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Y. Osada^a; J. P. Gong^a; K. Sawahata^a

^a Department of Chemistry, Ibaraki University, Mito, Japan

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SYNTHESIS, MECHANISM, AND APPLICATION OF AN ELECTRO-DRIVEN CHEMOMECHANICAL SYSTEM USING POLYMER GELS

Y. OSADA,* J. P. GONG, AND K. SAWAHATA

Department of Chemistry
Ibaraki University
Mito 310, Japan

ABSTRACT

When a water-swollen polyelectrolyte gel is interposed between a pair of electrodes and dc is applied, the gel undergoes electrochemomechanical contraction and concomitant water exudation. Micro-particles of crosslinked poly(acrylic acid) also undergoes reversible shrinkage by the electric field. The contraction was associated with the electrohydrodynamic transport of hydrated ions, and an equation expressing the rate of size change was derived as a function of voltage, charge density, and degree of swelling. Applications of this phenomenon to drug delivery systems, artificial muscles lifting and lowering a load, and some gel actuators walking in water are introduced.

1. INTRODUCTION

A system that undergoes shape change and develops a contractile force responding to outside stimulus is called a “chemomechanical (or mechanochemical) system” [1]. It refers to thermodynamic systems capable of transforming chemical energy directly into mechanical work or conversely of transforming mechanical into chemical potential energy

[2]. The isothermal conversion of all living organisms can easily be seen; for instance, in muscle, flagella, and ciliary movement.

During the last decade, a number of chemomechanical systems have been investigated. They include polyelectrolyte fibers and membranes which expand and contract upon changing their solubility and/or degree of ionization, noncharged polymer fibers which collapse upon changing temperature, and polymer membranes which associate cooperatively with "complementary" polymers.

Among them, a chemomechanical system actuated by electric stimulus seems to be particularly interesting in connection with the fact that the muscle can be considered the seat of the transformation of chemical into mechanical energy triggered by an electric signal. Detailed paths and processes at the molecular and cellular levels are the subject of many investigation nowadays.

Tanaka et al. [3] showed that a partially hydrolyzed polyacrylamide gel undergoes phase transition with the application of an electric field and collapses if the gel is placed in some solvent, e.g., a 50% acetone-water mixture. Grodzinsky [4] showed that collagen fibers immersed in an electrolyte bath can deform in the presence of an external electric field and thereby perform mechanical work. If the fiber is held to a constant length, the electric field generates a stress on the fibers. DeRossi [5], who used poly(vinyl alcohol) (PVA)-poly(acrylic acid) (PAA) composite membranes, found that a change in the shape of the membrane occurred when dc was applied. The phenomenon was related to a change in the ionization state of the membrane induced by an electrochemical reaction near the electrodes.

We have reported [6] that a water-swollen, crosslinked polyelectrolyte gel inserted between a pair of electrodes undergoes contraction and concomitant fluid (water) exudation in air. The applied electric field induces the migration of hydrated microions in the gel, thereby transporting water to the electrode.

This paper deals with the principle and behavior of contraction of some polymer gels. Modeling of the contraction was made on the basis of the electrokinetic process and Flory's theory. Examples of the application of the chemomechanical system are also briefly introduced.

2. CONTRACTILE BEHAVIORS OF GEL PARTICLES

In order to establish a system with a minimum response time, micro-particles of the sodium salt of poly(acrylic acid) gel were synthesized,

and the size change of the particles with time under various electric fields was measured [7].

A microparticle was placed between two SnO_2 electrodes of 10×10 mm which were mounted on a polymeric frame with a spacing of 1.3 mm. The space was filled with distilled water. A direct current with a $0\text{--}0.3$ mA/cm^2 density was applied via the SnO_2 electrodes, and the volume change of the microparticles was observed with an optical microscope.

No changes in the shape and size occurred while the microparticle underwent electrophoretic migration toward the anode. However, a quick contraction took place when the particle reached the anode and migration stopped.

