

Intelligent gels

Hiroki Nagasawa, Jian Ping Gong and Yoshihito Osada

Un gel polymère est un matériau mou et gonflé de solvant, capable de subir de grandes déformations. Lorsqu'un gel est déformé, son potentiel chimique est modifié ; il se comporte alors comme un transducteur d'énergie. En conséquence, un gel polymère présente une grande variété de réponses à des stimuli causés par des changements environnementaux. Dans cet article, les réponses originales à des stimuli électriques, thermiques, chimiques et magnétiques sont décrites. Les propriétés de frottement de surface sont également abordées.

Summary

Intelligent gels

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 outside environmental changes. In this article, unique electrical, thermal, chemical, and magnetic responses of polymer gels are described. The specific surface frictional property of gels is also briefly introduced.

Mots-clés

Key-words

Gel stimuable, frottement, déformation, mémoire de forme, gonflement.

Intelligent gel, friction, deformation, stimuli-response, shape memory, swelling.

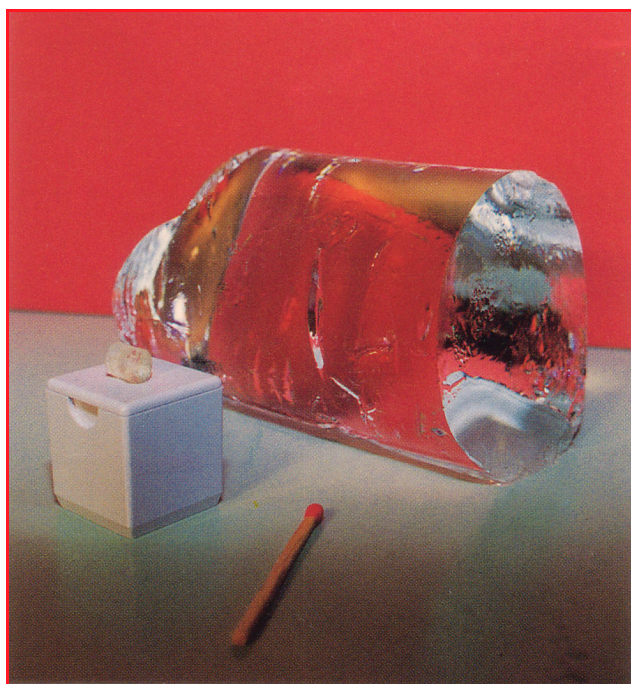


Figure 1 - Photograph of a synthetic polymer gel containing several thousand times of water.

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. A polymer gel consists of an elastic crosslinked 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 (*figure 1*). 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. This property is characteristic of gels, in contrast to most industrial materials such as metal, ceramics, and plastics, which are dry and hard.

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 membrane for separations, and modulators for delivery of drugs [1-6]. Since the studies on the fundamental process of gel volume transition as well as on its application have been extensively reported and we are not going to give a comprehensive review in this paper. This review is concerned with some examples of gels applied for possible artificial organs. Frictional specificities of gels are also briefly introduced.

Electric mechano responses of gels

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 [7-10]. *Figure 2* shows the shape change of an anionic gel with time under the electric field.

The electrically induced contraction of the gel is caused by a transport of hydrated ions and water in the network (an electrochemical phenomenon). When an external electric field is applied across the gel, both the macroions (polyelectrolyte gel) and the microions received electrical forces in the opposite direction. However, the macroions are stationary since they are chemically fixed to the polymer network, while the counter ions are mobile capable of migrating along the electric field and dragging water molecules with them.

