Soft and Wet Materials: Polymer Gels

By Yoshihito Osada* and Jian-Ping Gong

A polymer gel is a soft and wet material capable of undergoing large deformation. A deformed gel, in turn, changes its chemical potential, behaving as an energy transducer. Thus, a polymer gel shows a variety of stimuli-responsive actions, responding to external environmental changes. In this article unique electrical, thermal, and chemical responses of polymer gels are described. Recently observed frictional specificities of gels are also briefly introduced.

1. Introduction

A polymer gel consists of an elastic crosslinked network and a fluid filling the interstitial spaces 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 to most industrial materials such as metals, 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. This enables the organism to transport ions and molecules more easily and effectively while keeping its solidity.

Polymer gels can be easily deformed by external stimuli, and generate force or execute work on the external environment. If such responses can be translated from the microscopic level to a macroscopic scale, a conversion of chemical free energy into mechanical work should be realized. As early as 1948, Kuhn,[1] Breitenbach,[2] and Katchalsky[3] independently found that water-swollen polymer gels can convert chemical energy directly into mechanical work under isothermal conditions. The principle of reversible contraction and dilatation is based on the reversible ionization of suitable groups, for example, carboxylic acid groups, of a polyacid by alternating addition of alkali and acid, whereby the former produces an electrostatic repulsion of ions along the macromolecular chain and causes an expansion of the coiled polymer. Katchalsky denoted these transformations "mechanochemical reactions" or "mechanochemical systems".

The ability of polymer gels to undergo substantial swelling and collapsing as a function of their environment is one of the most remarkable properties of these materials. The phenomenon of gel volume transitions, which can be induced by temperature, pH, or ionic strength, has prompted researchers to investigate gels as potential actuators, sensors, controllable membranes for separations, and modulators for delivery of drugs.[4–9] Since studies on the fundamental process of the gel volume transition as well as on its application have been extensively reported we are not going to give a comprehensive review of this subject in this paper. This review is concerned with some examples of gels which significantly reflect their unique character.

2. Electrical Responses

2.1. Electrostatic Potential Distribution

Many polymer gels possess charges in their network. The polyelectrolyte gel can swell in water and absorbs a significant fraction (~2000 times the polymer weight) of water within its structure, but will not dissolve in water. Different from the linear polyelectrolyte solution, the polyelectrolyte gel exhibits a variety of unique properties, such as phase transition,[10] specific adsorption equilibrium,[11] the presence of unfrozen water,[12] and chemomechanical behavior.[13] The unique properties and behavior observed in the gel should be well characterized by the nature of the charged network together with its counterions.

Gels should, in general, be considered to be composed of heterogeneous structures of 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. In order to catch the electrical feature due to the crosslinkage of the ionic macromolecules, a two-dimensional lattice stacking model has been used to estimate the electrostatic potential energy distribution using the Poisson–Boltzmann equation.[14] According to this model, deep potential wells exist at crosslinking points and potential valleys near the polymer chains (Fig. 1). Counterions are mostly localized around the network knots as well as the polymer chains, due to the deep potential there. The charge density of counterions decreases very sharply with an increase in the distance from the polymer chain. Counterions located in the deep potential valley should be strongly bound to the polyion.

The mechanism of electrical conduction in a gel is essentially the same as that found in a linear polymer solution,[15,16] that is, the transport of loosely bound counterions plays the predominant role in electrical conduction.[17]

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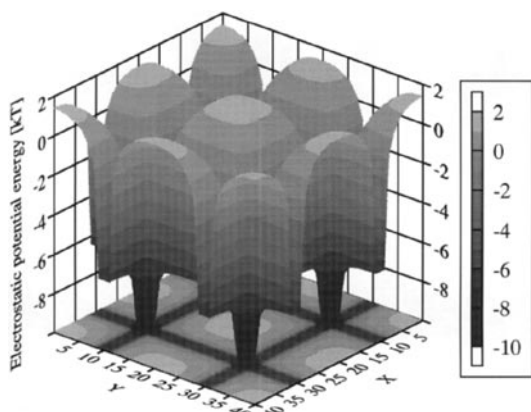Graduate School of Science, Hokkaido University
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Fig. 1. Spatial profile of the electrostatic potential energy in a polyelectrolyte gel. (From [14].)

2.2. Electrical Oscillation

Metal/polymer gel/metal structures, made of a water-swollen polymer gel sandwiched between two platinum wire electrodes, have the property of being able to switch on and off reversibly between two stable states, one characterized by high impedance, corresponding to the "off" state, and the other by low impedance, corresponding to the "on" state.[18–20]

Figure 2a shows a repetitive curve and its power spectrum when a DC voltage (7 V) was applied to a calcium alginate gel. The power spectrum of this oscillation shows a main peak at a frequency of 0.013 Hz with higher harmon-

ics. The magnitude of the main peak was about 9.80 % of that total energy within a range of 0.5 Hz. The maximum amplitude of current oscillation was about 0.22 mA.

Figure 2b–d shows the effects of an external sinusoidal voltage upon the current oscillation and the power spectrum when AC voltages of frequency 0.005–0.03 Hz and amplitude 2 V were superimposed afterwards onto the oscillation induced by DC voltage (5 V). The figure demonstrates that the entrainment of oscillation occurs in the gel when an AC current of a certain frequency is imposed, and the phenomenon is observed repeatedly for various polymer gels.

Repetitive oscillation also occurs in electroconductive gels swollen with organic solvents.[21] The nature of the oscillation is associated with the degree of crosslinking, the doping ratio of doped molecules, and temperature; an increase of these parameters enhances both the amplitude and frequency of the oscillation.

It is considered that the oscillation of a polyelectrolyte gel under an electric field is associated with the transfer process of micro- and macroions accompanying the synchronized dynamic segmentational motion of the charged network in the solvent. Thus, the appearance of periodical current oscillation seems to be an instinct of the cross-linked polymer network. The elucidation of the oscillation mechanism at the molecular level is at present difficult since the systems are multivariable with a nonlinear kinetic relation and complicated coupling mechanism and many more experiments are required to confirm these ideas conclusively.

Yoshihito Osada obtained his Bachelor's degree in applied chemistry from Waseda University, Japan, in 1966, and received his Ph.D. in polymer science from Moscow State University in 1970 under the supervision of Prof. V. A. Kabanov. He held the position of associate professor and later professor at Ibaraki University, Japan, from 1971 to 1991. From 1976 to 1978 he was a visiting scholar at the University of California at Berkeley, carrying out research on plasma polymerization. He joined the Department of Polymer Science at Hokkaido University as professor in 1992. His main research interests are chemomechanical systems from polymer gels (artificial muscles, artificial tactile sensors, etc.) and other functionalized gels.