Figure 1 shows time profiles of the contraction of a particle (180 μm diameter) in the cell when a direct current was applied. Below 2.4 V (18.5 V/cm), no contraction or detectable electric current was observed. Shrinkage started when the dc voltage reached 3 V or when the electric current reached 0.02 μA . The shrinkage rate increased with increasing electric field. Note that an increase in voltage increased not only the rate

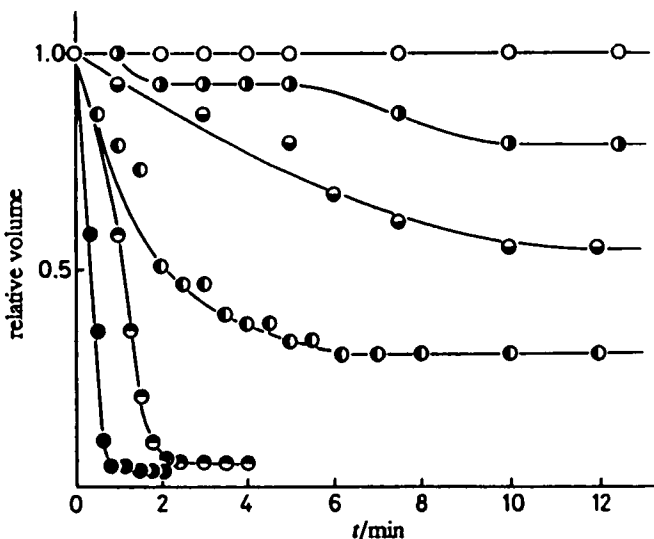


FIG. 1. Time profiles of volume change of the microparticles. Voltage: (○) 2.4 V (18.5 V/cm); (◐) 3.0 V (21.1 V/cm); (◑) 3.6 V (27.7 V/cm); (●) 4.2 V (32.3 V/cm); (⊙) 4.8 V (36.9 V/cm); (⊚) 6 V (46.2 V/cm). Microparticle diameter: 180 μm .

of contraction but also the final size (V_{\min}) that the particle could achieve.

Time profiles of the swelling process after the electric field was turned off are shown in Fig. 2. All microparticles, except for these at 4.2 V, recovered their original size and shape within 5–10 min and showed good reproducibility.

The dependence of the rate of volume change on the applied voltage is illustrated in Fig. 3. The current observed in the medium is also shown. Shrinkage of the microparticles occurs when the electric field exceeds the threshold overpotential (2.4 V). The rate of volume change increases in proportion to the current, and this fact evidently indicates that shrinkage of the particle is developed by the ion-transport process, accompanied by an electrochemical reaction.

The rate of volume change should be a function of the initial size of the particle, and the relative rate of volume change must increase with decreasing size of the particle. The experimental results are inversely proportional to the square of the particle size, as shown in Fig. 4. It was calculated that the time taken for a 96% volume change for a particle of 1 μm diameter is as low as 0.23 ms under these conditions.

In a previous paper [2, 6] we demonstrated that a water-swollen poly-electrolyte gel sandwiched between a pair of electrodes undergoes shrink-

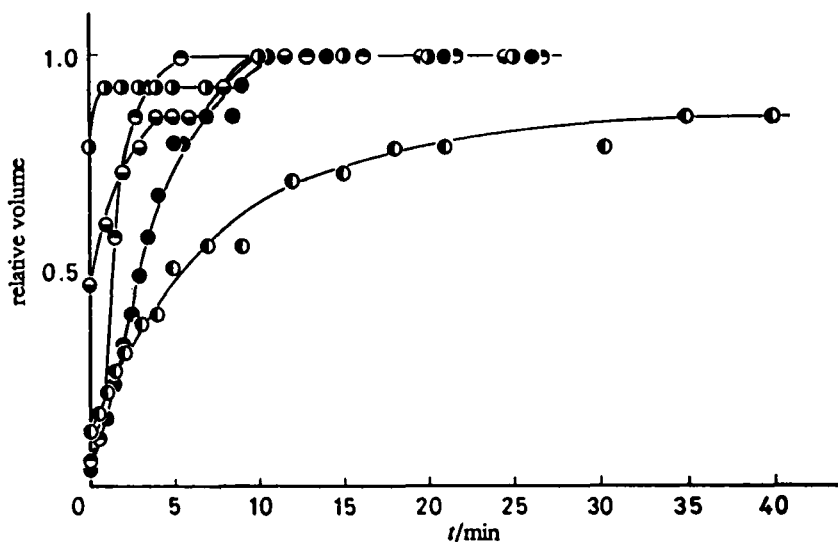


FIG. 2. Time profiles of the swelling process of the microparticles after the electric field was turned off. Symbols are the same as in Fig. 1.