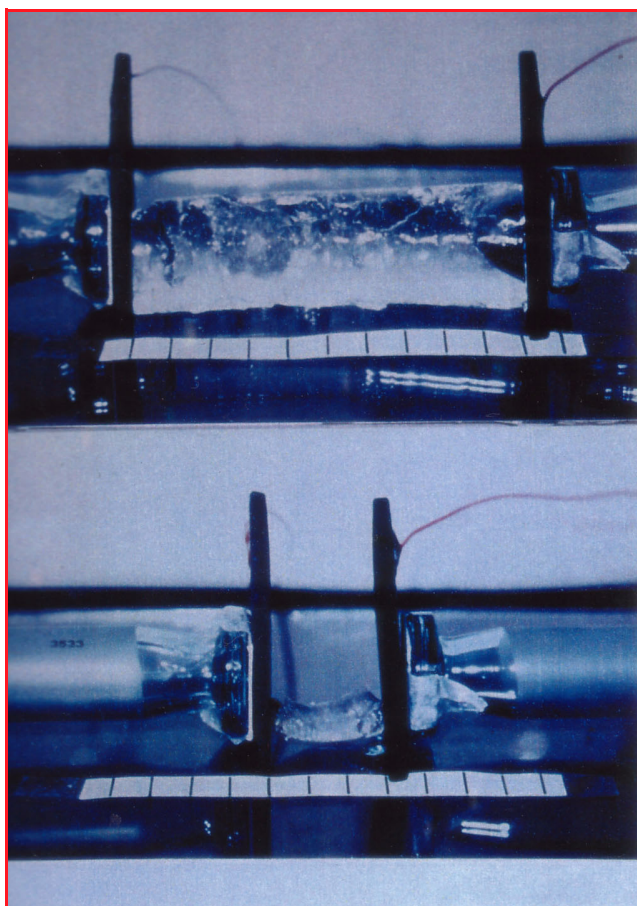


Figure 2 - Photographs of a poly(2-acrylamido-2-methyl-1-propanesulfonic acid) gel before (upper) and after (lower) imposing an electric field of 15 V for 10 h.

A capillary model has been proposed to describe the contraction process [11]. 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 the gel, i.e., on the quantity of electricity and is independent of electric field. The electrically induced contraction of the gel is dominated by electrokinetic processes of hydrated ions and water in the polymer gels.

The piezoelectric effect

In the previous section, we have described that a polyelectrolyte gel can contract under the electric stimulus, that is, a gel can convert the electrical energy into the mechanical work. The reverse process can also be observed in gels [12]. 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 carboxyl groups under deformation: being compressed in one direction, the gel 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 by the simultaneous increase in its degree of ionization.

In order to extract the change in electrical potential originated from the pH change 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, was inserted to measure the electrical potential by connecting the electrodes with a photo emission diode array through an amplifier (figure 3a). Figure 3b demonstrated that a soft and wet tactile-sensing system made of polymer gel could successfully light the array in proportion to the amplitude of the stress applied. 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. Figure 3b shows the potential difference thus obtained. The rate of contraction as well as the efficiency of the work increased with an increasing load to a maximum value. This anomalous lifting behavior of the gels can be explained in terms of a spontaneous ionization of ionizable groups leading to an increased current when the gel is stretched (mechanoelectric effect) [13].