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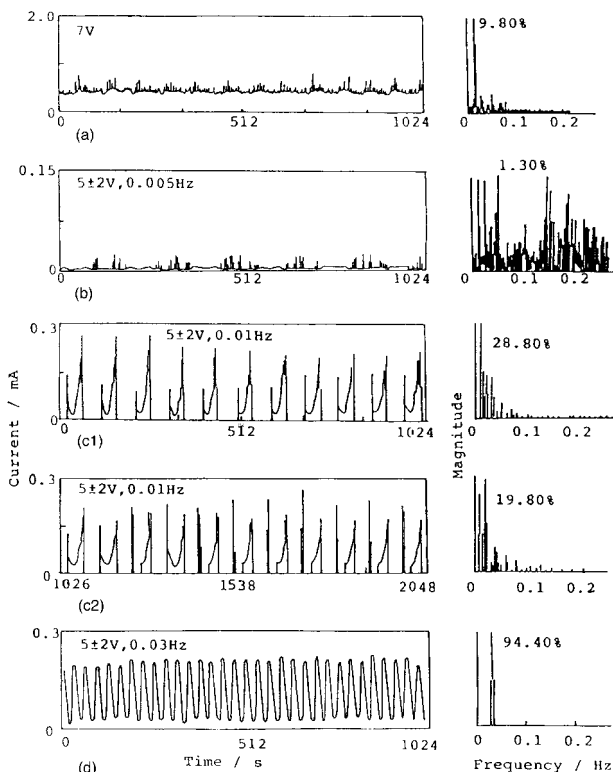
Fig. 2. The effects of the frequency of the external sinusoidal voltage on the current oscillation. Gel: calcium alginate, 24 mm in diameter, 11 mm long; degree of swelling: 40; electrode distance: 10 mm. a) DC: 7 V. b) DC 5 V; AC: 0.005 Hz, 2 V. c1,c2) DC: 5 V; AC: 0.01 Hz, 2 V. d) DC: 5 V; AC: 0.003 Hz, 2 V. Figures denoted in the power spectra indicate percent magnitude of the main peak of total energy generated within a range from 0 to 0.5 Hz. (From [20].)

2.3. Electrical Contraction

If the water-swollen crosslinked polyelectrolyte gel is inserted between a pair of planar electrodes and a DC voltage is applied, it undergoes anisotropic contraction and concomitant fluid (water) extrusion.[22,23] Figure 3 shows the shape change of an anionic gel with time under the electric field.

The electrically induced contraction of the gel is caused by the transport of hydrated ions and water in the network, and the contractile behavior observed is essentially an electrochemical phenomenon. When an external electric field is applied across the gel, the macro- and microions receive electrical forces in the opposite direction. However, the macroions are stationary since they are chemically fixed to the polymer network, while the counterions are mobile, capable of migrating along the electric field and dragging water molecules with them.

A capillary model has been proposed to describe the contraction process.[24] According to this theoretical analysis, the contraction efficiency is inversely proportional to the charge density of the network and increases with an increase of the degree of swelling. The theoretical analysis also predicts that the speed of gel contraction is dependent only on the amount of charge being transported through
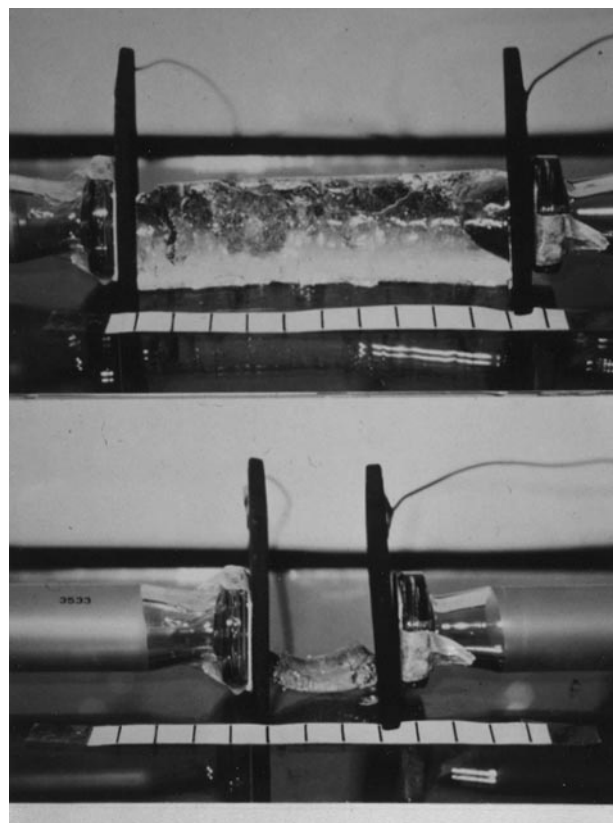

Fig. 3. Photographs of a poly(2-acrylamido-2-methyl-1-propanesulfonic acid) gel before (upper) and after (lower) imposing an electric field of 15 V for 10 h.

the gel, i.e., on the quantity of electricity, and is independent of the electric field. These predictions are in agreement with the experimental observations and demonstrate that the electrically induced contraction of the gel is dominated by electrokinetic processes of hydrated ions and water in the polymer gels.

2.4. The Mechanoelectric Effect

In the previous section, we described that a polyelectrolyte gel can contract or deform under an electrical stimulus, that is, a gel can convert the electrical energy into mechanical work. The reverse process can also been observed in gels.[25] This means that mechanical deformation can produce electrical potential.

When a piece of weak polyelectrolyte gel is pressed, the pH of the gel changes reversibly. The pH change is associated with an enhanced ionization of the carboxyl groups under deformation: being compressed in one direction, the gel expands 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, which should be compensated for by a simultaneous increase in its degree of ionization.

In order to extract the change in electrical potential originating from the pH change of the gel, a cell comprising

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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 (Fig. 4a). 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 is observed during this period. Figure 4b shows the potential difference thus obtained.

On the basis 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 (Fig. 4a). 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.
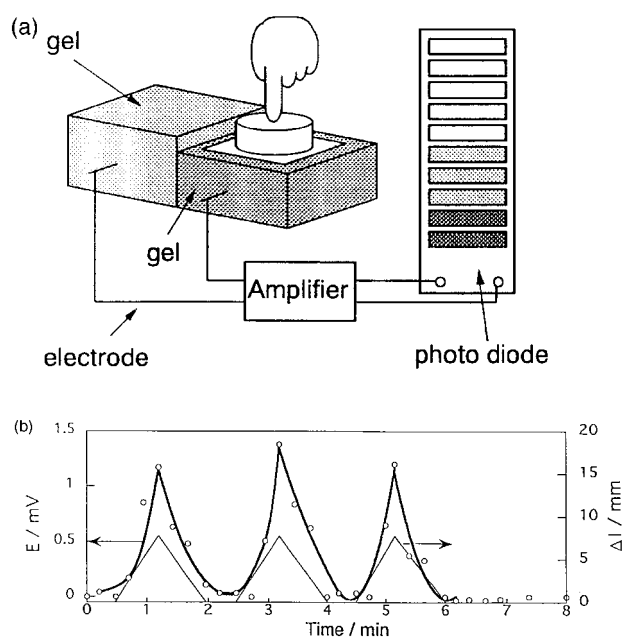

Fig. 4. a) Cell used to extract the electric potential and its application as an artificial tactile sensing system capable of lighting a photodiode array under the deformation. b) Time profile of electrical potential produced at the interface of two poly(acrylic acid) gels, one of which was deformed while the other was free-standing. Upper trace: electrical potential; lower trace: deformation length. Size of the gel: 15 mm × 10 mm × 10 mm; degree of swelling: 16. (From [25].)

