Electroconductive Organogel. 4. Electrodriven Chemomechanical Behaviors of Charge-Transfer Complex Gel in Organic Solvent

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ABSTRACT: The effect of 7,7,8,8-tetracyanoquinodimethane (TCNQ) doping on the electroconductivity of cross-linked poly[*N*-[3-(dimethylamino)propyl]acrylamide] (PDMAPAA) gel, swollen in *N*,*N*-dimethylformamide (DMF), was investigated. The gel showed ionic conductivity as high as 10^{-4} S cm^{-1} by TCNQ doping due to the formation of an ionic species of the charge-transfer (CT) complex between PDMAPAA gel and TCNQ. It was found that this type of CT gel undergoes rapid contraction by applying dc voltage, and the rate as well as the efficiency of the organogel much exceeded those of hydrogel. The mechanism of such an electrodriven chemomechanical contraction was explained in terms of an electrokinetic process, and the simple mathematical model of the contraction was postulated.

Introduction

In a previous paper from our laboratory we reported a new class of electroconductive organogels swollen in a nonvolatile organic solvent: dimethylformamide (DMF).[1,2] These gels are composed of an electron-donating polymer network: cross-linked poly[*N*-[3-(dimethylamino)propyl]-acrylamide] (PDMAPAA) and a low molecular electron acceptor: 7,7,8,8-tetracyanoquinodimethane (TCNQ), subsequently doped to the polymer network in DMF. The PDMAPAA gel showed extensive swelling and exhibited a green color when TCNQ was doped. The spectrophotometric and kinetic studies revealed that swelling and coloration are due to the formation of various kinds of ionic species formed by a CT complex between a polymeric network and TCNQ.

We have also found that this class of organogels, for example, PDMAPAA gel doped with 2,3,9,10,16,17,23,-24-phthalocyanineoctacarbonitrile (octacyanophthalocyanine, OCPc), as an electron acceptor undergoes electrophoretic migration toward the anode to give a two-dimensional orientation in the gel.[2] The polymer gel thus obtained as well as the dried one showed anisotropic electroconductivity as large as 3 orders of magnitude. It was also found that repetitive oscillations occurred in TCNQ–PDMAPAA gel when dc voltage was applied.[3] The nature of the oscillation varied with the change in degree of cross-linking, doping ratio of acceptor molecule, and temperature; an increase of these parameters enhanced both the amplitude and the frequency of the oscillation.

Thus, it is interesting to study the electrical and electrochemical behaviors of organogels and clarify the nature of organogel by comparison with corresponding solutions. The aim of this paper is to investigate the electrical conductivity of TCNQ–PDMAPAA gel and study the chemomechanical behaviors of the gels. It was found that TCNQ–PDMAPAA gel has the conductivity as high as 10^{-4} S/cm. The value is slightly lower than for the corresponding polymer solution, but higher than for the DMF solution of fully ionizable salt, tetra-*n*-butylammonium perchlorate (TBAPC). A study of the electrodriven chemomechanical contraction of the organogel was also made. It was found that the organogel undergoes contraction by applying an electric field, and the rate of contraction and the efficiency of the contraction were much higher than that of hydrogel.

Experimental Section

Material. *N*-[3-(Dimethylamino)propyl]acrylamide (DMAPAA) (from Kohjin Co., Ltd.), used as a monomer, *N*,*N'*-methylenebis(acrylamide) (MBAA) (from Tokyo Kasei Kogyo Co., Ltd.), used as a cross-linking agent, and azobis(isobutyronitrile) (AIBN) (from Tokyo Kasei Kogyo Co., Ltd.), used as an initiator, were purified in a manner described in the previous paper.[1] 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was the gift of Osaka Organic Chemical Industry, Ltd., and was recrystallized at 60 °C in acetonitrile. Dimethylformamide (DMF) (from Kanto Chemical Co.) was purified by vacuum distillation after standing overnight in KOH and CaO. Tetra-*n*-butylammonium perchlorate (TBAPC) (Tokyo Kasei Co., Ltd.) was recrystallized at 60 °C in a 1:1 mixture of ethyl acetate and hexane.

2-Acrylamido-2-methylpropanesulfonic acid (AMPS) (Nitto Chem. Co., Ltd.) was purified by repeated recrystallization. 2-Hydroxyethyl methacrylate (HEMA) was distilled prior to use under vacuum.

Preparation of the Gel. A cross-linked PDMAPAA gel was prepared by the same procedure described in the previous paper.[1] After polymerization, the product was cut in the form of a cylinder and immersed in a large amount of DMF until it reached an equilibrated size. Usually, it takes one week or more. During this procedure, DMF was repeatedly changed to remove the unreacted monomer and other chemicals.

Doping of TCNQ was done by immersing PDMAPAA gel into a large amount of the DMF solution of TCNQ.