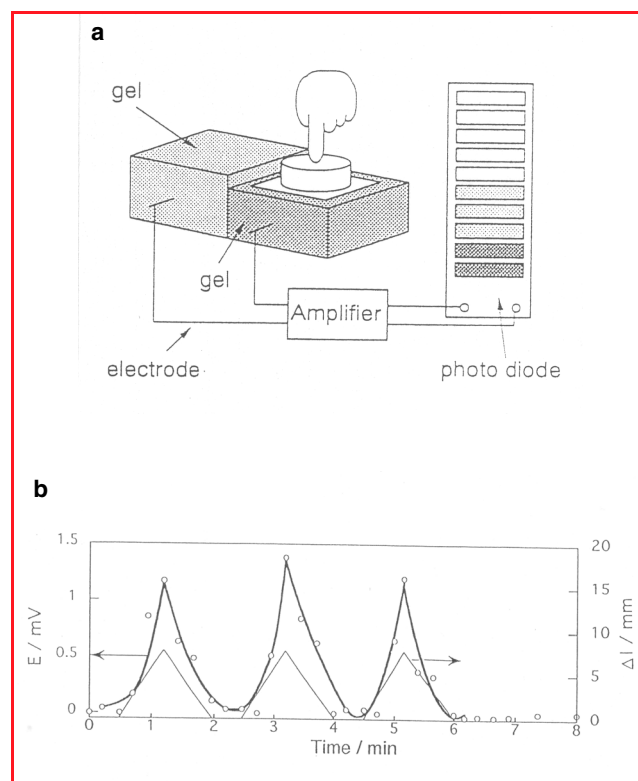


Figure 3 - a) Cell used to extract the electric potential and its application as an artificial tactile sensing system capable of lighting a photodiode array under the deformation; b) Time profile of electrical potential produced at the interface of two poly(acrylic acid) gels, one of which was deformed while the other was free-standing. Upper trace: electrical potential; lower trace: deformation length. Size of the gel: 15 mm X 10 mm X 10 mm; degree of swelling: 16. (From [12]).

We would like to emphasize that mechanoelectrical system made of polymer gel has similarities with the tactile perceptions in the living organism [14-15]. Both of them are dynamic processes in which the macroscopic deformation induces the ionic rearrangement which give rise 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.

Chemomechanical gels

Motility of gels driven by molecular assembly reaction

Since the polyelectrolyte gel has deep electrostatic potential valleys along the polymer chains and wells at the crosslinked points, it will attract the oppositely charged surfactants and form complexes [16]. Positively charged surfactant molecules bind with anionic polymer gel through electrostatic interactions and bring about contraction of the gel [17-19]. 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 [19-20].

Here, we introduce a newly designed moving system in which the PAMPS gel showed eel-like motion in the surfactant (Laurylpyridinium chloride) solution under an electric field [21-22]. The moving system was made using a styrofoam and pieces of PAMPS gel membrane. The body was made of styrofoam, which can be used at the same time as buoyancy. A pair of plastic sheets was attached to one end of the PAMPS gel and inserted to the styrofoam body. A pair of parallel carbon electrodes was 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 (*figure 4a*). Different from the movement made by a rigid machine, the gel exhibited an eel-like undulating motion and showed a propelling force with an order of 10^{-4} N.

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 schematically shown in *figure 4b*. The electric field drives and controls the direction of complexation equilibrium to give an 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 the 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 repeated swing. The movement of the gel is produced by a free energy change in the assembly reaction of the surfactant with the polymer network.

Fish have swimming capabilities far superior in many ways to what has been achieved by man-made technology. Using superbly well-designed bodies they exhibit extraordinary propulsion efficiencies, including acceleration, on the basis of hydrodynamic principle. Nevertheless, because of the prospective rewards, the effort should be put forth. Imitation of the motion of a fish by merely copying its shape and body