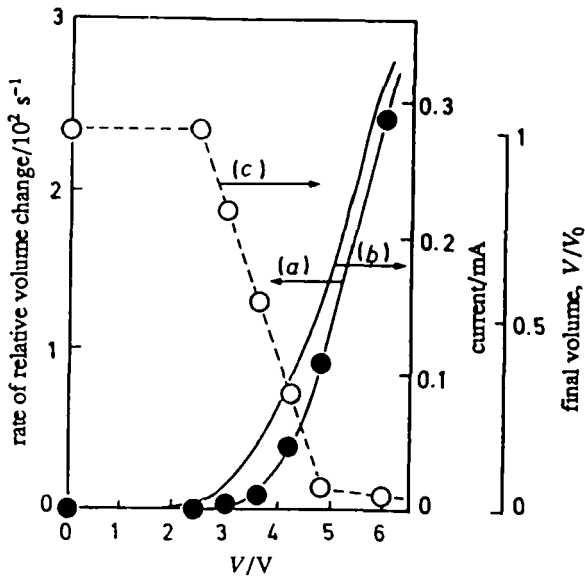


FIG. 3. Dependences of the rate of contraction of the microparticles (a), the current (b), and the final volume of the microparticles (c) on the voltage applied. Microparticle diameter: $180 \mu\text{m}$.

age under aerobic conditions and that the rate of shrinkage is proportional to the electric current [8]. The contraction was associated with the electrohydrodynamic transport of hydrated ions and concomitant water exudation. The shrinkage of the particles in the present case can be explained by the same reasons; i.e., the negatively charged microparticle moves to the anode, and sodium ions move to the cathode owing to electrophoretic migration. An electric-field gradient will produce a steady diffusion of mobile cations and carry sodium ions away from the carboxylates. Carboxylate anions thus undergo substitution with H^+ in the fluid and become largely undissociated. The carboxyl groups in this state are much less hydrated, and the gel can consequently contract. In fact, a decrease in pH was observed in the gel near the anode when a direct current was applied to a crosslinked rodlike Na-PAA gel [7].

3. MECHANISM OF CONTRACTION

As reported in earlier papers, we have several experimental facts supporting the interpretation that the chemomechanical behaviors observed are essentially electrochemical phenomenon. They are: 1) the absolute

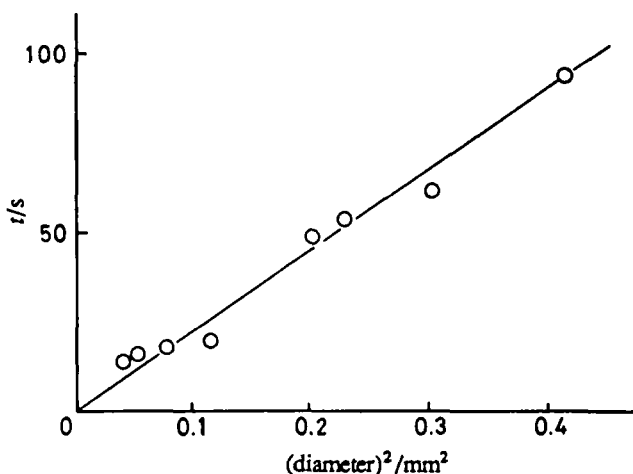


FIG. 4. Dependence of the time for a 96% volume change of the square of the microparticle size; dc voltage: 3.5 V (26.9 V/cm).

absence of contraction for neutral (noncharged) hydrogel; 2) swelling near the anode and contraction near the cathode when the gel is negatively charged, and the opposite observation for positively charged polyelectrolyte gel; 3) a parallel relationship of the rate of contraction and the amount of electric current. Thus, an electrokinetic process involving the transport of water and electric charges is accounted for.

However, the most striking support for the presumed electrokinetic nature is direct observation of water migration (electroosmosis) and of charged ions (electrophoresis) toward the electrode bearing a normal charge opposite in sign to the net charge borne by the gel. The observed chemomechanical behaviors of the hydrogels led us to consider the possibility that the external electric field underwent direct interaction with the internal electric field of the gel, particularly the coupling of the electroosmosis of water and the electrophoresis of the charged molecules [9].

The electroosmotic measurements were carried out with two measuring capillaries, as shown in Fig. 5. When dc was applied through the electrodes, the water level of the cathode quickly elevated and that of the anode lowered. The velocity of change in water level varied with the distance between the electrodes, and the value was almost proportional to the current. Flow was always in the direction of counterion movement