Poly(AMPS-*co*-HEMA) gel (AMPS:HEMA, 1:1) was prepared by plasma-initiated polymerization[4] of 5.0 mol % aqueous solutions of monomers.

Measurement. The degree of swelling, q, was calculated by measuring the diameters of equilibrated and original dry gels:

$$q = V/V_0 = (D/D_0)^3$$

where D, V and D_0, V_0 are the diameter and volume of equilibrated and original gels, respectively. The diameter of the gel was measured by a microscope with a calibrated scale.

The electronic spectra were measured using a Hitachi 320 spectrophotometer under nitrogen atmosphere.

Conductivity of the gel (10 × 10 × 10 mm cubic) was measured with a pair of platinum plate electrodes (10 × 10 mm) facing in parallel with 10-mm distance using a conductometric meter (CM-30, Shimadzu Ltd.). Conductivities of solutions were measured with a pair of platinum-black plate electrodes using a conductometric meter. All measurements were made in N_2 atmosphere at room temperature. We have studied the possibility of gas evolution accompanying the electrode reaction by using a microgasmeter within 0.1-μL accuracy and confirmed that no gas was produced at all when dc voltage up to 30 V/cm was applied to the gels or a DMF solution of TCNQ.[3]

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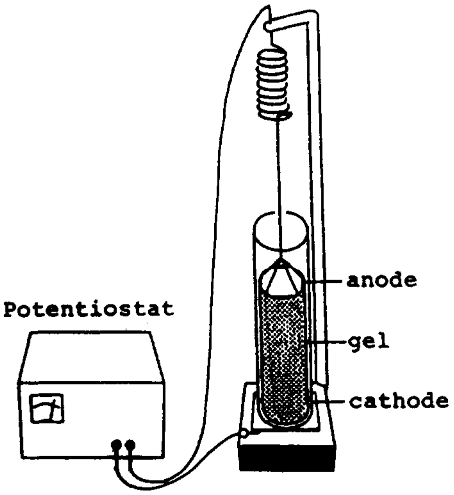

Figure 1. Apparatus for measurement of the contractile behavior of the gel under electric field. Gel: cylindrical, 10-mm long, 4 mm in diameter. Electrode: platinum plate; upper, 3.6 mm in diameter, lower, 10 × 10 mm.

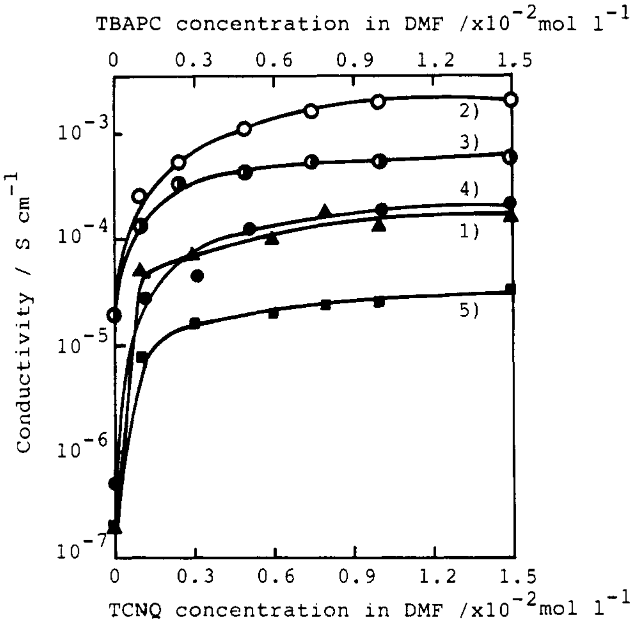

Figure 2. Effects of TCNQ (1–4) or TBAPC (5) on the conductivity of DMF. (1) DMF; (2) DMAPAA in DMF (10^{-2} mol/L); (3) PDMAPAA in DMF (10^{-2} mol/L); (4) PDMAPAA gel, degree of swelling (before doping), 410; (5) TBAPC in DMF (10^{-2} mol/L).

The configuration of the apparatus used in the measurement of the contraction of the gel is shown in Figure 1. A piece of solvent-swollen cylindrical polymer gel, 10-mm long and 4 mm in diameter, was placed in a glass tube. With the aid of two platinum plate electrodes, an electric field was applied across the gel from a dc power source. The change in length of the gel under the electric field was measured using a cathetometer with a calibrated scale. The electric field was simply calculated by dividing the voltage, U, by the distance of the two electrodes, assuming that the gel specimen is uniform.