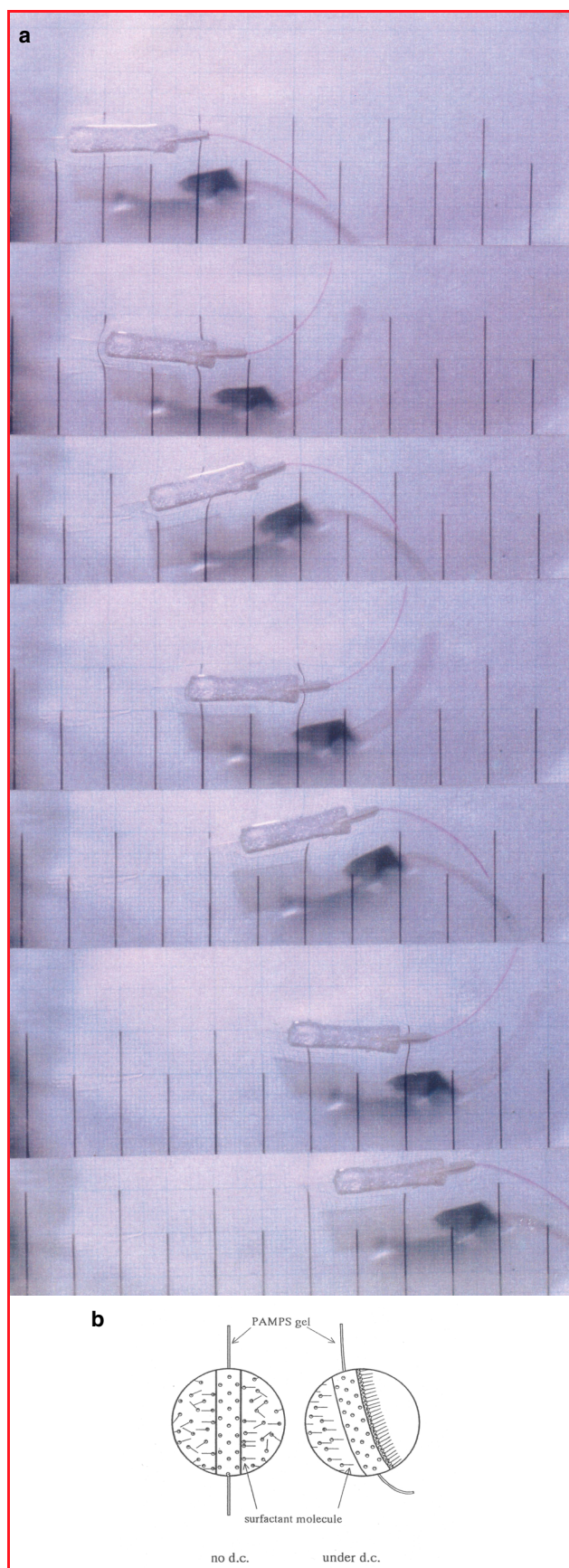


Figure 4 - a) Progressive change in motion of gel-eel under a voltage of 10 V. Electrode distance: 70 mm, 0.25 Hz, photographs were taken every 4s; b) The moving mechanism of the PAMPS gel. The left picture is free from the electric field and the right one is under a voltage of 10 V with the anode facing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