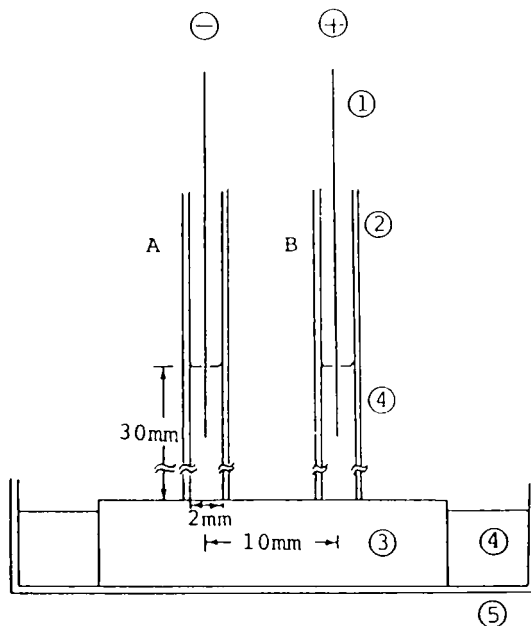


FIG. 5. Schematic representation of the apparatus for electroosmotic transport of water in the polyelectrolyte gel. (1) Platinum wire electrode, (2) measuring Pyrex-glass capillary, (3) polyelectrolyte gel (PAMPS gel), (4) water, (5) Petri dish.

(Fig. 6). When the electrode was placed on the surface of the gel (in this case, the electrode distance was 10 mm) and no water was poured into the capillary, elevation of the water level of the cathode was also observed, and the velocity was almost the same as in the case when water was poured. Thus, water undergoes electroosmotic migration from anode to cathode in a crosslinked anionic polymer network.

On the other hand, the movement of ions in an electric field (electrophoresis) also occurs. The velocity of the electrophoretic movement is ordinarily proportional to the electric field strength. This movement of ions is easily demonstrated by applying an electric field to the charged macromolecular solution; for example, 30 V for 15 min to a 1 wt% (0.12 mol/L) aqueous solution of PMAA and by measuring the amount of adsorbed PMAA on each of the electrodes. In this experiment it was found that PMAA adsorbed on the anode ca. 3.3 times larger than on

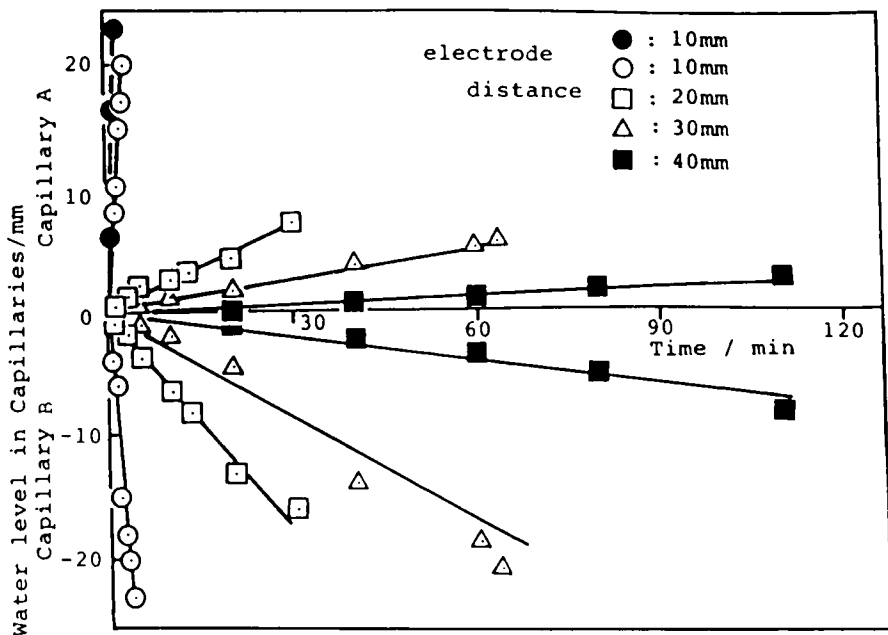


FIG. 6. Time dependences of water level in the measuring capillaries when a dc voltage (30 V) was applied. Electrode distance and current observed: (○) 10 mm, 4 mA; (●) 10 mm (no water was poured in the capillaries), 4 mA; (□) 20 mm, 0.1 mA; (△) 30 mm; 0.03 mA; (■) 40 mm, 0.01 mA. Sample; PAMPS gel.

the cathode and 2 times larger than on the electrode without an electric field.

A qualitative interpretation of the phenomena observed is that the application of an electric field causes a pumping of the mobile ions and the macronetwork ions, and the surrounding hydrated water in the opposite direction until they reach the electrode. As a result, an ion-exchange reaction takes place on the carboxylates and the state of hydration of the particles changes, as mentioned before.

Thus, shrinkage of the gel particle is attributed to a decrease in ionization of the sodium salt of PAA. On the basis of these experimental results, an attempt was made to deduce a mathematical formula expressing the process of collapse of the gel. Several assumptions were made:

- 1) Size change occurs homogeneously and reversibly, i.e., $dV/dt = dl^3/dt$ holds at any time.

