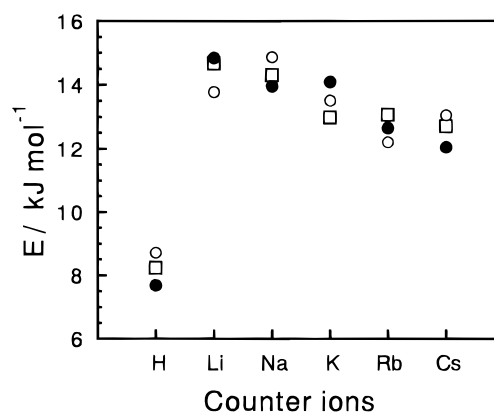
renesulfonic salts showed that the equivalent conductances of the polyion  $\lambda_p$  are 56–37 S cm<sup>2</sup> mol<sup>-1</sup> in the concentration range 0.005–0.1 M, and the transport number is 0.14–0.10.<sup>16</sup> These results indicate that the contribution of polyion to the conductance is not high but not low enough to be neglected.

If we assume that the mobility of charged network may be neglected in the case of gels, the fraction of counterion binding can be estimated by  $f = \Lambda/\lambda_c^0$ . It was found that  $f$  is around 0.5 for the PAMPS gel with various alkali-metal counterions at concentrations of 0.02M–0.4M.

**Activation Energy.** To study the transport process of microions in the gel, the temperature dependencies of the conductance of PAMPS as well as its alkali-salts gels have been studied. Figure 6b shows the Arrhenius plot of the equivalent conductance of the gels at a monomeric concentration of 0.1 M. The equivalent conductance of an AMPS monomer solution and a linear PAMPS solution at the corresponding concentration were also measured, and the results for the linear polymer solution are shown in Figure 6a. All of these three kinds of samples showed a good linearity in the Arrhenius plot, and the activation energies  $E$  were estimated from

$$\Lambda = A \exp\left(-\frac{E}{RT}\right)$$

Here,  $A$  is the frequency factor,  $T$  the absolute temperature, and  $R$  the gas constant. The activation energy of the gel and corresponding solutions of monomer and polymer are shown in Figure 7. No appreciable differences in the activation energy were observed among the solution of monomer, polymer, and network with the same counterion species. This result suggests that the electrical conduction occurs by essentially the same



**Figure 7.** Activation energies of electrical conduction of the AMPS monomer solution, PAMPS polymer solution, and PAMPS gel with various counterions. The monomeric concentration is 0.1 M. (□): Monomer solution; (○): polymer solution; (●): polymer gel.

mechanism for these three different kinds of samples and the transport process of counterions plays a predominant role for the electrical conduction. The fact that the activation energy of the proton sample was much lower than those of samples with alkali-metal counterions should be attributed to the specific conduction mechanism of proton ions. The activation energy of samples with alkali-metal counterions increased in the order  $\text{Cs}^+ \approx \text{Rb}^+ < \text{K}^+ < \text{Na}^+ \leq \text{Li}^+$ , which is of the same order as their Stokes radius. If the temperature dependence of  $\Lambda$  was due only to the change in the viscosity of water, the activation energy should not be different for different species of alkali metals according to Stokes' hydrodynamic theory. The slight increase in the activation energy in the order  $\text{Cs}^+ \approx \text{Rb}^+ < \text{K}^+ < \text{Na}^+ \leq \text{Li}^+$  might be attributed to the temperature effect on the Stokes radius.