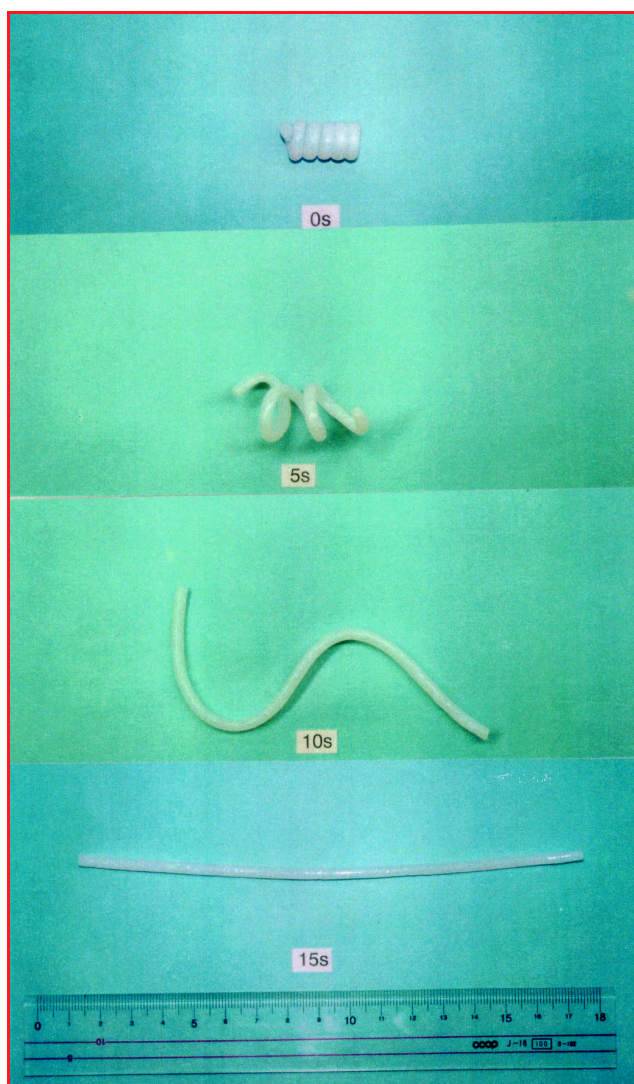


Figure 5 - Shape memory phenomenon of the gel. The copolymer gel was formed in a straight glass tube of diameter 5 mm and then swollen with water (dry samples do not show the shape memory effect). The gel was then heated to 50 °C, coiled and then cooled to the room temperature. The gel is rigid and retains its coiled shape (top panel). On heating again to 50 °C, the gel becomes soft and recovers its original, straight shape. (From [25]).

is realistic using today's machine technology; however, a smoothly and continuously flexing motion observed in the fish is difficult to make. The gel-membrane tail might be the first fish-inspired technological application.

Shape memory gel

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 in mechanical toughness and slow response to stimulus.

It has been demonstrated that the water-swollen polymer hydrogels with 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),

acryloylhexadecanoic acid (AHA) [23-24]. These gels undergo reversible order-disorder transition with a change in temperature, pH, and solvent properties.

Poly(SA-co-AA) gel exhibits shape memory behaviors with temperature (*figure 5*) [25]. 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 amorphous 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 [26].

The shape memory effect can be observed only for the water-swollen hydrogel and not for the dry sample. This is because AA units are substantially hydrated in water, and behave like a soft elastomer with a very low glass temperature. Under this condition, SA units are responsible for the mechanical toughness and render the material robust. Shape memory gel might be applied to biomedical materials such as temperature-activated surgical clamps or a thermally responsive valve.

Spontaneous motion in water

It has been discovered that crosslinked amphiphilic copolymer gels swollen in organic solvent undergo spontaneous motion when put on water [27-30]. The mode of motion largely depends on the shape of the gel. It has been found that the driving force of the gel motion is originated 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 for a prolonged time.

The motion of the amphiphilic gel has been successfully controlled by wrapping the gel up in aluminum foil and equipping it with a spouting foil. Tetrahydrofuran (THF)-swollen poly(SA) gel equipped with a pair of rudder and spouting hole behind (*figure 6a*). The flux of THF solvent can only spread out via this spouting hole. This model resembles a water beetle, has a pair of rudders that enable like the gel to undergo translational motion, and it behaves like the tail of kite. This gel underwent a controlled translational motion with a maximum velocity of 77 mm/s which exceeded the values obtained by the driven « gel looper » [20], and moved more than 30 minutes.

Next, a gel rotor with two spouting holes at two opposite sides was constructed. The rotor was settled around the stator which serves as a center pivot (*figure 6b*). This gel was comprised of a THF-swollen poly(SA-AA) gel, the THF-swollen rotor rotated with a maximum velocity of 400 rpm for nearly 30 min., but decreased the velocity with the time.

The prolonged gel motion obtained by the surface spreading of the organic solvent has several advantages and unique characteristics. They produce no noise and no unnecessary exhaust products like combustion or other chemical reactions. The motion is only obtained by the dilution of the

