JOURNAL OF
Materials
CHEMISTRY
Feature Article

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

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Received 1st November 2001, Accepted 11th April 2002

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I Introduction

A polymer gel consists of an elastic cross-linked network and a fluid filling the interstitial space of that 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 the water content is up to 90% (blood plasma). This enables the organism to transport ions and molecules easily and effectively while keeping its solidity. Polymer gels have attracted considerable attention in recent years.[1–10]

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 Section 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 with micro counter-ions that are localized in the network frame. A polyelectrolyte gel has the ability to swell in water and can absorb a significant amount ($\sim$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. The presence of potential wells at cross-linking points is predicted. The electrical conductance and the low frequency dielectric relaxation of the gel is measured and compared with the corresponding polymer solution; the effect of cross-linking points on counter-ion conduction is discussed.

Further, the specific electrical responses of polyelectrolyte gels are discussed. When a water-swollen polyelectrolyte gel is interposed between a pair of plate electrodes and a dc current is applied, it undergoes electrically-induced chemomechanical contraction and concomitant water exudation in the air.[11] 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 has been postulated.

Some kinds of weak polyelectrolyte gels, such as cross-linked poly(acrylic acid), show mechanoelectric properties and produce an electrical potential as large as a few millivolts.[12] Mechanical deformation is supposed to induce spontaneous ionization of carboxylic acids at a local level to produce an electrical potential.

In Section III, attempts to introduce ordered structure in the gels will be described. Two effective methods have been shown to introduce order into the structures of 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 Section III.

In Section IV, we demonstrate several applications of gels as soft and wet machines driven by chemical energy. These soft and wet machines may prove to be the basis for the development of 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 the Poisson–Boltzmann equation

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

DOI: 10.1039/b109981g

with a boundary condition of

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

where ε is the relative permittivity of the solvent, e is the charge of an elementary electron, k the Boltzmann constant, T the temperature, and ρ_0 the average counter-ion density. In eqn. (2), σ is the surface charge density of the chains and n denotes the normal derivation of potential on the surface of a polymer chain.

Gels should, in general, be considered to be composed of heterogeneous structures whose sizes range 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 identify the electrical properties caused by the cross-linkage of the ionic macromolecules, however, a periodical model has been proposed to estimate the electrostatic potential energy distribution in the polyelectrolyte gel.[13] In this model, the cross-linking points of the gel are proposed to be periodically distributed on the chain segments and the macro charges are evenly distributed on the chain. In addition, it is proposed that the polymer network is made of the periodical stacking of two-dimensional meshes, each a distance of $2r_0$ apart.

A numerical simulation of the electrostatic distribution in the polyelectrolyte gel has been carried out for a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) gel which is a fully ionized polyelectrolyte having sulfonic groups as macro-ions and H^+ as counter-ions. Fig. 1 shows the spatial profile of electrostatic potential energy in units of eV on the planes of mesh-like networks. The figure shows that potential energy wells exist at each of the 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, then

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

Hence, the 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 the counter-ions decreased very sharply with increasing distance from the polymer chain. Counter-ions located in a deep potential valley ($\gg kT$) should be strongly bound to the polyion. The amounts of these bound counter-ions increase with increasing cross-linking density.

The deep potential wells and high counter-ion densities at cross-linking points may cause instability and result in counter-ion condensation as predicted by Oosawa and Manning for linear polyelectrolyte solutions.[14,15]

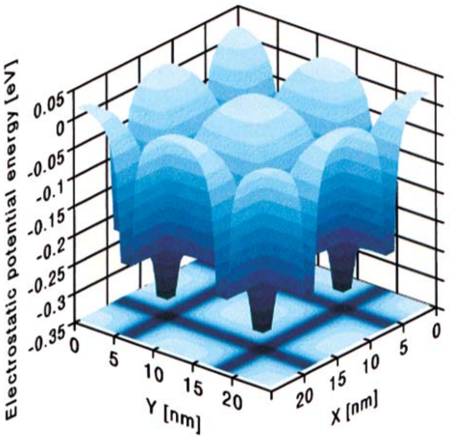

Fig. 1 Electrostatic potential energy distribution for the plane within the mesh-like network.

The presence of a deep electrostatic potential valley should strongly restrict the motion of water molecules which fill the interstitial space of the network and prevent the configuration that is favorable for crystal structure formation from being adopted. This may cause a decrease in 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 approach might over-simplify the problem. The presence of deep potential wells at cross-linking points could arise from this simplification; it would be helpful to understand the potential distribution of polyelectrolyte gels, especially in the absence of simple salts.