An attempt was also made to repeat the lifting of a load by applying an electric field. It was found that the rate of contraction as well as the efficiency of the work increases with increasing load to a maximum value. This anomalous lifting behavior of the gels can be explained in terms of a spontaneous ionization of the ionizable groups, leading to an increased current when the gel is stretched (mechano-electric effect).[26]

We would like to emphasize that a mechanoelectrical system made of polymer gel has similarities with tactile perception in living organisms.[27,28] Both of them are dynamic processes in which the macroscopic deformation induces the ionic rearrangement that gives rise to a certain amount of transmembrane potential. 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 mechanoelectrical system constructed from a polymer gel may open new possibilities in the investigation of artificial tissue-like tactile perception for prosthetics and robotics.

3. Molecular Assembly on the Polymer Gel

3.1. Interaction with Oppositely Charged Surfactants

Since the polyelectrolyte gel has deep electrostatic potential valleys along the polymer chains and wells at the crosslinked points, it will attract oppositely charged surfactants and form complexes. Surfactant binding to solvated and crosslinked polyelectrolytes having charges on the side chains as well as chain backbones has been extensively studied using various kinds of oppositely charged surfactants. It has been proposed that there are three categories of surfactant binding:[29] 1) cooperative and stoichiometric,[11,30] 2) non-cooperative and stoichiometric,[31] and 3) cooperative and non-stoichiometric.[32,33] The modes of these categories are predominantly determined by the 3D chemical structure of the surfactant, hydrophobicity, and the charge density of the polyelectrolyte.

For example, n-alkylpyridinium chloride (C_nPyCl, $n = 4$, 6, 8, 10, 12, 16, 18) stoichiometrically binds to the solubilized and crosslinked polyanion, poly[2-(acrylamido)-2-methylpropanesulfonic acid] (PAMPS). The binding is cooperative through the side-by-side hydrophobic packing of n-alkyl groups. Figure 5 shows the binding isotherms for C_nPyCl–PAMPS gel complex formation. The steep increase in binding at a critical surfactant concentration clearly demonstrates the cooperative binding. It is also seen that an increase in the alkyl chain length of the surfactant lowers the concentration at which the binding starts, indicating that the hydrophobic interaction favors the binding equilibrium and stabilizes the complex. With the binding of surfac-
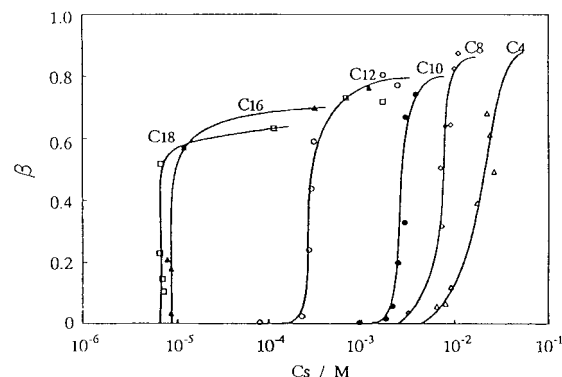

Fig. 5. Binding isotherms of surfactant molecules with the PAMPS gel in salt at 25 °C. Equilibration time 30 days. The degree of binding (β) is defined as the molar ratio of bound surfactant to total number of sulfonate groups in the gel. Na_2SO_4 (3×10^{-2} M). △: C_4PyCl, ◇: C_8PyCl, ●: $C_{10}PyCl$, ○: $C_{12}PyCl$, ▲: $C_{16}PyCl$, □: $C_{18}PyCl$. (From [30].)

tant, the gel loses its electrostatic energy, leading to a contraction in its volume. A supramolecular structure is formed in the surfactant-bound gel.[11,13]

In contrast, tetraphenylphosphonium chloride (TPPC), which has bulky, strongly hydrophobic groups, binds to PAMPS gel stoichiometrically but is not able to undergo cooperative binding to form an ordered structure in spite of its strong hydrophobicity. This indicates that the arrangement of the binding molecules to form a long sequence by the cooperative process is important to produce an organized structure.[31]

Examples of cooperative and non-stoichiometric binding involve the binding of C_nPyCl to amphiphilic polymers, such as *x,y*-ionene ($x = 6,12$; $y = 4, 6, 12$) bromide polymers, copolymers of acrylate, and those containing bulky hydrophobic groups exhibiting a lower critical solution temperature (LCST). They undergo non-stoichiometric two-step binding to give soluble complexes.[32,33]

3.2. Chemomechanical Gels

As described in the previous section, positively charged surfactant molecules bind to anionic polymer gels through electrostatic interactions and bring about contraction of the gel.[11,34,35] Using this phenomenon, an electrically driven artificial "worm-like muscle" and a swinging pendulum made of water-swollen synthetic polymer gel possessing motility in water have been reported.[13,35]