Results and Discussion

(a) Electric Conductivity of the Gel. Figure 2 shows the concentration dependences of TCNQ on the electric conductivity of DMF solution of DMAPAA (curve 2) and PDMAPAA (curve 3). It is seen that the electric conductivity of both solutions increases rapidly by addition of a small amount of TCNQ and then saturates. DMAPAA exhibits to some extent a higher conductivity than PDMAPAA. The increased conductivity is obviously due to the formation of an ionic species of the charge-transfer (CT) complex of TCNQ with DMAPAA or with PDMAPAA. According to the literature[5,6] and experimental results in our previous paper, TCNQ forms a CT complex with DMAPAA or PDMAPAA to give fully ionized PDMAPAAH$^+$, TCNQ$^{\bullet-}$ in a polar solvent like DMF. The source of the ammonium proton is most probably derived from amine through vinylamine intermediates together with the reduction product.[6] Formation of TCNQ^{2-} may also be possible as follows:

$$\mathrm{TCNQ} + 2\mathrm{PDMAPAAH} \rightarrow \mathrm{TCNQH_2} + \text{modified polymer}$$

$$\mathrm{TCNQH_2} + 2\mathrm{PDMAPAA} \rightarrow \mathrm{TCNQ^{2-}} + 2\mathrm{PDMAPAAH^+}$$

The electric conductivity of the TCNQ–PDMAPAA gel is also shown in Figure 2 (curve 4). In general, the measurement of electrical conductivity of a solvent-swollen polymer gel has a technical difficulty associated with a contact of the gel with electrodes, and so far as we know, there has been no report describing the electric conductivity of a polymer gel in detail. In fact, difficulty arose in slicing the gel smoothly and evenly to make perfect contact with electrodes. In addition we used polished platinum plate electrodes instead of platinum-black electrodes. Therefore, we are afraid that the values of the conductivity of the gel obtained may be to some extent lower than the actual value.

Nevertheless, the results of measurement showed the conductivity as high as 10^{-4} S/cm, as shown in Figure 2, and these values were slightly lower than those of the TCNQ–PDMAPAA solution. If molar conductivity of DMF solutions of TCNQ–DMAPAA, TCNQ–PDMAPAA, and TCNQ–PDMAPAA gel are plotted against the square root of TCNQ concentration, one can get an almost linear concentration dependence, which indicates that the complexes of these cases are strong electrolytes and fully ionized to give the corresponding cation and anion radicals (Figure 3a). This is in good agreement with our previous result[1,2] which demonstrated by using Flory's swelling equation that PDMAPAA gel is fully ionized in DMF to give TCNQ$^{\bullet-}$, TCNQ^{2-}, PDMAPAAH$^+$.

Therefore, these ions behave as the carriers of ionic electroconduction of the gel. The lower conductivity of the TCNQ–PDMAPAA solution or gel than that of the TCNQ–DMAPAA solution could be attributed to lower mobility of the polymeric cation PDMAPAAH$^+$ than that of DMAPAAH$^+$, since the mobility of macromolecular ions is usually much smaller than that of the corresponding low molecular weight ions.

Note that the conductivity of the DMF solution of TCNQ is nearly 10 times higher than that of tetrabutylammonium perchlorate (TBAPC) (Figure 2, curve 5). As noted before, DMAPAA and PDMAPAA exist as protonated cations in the presence of TCNQ. Therefore, it would be more suitable to compare their conductivities with the protonated ammonium ions with a planar polarizable anion. However, it may be interesting to compare the profile of concentration dependence of TCNQ and TBAPC to understand the conductivity behavior of these ions in DMF.

A plot of the molar conductivities of the DMF solution of TCNQ or TBAPC against the square root of TCNQ or TBAPC concentration was also made and is shown in Figure 3b. It is seen that the molar conductivity increases very rapidly with a decrease in TCNQ concentration. This result indicates that TCNQ behaves as a weak electrolyte