We have tried to estimate the temperature effect on  $f$  by using the relation  $f = \Lambda/\lambda_c^0$ , which neglects the contribution from polyions. The  $\lambda_c^0$  at various temperature were calculated from a second-order polynomial, which was obtained by fitting the polynomial with the data of  $\lambda_c^0$  at 0, 18, 25, and 100 in the literature.<sup>17</sup> It was found that for the linear polymer solutions with various counterions, a discernible minimum of  $f$  was observed around 40–50 °C. However, in the case of the gel, the temperature effect was not clear: in the temperature range 20–70 °C, the proton showed a moderate decreasing and  $\text{K}^+$  an increasing tendency, and other counterions showed no temperature dependence. All of the changes in  $f$  were within  $\pm 0.02$ , which is quite small. Therefore, the increase in the thermal energy have no much effect on helping the “condensed ions” to be released and increase  $f$  in the investigated temperature range.

In summary, the electrical conduction of a polyelectrolyte gel is predominately contributed by the “free” counterions which showed a conduction behavior similar to those of linear polymers and monomer solutions. The fraction of “condensed” counterions defined by the condensation theory seemed to be increased at an enhanced cross-linking density of gels. Although the effect brought about by the cross-linking of the polymer is still not so clear, this work might be useful in understanding the electrostatic interaction specific to a polyelectrolyte gel.

**Acknowledgment.** This research was supported in part by Grant-in-Aid for the Experimental Research Projects “Formation and Control of Superstructures in Polymer Gel” (07241202) and “Crosslinking Effect on the Ionic Conduction of Polyelectrolyte Gels” (08455446) from the Ministry of Education, Science and Culture, Japan. The authors also acknowledge to the Agency

of Science and Technology, Minister of International Trade and Industry (MITI) for the financial support.

## References and Notes

- (1) Umezawa, K.; Osada, Y. *Chem. Lett.* **1987**, 1795.
- (2) Miyano, M.; Osada, Y. *Macromolecules* **1991**, 24, 4755.
- (3) Sawahata, K.; Gong, J. P.; Osada, Y. *J. Macromol. Sci.* **1991**, 1189.
- (4) Osada, Y.; Hasebe, M. *Chem. Lett.* **1985**, 1285.
- (5) Osada, Y.; Kishi, R. *J. Chem. Soc., Faraday Trans.* **1989**, 85, 655.
- (6) Gong, J. P.; Nitta, T.; Osada, Y. *J. Phys. Chem.* **1994**, 98, 9583.
- (7) Nagasawa, M.; Noda, I.; Takahashi, T.; Shimamoto, N. *J. Phys. Chem.* **1972**, 76, 2286.
- (8) Dolar, D.; Span, J.; Pretnar, A. *J. Polym. Sci., Part C* **1968**, 16, 3557.
- (9) Oosawa, F. *J. Polym. Sci.* **1957**, 23, 421.
- (10) Manning, G. S. *J. Chem. Phys.* **1969**, 51, 934.
- (11) Manning, G. S. *J. Phys. Chem.* **1975**, 79, 262.
- (12) Gong, J. P.; Osada, Y. *Jpn. Chem. Lett.* **1995**, 449.
- (13) Jones, G.; Christian, S. M. *J. Am. Chem.* **1935**, 57, 272. It has been pointed out that both the equivalent condenser  $C_s$  and the resistance  $\Delta R$  introduced by the polarization at electrodes are inversely proportional to the square root of the frequency. According to this theory,  $\tan \psi = \Delta R C_s \omega = 1$ , and there is a phase displacement of  $-45^\circ$  at the electrodes. Therefore, if we plot  $R$  against  $1/\sqrt{\omega}$ , we should get a straight line whose intercept on the resistance axis would be the true resistance.
- (14) Ookubo, N.; Hirai, Y.; Ito, K.; Hayakawa, R. *Macromolecules* **1989**, 22, 1359.
- (15) Ito, K.; Yagi, A.; Ookubo, N.; Hayakawa, R. *Macromolecules* **1990**, 23, 857.
- (16) Kwak, J. C.; Hayes, R. C. *J. Phys. Chem.* **1975**, 79, 265.
- (17) *Chemistry Handbook* (Japanese), 2nd ed.; Chem. Soc. Jpn., Ed.; Maruzen Press: Tokyo, 1975.