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Description	

**Polymer gels as soft and wet chemomechanical systems**  
**- an approach to artificial muscles**

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## I Introduction

A polymer gel consists of an elastic cross-linked network and a fluid filling the interstitial space of the network. The network of long polymer molecules holds the liquid in place and so gives the gel what solidity it has. Gels are wet and soft and look like a solid material but are capable of undergoing large deformation. This property is in contrast with most industrial materials such as metal, ceramics, and plastics, which are dry and hard. Living organisms are largely made of gels. Except for bones, teeth, nails, and the outer layers of skin, mammalian tissues are highly aqueous gel materials largely composed of protein and polysaccharide networks, in which water contents range up to 90% (blood plasma). This enables the organism to transport ions and molecules more easily and effectively while keeping its solidity. Polymer gels are attracting considerable attention in recent years <sup>[1-10]</sup>.

This review article describes some of our results on the fundamental aspects and chemomechanical properties of polymer gels, which produce the motility of gels like muscle.

In chapter II of this review, we concentrate on the properties of a polyelectrolyte gel which is a charged polymer network with macro ions fixed on the polymer chains and the micro counter ions that are localized in the network frame. A polyelectrolyte gel exhibits ability to swell in water and absorbs a significant fraction (~2000 times the polymer weight) of water within its structure, but will not dissolve in water.

The electrostatic potential distribution as well as the counter-ion distribution of the charged network is theoretically estimated by the Poisson-Boltzmann equation, using a 2-dimensional stacking model. Presence of the potential wells at the cross-linking points is predicted. The electrical conductance and the low frequency

dielectric relaxation of the gel is experimentally measured and compared with the corresponding polymer solution, the effect of the cross-linking points on the counter-ion conduction is discussed.

Further, the specific electrical responses of the polyelectrolyte gels are discussed. When a water-swollen polyelectrolyte gel is interposed between a pair of plate electrodes and a D.C. current is applied, it undergoes electrically-induced chemomechanical contraction and concomitant water exudation in the air.<sup>[11]</sup> The electrically induced contraction of the gel is associated with the electrokinetic transportation of hydrated ions and water in the network, and a 1-dimensional electrokinetic model (1-D capillary model) for the contractile phenomenon was postulated.

Some kinds of weak polyelectrolyte gels, such as cross-linked poly(acrylic acid), show the mechanoelectric property and produce an electrical potential as large as a few millivolts.<sup>[12]</sup> The mechanical deformation was supposed to induce a spontaneous ionization of carboxylic acids in a local level to give out the electrical potential.

In chapter III, attempts to introduce ordered structure in the gels will be described. Two effective methods have been shown in introducing ordered structures in a water-swollen hydrogels: one is by the molecular assembly reaction between a polyelectrolyte gel and an oppositely charged surfactant. The other is by copolymerizing the hydrophilic moiety with a crystal moiety. The thermodynamics and the chemomechanical behavior of the ordered gels are described in chapter III.

In chapter IV, we demonstrate several applications of gels as soft and wet machines driven by chemical energy. These soft and wet machines might be the basis of the approach to artificial muscles.

## II Fundamental Properties and Electrical Responses of Polyelectrolyte Gels

### 1. Electrostatic Potential Distribution

The electrostatic potential distribution  $\psi(x, y, z)$  of a polyelectrolyte gel is determined by Poisson-Boltzmann equation

$$\Delta\psi(x, y, z) = -\frac{\rho_0}{\varepsilon} \exp\left[-\frac{e\psi(x, y, z)}{kT}\right] \quad (1)$$

with a boundary condition of

$$\frac{\partial\psi(x, y, z)}{\partial n} = -\frac{\sigma}{\varepsilon} \quad (2)$$

where  $\varepsilon$  is the dielectric constant of the solvent,  $e$  the charge of an elementary electron,  $k$  the Boltzmann constant,  $T$  the temperature, and  $\rho_0$  the average counter ion density. In equation (2),  $\sigma$  is the surface charge density of the chains and  $n$  denotes the normal derivation of potential on the surface of polymer chain.

Gels should, in general, be considered to be composed of heterogeneous structures in different orders from a few angstroms to several micrometers (structure hierarchy). This makes it extremely difficult to accurately calculate the electrostatic potential distribution in the gel by the Poisson-Boltzmann equation.

To catch the electrical feature due to the cross-linkage of the ionic macromolecules, however, a periodical model to estimate the electrostatic potential energy distribution in the polyelectrolyte gel has been proposed.<sup>[13]</sup> In this model, the cross-linking points of the gel are supposed to be periodically distributed on the chain segments and the macro charges are evenly distributed on the chain. Besides, it is supposed that the polymer network is made of the periodical stacking of two-dimensional meshes, each  $2r_0$  distance apart.

A numerical simulation of the electrostatic distribution in the polyelectrolyte gel has been carried out for a poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) gel

which is a fully ionized polyelectrolyte having sulfonic groups as macro-ions and  $H^+$  as counter-ions. Figure 1 shows a spatial profile of electrostatic potential energy in the unit of  $kT$  on the planes of mesh-like networks. The figure shows that there exist potential energy wells at every cross-linking points and valleys along the polymer chains.

Since the charge density of counter ions  $\rho(x, y, z)$  is determined by the Boltzmann distribution

$$\rho(x, y, z) = \rho_0 \exp\left[-\frac{e\psi(x, y, z)}{kT}\right] \quad (3)$$

Therefore, counter ions are mostly localized around the network knots as well as the polymer chains due to the deep potential wells and valleys. The charge density of counter ions decreased very sharply with an increase in the distance from the polymer chain. Counter ions located in the deep potential valley ( $\gg kT$ ) should strongly be bound to the polyion. The amount of these bound counter ions would increase with the increase in the cross-linking density.

The deep potential wells and high counter-ion densities at cross-linking points might bring about an instability and results in the counter-ion condensation as predicted by Oosawa and Manning for the linear polyelectrolyte solution. [14,15]

The presence of deep electrostatic potential valley should strongly confine the motion of water molecules which filling the interfacial space of the network and restrict the configuration favorable to form crystal structure. This might bring about decreased entropy and enthalpy changes of solvent molecules at crystallization, due to enhanced polarization and should decrease the melting temperature of water.

The treatment of a cross-linked polyelectrolyte gel with a rigid periodical structure and the interaction between small ions with a mean field might over-simplify

the problem. The presence of deep potential wells at cross-linking points could come from this simplification, it would be informative to understand the potential distribution of the polyelectrolyte gels, especially in the case of without the presence of simple salts.

## 2. Electrical Conductance of Polyelectrolyte Gels

From the calculated potential distribution of the polyelectrolyte gels, some effects of cross-linkage on the conductive behaviors of the gel can easily be expected. One is an enhanced counter-ion "binding" which should increase with the increase in the cross-linking density.<sup>[14,15]</sup> The potential wells at cross-linking point as predicted from the calculation should strongly localize or "condense" counter-ions through strong electrostatic interactions and affect the conductive behaviors of the gel. The other is a decreased contribution of ion transportation from the "giga" macromolecular network. The macro ions also make a contribution to the electrical conduction of polymer solution,<sup>[16,17]</sup> this contribution is expected to be depressed in the case of the networked gel.

Figure 2 shows the equivalent (molar) conductance of the strong polyelectrolyte gel PAMPS at various monomer concentrations.<sup>[18]</sup> The equivalent conductance of solutions of corresponding linear polymers (PAMPS) and monomer (AMPS) are also shown. The figure shows that a polyelectrolyte gel has an equivalent conductance approximately equals to that of the corresponding linear polymer solution which showed a slightly increasing tendency in the equivalent conductance with the concentration. Considerable coiling of the polymer chain at such high concentrations was considered to be responsible for the decreasing in the fraction of counter-ions condensed on the polyions, leading to higher values for the counter-ion mobility and the equivalent conductance.

However, the gels showed almost no distinct concentration dependencies of the equivalent conductance, which was somewhat smaller than that of linear polymer solutions when concentrations were higher than 0.25M. The presumable polymer chain coiling effect occurs at higher concentrations for polymer solutions may be canceled by the increasing cross-linking points which condense counter-ions and lead to decreases of counter-ion mobility and the equivalent conductance of gels.

According to the condensation theory <sup>[14,15,19]</sup>, the electrical conduction of a polyelectrolyte solution is due to the electrical drift of a fraction (f) of counter-ions that are located in a Debye-Huckel atmosphere. The remaining (1-f) fraction of counterions are considered to be bound to the macroions and do not contribute to the dc conductivity. In the latter case, the results of dc conductivity measurements are understandable if we take into account that the dc conductivity of gels and linear polymer solutions is largely dominated by the loosely bound counter-ions (free counter-ions). In other words, there should be no large difference in the state of free counter-ions between a gel and a linear polymer solution. To observe the behavior of bound counter-ions of gels and linear polymer solutions, the dielectric properties of the two systems were further studied.