Here, we introduce a newly designed moving system in which the PAMPS gel show eel-like motion in the surfactant solution under an electric field.[36] The moving system was made using a styrofoam and pieces of PAMPS gel membrane. The body was made of styrofoam (20 mm long, 2 mm wide, 2 mm thick), which can be used at the same time as buoyancy. A pair of plastic sheets (15 mm wide, 10 mm long) were attached to one end of the PAMPS gel (25 mm long, 5 mm wide, 0.4 mm thick) and inserted to the styrofoam body. A pair of parallel carbon electrodes (150 mm long, 15 mm wide, 2 mm thick) were placed with a separation distance of 90 mm in the surfactant solution and 10 V was applied. The eel moved forward slowly (ca. 15 cm/min) by repeated undulation of the PAMPS tail (Fig. 6a). Different from the movement made by a rigid machine, the gel exhibited an eel-like undulating motion and had a propelling force of the order of 10^{-4} N.
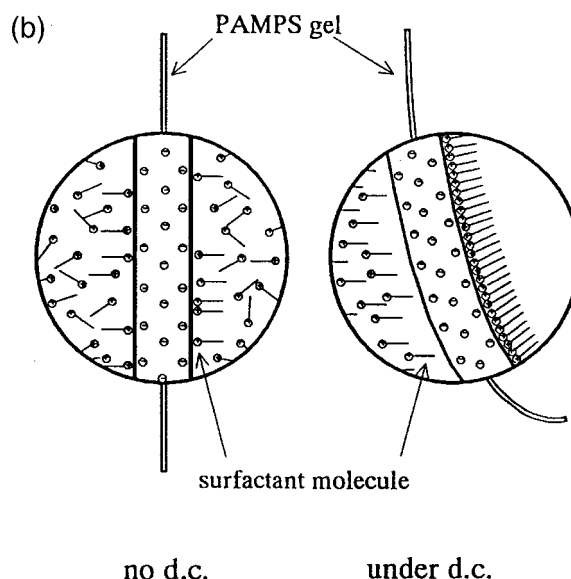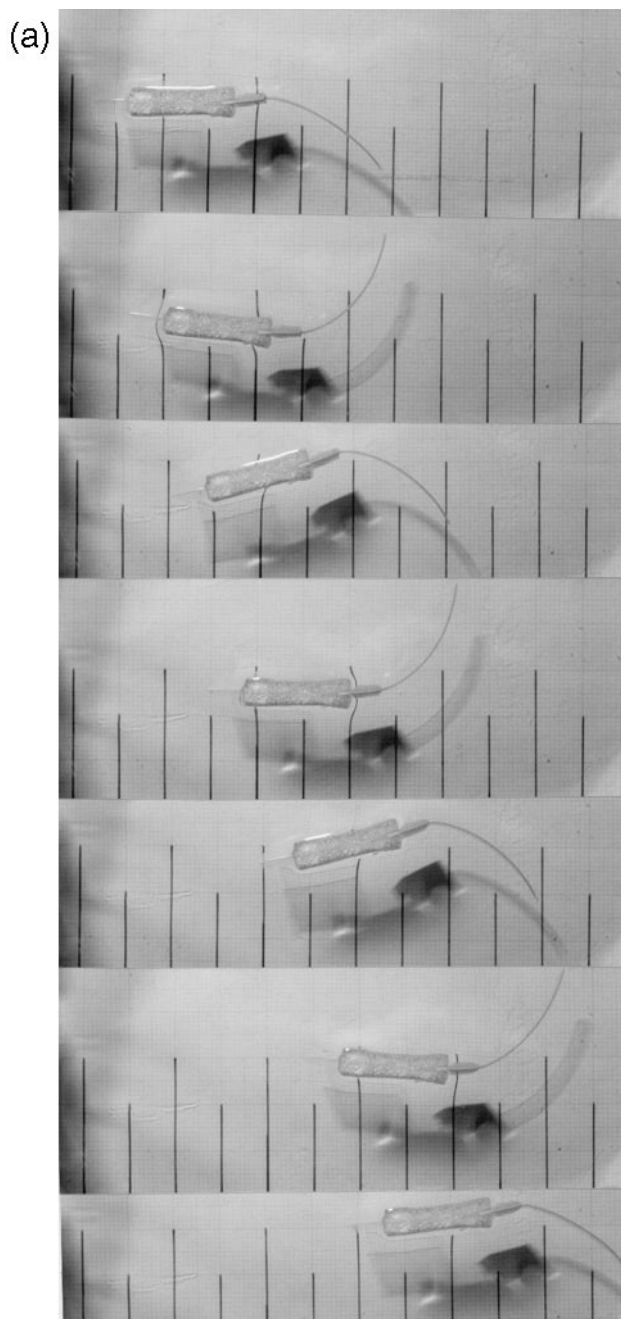

Fig. 6. a) Progressive change in motion of the gel eel under a voltage of 10 V. Electrode distance: 70 mm, 0.25 Hz; photographs were taken every 4 s. b) The moving mechanism of the PAMPS gel. The left picture shows the gel free from the electric field and the right picture under a voltage of 10 V with the anode facing the right side of the gel.

The principle of this eel-like swinging of the gel is associated with a reversible and cooperative complexation of the surfactant molecules on the surface of the polymer gel under the electric field; the mechanism is shown schematically in Figure 6b. The electric field drives and controls the direction of the complexation equilibrium to give anisotropic complex formation. When DC voltage is turned on, the positively charged surfactant molecules move electrophoretically 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 an anisotropic contraction and induces bending towards the anode. When the polarity of the electric field is reversed, the surfactant molecules absorbed on one side of the gel are released out of the gel and travel toward the cathode. Instead, new surfactant molecules form complexes on the opposite side of the gel and the gel bends to the other side. The periodical change in the electric field makes the gel repeatedly swing. The movement of the gel is produced by a free energy change in the assembly reaction of the surfactant with the polymer network.

4. Polymer Gels with Molecularly Organized Structures

4.1. Shape Memory Behavior

Water-swollen hydrogels are generally amorphous in nature and have no particular ordered structure at the molecular level, except for some biological gels where more highly ordered aggregates are observed in the "junction zones". This might be one of the reasons why synthetic polymer gels suffer from a lack of mechanical toughness and slow response to stimulus.

It was recently demonstrated that water-swollen polymer hydrogels with a molecularly ordered structure can be obtained by copolymerizing hydrophilic monomers such as acrylic acid (AA) with hydrophobic monomers that form crystals, for example, stearyl acrylate (SA) and acryloylhexadecanoic acid (AHA).[37,38] These gels undergo a reversible order–disorder transition with a change in temperature, pH, and solvent properties.

Investigation of the swelling process and the order–disorder transition of poly(AHA-*co*-AA) gel indicates that swelling of the network occurs first by disordering of the layer structure and then by the elimination of side chain crystallization (Fig. 7). Changes in the degree of swelling are produced either by changes of pH or by the addition of ethanol to the aqueous gel.

Poly(SA-*co*-AA) exhibits shape memory behavior with temperature (Fig. 8).[39] The principle of this phenomenon is based on a reversible order–disorder transition associated with the hydrophobic interactions between stearyl groups in water. Below the transition temperature (50 °C), stearyl side chains form crystalline aggregates and behave as a hard plastic, while above this temperature they transform to the amorphous state and the material abruptly becomes soft and flexible and is readily modified to a desired new shape. If the gel is cooled keeping its deformed shape, it becomes rigid and retains its new shape even after removing the load. When the modified gel is once again heated above the transition temperature, it is able to recover the original shape after a few seconds.

The shape memory effect can be observed only for the water-swollen hydrogel and not for the dry sample. This is because the AA units are substantially hydrated in water, and behave like a soft elastomer with a very low glass temperature. Under this condition the SA units are responsible for the mechanical toughness and render the material robust. In contrast, when the gel is dry, the AA units behave as a hard plastic even above the transition temperature and show no abrupt change in mechanical property by heating.

4.2. Spontaneous Motion on Water

It was discovered that crosslinked hydrophobic–hydrophilic copolymer gels swollen in organic solvent undergo spontaneous motion when put on water (Fig. 9).[40,41] The mode of motion largely depends on the shape of the gel: a disc-shaped gel exhibits translational motion while a triangular or a square-shaped one exhibits rotation. The velocity and duration of gel motion are strongly associated with the size and chemical structure of the gel. A gel weighing 0.1 g can stay in motion for more than 60 min. It was found that
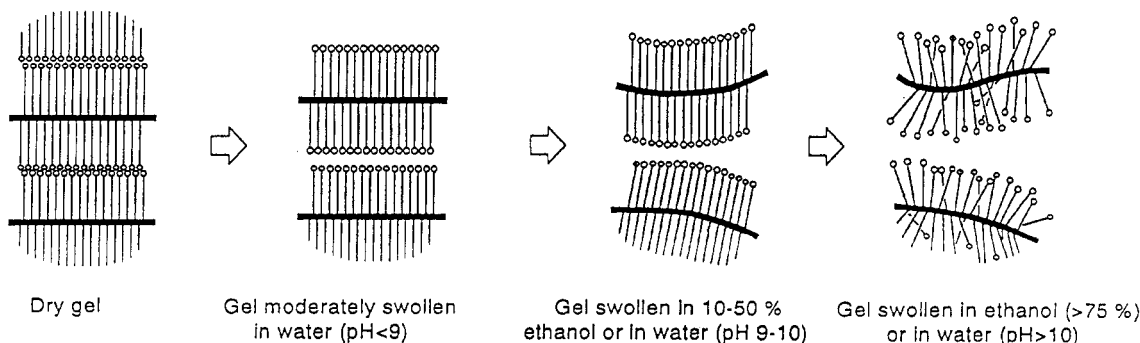