- 2) The rate of shrinkage of the gel is dominated by the electrokinetic process, i.e., the electrophoretic transfer of the ionized molecules is the rate-determining step.
- 3) The viscosity of the fluid in the gel (η) is proportional to the concentration of the polymer network C_p , i.e., $\eta = \alpha C_p$.

According to Flory's theory [10], the swelling of a polyelectrolyte gel is associated with the ionization of a polymer gel. If q is the degree of swelling, i.e., the volume ratio of ionized gel swollen in the solvent to that of the dry state, and i is the degree of ionization of the gel, then

$$q^{2/3} = ni + n(1/2 - \chi)V_u/(qv_1) \quad (1)$$

where n is the number of monomer units between two crosslinked points, χ is Flory's interaction parameter between polymer and solvent, and V_u and v_1 are the molar volume of a monomer unit and solvent, respectively.

When q is very large, the second term of Eq. (1) can be neglected since $ni \gg n(1/2 - \chi)V_u/(qv_1)$, and Eq. (1) becomes

$$q^{2/3} = (l^3/L^3)^{2/3} = ni \quad (2)$$

Based on our experimental assumption, both micro- and macroions are consumed by the electrode reaction and their concentration decreases when an electric field is applied to the gel. Therefore, if the moles of ions in the gel at time 0 and t are M_0 and M , respectively, we obtain the following equation under an electric field:

$$\begin{aligned} (l/L)^2 &= nM/M_p \\ &= n(M_0 - \int Idt/F)/M_p \end{aligned} \quad (3)$$

where l is the length of gel at time t , L is the length of dry gel, F is the Faraday constant, and M_p is the moles of monomer units in the gel.

If e is the charge of an electron and r is the effective diameter of solvated ions, the conductivity of the ionized gel σ is expressed as

$$\sigma = Fe(M/l^3)/(6\pi\eta r) \quad (4)$$

and the current I in the gel is associated with the voltage applied U by

$$I = \sigma(S/l)U = \sigma lU \quad (5)$$

where S is the cross-sectional area of the gel. Under the condition of constant voltage U , by differentiating Eq. (3) and combining it with Eqs. (4) and (5), we obtain

$$(dl/dt)/l^2 = -eU/(12\pi\alpha r M_p) \quad (6)$$

$$(1/l) - (1/l_0) = eU/(12\pi\alpha r M_p)t \quad (7)$$

where l_0 is the initial length of the gel. If ρ is the density of polymer gel and M_w is the molecular weight of the monomer unit, $M_p = \rho L^3/M_w = \rho l_0^3/qM_w$, and Eq. (7) becomes

$$(1/l) - (1/l_0) = \omega qEt/l_0^2 \quad (8)$$

where $\omega \equiv eM_w/(12\pi\alpha\rho r)$ and $E = U/l_0$. Generally, $\omega qEt/l_0 \ll 1$, therefore,

$$l = l_0 - \omega qEt \quad (9)$$

and the equation of the rate of contraction of the gel becomes

$$\nu = dl/dt = -\omega qE \quad (10)$$

where ν is the rate of shrinkage.

This is the quantitative expression of the rate of shrinkage of polyelectrolyte gels caused by applying an electric field.

Figure 7 shows the relationship of the rate of shrinkage of gel particles to the electric fields. The linear relationship obtained shows fairly good agreement with the equation derived, indicating that the size change occurred by an electrokinetic process.

4. APPLICATIONS OF CHEMOMECHANICAL DEVICES

(A) Drug Delivery System (DDS) Using Microparticles

When drug molecules are trapped within gel particles which exhibit reversible shrinking and swelling as an electric stimulus is turned on and off, the drug may be switched on and off since the substrate diffusion rate should be altered by the solvent flow caused by contracting stress of the gel and by the change in the crosslinked network density. This stress

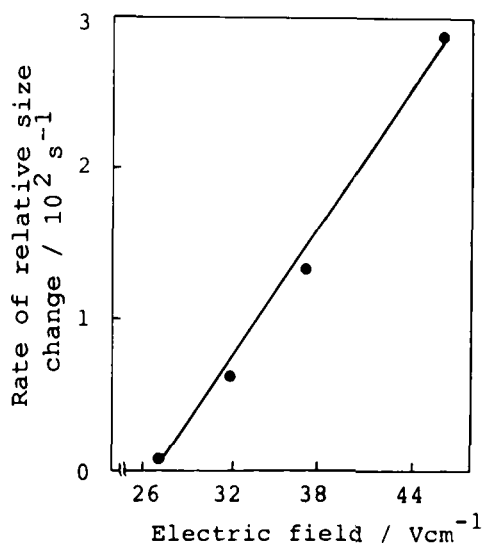


FIG. 7. Dependence of the rate of contraction of the microparticles on the electric field applied. Microparticle diameter: 180 μm .

will also “squeeze” out the swelling fluid containing drug as the gel shrinks [11].