### **3. Low Frequency Dielectric Relaxation of Polyelectrolyte Gels**

It is well known that the dielectric relaxation spectrum gives us information about ions which move under an alternative electric field. The dielectric relaxation spectroscopy of the polyelectrolyte solutions shows two kinds of relaxation processes: the high-frequency relaxation in MHz frequency range and the low-frequency one in radio-wave frequency range. The high frequency relaxation is due to the fluctuation of free counter-ions that exist far from macro-ions. <sup>[20-23]</sup> The low-frequency relaxation



arises from the fluctuation of bound counter-ions that exist in the vicinity of macro-ions. [20,21,24]

The low-frequency relaxation should also be observed in the polyelectrolyte gels, as like in the polyelectrolyte solutions. Moreover, we are able to speculate that the polyelectrolyte gel shows a slower relaxation process than the linear polymer solution, because of the strong network-counter-ion interaction, although the loosely bound counter-ions showed no difference between in the networked gels and in the linear polymer solutions, as elucidated by the results of the electrical conductance.

Figure 3 shows the concentration dependencies of the mean relaxation time,  $\tau_0$ , of sodium salt of poly(2-acrylamido-2-methylpropane sulfonic acid) (PNaAMPS) gels and their corresponding linear polymer solutions. The relaxation time of gels decreases with increasing the concentration, while that of linear polymer solutions is almost independent of the concentration. According to the literatures [20,21], the observed low-frequency relaxation of the linear polymer solution is associated with the tightly bound counter-ion fluctuation along the polymer chain. This low frequency relaxation strongly depends on the molecular weight but is almost independent of the concentration. [25]

Supposing a square type potential well along the polymer chain,  $\tau_0$  of the linear polymer solution is given by [26]

$$\tau_0 = \frac{L_f^2}{D} = \frac{L_c^2}{12D} \quad (4)$$

where  $L_f$  and  $D$  are the fluctuation length and the diffusion constant of the bound counter-ion, respectively.  $L_c$  is the contour length of the macro-ion. Using the degree of polymerization  $N$  as 3100 and the monomer unit length  $b$  as 2.55 Å, one gets  $L_c$

and  $L_f$  as 801nm and 231nm, respectively, from equation (4). The mean diffusion constant,  $D_m$ , is determined to be  $2.1 \times 10^{-10} \text{ m}^2/\text{s}$  which is an order of magnitude smaller than the diffusion constant  $D_0 (=1.22 \times 10^{-9} \text{ m}^2/\text{s})$  of  $\text{Na}^+$  ion in water. This result is in good agreement with the data of sodium salts of poly(styrene sulfonate) (PNaPSS) solution reported by N.Ookubo et al.. [27]

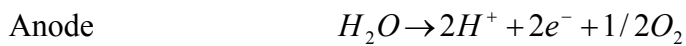
The observed relaxation of gels is considered correspond to the counter-ion fluctuation along the polymer network by crossing through the cross-linking points. Thus, the observed relaxation time consists of the two relaxation times, i.e. the time for fluctuating along the linear part of the polymer network and the time for exceeding the energy barrier which is based on the electrostatic potential well at the cross-linking points. According to this explanation, the diffusion constant at the cross-linking point is found to be 3 orders lower in magnitude in comparison with that alongs the polymer chain. This might be a proof of the presence of deep potential wells at cross-linking points. It is also found that the bound counter-ions can fluctuate across over about 100 cross-linking points. The energy barrier of the cross-linking points are neither sensitive to the degree of cross-linking density, nor to the polymer concentration. This is in accordance with the fact that the diffusion constant of bound counter-ions along a linear polymer chain is not sensitive to the polymer concentration. These results suggest that the state of bound counter-ions in the vicinity of the polymer chain or in the cross-linking points is not affected by the presence of other polymers or their counter-ions.

#### **4. Electrical Contraction of Polyelectrolyte Gels**

When a polyelectrolyte gel is inserted between a pair of electrodes and a D.C. voltage is applied, it undergoes anisotropic contraction and concomitant fluid (water) exudation. <sup>[11,27]</sup> Figure 4 shows the schematic view of the shape change of an anionic gel with time under the electric field. <sup>[28]</sup> There are several features of the contraction.

- 1) The contraction occurs only for polyelectrolyte gels and not for non-charged hydrogel.
- 2) The anionic gel slight swells near the cathode and extensively contracts near the anode, the reverse occurs for the cationic gel.
- 3) The rate of contraction is proportional to the electrical current.
- 4) The contraction of the gel is reversible, i.e., it swells in water after the electric field is removed.

Figure 5-(a) shows the electric quantity dependence of the relative weight change of PAMPS gels with various degree of swelling under a D.C. electric field. PAMPS gel is a strong acid polymer with fully ionized sulfonic groups as macroions and  $H^+$  as counterions. When an electric field is applied, hydrated  $H^+$  ions (more exactly  $H_3O^+$ ) migrate towards the cathode and are reduced, liberating  $H_2$ . The water migrates together with  $H^+$  ions and exits the gel near the cathode. The overall electrode reactions are expressed as follows:



The oxygen and hydrogen liberated can be observed throughout the course of the contraction. It has been verified that the amount of gases released was consistent with the theoretical value derived by Faraday's law according to the above equations. The overall population of ions should not significantly change during the contraction,

because at every moment, the amount of  $H^+$  generation and consumption should be balanced at both electrodes.

The electrically induced contraction of the gel is caused by a transport of hydrated ions and water in the network, and the contractile behaviors observed are essentially electrochemical phenomena. When an outer electrical field is applied across the gel, both the macro- and the micro-ions get electrical forces in an opposite direction. However, the macro-ions are stationary phase since they are chemically fixed to the polymer network, while the counter ions are mobile capable of migrating along the electric field and drag water molecules with them. In other words, application of an electric field causes a pumping of mobile counter-ions and macro network ions together with the surrounding water in opposite directions until mobile ions reach the electrode, whereupon the velocity of migration and the velocity of gel contraction are governed both by the quantity of mobile ions and the electric field.

A one-dimensional capillary model has been proposed to quantitatively analysis the electro contractile behave of the gel (Figure 6).<sup>[29]</sup> In this model, only the macro-ions located along the chains parallel to the electric field applied were considered and the effects of cross-linking points as well as the chains located perpendicular to the electric field were neglected. Under such a simplification, the problem of water transportation under the electric field in the polymer network is simplified to a problem of the transportation along the rod-like polymer chain, which is analogous to that of liquid flow through a capillary under the influence of electric field. The numerical simulation of contraction has been made for PAMPS gel, and Figure 5-(b) is theoretically obtained electric quantity dependence of relative weight change of PAMPS gels ( $W/W_w$ ) with various degree of swelling  $q$ . Comparing with Figure 5-(a), both figures show that  $W/W_w$  is proportional to the amount of charges transported

through the gel and the rate of contraction increases with increase in the degree of swelling.

Here it should be noted that the values obtained by simulation are somehow several times larger than those of experimental data. One reason for this should be attributed to the simplification of the problem to 1-dimensional model, whereupon the effect of cross-linking points, and of the macromolecular ions located perpendicular to the electric field have not been taken into account. In addition, neglecting of the counter flow of water might also overestimate the migration ability of water and lead to a large contraction rate. This model satisfactorily illustrates the characteristics of the contraction phenomenon and demonstrates that the contraction of a gel under the electric field occurs due to electro-kinetic mechanism.

## **5. Mechanoelectrical Effects of Polyelectrolyte Gels**

In the previous section, we have described that a polyelectrolyte gel can make contraction or deformation under the electric stimulus, that is, a gel can convert the electrical energy into the mechanical work. The reverse process has also been observed in gels. <sup>[12]</sup> It has been found that mechanical deformation can produce electrical potential as large as a few millivolts. This property of gel is similar as that of soft tissue in the mechanically induced biological systems such as touch-sensing system of human fingers. It has been clarified that stress generates potentials (SGP) in human skin, which are then transmitted to the central nervous system for further processing. <sup>[30,31]</sup> Hence, like a human skin, the gel is able to convert mechanical energy into electrical one behaving like a soft and wet piezoelectric material.

When the ionizable polymer is chemically cross-linked to form a three-dimensional network, an increase in the ionization of the network brings about an extensive swelling of the gel that can visually be observed on the macroscopic level. The expansion of the conformation is due to the increase in the electrostatic potential appeared on the macromolecules. On the base of swelling and contraction of a weak polyelectrolyte gel, Katchalsky and Kuhn <sup>[32-34]</sup> proposed a so called "muscle" model which referred to as "mechanochemical" or later as to "chemomechanical" system. <sup>[1,35]</sup>

The reverse process, i.e., mechanically induced shape change of any cross-linked weak polyelectrolyte should cause a change in its ionization state. When a piece of weak polyelectrolyte gel is placed in a cell and compressed from the vertical direction using a glass piston ([Figure 7-\(a\)](#)), the pH of the gel changes as shown in [Figure 8](#). When the gel was unloaded, the pH quickly obtained the original pH value with some overshooting.

Since there was no water outlet in the course of the deformation, the pH change should be associated with an enhanced ionization of carboxyl groups under deformation: being compressed in one direction, the gel is subjected to expand laterally and induces a one-dimensional dilatation of the polymer network in this direction. This brings about an increased chemical free energy (a decrease in entropy) of the polymer chain that should be compensated by the simultaneous increase in its ionization.