Dry gel   Gel moderately swollen in water (pH<9)   Gel swollen in 10-50 % ethanol or in water (pH 9-10)   Gel swollen in ethanol (>75 %) or in water (pH>10)

Fig. 7. Schematic illustration of the change in organized structure of the poly(AHA-*co*-AA) gel by swelling in various media. (From [37].)
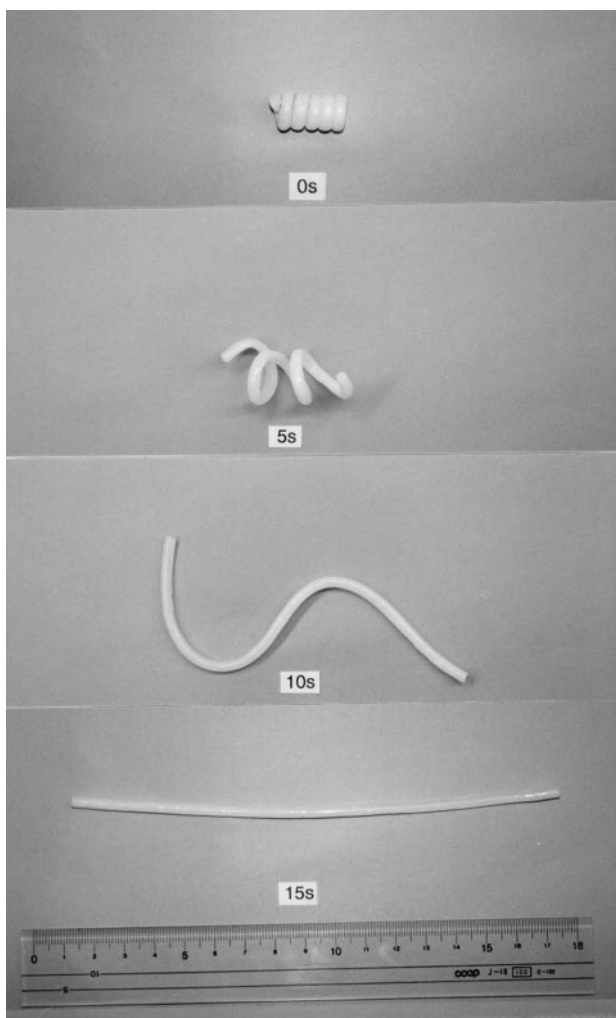
Fig. 8. Shape memory phenomenon of the gel. The copolymer gel was formed in a straight glass tube of diameter 5 mm and then swollen with water (dry samples do not show the shape memory effect). The gel was then heated to 50 °C, coiled and then cooled to room temperature. The gel is rigid and retains its coiled shape (top panel). On heating again to 50 °C, the gel becomes soft and recovers its original, straight shape. (From [39].)
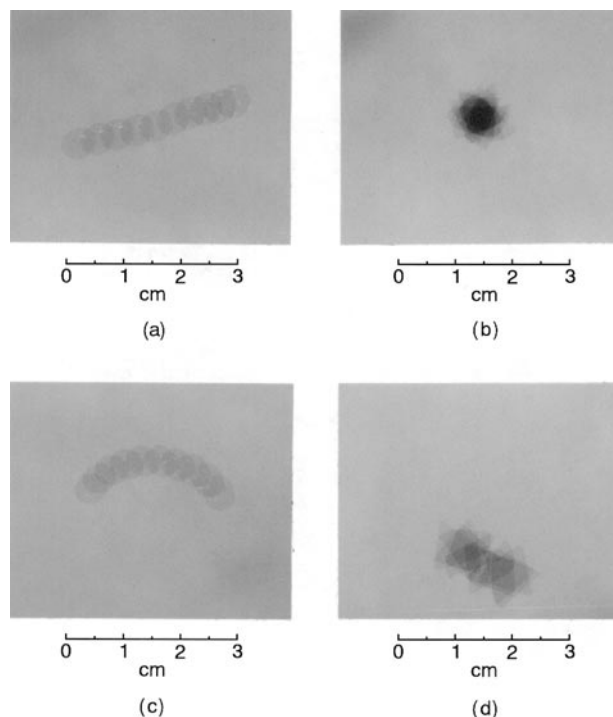

Fig. 9. Gels of various shapes in motion. Photographs were taken by multi-exposure with a stroboscope flashing at 10 Hz for 1 s. a) Translational motion of a disc-shaped gel. b) Rotational motion of a square gel. c,d) Motion composed of translation and rotation of a disc (c) and a triangle (d). (From [41].)

the driving force of the gel's motion originates from the surface spreading of the organic solvent. The gel, immersed in water, rapidly forms a partially organized structure on its outer surface and gradually shrinks, simultaneously producing high osmotic pressure and hydrostatic pressure. By virtue of these two pressures, the organic solvent is pumped out of the gel over a prolonged period of time (Fig. 10a). Once the water-miscible organic solvent is released from the gel, it quickly spreads on the water surface due to its lower surface tension compared to that of water (Fig. 10b). Therefore, the gel obtains a net reaction force to induce motion, presumably due to its heterogeneous structure.

The prolonged gel motion obtained by the surface spreading of the organic solvent has several advantages and unique characteristics. It produce no noise and no unnecessary exhaust products such as those obtained from combustion or other chemical reactions. The motion is only obtained by the dilution of the organic fluid, which can be recovered using separation technologies such as distillation or membranes.

In contrast to motors and hydrodynamic pumps, the motion made by the polymer gel is produced by the chemical free energy change, whereupon the electrical or thermal energy is used to drive the direction and control the state of the equilibrium. Thus, the chemomechanical gel driven by the outside stimulus is able to exhibit "gentle" and "flexible" action, and its movement is more like that observed in muscle than in metallic machine systems, and may lead to approaches to "biomechanics".