2. Electrical conductance of polyelectrolyte gels

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

Fig. 2 shows the equivalent (molar) conductance of the "strong" polyelectrolyte gel PAMPS at various monomer concentrations.[18] The equivalent conductance of solutions of the corresponding linear polymer (PAMPS) and monomer (AMPS) are also shown. The figure shows that the equivalent conductance of the polyelectrolyte gel approximately equals that of the corresponding linear polymer solution which showed a slight increase in the equivalent conductance with concentration. Considerable coiling of the polymer chain at such high concentrations is considered to be responsible for the decreasing fraction of counter-ions condensed on the polyions, leading to greater counter-ion mobility and higher valuesequivalent conductance.

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

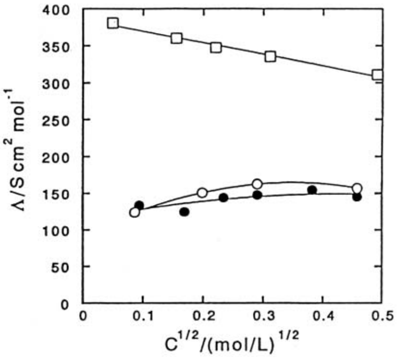

Fig. 2 Equivalent conductance of AMPS monomer solution (□), PAMPS linear polymer solution (○), and PAMPS polymer gel (●) at various monomer concentrations. $T = 25$ °C.

decreases in counter-ion mobility and the equivalent conductance of gels.

According to the condensation theory,[14,15,19] 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 counter-ions are considered to be bound to the macro-ions 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 the fact 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 dielectric relaxation spectra provide information about ions which move under an alternating electric field. Dielectric relaxation spectroscopy of polyelectrolyte solutions shows two kinds of relaxation processes: high-frequency relaxation in the MHz frequency range and low-frequency relaxation in the radiowave frequency range. The high frequency relaxation is due to the fluctuation of free counter-ions that exist at a distance from macro-ions.[20–23] The low-frequency relaxation arises because of the fluctuation of bound counter-ions that exist in the vicinity of macro-ions.[20,21,24]

Low-frequency relaxation should also be observed in polyelectrolyte gels, as in the polyelectrolyte solutions. Moreover, we can speculate that the polyelectrolyte gel shows a slower relaxation process than the linear polymer solution because of the strong network–counter-ion interaction, although there was no difference between the behaviour of the loosely bound counter-ions in the networked gels and in the linear polymer solutions, as elucidated from the electrical conductance results.

Fig. 3 shows the concentration dependencies of the mean relaxation time, τ_0, of the sodium salt of poly(2-acrylamido-2-methylpropanesulfonic acid) (PNaAMPS) gels and their corresponding linear polymer solutions. The relaxation time of gels decreases with increasing concentration, while for linear polymer solutions the relaxation time is almost independent of the concentration. According to the literature,[20,21] the observed low-frequency relaxation of the linear polymer solution is associated with the fluctuation of tightly bound counter-ions along the polymer chain. This low frequency relaxation strongly depends on the molecular weight but is almost independent of the concentration.[25]

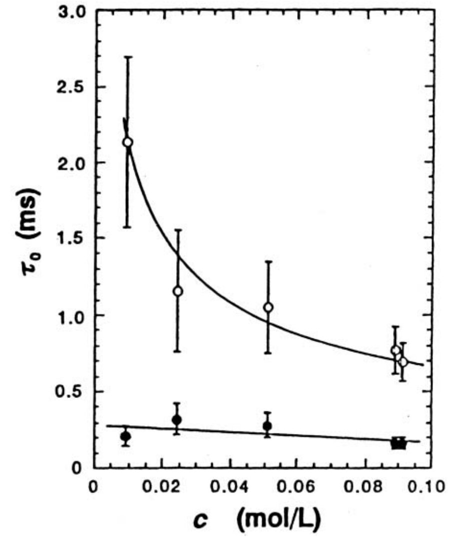

Fig. 3 Concentration dependencies of the mean relaxation time τ_0 of PNaMPS gels (○) and their corresponding linear polymer solutions (●).