The mechanically induced ionization was observed only for weak polyelectrolyte gels that are able to sensitively change their ionization state in respect to their conformation and not for the fully-ionized strong polyelectrolyte gels.

In order to extract the change in electrical potential originated from the pH decrease of the gel, a cell comprising of two polymer gels facing each other was made. A pair of needle-like platinum wire electrodes, one as reference, the other as working

electrode, were inserted to measure the electrical potential. When the gel is deformed, the extra protons migrate to the undeformed gel through the interface until the Donnan equilibrium is reached and an electrical potential difference was observed during this period.

On the base of this principle, a soft and wet tactile-sensing device was constructed by connecting the electrodes with a photo emission diode array through an amplifier (Figure 7-(b)). Experiments demonstrated that the tactile-sensing system made of polymer gel could successfully light the array in proportion to the amplitude of the stress applied.

It should be emphasized that mechano-electrical system made of polymer gel has similarities with the tactile perceptions in the living organism. Both of them are dynamic processes in which the macroscopic deformation induces the ionic rearrangement which give rise to a certain amount of trans-membrane potentials. The gel also possesses common features with the natural tissue: softness, wetness, elasticity and some other rheologically specified characteristics.

Because of these similarities, the soft mechano-electrical system constructed from a polymer gel may open new possibilities in investigating artificial tissue-like tactile perception for prosthetics and robotics.

### **III Formation of Ordered Structure in Hydrogels**

#### **1. Molecular Assembly Reaction Between Polyelectrolyte Gels and Oppositely Charged Surfactants**

A number of studies on the structure of the complex of the polyelectrolyte gels with oppositely charged surfactants with a long alkyl tail or a planar component have been made. Complexes of polyelectrolytes <sup>[36,37]</sup> with surfactants formed well-organized

structures. Kabanov et al. have reported that the structure of the stoichiometric complexes formed between cross-linked poly(acrylic acid) (PAA) and cationic surfactants, cethyltrimethyl ammonium bromide, form a layer structure. The layer structure [38] and its function for many other complexes were also investigated. [39-43] The complex of polycation gels with anionic phthalocyanine formed a hexagonal columnar structure. [44]

The principle of the complex formation between a polyelectrolyte gel and an oppositely charged surfactant molecules is based on the electrostatic and hydrophobic interactions. A remarkable contraction of the gel is observed only above a certain critical concentration of the surfactant, which indicates that the surfactant-gel complex formation has a cooperative nature associated with the hydrophobic interaction between surfactant molecules.

We have systematically studied the thermodynamics and structure of complex formation between PAMPS gels and alkyl pyridinium chloride ( $C_n\text{PyCl}$ ). If the degree of binding,  $\beta$  (the molecular ratio of surfactant adsorbed to the sulfonic acid group in the gel), derived from the concentration change is plotted as a function of the surfactant concentration,  $C_s$ , a binding isotherm is obtained as shown in [Figure 9](#).

As is well established, the overall stability constant,  $K$ , for the complexation can be calculated as follows when the surfactant undergoes a stoichiometric reaction with the gel in the concentration range  $10^{-4} - 10^{-2}$  M:

$$K = (C_{s0} - C_s) / [\{C_p - (C_{s0} - C_s)\}C_s] \quad (5)$$

where  $C_p$  is the exchanged molar concentration, defined as the amount of sulfonic acid groups in the total volume of the solution,  $C_0$  is the surfactant concentration surrounding the polymer gel at equilibrium.



On the basis of the Zimm-Bragg theory for a helix-coil transition, Satake and Yans<sup>[45]</sup> derived the following expression for the cooperative binding:

$$K = K_0 u = 1/(C_s)_{0.5} \quad (6)$$

where  $K_0$  is the binding constant of a surfactant molecule bound to an isolated binding site on a polymer, and  $u$  is the cooperativity parameter characterizing interaction between adjacently bound surfactants. Thus,  $K$  can be calculated as the value of the reciprocal of the equilibrium free surfactant concentration,  $C_s$  at  $\beta = 0.5$ . Table 1 shows the stability constant, binding constant and cooperativity parameter for the complexation obtained by this method for surfactant molecules of various alkyl chain lengths. It is seen that the stability constant,  $K$ , of the surfactant molecules increases significantly with increasing alkyl chain length, and the value of C<sub>16</sub>PyCl is about 5000 times larger than C<sub>4</sub>PyCl and more than four times larger than C<sub>12</sub>PyCl.

These results indicate that the hydrophobic interaction of alkyl chains plays an important role in effective complexation. The positively charged surfactant molecules complex with the sulfonate moiety through an electrostatic salt formation, but the alkyl chains make an additional, side-by-side, hydrophobic binding to give a micellar-like structure of surfactant within the gel.

The effect of cross-linking on the cooperative binding has been theoretically analyzed. The hydrophobic interaction has been treated using the nearest neighbor interaction model, while the electrostatic interaction has been calculated using the rod-like model. The general formulas derived on the basis of the free energy minimum principle predicted that the cross-linkage enhances the initiation process but strongly suppresses the cooperativity due to the osmotic pressure in the network domain. The theoretical results showed fairly good agreement with the experimental data, confirming the essential features of the theory.<sup>[46]</sup>

## 2. Hydrogels with Crystalline Ordering

The water-swollen polymer hydrogel with molecularly ordered structure can be obtained by copolymerizing hydrophilic monomers such as acrylic acid(AA) with hydrophobic monomers which form crystals such as stearyl acrylate(SA), acryloylhexadecanoic acid(AHA).<sup>[47,48]</sup> These gels undergo reversible order-disorder transition with change in temperature, pH and solvent properties.

Effect of crosslinkage on the formation of the organized structure has been studied using poly(n-stearyl acrylate(SA)-co-AA) gel samples with the same swelling ratio ( $q = 12$ ) but with a different degree of crosslinking (0, 0.3, 1.0, 3.0, 10 mol%, degree of crosslinking = 0 % corresponds to the linear polymer.) It was found that  $d_2$  (long-range ordering) spacing disappeared at degree of crosslinking = 3.0 mol%, while  $d_1$  (short-range ordering) spacing destructed only at degree of crosslinking = 10 mol%. These facts suggest that increasing degree of crosslinking, similarly to the effect of water, destroys first the long-range organization, then the short-range organization.<sup>[49]</sup>

WAXD and SAXD results showed that poly(SA-co-AA) gels showed crystalline structure in which the long alkyl side chains are in a tail-to-tail alignment arranged perpendicular to the main chains. DSC thermograms of the poly(SA-co-AA) gels showed the endothermic and exothermic peaks at 48 and 42°C upon heating and cooling, respectively, which was confirmed to be the reversible order-disorder transition together with the results of X-ray study. In every poly(SA-co-AA) gel, hysteresis was observed whereupon the melting temperature was higher than the crystallization temperature, but the transition temperature was independent of the copolymer composition.

Temperature dependence of Young's modulus, E of the poly (SA-co-AA) gel is

shown in [Figure 10](#).  $E$  decreased gradually with increasing temperature from 30 to 47°C and decreased abruptly from  $1.7 \times 10^7$  to  $2.2 \times 10^5$  Pa above 49°C. The temperature at which  $E$  decreased abruptly coincides with the order-disorder transition temperature of the gel obtained by a DSC measurement. The gel showed a typical jelly-like softness above the temperature. The drastic change observed in mechanical property is reversible.

Fluorinated water-swollen hydrogels with molecular and supramolecular organization have also been synthesized. <sup>[50]</sup> Moderately water-swollen hydrogels were prepared by copolymerizing SA, 2,2,2-trifluoroethyl acrylate (TFEA), and acrylic acid (AA), and the effects of water and TFEA on the molecular and supramolecular structure were investigated. An incorporation of TFEA brought about a decrease in  $d_2$  spacing presumably due to a local order becoming amorphous while  $d_1$  was kept constant. Enhanced effects of water and stretching on the supramolecular organization were demonstrated. Although the melting temperature of cross-linked poly(SA-co-AA) was independent of the SA content, that of the cross-linked poly(SA-co-TFEA-co-AA) can be modulated by changing the TFEA content  $F$  in the gel. As shown in [Figure 11](#), the transition temperature at which Young's modulus abruptly changes decreased with an increasing in TFEA.

## **IV Chemomechanical Systems Constructed from Gels**

### **1. Gel-looper – The First Man-made Soft Machine**

In contrast to motors and hydrodynamic pumps, the movement made by the polymer gel is produced by the chemical free energy of the polymer network, whereupon electrical or thermal energy is used to drive the direction and control the state of the equilibrium. Thus, the chemomechanical gel driven by an outside stimulus is

able to exhibit gentle and flexible action and its movement is more like that observed in muscle than in metallic mechanical systems, and may serve as a new type of soft-actuator or molecular machine.