5. Surface Friction of Polymer Gels

In the previous sections, we discussed several moving systems made of polymer gels, in which surface friction of gels with other medium is apparently important. The fact that the gel is receptive to the surroundings suggests that it has specific surface and interface properties. Recently, the surface friction of various kinds of hydrogels was investigated and compared with that of solid materials. Amonton's law states that the frictional force F between two solids is proportional to the load W forcing them together, $F = \mu W$.[42] According to this law, the coefficient μ, known as the frictional coefficient, depends neither on
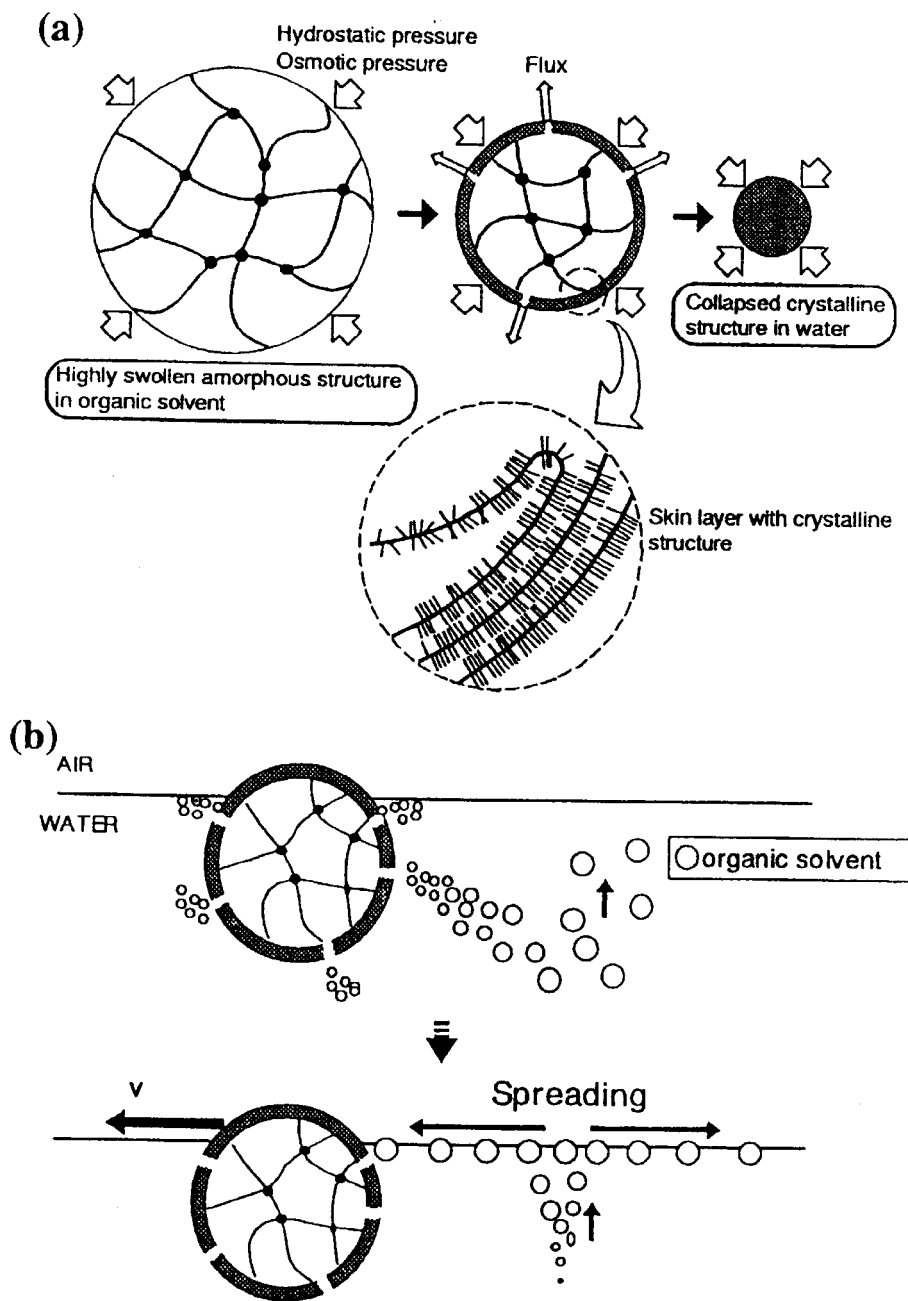
(a)

(b)

Fig. 10. Schematic illustration of the mechanism for the spontaneous motion of the gel on water. a) Releasing and b) surface spreading processes of the organic solvent. (From [41].)

the sliding velocity nor the apparent contact area of the two surfaces but depends only on the moving materials. It usually lies in the range 0.5–1.0.[43] However, it is found that the frictional relations of gels cannot simply be represented by Amonton's law.[44] When a polymer gel slides against a solid surface, the frictional force of the gel is slightly dependence on the load W (Fig. 11a), but strongly depends on the sliding velocity v. Most importantly, some gels have frictional coefficients of $\sim 10^{-3}$, which is much lower than that observed in friction between solids (Fig. 11b). This unique frictional behavior of gels should be attributed to the strong water solvation of the polymer network, which might sustain hydrodynamic lubrication

even at a very low sliding velocity and under a high pressure.

The behavior of gels seems to have some similarities with that of cartilage in human and animal joints. The cartilage consists of cells distributed throughout a three-dimensional collagen network filled with a synovial fluid and has a coefficient of friction in the range 0.001–0.03.[45] Although the true mechanism of cartilage friction is not fully understood, theories of boundary, weeping, and elastohydrodynamic lubrication have been proposed. A systematic investigation of gel tribology may be merited for the elucidation of the mechanism of joint motion and serve for the construction of comfortable artificial human joints.
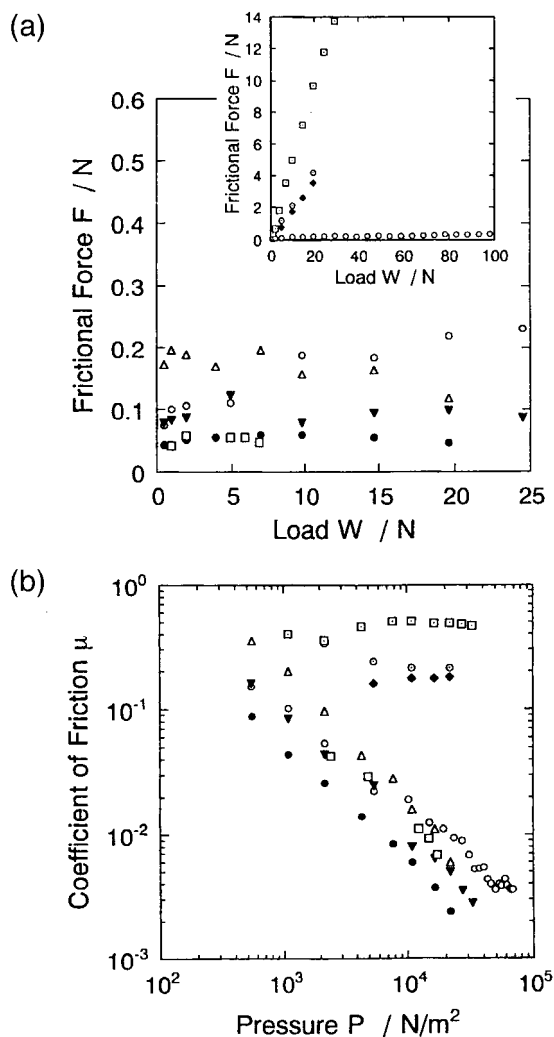
(a)

(b)

Fig. 11. Frictional force *F* as a function of load *W* (a) and the frictional coefficient μ as a function of pressure *P* normal to the surface (b). Sliding velocity: 7 mm/min. (●) gellan gel on glass; (▼) gellan gel on steel; (△) gellan gel on gellan gel; (□) κ-carrageenan gel on glass; (○) PVA gel on glass; (◎) water-soaked sponge on glass; (⊡) wet rubber on glass; (◆) wet glass on glass; Young's modulus: gellan gel, 6×10^4 Pa; κ-carrageenan gel, 5×10^4 Pa; PVA gel, 1.5×10^5 Pa; contact area: 30 mm × 30 mm except κ-carrageenan gel (20 mm × 20 mm). (From [44].)