Figures 8(a) and 8(b) shows the changes in concentration of pilocarpine hydrochloride (Pil) released from NaPAA microparticles as a function of time. A rapid and sharp increase in concentration of Pil was observed when the electric field was applied. The rate of Pil release during “on” time was $9.8 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$, which was 5.4-fold greater than the rate during the “off” time ($1.8 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$). The rate of release increased with increasing electric field, and the rate of Pil release at 5.6 V/cm was about 4 times that at 3.3 V/cm. This factor coincides with the ratio of the rate of contraction of microparticles at 5.6 and 3.3 V/cm.

(B) Gel Actuators

A chemomechanical system capable of moving a load up and down automatically and repeatedly is the simplest application of electro-shrinkable gels. The interesting feature was that the rate of contraction of the gel increased with load. The rate of contraction initially decreased from 0.4 to 0.1 cm/h when 50 V was applied to a PMAA gel (60 mm

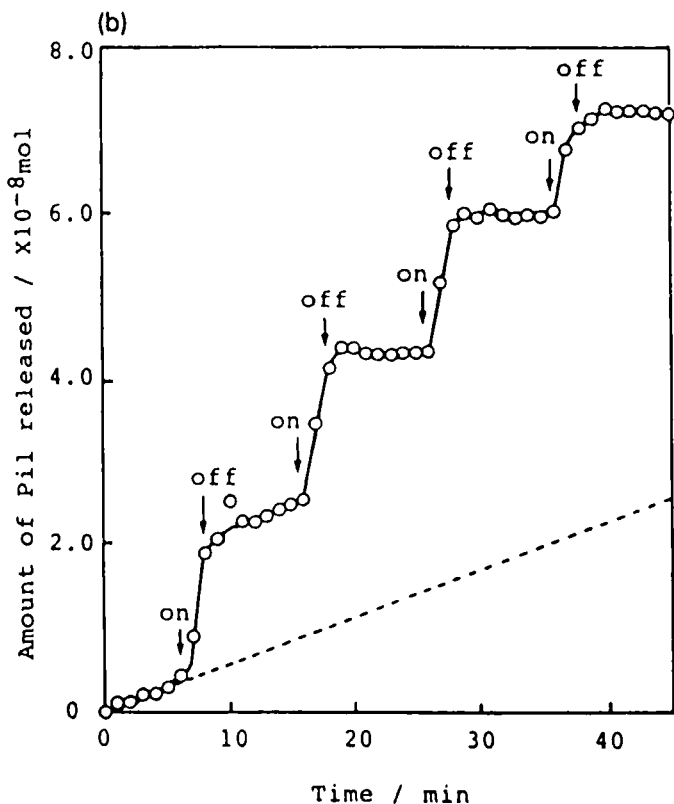
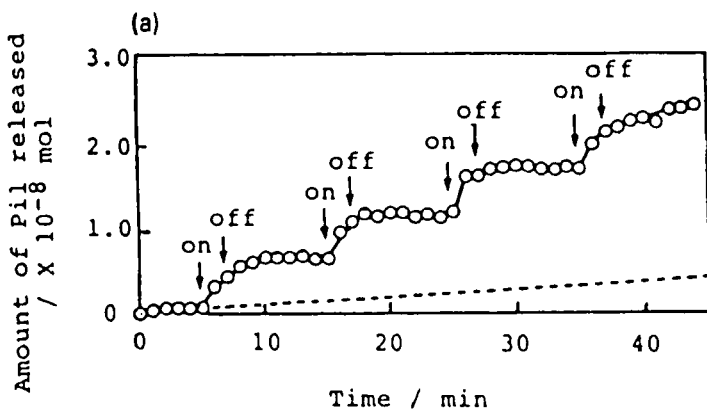


FIG. 8. Time profiles of Pil release from PAA microparticles. Field strength: (a) 3.3 V/cm, (b) 5.6 V/cm; current density: (a) 8.8 $\mu\text{A}/\text{cm}^2$, (b) 25 $\mu\text{A}/\text{cm}^2$; in the presence of 5.1×10^{-4} mol/L of Pil in the external solution. Weight of dry microparticles: 7.4×10^{-5} g; water: 4 mL; amount of Pil entrapped: 2.5×10^{-7} mol. Dashed lines indicate the spontaneous release of Pil without application of dc.

long, 17 mm in diameter) and the load from 0 to 5.5 g, but beyond that the lifting rate increased with increasing load (Fig. 9). Thus, a weight of 22 g was lifted 6 times faster than that of 5.5 g. The efficiency of the work done by the gel with a 22-g load was 24 times larger than that of 5.5 g.