Assuming a square type potential well along the polymer chain, τ_0, of the linear polymer solution is given by[26]

$$\tau_0 = \frac{L_f^2}{D} = \frac{L_c^2}{12D} \tag{4}$$

where L_f and D are the fluctuation length and the diffusion constant of the bound counter-ion, respectively, and L_c is the contour length of the macro-ion. With a degree of polymerization N of 3100 and a monomer unit length b of 2.55 Å, one obtains L_c and L_f values of 801 nm and 231 nm, respectively, from eqn. (4). The mean diffusion constant, D_m, was determined to be 2.1×10^{-10} m^2 s^{-1}, which is an order of magnitude smaller than the diffusion constant D_0 ($= 1.22 \times 10^{-9}$ m^2 s^{-1}) of Na$^+$ ions in water. This result is in good agreement with the data for sodium salts of poly(styrene sulfonate) (PNaPSS) solutions reported by Ookubo *et al.*[27]

The observed relaxation of gels is considered to correspond to the fluctuation of counter-ions along the polymer network by crossing through the cross-linking points. Thus, the observed relaxation time comprises of 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 related to the electrostatic potential well at the cross-linking points. Following from this explanation, the diffusion constant at the cross-linking point for the counter-ions is found to be 3 orders lower in magnitude than it is along the polymer chain. This might be proof of the presence of deep potential wells at cross-linking points. It has also been found that the bound counter-ions can fluctuate 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 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 dc voltage is applied, it undergoes anisotropic contraction and concomitant fluid (water) exudation.[11,27] Fig. 4 shows the schematic view of the shape change of an anionic gel with time in an electric field.[28] There are several features of the contraction.

1) Contraction occurs only for polyelectrolyte gels and not for uncharged hydrogels.

2) An anionic gel slightly swells near the cathode and

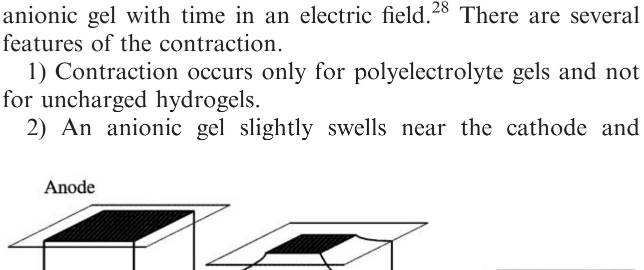

Fig. 4 Schematic view of shape change of a polyanion gel with time under the electric field.

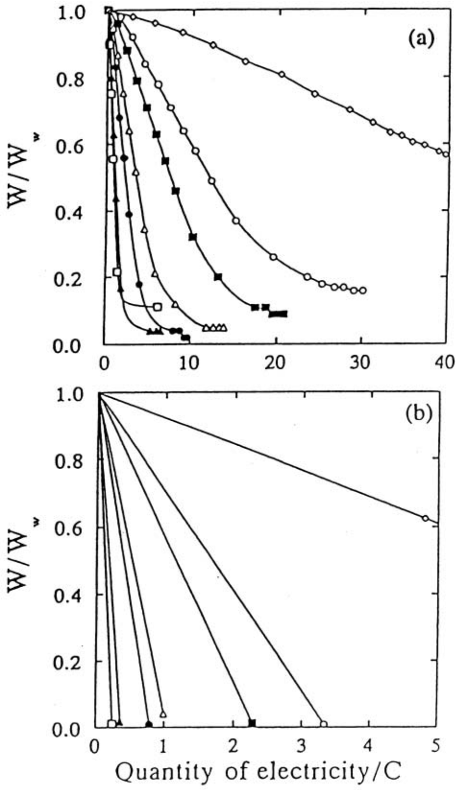

Fig. 5 Relative weight change of the PAMPS gel as a function of the quantity of electricity for gels with various degree of swelling, q. (a) Experimental observation, (b) theoretical simulation using the 1-D capillary model. $q = 25$ (◇), $q = 70$ (○), $q = 100$ (■), $q = 200$ (△), $q = 256$ (●), $q = 512$ (▲), $q = 750$ (□).

extensively contracts near the anode, the reverse occurs for a 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.

Fig. 5(a) shows the electricity quantity dependence of the relative weight change of PAMPS gels with various degrees of swelling under a dc electric field. The PAMPS gel is a strong acid polymer with fully ionized sulfonic groups as macro ions and H^+ as counter-ions. When an electric field is applied, hydrated H^+ ions (more exactly H_3O^+) migrate towards the cathode and are reduced, liberating H_2. The hydrated H^+ ions migrate and leave the gel near the cathode. The overall electrode reactions are expressed as follows:

$$\text{Anode} \quad H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2$$

$$\text{Cathode} \quad 2H^+ + 2e^- \rightarrow H_2$$

The oxygen and hydrogen liberated can be observed throughout the course of the contraction. It has been verified that the amount of gas released is consistent with the theoretical value derived by Faraday's law according to the above equations. The total population of ions should not significantly change during the contraction, because at every moment, H^+ generation and consumption should be balanced at both electrodes.