6. Synthesis and Properties of Structure-Controlled Gels

6.1. Fast Deswelling Gels with a Comb-Like Structure

Many polymeric hydrogels undergo abrupt changes in volume in response to external stimuli, such as changes in solvent composition,[46] pH,[47] and temperature.[48,49] For several of the potential applications of these materials, such as "smart" actuators, a fast response is needed. The kinetics of swelling and deswelling in these gels are typically governed by diffusion-limited transport of the polymeric components of the network in water, the rate of which is inversely proportional to the square of the smallest dimension of the gel.[50] Several strategies have been explored for in-

creasing the deswelling dynamics, such as introducing porosity.[51] Okano et al. have demonstrated that the rapid deswelling of a hydrogel can be introduced by tailoring the gel architecture at the molecular level.[52] They have prepared a crosslinked poly(*N*-isopropylacrylamide) (PIPAAm) gel in which the polymer chains bear grafted side chains (Fig. 12). Conventional IPAAm homopolymer gels shrink very slowly after the temperature is increased from 10 °C to 40 °C, requiring more than a month to reach equilibrium (Fig. 13). In contrast to the IPAAm homopolymer gel, the comb-type grafted hydrogel shrinks rapidly to its equilibrium state. In the process, the gel undergoes large, rapid volume changes, indicating a much greater aggregation force operating within the grafted gel. Trapped water is rapidly squeezed out from the gel. This is supported by the change in the amount of freezable water within the two types of gel matrices, determined by differential scanning calorimetry (DSC, Fig. 13).

6.2. Gels with Modulated Structure

Hu et al. have proposed a class of environmentally responsive gels based on the spatial modulation of the chemical nature of gels.[53] The modulation was achieved by limiting the interpenetration of the poly(acrylamide) gel network with the poly(*N*-isopropylacrylamide) gel network. The gels thus produced have an internally heterogeneous or modulated structure. Several simple applications based on the modulated gels are demonstrated. A bi-gel strip bends almost to a circle in response to a temperature increase or a change in solvent properties. A shape memory gel reversibly changes its shape from a straight line to a pentagon to a quadrangle as the temperature increases. The gel functions obtained from the modulation method are based on the fact that the volumes of different gels are sensitive to different aspects of the external environment. Applications of the modulation method could be extensive. For example, a modulated pH-sensitive bi-gel could bend in a pH environment as well. Because a large amount of strain can be produced, structurally modulated gels may find use in gel display devices, switches, or valves.

7. Conclusion

Unlike motors and hydrodynamic pumps, the movement in a polymer gel system is produced by the chemical free energy of the polymer network, whereby the electrical or thermal energy is used to drive the direction of movement and control the state of equilibrium. A chemomechanical gel driven by an outside stimulus is able to exhibit "gentle" and "flexible" action and its movement reminds us of muscle rather than metallic machine systems; the gel may serve as a new type of "soft-actuator" or "molecular machine". As this system can transform chemical free energy directly

Homopolymer gel
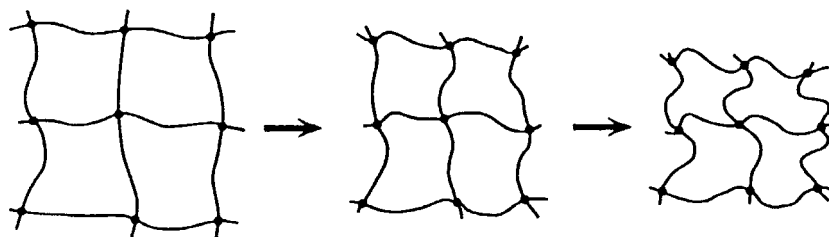
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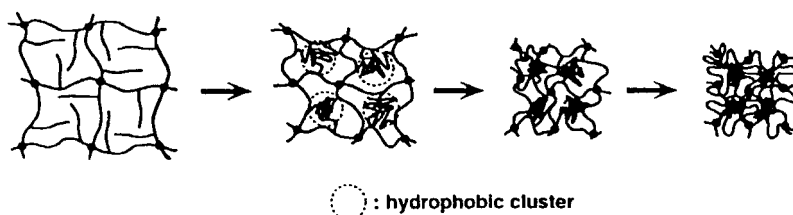

⊙ : hydrophobic cluster

Fig. 12. Structure and shrinking mechanism for conventional homopolymer and comb-type grafted PIPAAm gels undergoing temperature-induced collapse in aqueous media. (From [52].)

ties of gels to create self-sensing and self-regulating machines that respond intelligently to changes in their surroundings.
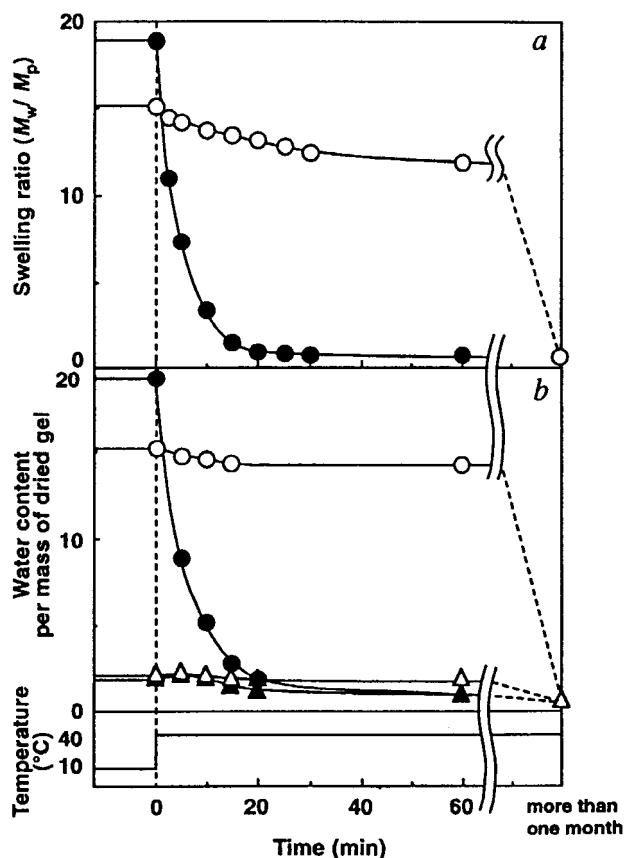
Fig. 13. a) Shrinking kinetics for homopolymer (○) and comb-type grafted PIPAAm (●) gels. b) Changes in water structure and content for shrinking homopolymer (○: freezable water; △: non-freezable water) and comb-type grafted (●: freezable water; ▲: non-freezable water) gels at 40 °C. (From [52].)