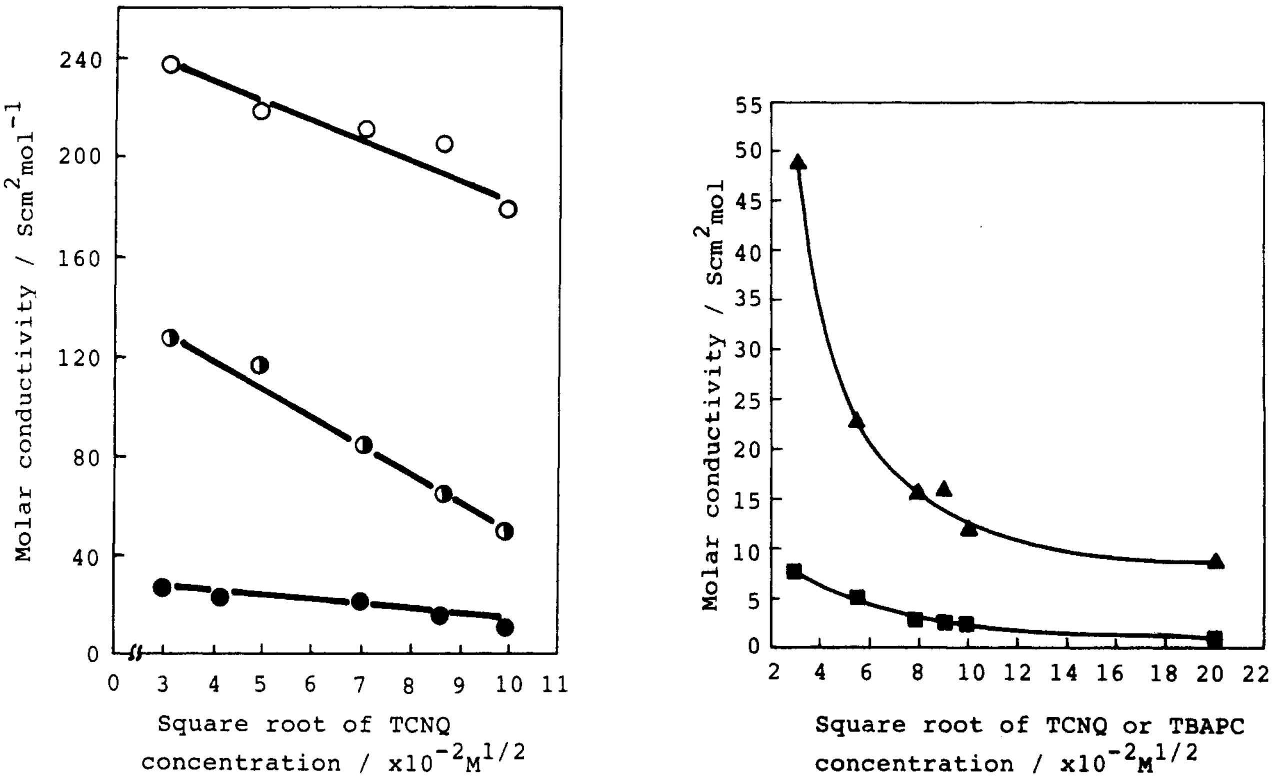

Figure 3. (a, left) Plot of the molar conductivity against the square root of TCNQ concentration. DMF solutions of (○) TCNQ–DMAPAA, (◑) TCNQ–PDMAPAA, and TCNQ–PDMAPAA gel (●); [DMAPAA] = [PDMAPAA] = 10^{-2} mol/L. (b, right) Plot of the molar conductivity against the square root of TCNQ (▲) or TBAPC (■) concentration in DMF.

in DMF and that a decrease in TCNQ concentration enhances the dissociation to give corresponding free ions. This result also coincides with the fact that DMF behaves as a weak electron donor.[1]

Contrastly, the molar conductivity of the TBAPC solution showed a very low and almost linear concentration dependence, even though TBAPC is a strong electrolyte. Thus, the carrier concentration of TBAPC should be higher than that of TCNQ in DMF. Nevertheless, the TCNQ solution exhibited a higher conductivity than TBAPC, and this might be attributed to the higher mobility of carrier ions of TCNQ than that of TBAPC since the electric conductivity is expressed as the product of carrier concentration and ionic mobility.

(b) Contractile Behaviors of the Gel. It is known that a polyelectrolyte gel undergoes contraction when an electric field is applied,[7,8] and this phenomenon was associated with an electrokinetic process.[9] We have found that the electroconductive TCNQ–PDMAPAA gel showed significant and rapid contraction by applying an electric field. When the electric field was applied by using the apparatus shown in Figure 1, the gel contracted from the cathode and spread throughout the whole area of the gel. While contraction occurs, DMF is released near from the anode. No gas evolution occurred at both electrodes throughout the whole period of the experiment of contraction.

Figure 4 shows time dependence of size changes of the gel (doping ratio: 0.2) for various dc voltages, U. It is seen that the rate of contraction, v, increased with an increase in the voltage, and if v is plotted against electric field E ($E = U/L$), one can get a straight line, indicating that v is proportional to E as shown in Figure 5. This electric field dependence of v is the same as obtained for hydrogels.[10,11]

The effect of charge density on v was also studied by varying the doping ratios of the gel r. As seen in Figure 5, the rate of contraction was quite insignificant if $r = 0.1$ or less. The small v value in this range is obviously due to the low conductivity of the gel as seen in Figure 2. However, when r becomes higher, rapid contraction occurred, and in the range of $r = 0.1$–0.5, r increased with increase in v. Thus, the electric contraction of the gel can be associated with the charge density of the gel.