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

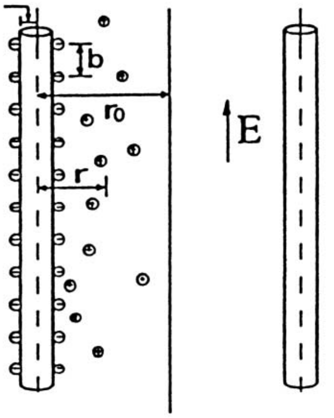

Fig. 6 Schematic model of the 1-D capillary model. As described in the text, only the macro-ions parallel to the electric field are considered.

A one-dimensional capillary model has been proposed to quantitatively analyse the electro-contractile behaviour of the gel (Fig. 6).[29] In this model, only the macro-ions located along the chains parallel to the applied electric field 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 in the polymer network under an electric field is simplified to a problem of transportation along the rod-like polymer chain, which is analogous to that of liquid flow through a capillary under the influence of an electric field. A numerical simulation of contraction has been made for PAMPS gels, and Fig. 5(b) shows the theoretical electricity quantity dependence of the relative weight change of PAMPS gels (W/W_W) at various degrees of swelling q. Comparing with Fig. 5(a), both figures show that W/W_W is proportional to the amount of charge transported through the gel and the rate of contraction increases with an increase in the degree of swelling.

Here it should be noted that the values derived by simulation are somehow several times larger than those obtained from the experimental data. One reason for this may be attributed to the simplification of the problem to a 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 the counter flow of water might also overestimate the migration ability of water and lead to a large contraction rate. However, the model satisfactorily illustrates the characteristics of the contraction phenomenon and demonstrates that the contraction of a gel under an electric field occurs due to an electrokinetic mechanism.

5. Mechanoelectrical effects of polyelectrolyte gels

In the previous section, we described a polyelectrolyte gel that can contract or deform under electrical stimulus, that is, a gel that can convert electrical energy into mechanical work. The reverse process has also been observed in gels.[12] It has been found that mechanical deformation can cause electro-mechanical deformation of a weak polyelectrolyte gel producing an electrical potential as large as a few millivolts. This property of gels is similar to that of soft tissue in mechanically induced biological systems such as the touch-sensing system of human fingers. It has been proven that stress generates potentials in human skin, which are then transmitted to the central nervous system for further processing.[30,31] Hence, like human skin, a gel is able to convert mechanical energy into electrical energy, thus behaving like a soft and wet piezoelectric material.

When an 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 an increase in the electrostatic potential on the macromolecules. On the basis of swelling and contraction of a weak polyelectrolyte gel, Katchalsky and Kuhnand and their co-workers[32–34] proposed a so called ''muscle'' model which is referred to as a ''mechanochemical'' or later as a ''chemomechanical'' system.[1,35]

The reverse process, *i.e.*, a 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 in a vertical direction using a glass piston (Fig. 7(a)), the pH of the gel changes as shown in Fig. 8. When the gel was unloaded, the pH quickly returned to the original pH value with some overshooting.

Since there was no water outlet during deformation, the pH change may be associated with enhanced ionization of the carboxy groups under the deformation: being compressed in one direction, the gel is subjected to lateral expansion and induces one-dimensional dilatation of the polymer network in this direction. This causes an increase in the 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 make use of the change in electrical potential originating 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 the reference, the other as the working electrode, were inserted into the cell 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; an electrical potential difference was observed during this period.

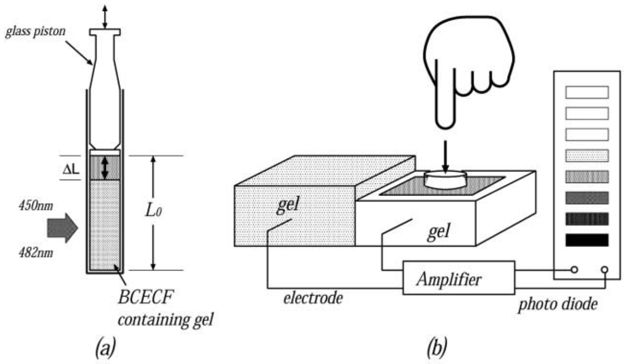

Fig. 7 Cell used to extract the electrical potential and its application as an artificial tactile sensing system capable of lighting a photodiode array under deformation.

