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ELECTRICALLY ACTIVATED MECHANOCHEMICAL DEVICES USING POLYELECTROLYTE GELS

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We report the first model of electrically activated mechanochemical system made of polyelectrolyte gels which contracts, oscillates, and bends reversibly. On the basis of this principle a variety of devices which function under electric stimulus, i.e., a "chemical valve" membrane expanding and contracting the pore size, a switching oscillating 15 to 100 times per minute, and a composite bending like "bimetal" were developed.

A.Katchalsky and his school have developed several types of mechanochemical engine which is actuated by a collagen fiber in the form of a loop, a portion of which is wrapped around a pair of pulley or spindles.$^{1-3)}$ We have developed a "chemical valve" membrane mechanochemically expanding and contracting its micropores and permeates selectively macromolecular and molecular solutes according to their molecular size.$^{4-6)}$ We report here the first model of electrically activated artificial muscle system which contracts by the electric stimulus under isothermal condition. A method of electrical control which is being developed in this article makes use of the water-swollen crosslinked polyelectrolyte gels.

A polymer gel$^{7)}$ was inserted between a pair of parallel plate carbon electrodes connected to a DC source (Fig. 1). When the electricity was turned on, the polymer gel started to shrink releasing water droplet one after another. For example, a water swollen poly(2-acrylamido-2-methyl-1-propanesulfonic acid;AMPS) gel(12 mm wide, 19 mm long, 30 mm high, 5.6 g weight, 1 g dry poly(AMPS) adsorbed 2250 g water), reduced in weight as large as 70% of its original weight due to loss of water when 6.3 V/cm electric field or 0.7 mA/cm^2 DC current was imposed for 20 min(Fig. 1). The minimum value of electric field to induce contraction of the gel was 1.6 V/cm and the rate of water release increased with increasing electric field An addition of NaCl(0.1 mol /l or less) also increased the rate of water release whereas the presence of organic solvent, such as ethanol or acetone, decreased both the rate and the extent of the contraction as shown in Fig. 1. The rate of water release of poly(AMPS) gel in 50 and 100% ethanol was only 38 and 17% of that in water, respectively. No contraction was observed at all when an AC field was applied at 10 V/cm in the range between 6 Hz and 5 kHz. Gels prepared from polymers and copolymers that contain ionizable group, for examples:poly(methacrylic acid),

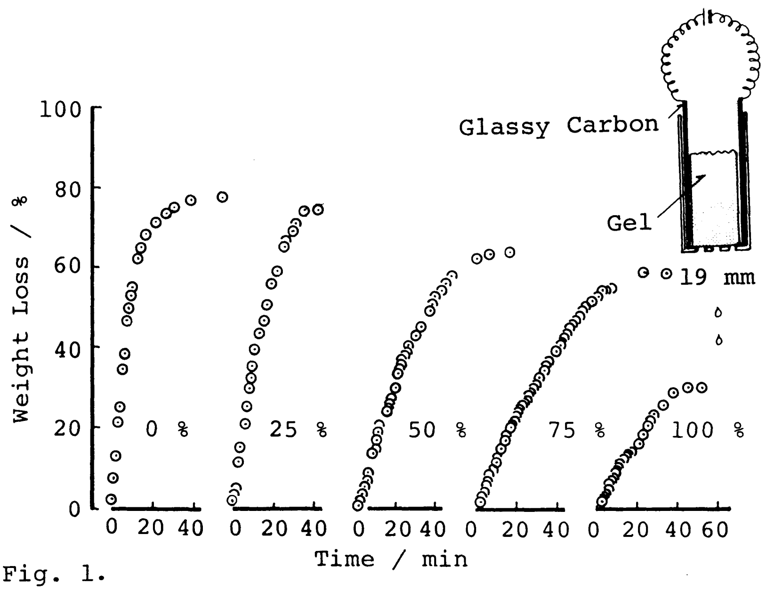

Fig. 1.

Apparatus for the electro-activated mechanochemical system and time profile of weight change of the gel equilibrated in water-ethanol mixture.

gel: poly(2-acrylamido-2-methyl-1-propanesulfonic acid), electric field: 6.3 V/cm, Degree of swelling of the gel used decreased from 2250 times in water to 1000 times in ethanol. Figures denote volume % of ethanol.