A sheet of PAMPS gel was suspended from a long plastic ratchet bar, followed by immersion in a dilute solution. N-(n-dodecyl) pyridinium chloride ( $C_{12}PyCl$ ) containing  $3 \times 10^{-2}$  mol/l sodium sulfate. When 20V D.C. (1.0 V/cm) voltage was applied through a pair of long carbon plate electrodes placed at the upper and lower positions of the ratchet bar, and the polarity was altered at 2 s intervals, the gel moved forward in the water like a 'looper' by repeated bending and stretching.<sup>[51,52]</sup> [Figure 12](#) shows time profiles of 'gelooper' walking with a constant velocity of 25cm / min in water at 20V D.C.

The principle of motility of this gel-looper is associated with a reversible and cooperative complexation of surfactant molecules on the polymer gel under an electric field to give rise to shrinkage of the gel. The electric field drives and controls the direction of this equilibrium to give anisotropic complex formation. When the D.C. voltage is turned on, the positively charged surfactant molecules move by electrophoresis, towards the cathode and form a complex with the negatively charged gel, preferentially on the side of the PAMPS strip facing the anode. This causes anisotropic contraction, bending the gel towards the anode ([Figure 13](#)). When the polarity of the electric field is reversed, the surfactant molecules absorbed on the gel are released and electrophoretically travel towards the anode. Instead, new surfactant molecules complex preferentially on the opposite side and straighten the gel. The polymer gel can be made to bend and stretch repeatedly. It thus inches forward along the ratchet bar by means of the hooks from which it is suspended.

## 2. Shape Memory Gels

A material is said to show shape memory if it can be deformed to a new shape (which it retains), only to revert to its original shape when heated above a certain critical temperature. The most famous example of such a material is titanium-nickel alloy, produced by a reversible martensitic structural transformation. <sup>[53]</sup> The mechanism of the shape memory gel is very different.

The mechanical properties of the water-swollen poly(SA-co-AA) gels containing the long alkyl side chain drastically changed due to the reversible order-disorder transition, which allowed one to expect “shape memory” behaviors. If the gel is heated above the transition temperature (50°C) under its ‘soft’ state, it can be readily deformed to a new shape. As far as the gel is kept cooled in its deformed state, it is rigid and retains its new shape. The crystalline aggregates formed among the side chains lock and keep the new shape. If the gel is then once again heated above the transition, it spontaneously recovers its original size and shape in a few seconds. This behavior is illustrated in the [Figure 14](#). The hydrogels containing the long alkyl side chain with the ionizable group, poly(AHA-co-AA) gels, show the similar shape memory effect by changing temperature or pH.

Based on the shape memory effect, gel valve has been constructed. The load was placed on the plate of the poly(SA-co-AA) gel which has a slit at the center. The gel was tough enough to support the loads at 25°C. When the gel is heated up to 40°C, the gel plate became soft and unable to hold the load any more and open the slit to drop the load. The gel plate automatically closes by the shape memory effect when all the glass beads used as a load has been dropped.

## 3. Chemical Motor

A new class of motor and generator system using order-disorder transition has been constructed, which directly changes the chemical energy into mechanical work. The driving force of the motion of the gel is originated from the surface tension of spreading organic fluid, which is pumped out of the gel due to high osmotic and hydrostatic pressures in the gel. If a poly(SA) gel swollen in THF which is in amorphous state is placed on the water surface, it transfers to ordered state from the surface and simultaneously undergoes translational and rotational motions for a long time (more than 2 hours). The process of a prolonged motion of the gel on the water surface was related to two steps: the first step is the releasing of organic solvent from the gel by osmotic pressure and hydrostatic pressure. When the gel swollen in THF is placed on water, it quickly forms a crystalline skin layer and an osmotic pressure is produced between the inside and outside of the gel. Since the formation of the crystalline surface skin layer additionally produces a large hydrostatic pressure difference, the organic solvent was ejected for a long period. The organized layer behaves as a permselective membrane which allows the organic solvent to diffuse out but does not allow the water to come in. The formation of organized structure of the gel starts from the outer surface of the gel and develops into its inner part. By virtue of this, the skin layer keeps "pumping out" the organic solvent for a prolonged period of time. Here, an important fact is that the crystalline skin layer formed at the gel-water interface can act as a "molecular orifice" through which the organic solvent in the gel flows out.

The second step is the spreading of the organic solvent on the surface of the water and imparting motion to the gel. Once the THF, which is water mixable, is ejected out of the gel, it rises up onto the water surface because of its lower density and rapidly spreads on it because of the large difference in their surface tensions. The

surface spreading of the organic solvent imparts a reaction force to the gel and makes the gel do motion.

When two gels are wrapped by an aluminum foils and two spouting holes are settled oppositely at sides of the rotor to generate the torque, the rotational motion is obtained. Using the rotational motion, a generator to produce an electric power has been constructed using the amphiphilic gel equipped with a pair of permanent magnet, solenoid coil, stator and a schale filled with water (Figure 15). When the rotor rotates clockwise on the surface of water, the magnetic flux in the solenoid coil changes to give an electromotive force. Figure 15 demonstrates a lighting of photodiode array by this amphiphilic gel generator. Numbers of photodiode to be lighted is determined by the rotation velocity of the gel-rotor. The instantaneous electromotive force reached a maximum about 15 mV if four pieces of coils is used. The instantially induced current was 83  $\mu$  A and the electric power by the electromagnetic energy was 0.2  $\mu$  W.

Since, the kinetic energy of these systems comes form the free-energy change of water-organic solvent mixing, neither noise nor exhaustion is produced. Besides, they can be used many times if the organic solvent is recovered.

The successful fabrication and operation of chemomechanical gel may produce such variety of soft machining technologies as soft-touch manipulators, targeted drug injection, osmotic pumping devices, and micro actuators.

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**Table 1**

Interaction parameters of various surfactants with polymer gel

Surfactant	Stability Constant, $K/10^3 \text{ l mol}^{-1}$	Binding constant, $K_b/10^3 \text{ l mol}^{-1}$	Cooperativity parameter, $u$
C <sub>4</sub> PyCl	0.016	0.32	0.051
C <sub>8</sub> PyCl	0.66	2.6	0.26
C <sub>10</sub> PyCl	4.5	10	0.43
C <sub>12</sub> PyCl	28	38	0.74
C <sub>16</sub> PyCl	79	56	1.4
C <sub>18</sub> PyCl	420	110	3.8

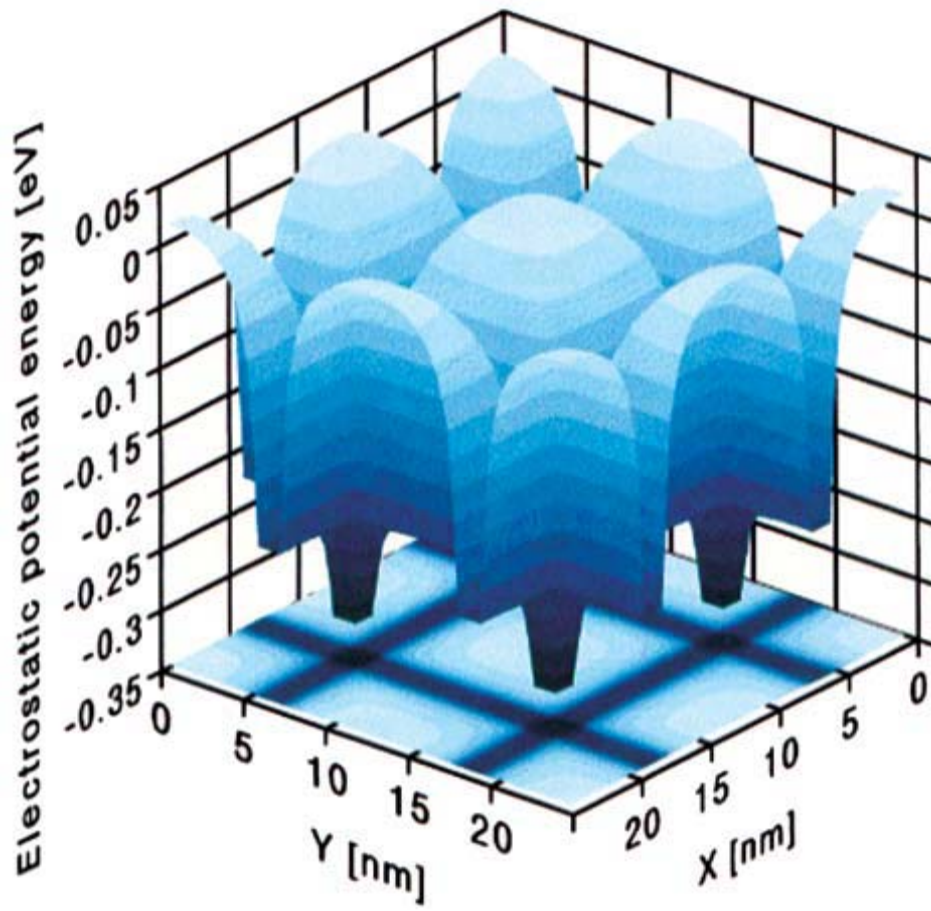


Fig. 1 Electrostatic potential energy distribution for the plane within the mesh-like network.