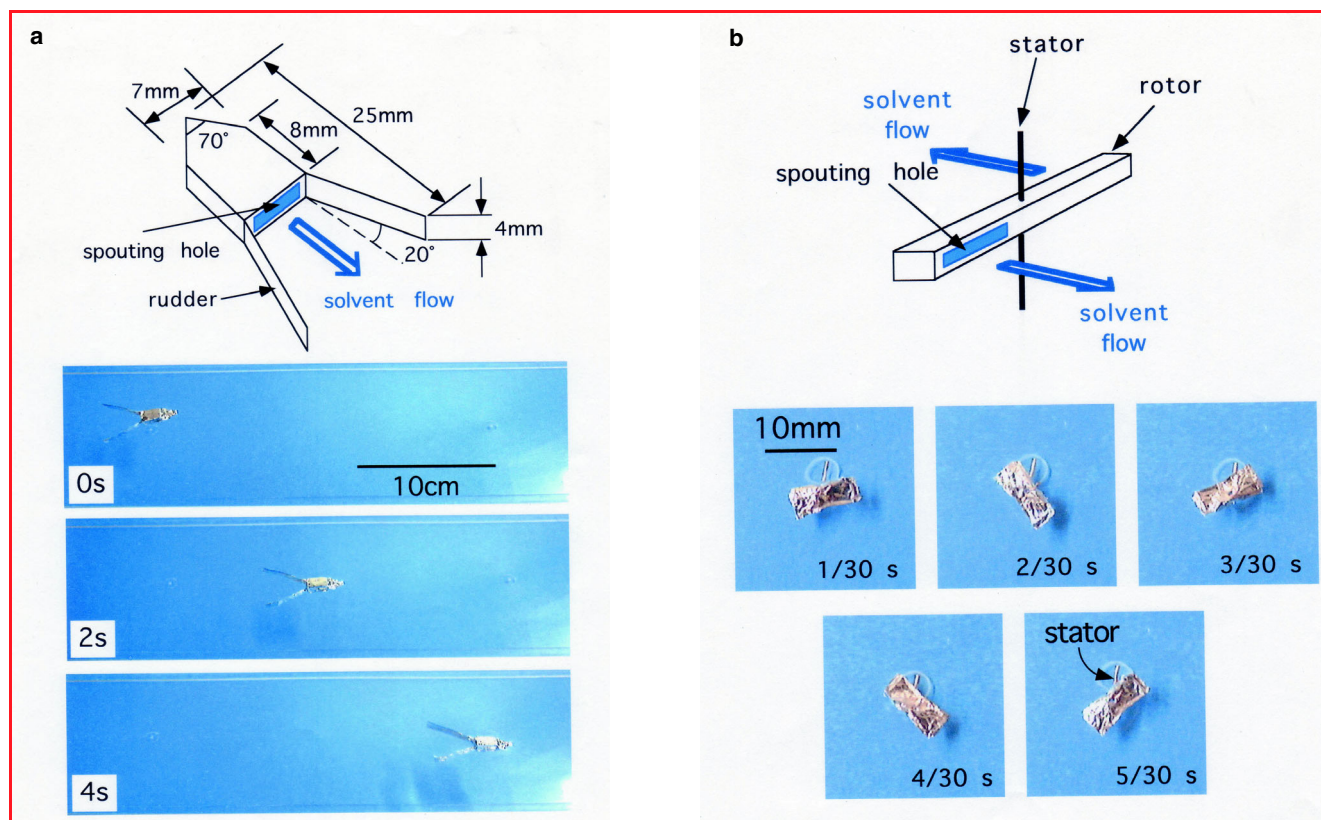


Figure 6 - Schematic illustration and photographs of the gels swollen in THF: a) the translational motion; b) the rotation. (From [29]).

organic fluid, which can be recovered by 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. The chemomechanical gel driven by an outside stimulus is able to exhibit « gentle » action, and its movement is more like that observed in muscle than in the metallic machine systems, and this may lead to applications in « biomechanics ». From this point of view, the application of chemomechanical gel as an « actuator » for robots and other machine systems has special interests. Robots made of these soft gels would behave more softly, more carefully, and more gently.

Fast deswelling gel with a comb-like structure

Many polymeric hydrogels undergo abrupt changes in volume in response to external stimuli, such as changes in solvent composition [31], pH [32], and temperature [33-34]. 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 [35]. Several strategies have been explored for increasing the deswelling dynamics, such as introducing porosity [36]. Okano *et al.* have demonstrated that a rapid deswelling of hydrogel can be introduced by tailoring the gel architecture at the molecular level [37]. They have prepared a crosslinked poly(N-isopropylacrylamide, IPAAm) gel in which the polymer chains bear grafted side