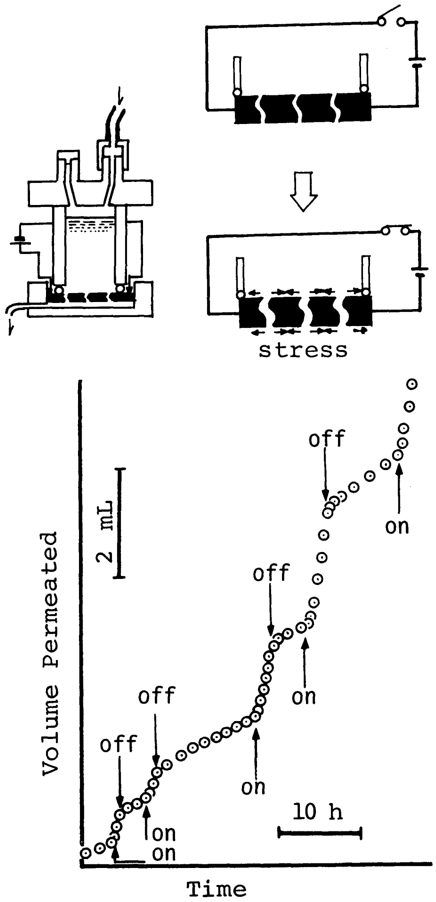

Fig. 2.

Apparatus for the electroactivated "chemical valve" membrane and change in water permeability by alternative "on" and "off" of electric field. electric field: 2.6 V/cm. Membrane was prepared by the polymerization of AMPS in the presence of porous (average pore size 8 µm) poly(vinyl alcohol) sheet.

partially-hydrolyzed poly(acrylamide), poly(styrene sulfonic acid), quarternized poly(4-vinyl pyridinium chloride), poly(vinylbenzyltrimethyl ammonium chloride), exhibited marked contraction.

Gels from proteins such as gelatine, collagen and sugars such as alginic acid and its salts, ager-ager, and gum arabic also contracted under electric stimulus. At that time, a migration of the gel to the counter electrode was observed, i.e., a negatively-charged polymer gel migrated to the anode and, consequently, the volume of the gel near anode swelled slightly. In this case, water droplet preferentially dripped near the cathode. Polymer gels containing no ionizable moieties such as poly(2-hydroxyethyl methacrylate;HEMA), poly(acrylamide), poly(vinyl alcohol), and starch showed no contraction at all.

The phenomenon of contraction of gels and the concomitant of water is rather simple and unique. Tanaka[8,9] described in his paper that a phase transition occurs to suddenly collapse the gel when an electric field was applied across the partially hydrolyzed poly(acrylamide)gel in 50% mixture of acetone and water. The behavior that we observed seems to be different from that observed by Tanaka, since the contraction of our gel is not induced by a phase transition. Similar to the poly(AMPS) gel described previously, the gel from partially hydrolyzed poly-

(acrylamide) gel shrinked most significantly and most rapidly in water while increasing the acetone content resulted in a gradual decreases in the rate and extent of contraction. Increasing the electric field leads to a corresponding increase in contraction, but no critical electric field which induce sudden substantial shrinkage as described by Tanaka was observed. We tentatively believe that the contraction resulted from the electrostatic interaction between charged macromolecules and the electrode leads extensive desolvation(dehydration) of the gel. Under an applied electric field, the charged polymer network migrates electrophoretically to the counter-electrode and is adsorbed to the electrode surface loosing the hydration power at the same time due to the neutralization of the net electrostatic potentials of the macro-charges.

A variety of potential applications can be depicted using this kind of electrically activated mechanochemical gels. Figure 2 is the schematic diagram for electrically-activated "chemical valve" membrane[10)] which reversibly expands and contracts the pore-size by the electric stimulus. When the mechanochemical contraction described is developed isometrically, i.e., keeping the membrane dimensions constant, the contractile stress appearing in the membrane should expand the pore channels through which water may permeate.[4)] Figure 2 shows the effect of a mechanochemical contraction of the poly(AMPS) membrane on the water permeation when 6.5 V DC was alternatively imposed through platinum wire electrodes. It is seen that the "chemical valve" membrane could increase and decrease the water permeability repeatedly by electric stimulus. This type of electrically-activated "chemical valve" membrane exhibited long term stability and could work continuously for more than one month.