This anomalous lifting behavior of the gel can be explained in terms of a spontaneous ionization of ionizable groups, leading to a spontaneous increase in electric current when the gel is stretched (reverse chemomechanical reaction).

It is known that the dissociation of a weak polyelectrolyte results in a more expanded conformation of a polymer chain. Conversely, the stretching of a macromolecular chain by an applied stress induces an additional ionization. This should also be observed in polyelectrolyte networks. In fact, we observed the ionization of carboxylic groups, i.e., a decrease of pH of the gel when a stress was applied. Figure 10 shows the pH change of PMAA gel when a load of 20 g was applied. A rapid decrease in pH was observed almost simultaneously with loading, fol-

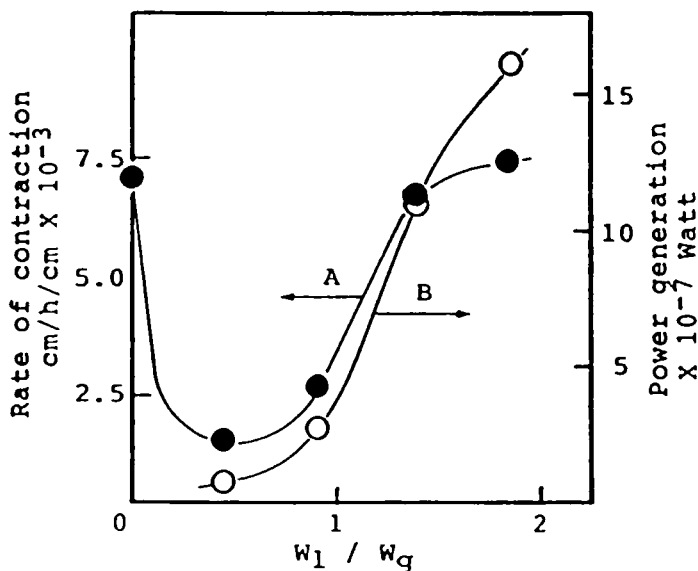


FIG. 9. Rate of contraction (A) and power generated (watts) (B) vs load applied (W_1) per weight and length of PMAA gel sample (W_g). Gel: 60 mm long, 17 mm in diameter, wet weight 12 g; electric field: 50 V dc.

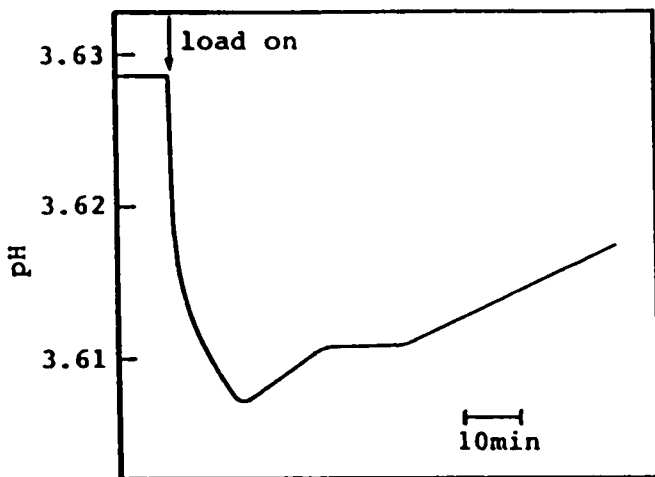


FIG. 10. pH profile of the PMAA gel sample under a tensile stress of 20 g. Sample dimensions: length, 100 mm; diameter, 17 mm; wet weight, 20 g.

lowed by a gradual recovery to the initial pH value. The decrease in pH corresponded to an increase in the degree of ionization from $2.03 \times 10^{-4}\%$ to $2.13 \times 10^{-4}\%$. The gradual recovery of pH with time may be associated with relaxation of the water-swollen and highly elastic network. This assumption was further supported by contractile experiment of the gel under isotonic conditions. The experiment was carried out by using a gel with different degrees of swelling, and it was found that a PMAA gel that stretched more showed a faster lifting.