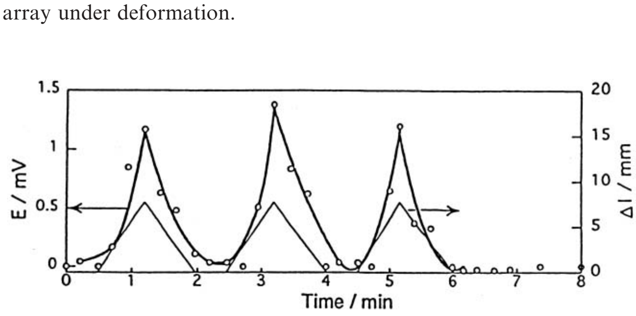

Fig. 8 Time profile of electrical potential produced at the interface of two poly(acrylic acid) gels, one of which was deformed and the other was free-standing. Size of the gel: 15 × 10 × 10 mm, degree of swelling: 16.

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

It should be emphasized that the mechanoelectrical system made of a polymer gel has similarities with tactile perceptions in living organisms. Both of them are dynamic processes in which the macroscopic deformation induces an ionic rearrangement which gives rise to *trans*-membrane potentials. Gels also share common features with natural tissues: softness, wetness, elasticity and some other rheologically specified characteristics.

Because of these similarities, soft mechanoelectrical systems constructed from polymer gels may open new possibilities for investigating artificial tissue-like tactile perception in 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 complexes of polyelectrolyte gels and oppositely charged surfactants with long alkyl tails or planar components have been made. Complexes of polyelectrolytes[36,37] with surfactants form 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, *e.g.* cetyltrimethylammonium bromide, is a layered structure. This layered structure[38] and its function have also been investigated for many other complexes .[39–43] The complexes of polycation gels with anionic phthalocyanine formed hexagonal columnar structures.[44]

Complex formation between a polyelectrolyte gel and an oppositely charged surfactant molecules arises due to electrostatic and hydrophobic interactions. Significant contraction of the gel is observed only above a certain critical concentration of the surfactant, which indicates that surfactant–gel complex formation has a cooperative nature associated with the hydrophobic interaction between surfactant molecules.

We have systematically studied the structures of complexes of PAMPS gels and alkylpyridinium chloride (C_nPyCl) and the thermodynamics of complex formation. If the degree of binding, β (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 Fig. 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:

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

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

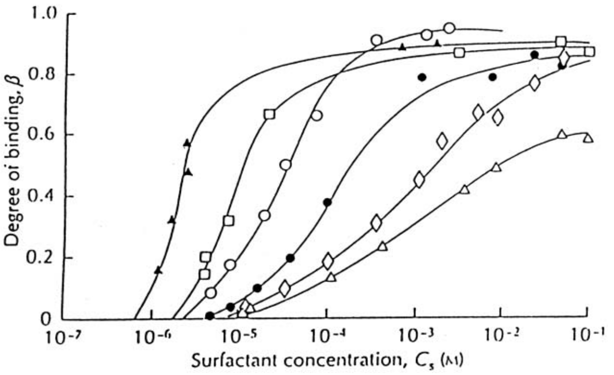

Fig. 9 Binding isotherms of surfactant molecules with the PAMPS gel in salt at 25 °C. Equilibration time 30 days. The degree of binding (β) is defined as the molar ratio of bound surfactant to the total sulfonate group in the gel. Na_2SO_4 (3×10^{-2} M). △: C_4PyCl, ◇: C_8PyCl, ●: C_{10}PyCl, ○: C_{12}PyCl, ▲: C_{16}PyCl, □: C_{18}PyCl.

Table 1 Interaction parameters of various surfactants with polymer gel

Surfactant	Stability Constant, $K/10^{-3}$ l mol^{-1}	Binding constant, $K_0/10^{-3}$l mol^{-1}	Cooperativity parameter, u
C_4PyCl	0.016	0.32	0.051
C_8PyCl	0.66	2.6	0.26
C_{10}PyCl	4.5	10	0.43
C_{12}PyCl	28	38	0.74
C_{16}PyCl	79	56	1.4
C_{18}PyCl	420	110	3.8

On the basis of the Zimm–Bragg theory for a helix–coil transition, Satake and Yang[45] derived the following expression for the cooperative binding:

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

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 interactions 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 constants, binding constants and cooperativity parameters for the complexation for surfactant molecules of various alkyl chain lengths. It is seen that the stability constants, K, of the surfactant molecules increase significantly with increasing alkyl chain length, and the value of C_{16}PyCl is about 5000 times larger than C_4PyCl and more than four times larger than C_{12}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 electrostatic salt formation, but the alkyl chains lead to 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 formulae derived on the basis of the free energy minimum principle predicted that cross-linking 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.[46]

2. Hydrogels with crystalline ordering

A water-swollen polymer hydrogel with a 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).[47,48] These gels undergo reversible order–disorder transitions with changes in temperature, pH and solvent.