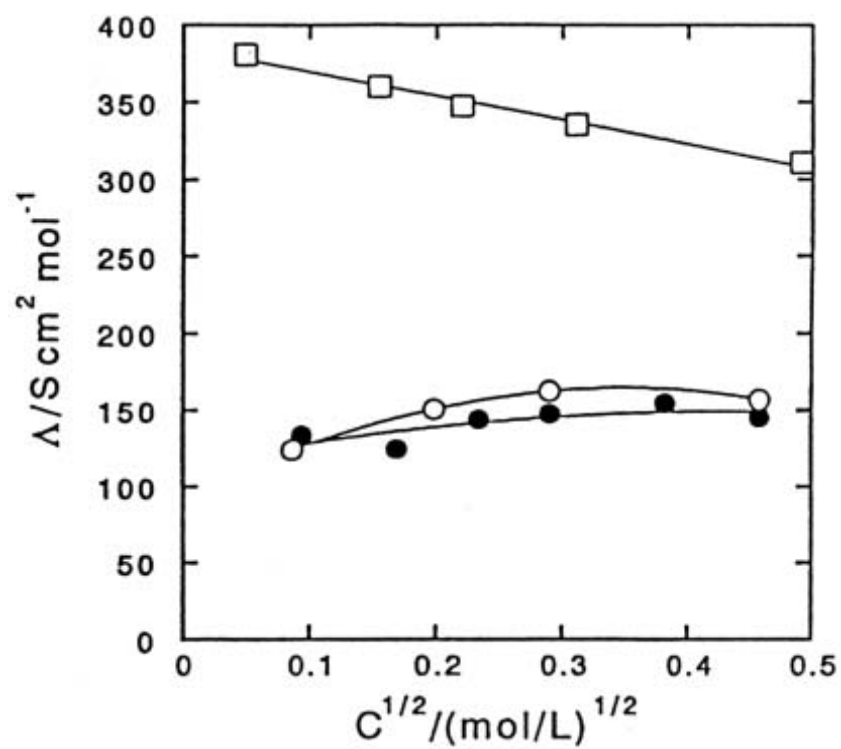


Fig. 2 Equivalent conductance of AMPS monomer solution ( $\square$ ), PAMPS linear polymer solution ( $\circ$ ), and PAMPS polymer gel ( $\bullet$ ) at various monomer concentrations.  $T \sim 25^\circ\text{C}$ .

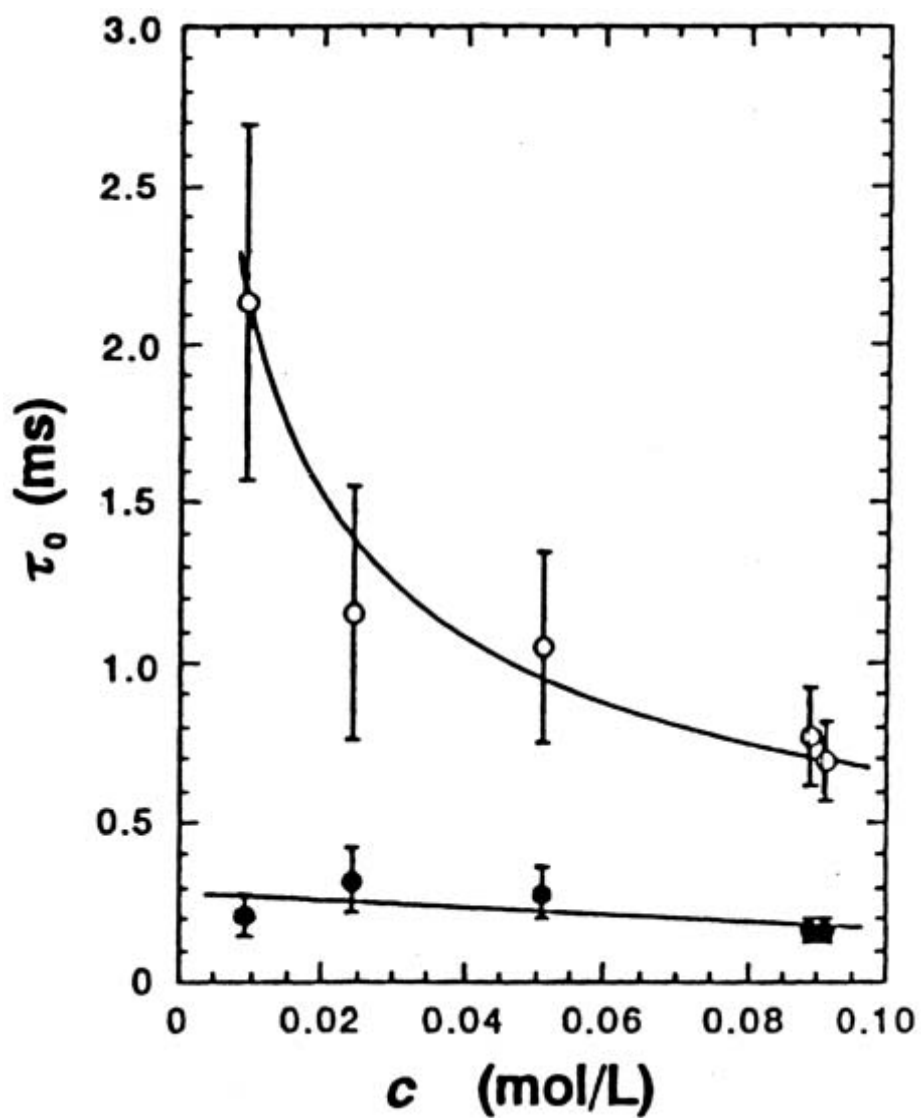


Fig. 3 Concentration dependencies of the mean relaxation time  $\tau_0$  of PNaMPS gels (○) and their corresponding linear polymer solutions (●).

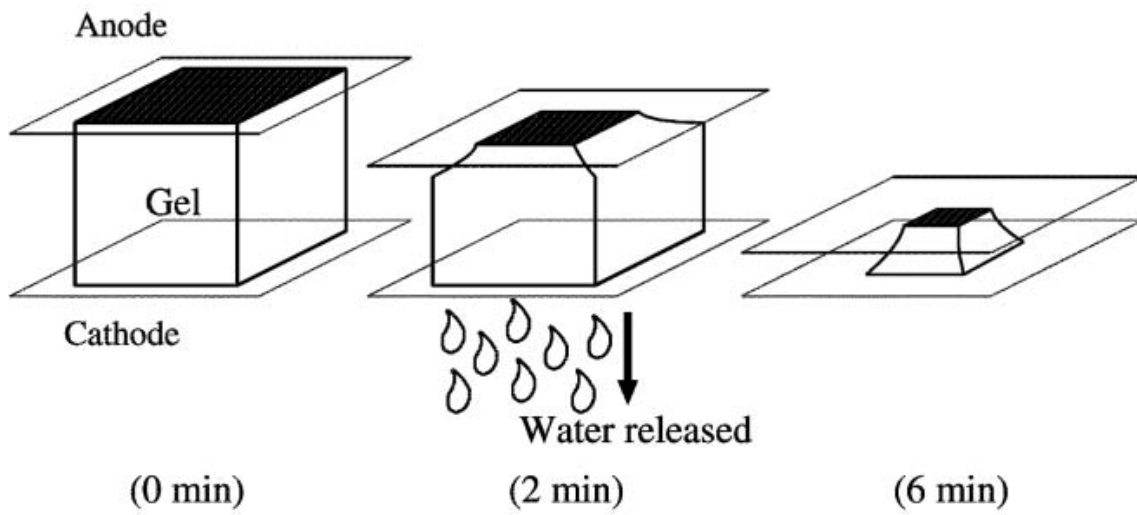


Fig. 4 Schematic view of shape change of a polyanion gel with time under the electric field.