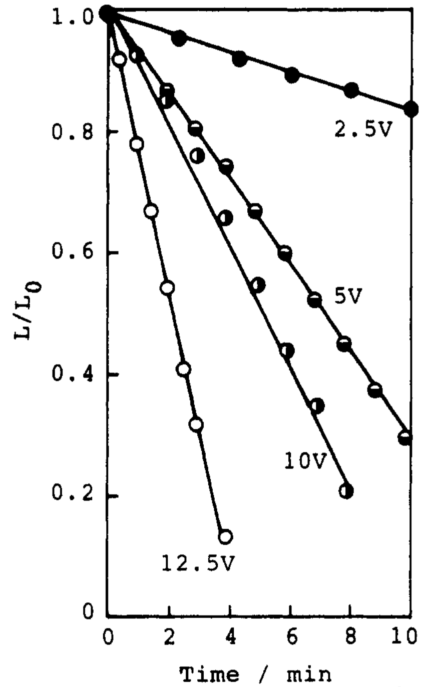

Figure 4. Time profiles of the size change of TCNQ–PDMAPAA gel under various electric fields. Degree of cross-linking, 0.2 mol %; doping ratio (r), 0.2.

The effect of electric contraction on the degree of cross-linking (f) was also studied using polymer gels with various

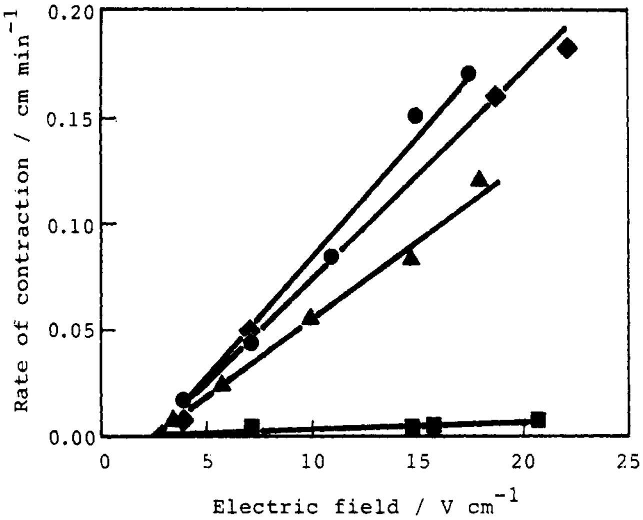

Figure 5. Dependence of the rate of contraction on the electric field. Degree of cross-linking, 0.2 mol %; doping ratio r (■) 0.05, (▲) 0.2, (◆) 0.3, (●) 0.5.

cross-linking ratios. As shown in Figure 6a, the increase in cross-linkage rapidly decreased the rate of contraction.

It should be noted that when a dc electric field was applied, the color of the gel near the cathode changed from green to transparent and moved through the whole area of the gel. This result indicates that the TCNQ$^{\bullet-}$ anion radical undergoes electrophoretic migration from the cathode to the anode under the electric field and oxidized to give neutral TCNQ. Therefore, the contraction and the release of DMF should apparently be associated with the electrokinetic behaviors.

In order to investigate the reaction occurring at the electrodes, spectrophotometric analysis of the chemical species of the DMF solution released from anode was made, and the result is shown in Figure 7. A very strong peak with a maximum at 394 nm due to neutral TCNQ (Figure 7c) is observed, and no absorption in the range of 700–900 nm characteristic of the CT complex (see Figure 7b)[1,2] was observed. This result indicates that the highly solvated TCNQ$^{\bullet-}$ has been oxidized, and after reaching the anode, has formed neutral TCNQ and consequently liberated DMF from the gel. PDMAPAAH$^+$ is reduced at the cathode to give the corresponding PDMAPAA. Thus, the overall reaction at both electrodes may be expressed as follows:

$$\mathrm{TCNQ}^{\bullet-} \rightleftharpoons \mathrm{TCNQ} + e^- \tag{1a}$$

$$\underset{\text{(modified polymer)}}{\mathrm{PDMAPAAH}^+} + e^- \rightleftharpoons \mathrm{PDMAPAA} \tag{1b}$$

We have several other experimental facts supporting an interpretation that the chemomechanical behaviors observed are essentially electrokinetic phenomenon. They are (1) no contraction for neutral (noncharged) PDMAPAA gel in DMF, (2) preferential contraction in the region of the cathode and no contraction in the anode area, (3) contraction rate proportional to electric field applied, and (4) the direct observation of the migration of TCNQ$^{\bullet-}$ toward the anode due to electrophoresis.

A qualitative interpretation of the process is that the application of the electric field causes electrophoretic migration of the positively charged polymer network toward the cathode and the negatively charged counterions (TCNQ$^{\bullet-}$) and surrounding DMF molecules to the anode. Here, electroosmotic travel of DMF may additionally help the transport of solvent molecules to the anode. As a result, the redox reaction takes place on both electrodes and the carrier ions in the gel lose their charges and liberate DMF. The contraction of the gel, therefore, can be associated with the decrease of charges.