The effect of cross-linkage 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 when the degree of crosslinking = 3.0 mol%, while d_1 (short-range ordering) spacing was destroyed only when the degree of crosslinking = 10 mol%. These facts suggest that an increasing degree of crosslinking, similar to the effect of water, destroys first the long-range organization, then the short-range organization of the structure.[49]

WAXD and SAXD results showed that poly(SA-*co*-AA) gels have crystalline structures 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 endothermic and exothermic peaks at 48 and 42 °C upon heating and cooling, respectively, which was confirmed to correspond to the reversible order–disorder transition in agreement 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.

The temperature dependence of Young's modulus, E, of the poly (SA-*co*-AA) gel is shown in Fig. 10. E decreases gradually with increasing temperature from 30 to 47 °C and then decreases sharply from 1.7×10^7 to 2.2×10^5 Pa above 49 °C. The temperature at which E decreases sharply coincides with the order–disorder transition temperature of the gel obtained by DSC measurement. The gel showed a typical jelly-like softness above this temperature. The drastic change observed in the mechanical property is reversible.

Fluorinated water-swollen hydrogels with molecular and supramolecular organization have also been synthesized.[50] Moderately water-swollen hydrogels were prepared by copolymerizing SA, 2,2,2-trifuoroethyl acrylate (TFEA), and acrylic acid (AA), and the effects of water and TFEA on the molecular and supramolecular structure were investigated. Incorporation of TFEA brought about a decrease in d_2 spacing presumably

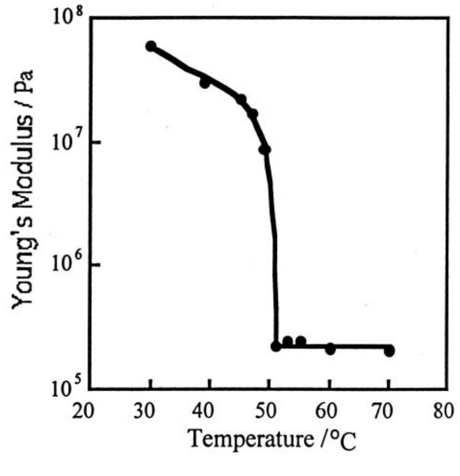

Fig. 10 Temperature dependence of Young's modulus (E) of the poly(SA-*co*-AA)s gel with $F_{SA} = 0.25$ (where F is the TFEA content in the gel).

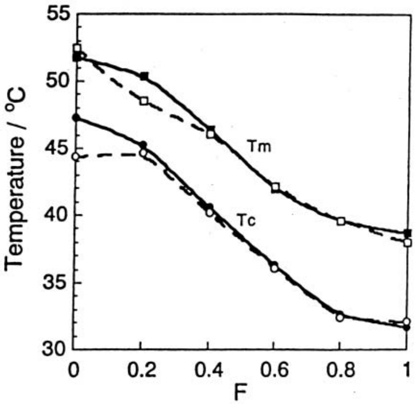

Fig. 11 Transition temperature of poly(SA-*co*-TFEA-*co*-AA) gels as a function of TFEA content, F. T_m and T_c denote the temperature of melting and crystallization, respectively. Full line, wet sample; dotted line, dry sample. F = [TFEA]/([TFEA] + [SA]); [SA] : [AA] = 1 : 3.

due to small areas being rendered 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 Fig. 11, the transition temperature at which Young's modulus changes sharply decreased with increasing 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 polymer gels 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, a chemomechanical gel driven by an outside stimulus is able to exhibit a 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 and immersed in a dilute solution of *N*-(*n*-Dodecyl)pyridinium chloride (C_{12}PyCl) containing 3 × 10^{-2} mol l^{-1} sodium sulfate. When 20 V dc (1.0 V cm^{-1}) 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' (inch worm) by repeated bending and stretching.[51,52] Fig. 12 shows time profiles of 'gelooper' walking with a constant velocity of 25 cm min^{-1} in water at 20 V dc

The principle of motility of this gel-looper is associated with reversible and cooperative complexation of surfactant molecules on the polymer gel under an electric field to cause shrinkage of the gel. The electric field drives and controls the direction of this equilibrium to give anisotropic complex formation. When the dc 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 (Fig. 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 to 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.