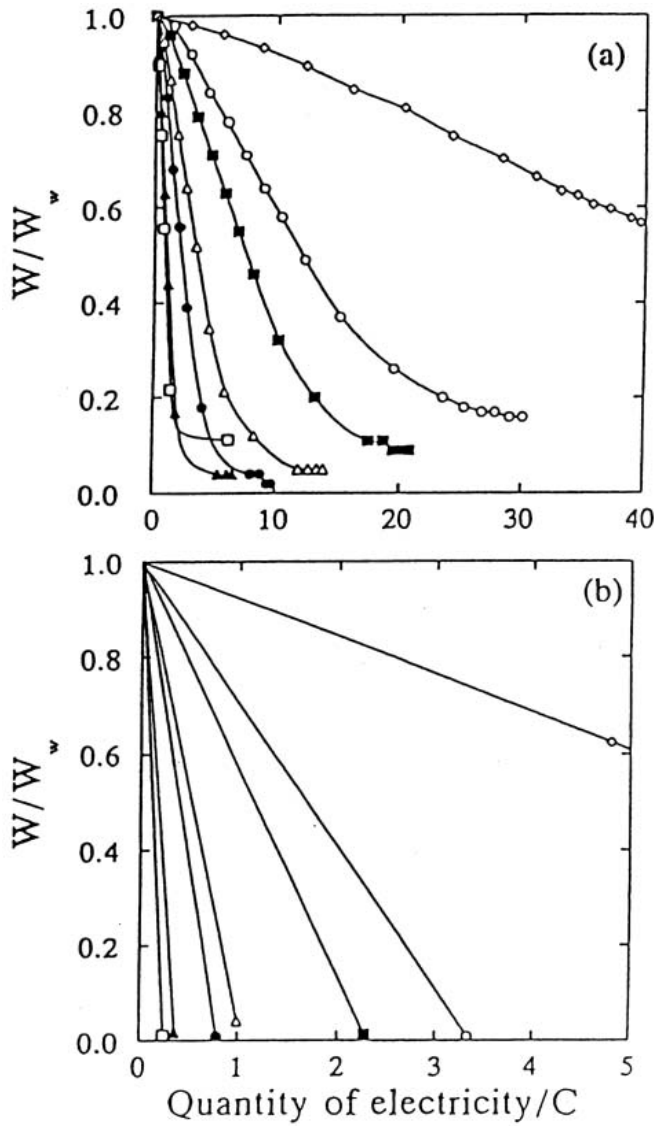


Fig. 5 Relative weight change of the PAMPS gel as a function of the quantity of electricity for gels with various degree of swelling,  $q$ . (a) Experimental observation, (b) theoretical simulation using the 1-D capillary model.  $q \sim 25$  ( $\diamond$ ),  $q \sim 70$  ( $\circ$ ),  $q \sim 100$  ( $\blacksquare$ ),  $q \sim 200$  ( $\Delta$ ),  $q \sim 256$  ( $\bullet$ ),  $q \sim 512$  ( $\blacktriangle$ ),  $q \sim 750$  ( $\square$ ).



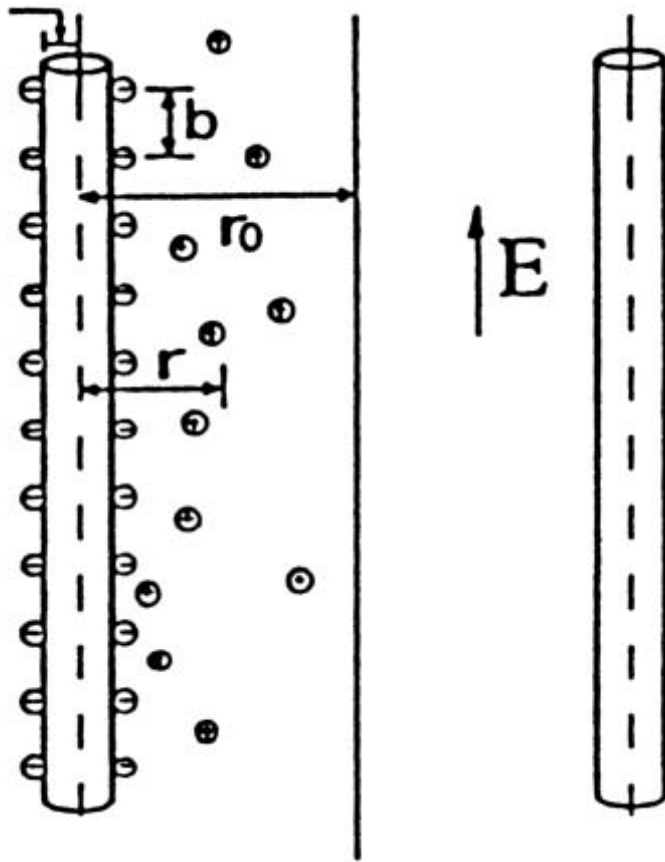


Fig. 6 Schematic model of the 1-D capillary model. As described in the text, only the macro-ions parallel to the electric field are considered.

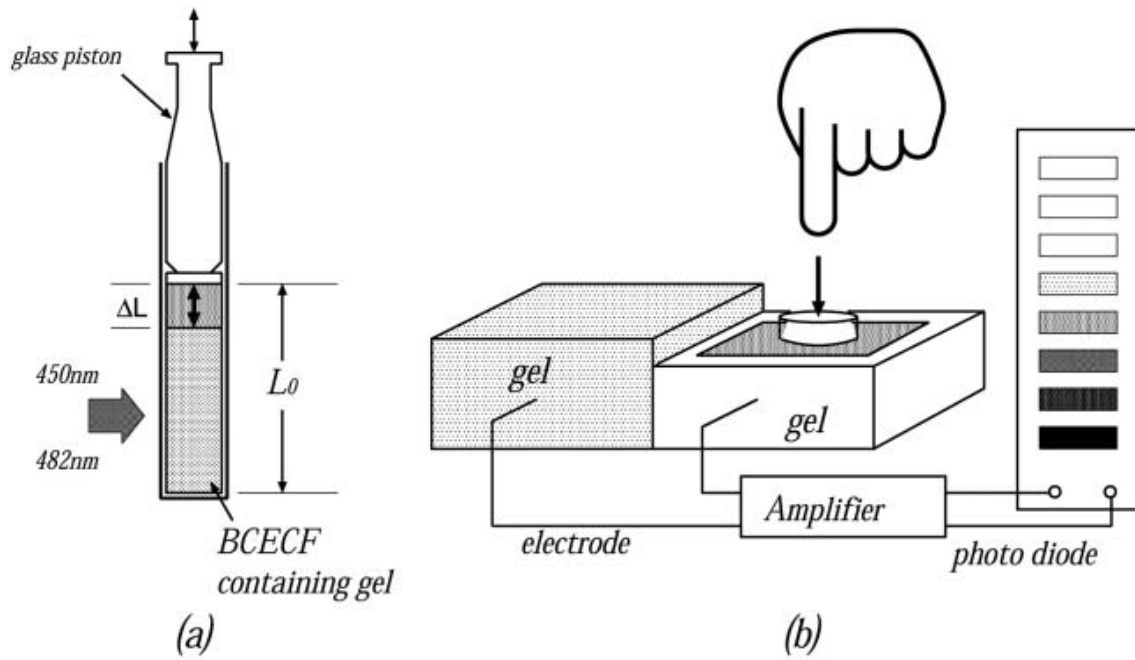


Fig. 7 Cell used to extract the electrical potential and its application as an artificial tactile sensing system capable of lighting a photodiode array under deformation.

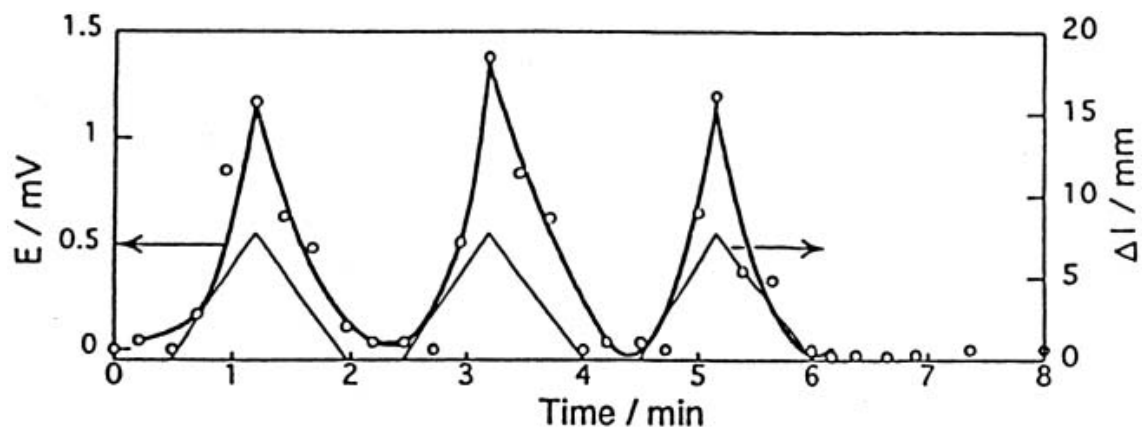


Fig. 8 Time profile of electrical potential produced at the interface of two poly(acrylic acid) gels, one of which was deformed and the other was free-standing. Size of the gel:  $15 \times 10 \times 10$  mm, degree of swelling: 16.