We have found that metal-polymer gel-metal structures, made of a water swollen polymer gel sandwiched between two platinum wire electrodes, have the property to switch reversibly between two stable states, one characterized by high impedance corresponding "off" state, and the other one by a low impedance corresponding "on" state. The "off" and "on" states are performed by reversible shrinking and expanding of the gel driven by electric stimulus. Figure 3 shows schematics for the dynamic oscillation or switching device. The amplitude of voltage at "on" and "off" states was more than 10^3 times and the structure was reproducible which could be switched from 300 to 2000 times within 20 min(Fig. 3). The frequency of the switching and shape of the signal depended on the electric field

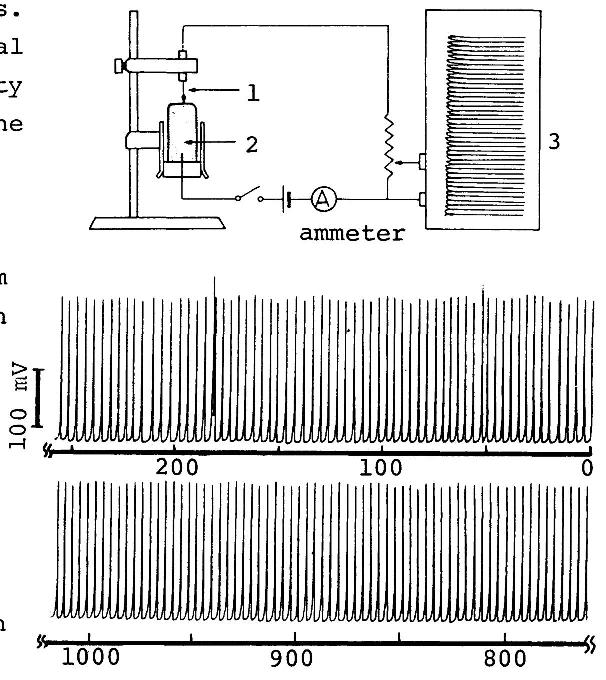

Fig. 3. Circuit for the display of dynamic oscillation and its characteristics. 1: gel, 2: platinum wire electrode, 3: amplifier and recorder.
gel: poly(AMPS-co-HEMA), 12 mm diameter, 10 mm long, degree of swelling: 45 times electric field: 1.4 V/cm.

imposed as well as on the degree of swelling of the gel. The higher electric field resulted in the higher frequency. The higher frequency was also obtained from the gel of high swellability. Switching and memory phenomena have been observed originally in the films of certain metal oxides and afterwards in amorphous semiconductors, but until now, to our knowledge, these phenomena have not been observed in water-containing organic materials.

We also constructed polymeric device which functions as "bimetal" or "piezoelectric" material from gel-plastic laminated structure(Fig.4) The contractile force developed in the gel by an electric stimulus through a pair of platinum wire electrodes could bend the "nonshrinkable" poly(vinyl chloride) tube.$^{11)}$ The composite device consisting of crosslinked poly(methacrylic acid) (degree of swelling; 3 times) and poly(vinyl chloride) tube as illustrated in Fig. 4 bent as large as 20° after ca. 30 min. It recovered the original straight form by dipping in water.

The mechanochemical devices described may have a variety of potential applications such as pH-sensitive electrodes, sensor, actuator and others.

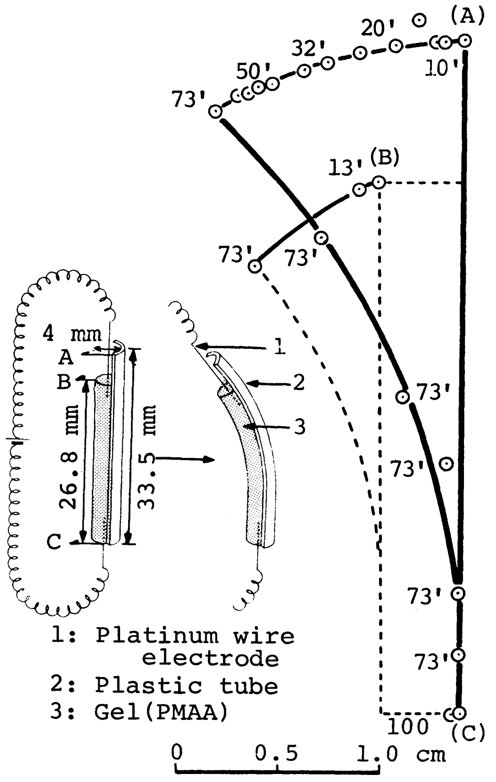

Fig. 4.
Schematic illustration of polymer composite functioning as "bimetal" and the profile of its "bending". gel: poly(methacrylic acid), electric field: 0.25 V/cm, Figures indicate time(min) after electric field was imposed.

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