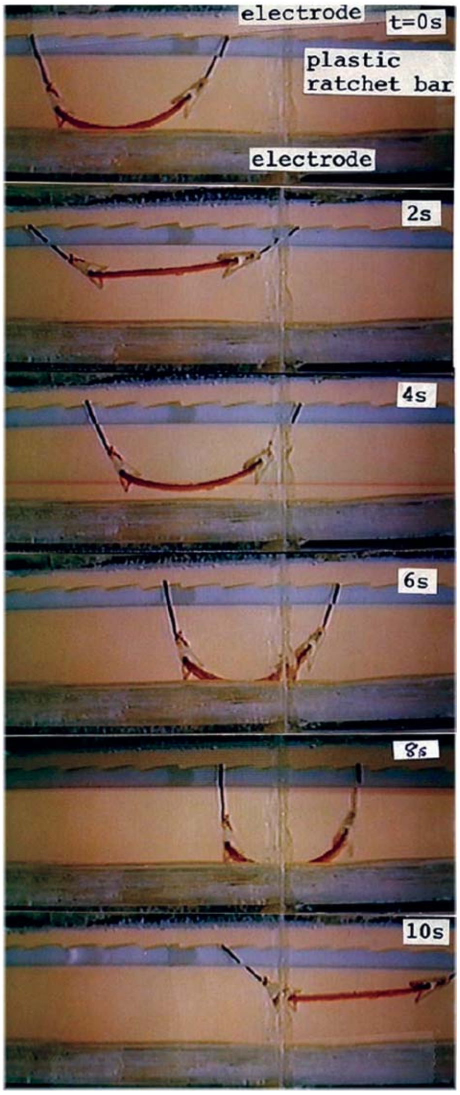

Fig. 12 An inchworm-like device that moves by repeatedly curling and straightening itself was developed by Osada.

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

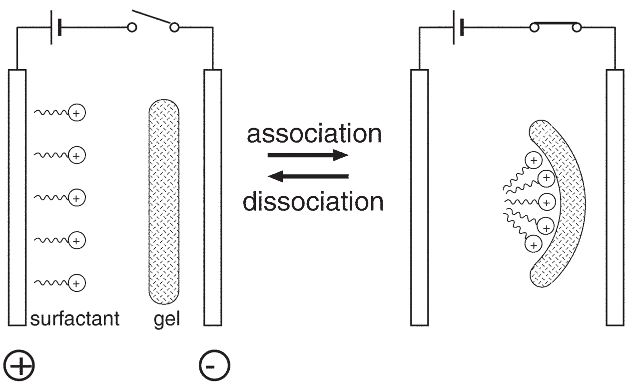

Fig. 13 Schematic illustration of a bending mechanism by anisotropic association and dissociation of surfactant molecules under an electrical field.

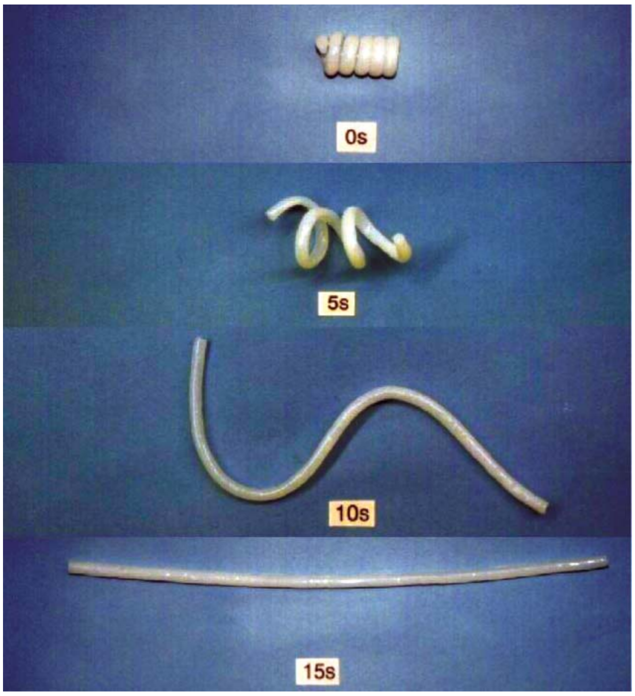

Fig. 14 Shape memory phenomena of the gel. The copolymer gel was formed in a straight glass tube of diameter 5 mm and then swollen with water (dry samples do not show the shape memory effect). The gel was then heated to 50 °C, coiled and then cooled to room temperature. The gel is rigid and retains its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