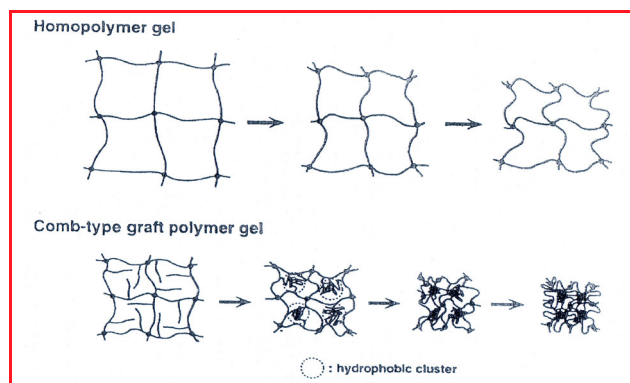


Figure 7 - Structure and shrinking mechanism for conventional homopolymer and combtype grafted PIPAAm gels undergoing temperature-induced collapse in aqueous media. (From [37]).

chains (figure 7). The comb-type grafted hydrogel shrinks more rapidly to its equilibrium state than the IPAAm homopolymer gel. 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.

To take advantage of this fact, new application to drug delivery system might be thought. A.S. Hoffman *et al.* tried to synthesize novel bioadhesive, pH- and temperature-sensitive graft copolymer gels for prolonged mucosal drug delivery [38].

Surface friction of polymer gels

In the previous sections, we have demonstrated several moving systems made of polymer gels, where surface

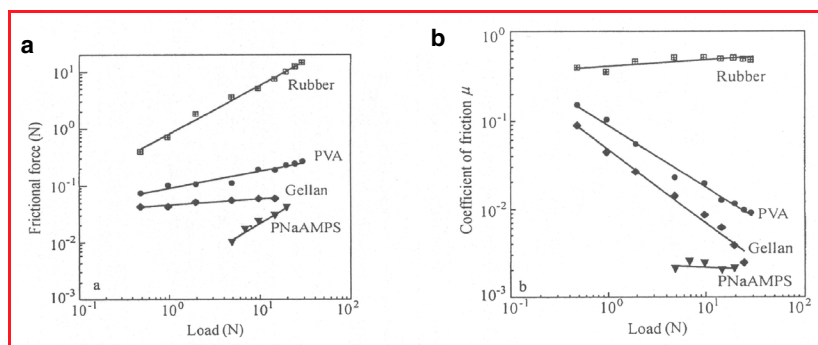


Figure 8 - Dependence of friction (a) and the coefficient of friction (b) on load for various kinds of hydrogels sliding on a glass surface in air. Sliding velocity: 7 mm/min.; sample constant area: PVA, gellan and rubber; $3 \times 3 \text{ cm}^2$, PNaMPS, $2 \times 2 \text{ cm}^2$, degree of swelling q : PVA, 17; gellan, 33; PNaMPS, 15. (From [47]).

friction of gels with other medium is apparently important. The fact that gel is receptive to surroundings suggests that it has specific surface and interface properties. Recently, the surface friction of various kinds of hydrogels have been investigated and compared with that of solid materials. Amontons's law says that the frictional force F between two solids is proportional to the load W forcing them together $F = \mu W$ [39]. According to this law, the proportional coefficient μ usually lies in a range of 0.5-1.0 [40]. However, it is found that the frictional relations of gels can not simply be represented by Amontons's law [41]. When a polymer gel slides against a solid surface, the frictional force of the gel is slight dependence on the load W (figure 8a), 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 (figure 8b). This behavior of gel seems to have some similarities with that of cartilage in human and animal joints. The cartilage consists of cells distributed throughout a