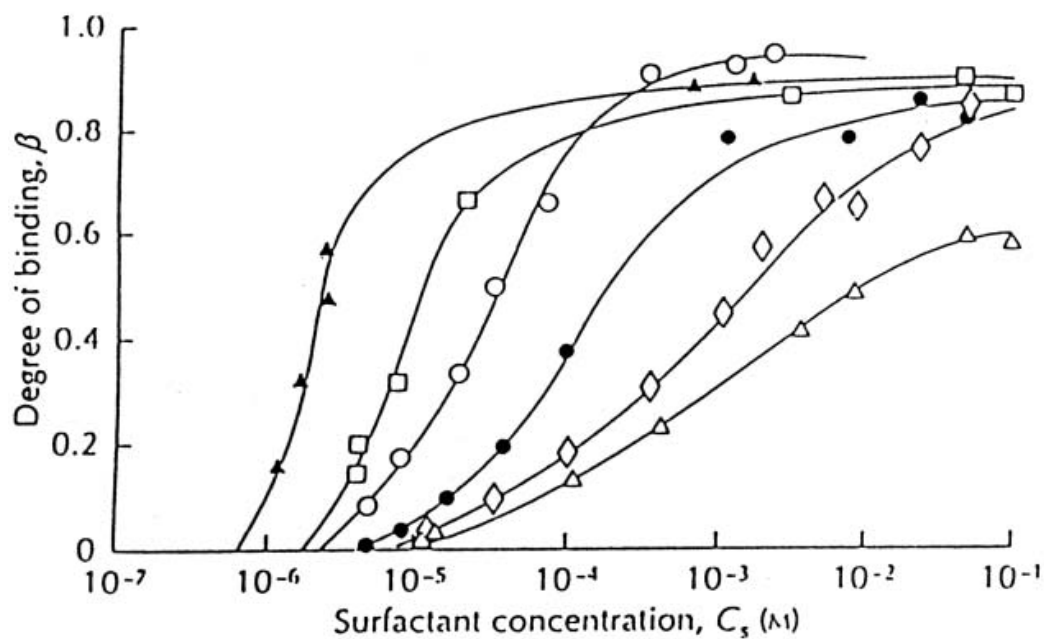


Fig. 9 Binding isotherms of surfactant molecules with the PAMPS gel in salt at 25°C. Equilibration time 30 days. The degree of binding ( $\beta$ ) is defined as the molar ratio of bound surfactant to the total sulfonate group in the gel.  $\text{Na}_2\text{SO}_4$  ( $3 \times 10^{-2}$  M).  $\Delta$ :  $\text{C}_4\text{PyCl}$ ,  $\diamond$ :  $\text{C}_8\text{PyCl}$ ,  $\bullet$ :  $\text{C}_{10}\text{PyCl}$ ,  $\circ$ :  $\text{C}_{12}\text{PyCl}$ ,  $\blacktriangle$ :  $\text{C}_{16}\text{PyCl}$ ,  $\square$ :  $\text{C}_{18}\text{PyCl}$ .

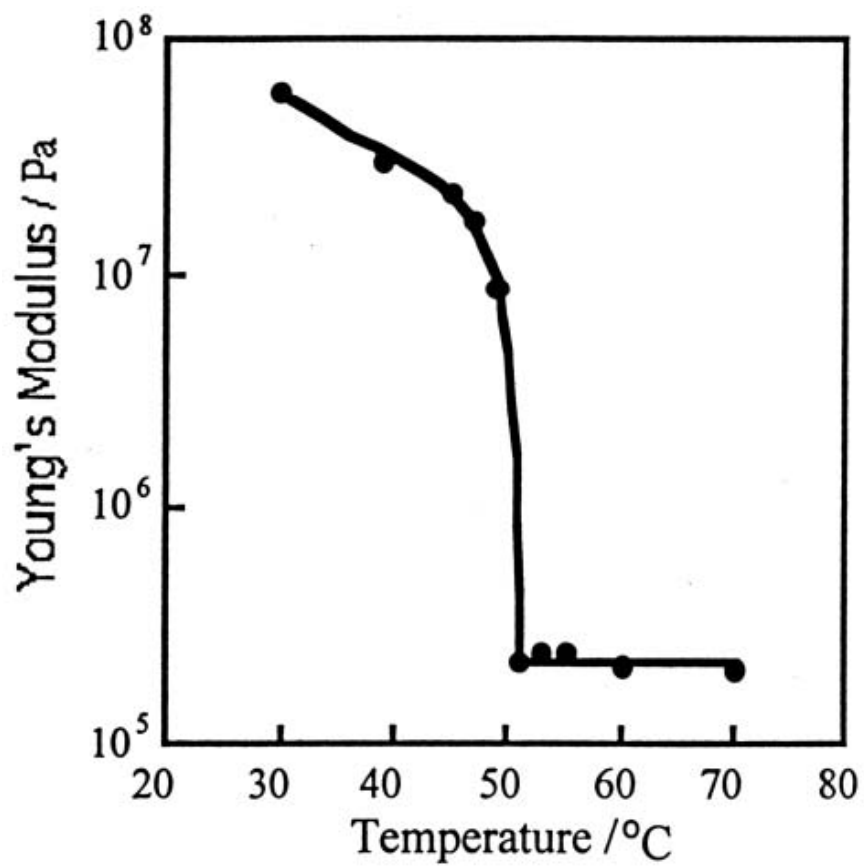


Fig. 10 Temperature dependence of Young's modulus ( $E$ ) of the poly(SA-co-AA)s gel with  $F_{SA} \sim 0.25$  (where  $F$  is the TFEA content in the gel).

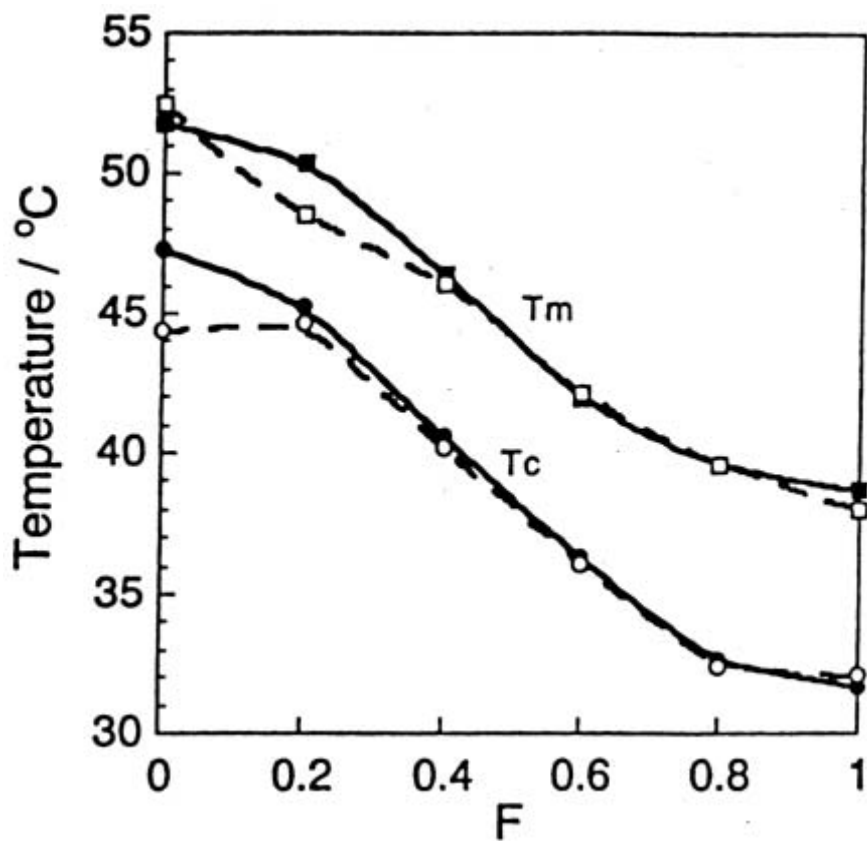


Fig. 11 Transition temperature of poly(SA-co-TFEA-co-AA) gels as a function of TFEA content,  $F$ .  $T_m$  and  $T_c$  denote the temperature of melting and crystallization, respectively. Full line, wet sample; dotted line, dry sample.  $F = [\text{TFEA}] / ([\text{TFEA}] + [\text{SA}])$ ;  $[\text{SA}] : [\text{AA}] = 1 : 3$ .

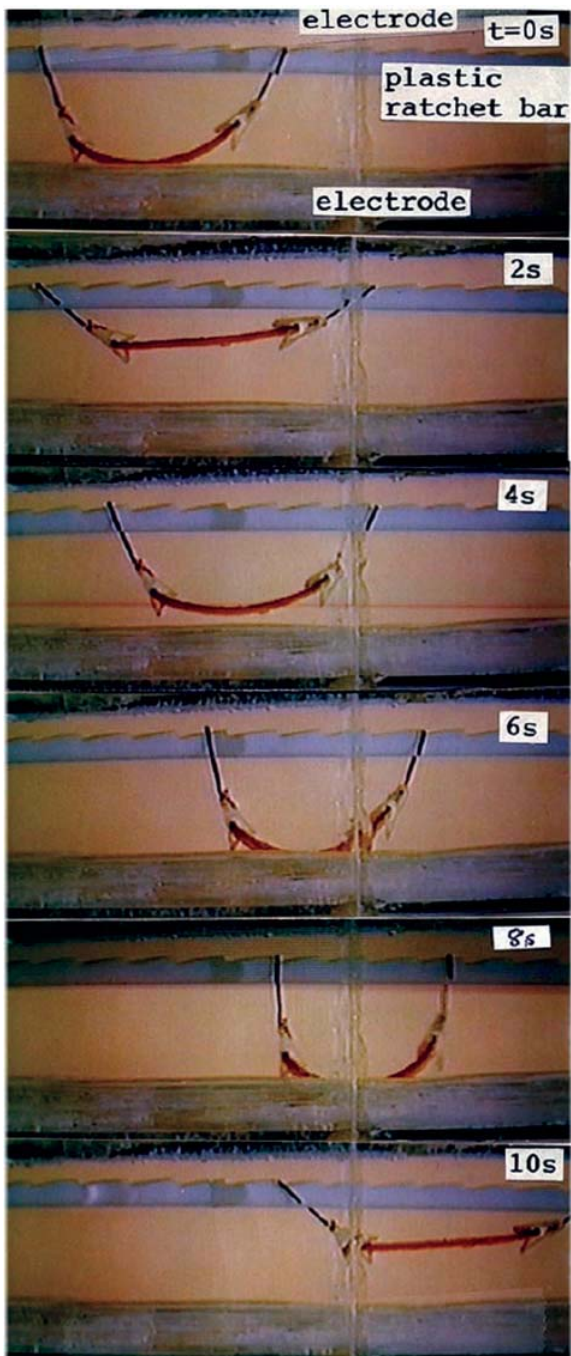


Fig. 12 An inchworm-like device that moves by repeatedly curling and straightening itself was developed by Osada.