In order to compare the contractile behaviors between an organogel and a hydrogel, an electrodriven contraction experiment was carried out using a hydrogel having the same swelling ratio as the TCNQ–PDMAPAA gel. Poly(AMPS-*co*-HEMA) gel was used because of its largest contraction rate among the hydrogels measured. As showing in Figure 8, the organogel showed very rapid contraction and completed more than 95% shrinkage of its initial length in 4 min, while the hydrogel contracted much more slowly and completed only 35% contraction in the same time. In addition, the hydrogel showed an

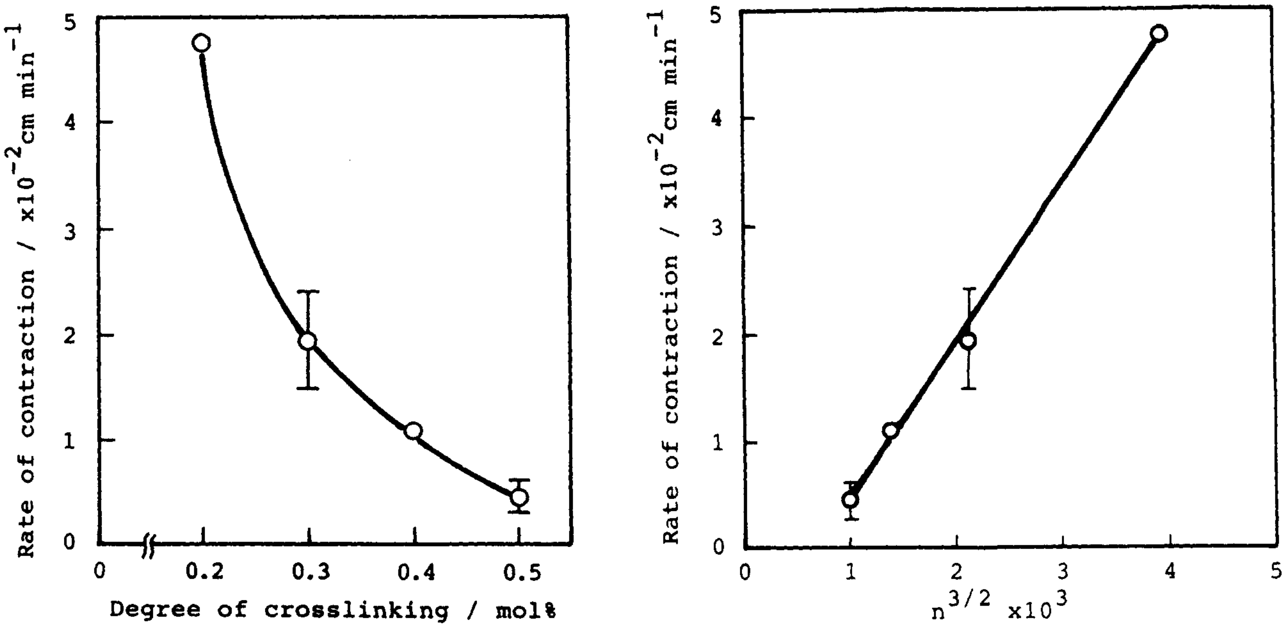

Figure 6. (a, left) Dependence of the rate of contraction on the degree of cross-linking (f): $r = 0.5$, $E = 7$ V/cm. (b, right) Dependence of the rate of contraction on the number of segments between two cross-linking points.

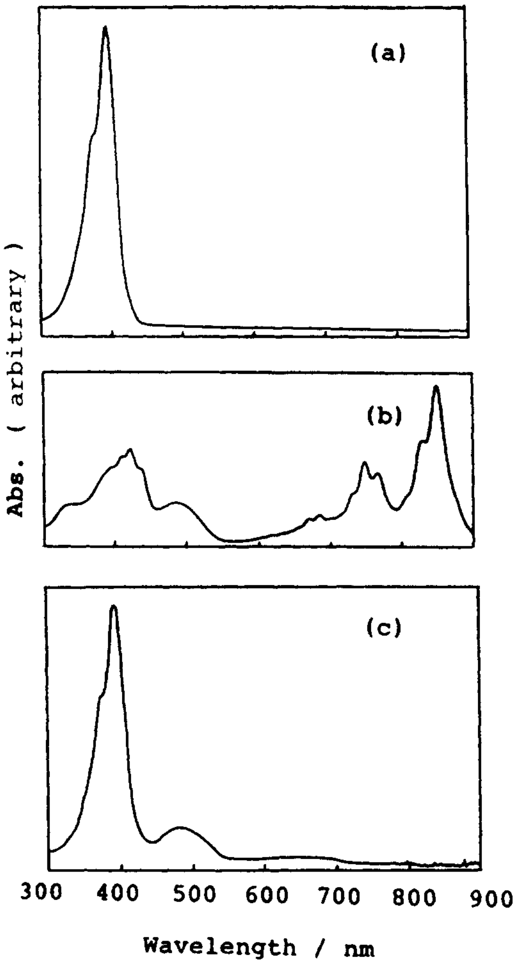

Figure 7. Electronic spectra of a DMF solution of (a) TCNQ; (b) TCNQ-PDMAPAA equimolar mixture; and (c) liquid released from the gel concomitant with the contraction of the gel.

extensive gas evolution due to water hydrolysis throughout experimental period.