into mechanical work without producing heat, high efficiency of energy conversion may be promised. We believe it will eventually be possible to make use of these proper-

[1] W. Kuhn, *Experimentia* **1949**, *5*, 318.
[2] J. W. Breitenbach, H. Karlinger, *Monatsh. Chem.* **1949**, *80*, 211.
[3] A. Katchalsky, A. Oplatka, in *Proc. of the 4th Int. Cong. on Rheology* (Eds: E. H. Lee, A. L. Copley), Interscience, New York **1965**.
[4] Y. Osada, *Advances in Polymer Sciences*, Springer, Berlin **1987**, Vol. 82, p. 1.
[5] *Polymer Gels* (Eds: D. DeRossi, K. Kajiwara, Y. Osada, A. Yamauchi), Plenum, New York **1991**.
[6] Y. Osada, J. P. Gong, *Prog. Polym. Sci.* **1993**, *18*, 187.
[7] Y. Osada, S. B. Ross-Murphy, *Sci. Am.* **1993**, *268*, 82.
[8] A. Wassermann, *Size and Shape Changes of Contractile Polymers*, Pergamon, New York **1960**.
[9] A. H. Clark, S. B. Ross-Murphy, *Adv. Polym. Sci.* **1987**, *83*, 57.
[10] T. Tanaka, I. Nishio, S. T. Sun, S. V. Nishio, *Science* **1973**, *218*, 467.
[11] a) H. Okuzaki, Y. Osada, *Macromolecules* **1994**, *27*, 502. b) H. Okuzaki, Y. Osada, *Macromolecules* **1995**, *28*, 380. c) H. Okuzaki, Y. Osada, *Macromolecules* **1995**, *28*, 4554.
[12] D. E. Woessner, B. S. Snowden, *J. Colloid Interface Sci.* **1970**, *34*, 290.
[13] Y. Osada, H. Okuzaki, H. Hori, *Nature* **1992**, *355*, 242.
[14] J. P. Gong, Y. Osada, *Chem. Lett.* **1995**, 449.
[15] F. Oosawa, *J. Polym. Sci.* **1957**, *23*, 421.
[16] G. S. Manning, *J. Chem. Phys.* **1969**, *51*, 924.
[17] J. P. Gong, N. Komastu, T. Nitta, Y. Osada, *J. Phys. Chem.* **1997**, *101*, 740.
[18] K. Umezawa, Y. Osada, *Chem. Lett.* **1987**, 1795.
[19] Y. Osada, K. Umezawa, *Macromol. Chem.* **1988**, *189*, 597.
[20] Y. Osada, K. Umezawa, A. Yamauchi, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3232.
[21] M. Miyano, Y. Osada, *Macromolecules* **1991**, *24*, 4755.
[22] Y. Osada, M. Hasebe, *Chem. Lett.* **1985**, 1285.
[23] R. Kishi, Y. Osada, *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 655.
[24] J. P. Gong, T. Nitta, Y. Osada, *J. Phys. Chem.* **1994**, *98*, 9583.
[25] K. Sawahata, J. P. Gong, Y. Osada, *J. Macromol. Sci.* **1991**, 1189.
[26] Y. Osada, R. Kishi, M. Hasebe, *J. Polym. Sci., Part C: Polym. Lett.* **1987**, *25*, 481.
[27] M. H. Shamos, L. S. Lavine, *Nature* **1967**, *213*, 267.
[28] H. Athenstaedt, H. Claussen, D. Schaper, *Science* **1982**, *216*, 1018.
[29] N. Isogai, T. Narita, L. Chen, K. B. Kim, M. Hirata, J. P. Gong, Y. Osada, *Colloids Surf. A: Physicochem. Eng. Aspects*, in press.
[30] H. Okuzaki, Y. Osada, *J. Biomater. Sci. Polymer Ed.* **1994**, *5(5)*, 485.
[31] N. Isogai, J. P. Gong, Y. Osada, *Macromolecules* **1996**, *29*, 6803.

ADVANCED MATERIALS

[32] S. Y. Yu, M. Hirata, L. Chen, S. Matsumoto, M. Matsukata, J. P. Gong, Y. Osada, *Macromolecules* **1996**, *29*, 8021.

[33] L. Chen, S. Y. Yu, J. P. Gong, Y. Osada, *Macromolecules* **1998**, *31*, 787.

[34] A. R. Khokhlov, E. Y. Kramarenko, E. E. Makhaeva, S. G. Starodubtzev, *Makromol. Chem., Theory Simul.* **1992**, *1*, 105.

[35] H. Okuzaki, Y. Osada, *J. Intelligent Mater. Syst. Struct.* **1993**, *4*, 50.

[36] Y. Ueoka, J. P. Gong, Y. Osada, *J. Intelligent Mater. Syst. Struct.* **1997**, *8*, 465.

[37] M. Uchida, M. Kurozawa, Y. Osada, *Macromolecules* **1995**, *28*, 4583.

[38] A. Matsuda, J. Sato, H. Yasunaga, Y. Osada, *Macromolecules* **1994**, *27*, 7695.

[39] Y. Osada, A. Matsuda, *Nature* **1995**, *376*, 219.

[40] Y. Osada, J. P. Gong, M. Uchida, N. Isogai, *Jpn. J. Appl. Phys.* **1995**, *34*, L511.

[41] J. P. Gong, S. Matsumoto, M. Uchida, N. Isogai, Y. Osada, *J. Phys. Chem.* **1996**, *100*, 11 092.

[42] M. Amontons, *Mem. Acad. R. Sci.* **1699**, 206.

[43] A. W. Adamson, *Physical Chemistry of Surfaces*, Wiley, New York **1990**.

[44] J. P. Gong, M. Higa, Y. Iwasaki, Y. Katsuyama, Y. Osada, *J. Phys. Chem.* **1997**, *101*, 5487.

[45] C. W. McCutchen, *Lubrication of Joints, The Joints and Synovial Fluid*, Academic, New York **1978**, *10*, 437.

[46] E. Hirokawa, T. Tanaka, *J. Chem. Phys.* **1984**, *81*, 6379.

[47] T. Tanaka, D. J. Fillmore, S. T. Sun, I. Nishino, G. Swislow, A. Shah, *Phys. Rev. Lett.* **1980**, *45*, 1636.

[48] A. S. Hoffman, *J. Controlled Release* **1987**, *6*, 297.

[49] *Responsive Gels: Volume Transitions II* (Ed: K. Dusek), Springer, Berlin, **1993**.

[50] T. Tanaka, D. J. Fillmore, *J. Chem. Phys.* **1979**, *70*, 1214.

[51] L. C. Dong, A. S. Hoffman, *J. Controlled Release*, **1990**, *13*, 21.

[52] R. Yoshida, K. Uchida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai, T. Okano, *Nature* **1995**, *374*, 240.

[53] Z. Hu, X. M. Zhang, Y. Li, *Science* **1995**, *269*, 525.