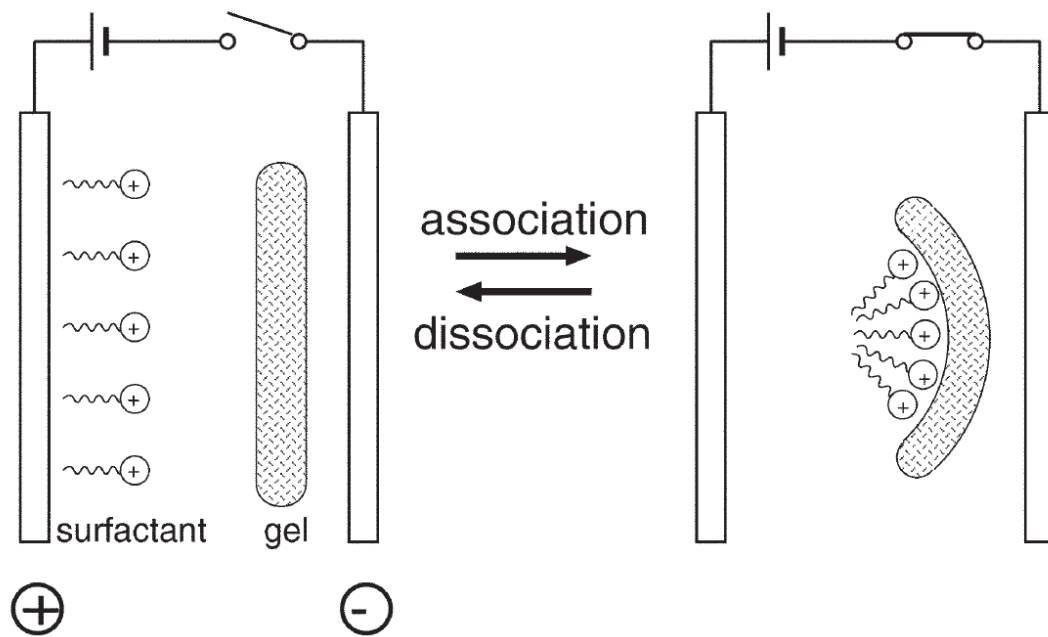


Fig. 13 Schematic illustration of a bending mechanism by anisotropic association and dissociation of surfactant molecules under an electrical field.



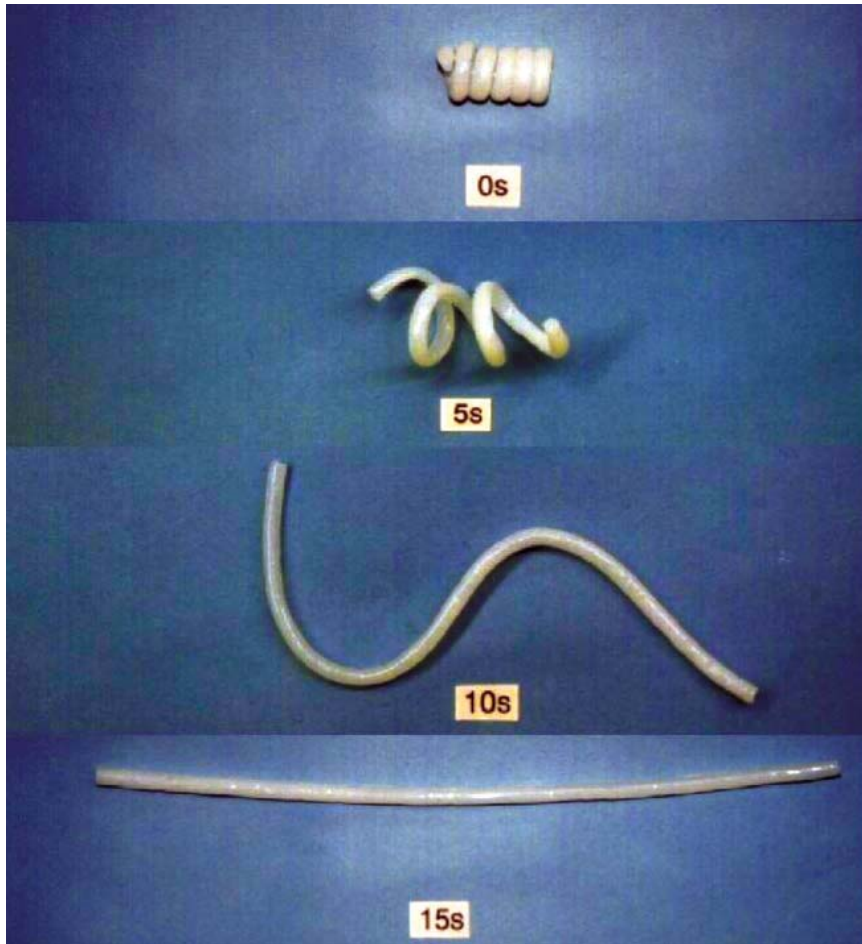


Fig. 14 Shape memory phenomena of the gel. The copolymer gel was formed in a straight glass tube of diameter 5 mm and then swollen with water (dry samples do not show the shape memory effect). The gel was then heated to 50 uC, coiled and then cooled to room temperature. The gel is rigid and retains its coiled shape (top panel). On heating again to 50 °C, the gel becomes soft and recovers its original, straight shape.

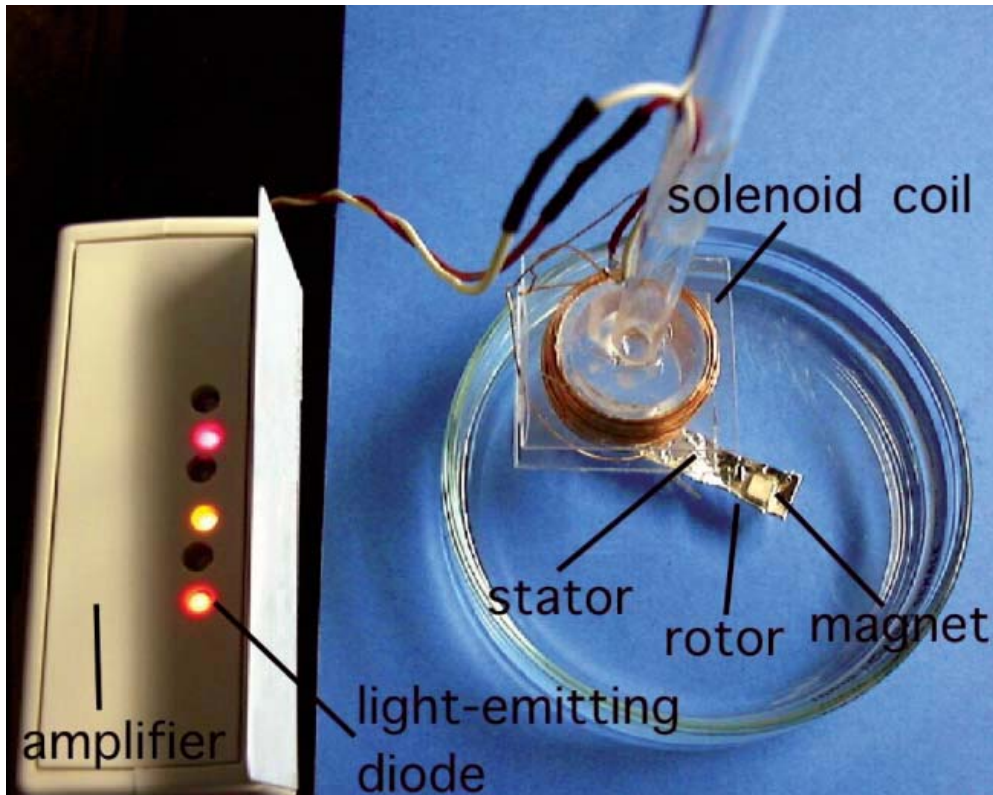


Fig. 15 Photograph of the experimental set up used to produce electric power and to light a photodiode array. The size of the rotor is 40 mm long, 6 mm wide, 2 mm thick, and the total weight of the rotor is 434 mg. The flux density of the permanent magnet is equal to 2300 Oe. The stator is made of a copper wire. The solenoid coil was wound with  $5 \times 10^3$  turns  $\text{m}^{-1}$ . (For the lighting of the photodiode, the output signal was amplified about 1500 times.)