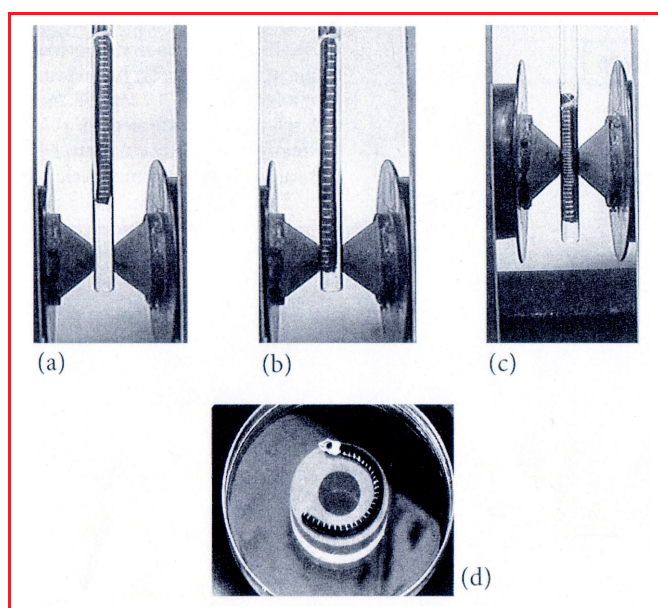


Figure 9 - Shape distortion of ferrogels due to non-uniform magnetic field; a) no external magnetic field; b) the maximal field strength is located under the lower end of the gel; c) the maximal field strength is focused in the middle of the gel along its axis; d) bending induced by a permanent magnet. (From [51]).

three-dimensional collagen network filled with a synovial fluid and has a coefficient of friction in the range 0.001~0.03 [42]. Although the true mechanism of the cartilage friction is not fully understood, theories of boundary, weeping and elastohydrodynamic elubrication have been proposed [43-48]. A systematic investigation of gel tribology may merit the elucidation of the mechanism of joint motion and serve for construction of comfortable artificial human joints.

Magnetic field sensitive polymeric actuators

In previous articles, most of the polymeric gel actuators are based on discontinuous volume phase transitions by external stimuli. Recently, M. Zrinyi *et al.* have developed a completely different type of polymeric actuators by introducing magnetic nanoparticles into a gel [49-51]. They call magnetic field sensitive gels « ferrogels ».

Ferrogels are composed of chemically crosslinked polyvinyl alcohol (PVA) hydrogels (6.3 wt %) filled with magnetite (Fe_3O_4) particles (4.25 wt %). When magnetic field is turned on, the shape of ferrogels is changed; bending, elongation, contraction and a combination of these basic distortion (figure 9). Magnetic sensitive gels can change the shape repeatedly many times without damaging the gels. The response time to obtain the new equilibrium shape was found to be less than 0.1 s and seems to be independent of the size of gel.

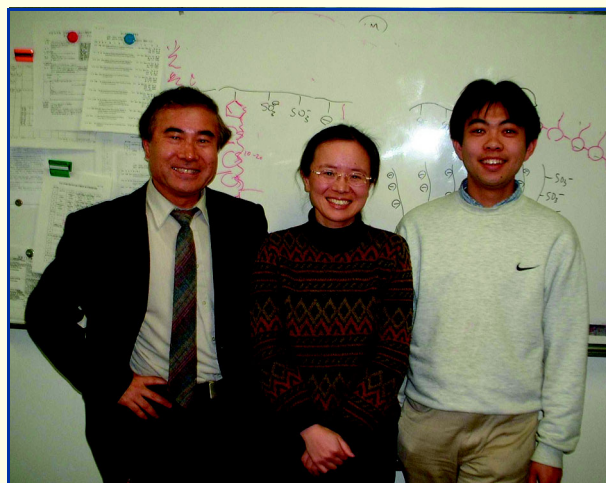
The principle of ferrogel's shape transformation and motility lies in a unique magnetoelastic behavior. The magnetic field drives and controls the displacement of the individual particles and the final shape is set by the balance of magnetic and elastic interactions.

The ability of magnetic field sensitive gels to undergo a quick controllable change of shape can be used to create an artificially designed system possessing the sensor and actuator functions internally in the gel itself. The peculiar magneto-elastic properties may be used to create a wide angle of motion and to control the shape change and movement, that are smooth and gentle, and similar to that observed in muscle. If the magnetic field is created inside the gel by incorporated small powerful electromagnets and the field is co-oriented and controlled by a computer, then magneticfield-sensitive gel may be used as an artificial muscle.

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