If the electric energy consumed during the experiment is plotted against the size change of the gel, we obtain Figure 9 which indicates that the electrochemical energy consumed for the chemomechanical contraction of the organogel is much less than that consumed for the hydrogel.

These results demonstrate that the electroconductive organogel is able to convert electric energy more efficiently into mechanical energy than the hydrogel. The reason is partly attributed to the enhanced stability of DMF which is not sustained electrochemical decomposition.

(c) Mechanism of Contraction. As described in the preceding section, the contraction of the gel described is attributed to a decrease in the charges of the gel. On the basis of this contraction mechanism, an attempt to deduce a mathematical formula expressing the collapse of the gel was made.

Several assumptions were made; they are as follows: (1) Size change occurs only in the direction of the electric field and $dV/dt = d(SL)/dt = S\,dL/dt$ holds at any time, where S is the cross-sectional area and L is the length of the gel. (2) The rate of shrinkage of the gel is dominated by the electrokinetic process, i.e., by the electrophoretic transfer of the ionized molecules. (3) The viscosity of the fluid in the gel, η, is proportional to the concentration of the polymer network C_p, i.e., $\eta = \alpha C_p$.

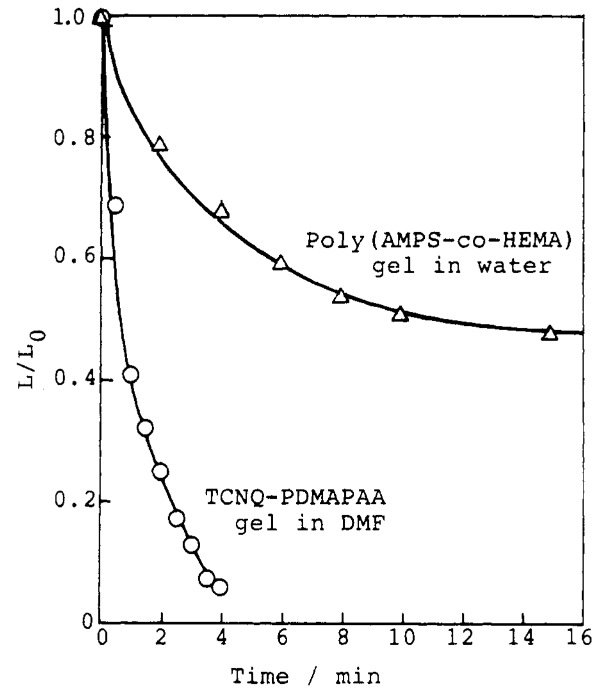

Figure 8. Time profiles of size change (L/L_0) of TCNQ-PDMAPAA organogel (○) and poly(AMPS-*co*-HEMA) hydrogel (△), under a constant current (0.3 mA). Degree of swelling: poly(AMPS-*co*-HEMA) gel, 400; TCNQ-PDMAPAA gel, 340; doping ratio (r) = 0.9.

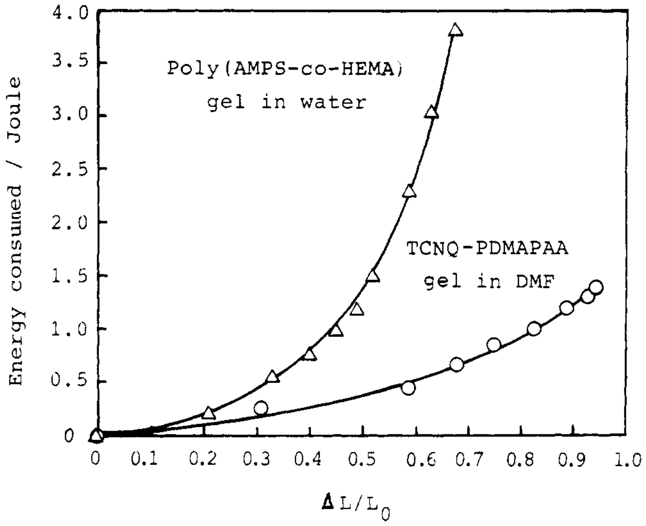

Figure 9. Relations between size changes of the gel and energy consumed. (△) TCNQ-PDMAPAA gel, (○) poly(AMPS-*co*-HEMA) gel. Experimental conditions are the same as noted in Figure 8.