Thus, the increased efficiency of a PMAA gel is due to additional ionization produced by stretching of the polyelectrolyte network, which as a result enhanced the electric current. This anomalous behavior may well provide the basis for an automatic or inherent control sensor which spontaneously adjusts the energy absorbed by a synthetic muscle system to that required to do the work, i.e., a heavier load absorbs more energy without external stimulus. In this respect, it is similar to mechanical devices with a sensor feedback control system. One can speculate about similarity to a biological muscle system where the force applied to accomplish work is proportional to that required.

Various types of actuators, such as gel-looper, oaring boat, gel-pendulum, gel-plotter, and others, using an electro-driven chemomechanical gel were recently created. For example, a gel-looper made of cross-

linked PMAA, was hung over an unsymmetrically notched plastic bar and placed in a tank filled with a 5-mM aqueous solution of sodium sulfate. A constant voltage was applied from two carbon electrodes (150 mm long) placed at the upper and lower sides of the gel-looper and the polarity changed at 1.4-min interval. The PMAA stretched when the upper electrode was the anode and moved the "head" forward. When the polarity of the electrode was changed, the gel-looper hooked the tail. Thus, the gel-looper moves 150 mm in 10 min by alternatively repeating stretching and bending.

5. EXPERIMENTAL

(A) Materials

The sodium salt of poly(acrylic acid) (Na-PAA) microparticles was prepared by the inverse emulsion polymerization of a solution of 136 mmol of the sodium salt of acrylic acid and 0.065 mmol of *N,N*-methylenebis(acrylamide) (MBAA) in 68.5 cm³ of cyclohexane in the presence of 0.48 g Span 80 (sorbitan mono-oleate). The suspension was stirred with a velocity of 180–200 rpm under a nitrogen atmosphere, and the polymerization was carried out at 60°C for 6 h. Potassium persulfate (0.03 g) was used as the radical initiator. Following polymerization, the microparticles were washed in MeOH and equilibrated in distilled water for 1 day. The microparticles were spherical, and the diameter of the swollen samples in distilled water was between 150 and 300 μm.

Entrapment of pilocarpine hydrochloride (Pil) was carried out by immersing the dry NaPAA microparticles in the Pil solution. The release test of Pil was carried out as follows: The microparticles containing Pil were placed in a quartz cell containing 4 mL water. With the aid of two carbon electrodes, a constant voltage was applied from a dc source. The solute concentration in the water was monitored spectrophotometrically by measuring the change in absorption at 510 nm as a function of time.

Crosslinked water-swollen gels of poly(2-acrylamido-2-methylpropane-sulfonic acid) (PAMPS) were prepared by radical polymerization of a 5.0-mol% aqueous solution of the corresponding monomers in the presence of 5×10^{-2} mol% MBAA. In a similar manner, a crosslinked poly(methacrylic acid) (PMAA) gel used for the gel-looper was prepared by polymerizing a 3.0-mol/L aqueous solution of MAA in the presence of 5.0×10^{-3} mol% MBAA.

(B) Measurements

A microparticle was placed between a pair of parallel Pt-wire electrodes 11 mm apart, and the space was filled with 107 cm³ of distilled water. A dc voltage ranging from 0 to 4 V was applied across the electrodes. The migration velocity of the microparticle was measured with an optical microscope.

An experiment on electroosmosis was carried out with two measuring vertical capillaries, and the apparatus used is shown in Fig. 5. A disk-shaped PAMPS gel, 80 mm in diameter and 20 mm thick, was placed in a Petri dish and partly immersed in water. Two glass capillaries with 2 mm inner diameters were stood in parallel on the top of the gel at a distance of 10 mm. Water was then poured into both capillaries and a pair of Pt wire electrodes was placed in each of them. The distance of the electrodes was controlled by changing the position of the electrode in water. A dc voltage (30 V) was applied, and the positions of the liquid levels in the measuring capillaries were determined with time by using a cathetometer.

Experiments in load lifting through the application of an electric field were carried out by using a PMAA gel 60 mm long and 17 mm in diameter. The change in length of the PMAA gel was measured by using a cathetometer. The pH change in the PMAA gel was measured by inserting a microcombination pH probe (MI-410) when a 20-g load was applied.

REFERENCES AND NOTES

- [1] We prefer the terms "chemomechanical reaction" and "chemomechanical system" instead of "mechanochemical" proposed by A. Kachalsky because they are more precise and avoid confusion with other terminology. Note that mechanochemical reaction often refers to a chemical reaction induced by mechanical stress fracture to give radicals and a crosslinked formation.
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