alloy, produced by a reversible martensitic structural transformation.[53] The mechanism used in 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 a reversible order–disorder transition, which allowed one to expect 'shape memory' behavior. If the gel is heated above the transition temperature (50 °C) in its 'soft' state, it can be readily deformed to a new shape. As long as the gel is kept cool 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 temperature, it spontaneously recovers its original size and shape in a few seconds. This behavior is illustrated in Fig. 14. Hydrogels containing a long alkyl side chain with an ionizable group, *e.g.* poly(AHA-*co*-AA) gels, show a similar shape memory effect on changing temperature or pH.

Based on the shape memory effect, a gel valve has been constructed. A load was placed on the plate of a 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 was unable to hold the load any more and the slit opened to drop the load. The gel plate automatically closes by the shape memory effect when all the glass beads used as a load have been dropped.

3. Chemical motor

A new class of motor and generator system using the order–disorder transition has been constructed, which directly changes chemical energy into mechanical work. The driving force of the motion of a gel originates from the surface tension of the 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 with THF, which is in an amorphous state, is placed on the surface of water, it transfers to the ordered state from the surface and simultaneously undergoes translational and rotational motions for a long time (more than 2 hours). The prolonged motion of the gel on the water surface can be explained by two facts: the first step involves the release of organic solvent from the gel by osmotic pressure and hydrostatic pressure. When the gel swollen with THF is placed in 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 also 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 the organized structure in the gel starts from the outer surface of the gel and works inwards. Because of this, the skin layer keeps ''pumping out'' 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 reason is the spreading of the organic solvent on the surface of the water causing the gel to move. Once the THF, which is water miscible, is ejected from the gel, it rises to the water surface because of its lower density and rapidly spreads on it because of the large difference in their surface tensions. The spreading of the organic solvent at the surface imparts a reaction force on the gel causing the gel to move.

When two gels are wrapped in aluminum foil and two spouts are created on opposite sides of the rotor to generate a torque, rotational motion is obtained. Using the rotational motion, a generator has been constructed to produce electric power using an amphiphilic gel equipped with a pair of permanent magnets, solenoid coil, stator and a schale filled with water (Fig. 15). When the rotor rotates clockwise on the surface of the water, the magnetic flux in the solenoid coil changes to give an electromotive force. Fig. 15 shows the lighting of a photodiode array using this amphiphilic gel generator. The number of photodiodes that can be lighted is determined by the rotation velocity of the gel-rotor. The instantaneous electromotive force reached a maximum of about 15 mV if four pieces of coil were used. The instantaneously induced current was 83 μA and the electric power produced from the electromagnetic energy was 0.2 μW.

Since, the kinetic energy of these systems comes form the free-energy change of water–organic solvent mixing, neither

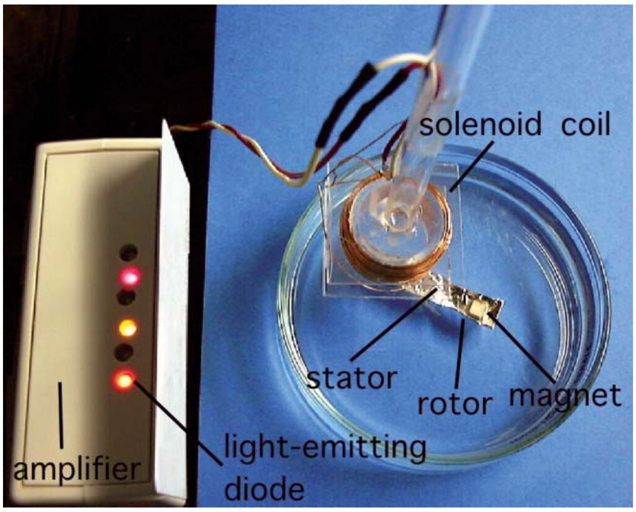

Fig. 15 Photograph of the experimental set up used to produce electric power and to light a photodiode array. The size of the rotor is 40 mm long, 6 mm wide, 2 mm thick, and the total weight of the rotor is 434 mg. The flux density of the permanent magnet is equal to 2300 Oe. The stator is made of a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

noise nor exhaustion is produced. Also, they can be used many times if the organic solvent is recovered.

The successful fabrication and operation of chemomechanical gels may lead to a variety of soft machine technologies, such as soft-touch manipulators, targeted drug injection, osmotic pumping devices, and micro-actuators.

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