According to Flory's theory,[12] the swelling of the polyelectrolyte gel is associated with the ionization of the polymer gel. If q is the degree of swelling, i.e., the volume ratio of the gel in the swelling state to that in the dry state, and i is the degree of ionization of the gel, then we have

$$q^{2/3} = ni + n(^1/_2 - \chi)V_u/(qv_1) \qquad (2)$$

where n is the number of monomer units between two cross-linked points, χ is the Flory interaction parameter between the polymer and solvent, and V_u and v_1 are the molar volume of a monomer unit and solvent, respectively. In the given case, the degree of ionization i can be assumed to be equal to the TCNQ doping ratio r because the TCNQ-PDMAPAA complex is fully ionized in DMF.

When q is very large, the second term of eq 2 is neglected since $ni \gg n(^1/_2 - \chi)V_u/(qv_1)$, and eq 2 becomes simply

$$q^{2/3} = (SL/V_0)^{2/3} = ni \qquad (3)$$

where V_0 is the volume of the gel in the dry state.

On the basis of our experimental assumption, both micro- and macroions are consumed by the electrode reaction and decrease their concentration. Therefore, if the number of moles of ions in the gel at time 0 and t are M_0 and M, respectively, we get the following equation under an electric field:

$$(SL/V_0)^{2/3} = nM/M_p = n(M_0 - \int I\,dt/F)/M_p \quad (4)$$

where F is the Faraday constant and M_p is the number of moles of monomer units in the gel.

If e is the charge of an electron and r_i is the effective radius of solvated ions, the conductivity of the ionized gel, σ, is expressed as[13]

$$\sigma = Fe[M/(SL)]/(6\pi\eta r_i) \quad (5)$$

and the current, I, is associated with the voltage applied, U, as

$$I = \sigma(S/L)U \quad (6)$$

where S is the cross-sectional area of the gel. Under the condition of constant voltage, U, by differentiating (4) with time and combining with (5) and (6), we get

$$dL/dt = -eSU/(4\pi\alpha r_i M_p) \quad (7)$$

If ρ is the density of the polymer gel and MW is the molecular weight of the monomer unit, we have

$$M_p = \rho V_0/\mathrm{MW} = \rho S_0 L_0/(q\mathrm{MW}) = \rho S_0 L_0/[(ni)^{3/2}\mathrm{MW}] \quad (8)$$

where S_0 and L_0 are the initial ($t = 0$) cross-sectional area and length of the gel, respectively. Using (8) and $S = S_0$, we get the length change of the gel under the electric field in the following form by integrating (7):

$$L = L_0 - k(ni)^{3/2}Et \quad (9)$$

where $k = e\mathrm{MW}/(4\pi\alpha\rho r_i)$ is a constant determined by the properties of polymer and the solvent and $E = U/L_0$ is the strength of the electric field applied on the gel.

Finally, a simple equation for the rate of contraction of the gel, v, is obtained by differentiating (9):

$$v = dL/dt = -k(ni)^{3/2}E \quad (10)$$

Equations 9 and 10 are the quantitative expression of the contraction of TCNQ–PDMAPAA gel that occurred by applying an electric field. They indicate that the rate of contraction of a gel is directly proportional to the electric field applied on the gel. They also indicate that the rate of contraction depends on the degree of ionization of the gel and the degree of cross-linking under certain electric fields. From Figure 6b it is seen that the experimental results are in good agreement with the results from the equations derived except that the contractions start at the electric field of 2.5 V/cm. This is due to overpotential of the electrodes required for electrochemical reaction. If we consider this, we obtain (11) and (12) by replacing E with $E - E_0$, where E_0 is the value of the overpotential for electrochemical reaction.

$$L = L_0 - k(ni)^{3/2}(E - E_0)t \quad (11)$$

$$v = -k(ni)^{3/2}(E - E_0) \quad (12)$$

It is seen from Figure 5 that the rate of contraction increases with an increase in TCNQ concentration in the range of $r = 0.1–0.5$. Figure 6b also indicates that v is proportional to $n^{3/2}$. Since n is equal to $1/(2f)$ where f is the degree of cross-linking, one should get a linear relation by plotting v and $n^{3/2}$. The v–$n^{3/2}$ plot using the experimental data in Figure 6a gives a straight line as shown in Figure 6b and indicates that eq 12 is valid.

Thus, both the experimental and the theoretical results indicate that the electrodriven chemomechanical size change of the CT gel is essentially explained by an electrokinetic process and can be associated with the electrophoretic transfer of charged molecules toward the counter electrode where electrode reaction takes place rather quickly.

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