Macromolecules **1991,** *24,* 4755–4761 **4755**

Electroconductive Organogel. 2.[†] Appearance and Nature of Current Oscillation under Electric Field

Mari Miyano and Yoshihito Osada*

Department of Chemistry, Ibaraki University, Mito 310, Japan

Received December 13, 1990 ; Revised Manuscript Received March 22, 1991

ABSTRACT: An artificial oscillation system consisting of an acceptor-doped electroconductive organogel, to which a constant electric potential was applied, is described. This organogel is made of cross-linked polymer donor subsequently doped with low molecular acceptor and swollen in *N,N*-dimethylformamide. It was found that repetitive oscillations occurred in these gels above a certain threshold potential in organic solvent. The nature of the oscillation was associated with the degree of cross-linking, the doping ratio of acceptor molecule, and temperature; an increase of these parameters enhanced both the amplitude and frequency of the oscillation. A possible mechanism of the oscillation is also briefly described.

Introduction

In recent years, marked attention has been paid to oscillatory processes typically in biological objects at organ, cellular, subcellular, and molecular levels. For example, self-sustained oscillation with a frequency of 145 Hz occurs in the squid giant axon by exchanging seawater for a mixture of seawater and 550 mM NaCl solution (1 M = 1 mol dm^{-3}).[1] Artificial oscillating systems consisting of chemical reactions are the simple artificial model for these oscillative systems observed in biological systems. The so-called Belousov–Zhabotinsky-type oscillation reaction is the typical reaction in this context, and many people are involved in investigating it both experimentally and theoretically.[2] The thermodynamic bases of oscillatory systems have been laid out by Prigogine and his colleagues.[3]

The Teorell oscillator is a device that makes use of the coupling of ion and water fluxes within a highly porous membrane.[4] In this case, the membrane separates two well-stirred electrolyte solutions of different concentrations. Each solution is contained in a compartment with a vertical capillary on the top. A net movement of solution through the membrane therefore generates an electroosmotic flow in the direction of the cathode.

The solutions are arranged so that this flow takes place from the dilute side to the concentrated side. The oscillatory phenomena were explained as an electroosmotic process, causing periodic resistance changes of the membrane.

There have been many other theoretical and experimental investigations of current oscillation. The generation of pulses superimposed on dc was observed by Seno in ion-exchange membranes dipped in aqueous sodium chloride solution.[5] The phenomenon was associated with the formation of a salt-depletion diffusion layer. Shashoua reported the generation of current oscillations under constant dc electric field in the membranes consisting of polymeric acid and base composite facing each other.[6] In these cases, the presence of salt of both sides of the membrane was one of the requirements in order to generate spikes. Katchalsky[7] explained the appearance of these oscillative phenomena as follows: the current flow through the membrane induces salt accumulation in the polymer membranes, which, at a certain concentration, leads to the shrinkage of the membrane and a breakdown region is formed. The excess ions are washed off to reestablish the original state of the membrane. The sustained electromedionical oscillations were observed on bimolecular lipid membranes by Pant and Rosenberg.[8] In this case, lipid molecules arranged in a bimolecular structure are in an excited state and involved in the charge-transfer processes at the membrane–electrode interfaces.

We found that repetitive current oscillation occurred in hydrogel[9,10] when a dc was applied through electrodes, and semiquantitative analyses of the oscillation were made by use of fast Fourier transformation (FFT). It was also found that entrainment of oscillation occurred in the polymer gels when the frequency of the sinusoidal stimulation was close to that of parent current oscillation.[11]

In this paper, we present a new and simple oscillation system that is considered to be perturbed by small parameters. The system consists of a cross-linked electroconductive organogel, swollen in nonvolatile organic solvent *N,N*-dimethylformamide (DMF), which shows current oscillations when imposing dc electric field above a certain minimum potential.

Experimental Section

Materials. [(Dimethylamino)propyl]acrylamide (DMAPAA) (Kojin Co., Ltd.) was distilled at 120 °C under reduced pressure of 532 before use. *N,N'*-Methylenebis(acrylamide) (MBAA) (Tokyo Kasei Kogyo Co., Ltd.) was used as a cross-linking agent and was recrystallized twice from ethanol. Azobis(isobutyronitrile) (AIBN) (Tokyo Kasei Kogyo Co., Ltd.), which was used as a radical initiator, was recrystallized from ethanol. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was kindly provided by Osaka Organic Chemical Industry Ltd. and was recrystallized at 60 °C in tetrahydrofuran. Tetra-*n*-butylammonium perchlorate (TBAPC) (Tokyo Kasei Kogyo Co., Ltd.) was recrystallized at 60 °C in a 1:1 solvent mixture of ethyl acetate and hexane. 2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS) (Nitto Chemical Co., Ltd.) was purified by repeated recrystallization.

Preparation of the Gel. A cross-linked poly[[(dimethylamino)propyl]acrylamide] PDMAPAA gel was prepared by radical polymerization of a solution of 3.0 M DMF with corresponding monomers in the presence of a calculated amount of MBAA and AIBN. The polymerization was carried out in an ampule (12 mm in diameter, 50 mm in length) at 60 °C for 12 h under nitrogen atmosphere. Linear polymers were prepared in a similar manner but without MBAA.

After polymerization, the gel was immersed in a large amount of DMF until it reached an equilibrated size. Doping with TCNQ was made by immersing PDMAPAA gel into a large amount of DMF solution of TCNQ. The doping ratio (DR) was defined as the molar ratio of TCNQ to unit moles of PDMAPAA. Significant swelling of the gel occurred. The degree of swelling (DS) was calculated by weighing dry and DMF-swollen gels, respectively. Doping of linear polymer solutions was made by adding various

---

[†] Previous paper in this series: Electroconductive Organogel. 1. Electrophoretic Orientation of Phthalocyanine Molecules in Polymer Gel. Osada, Y.; Ohnishi, S. *Macromolecules* **1991,** *24,* 3020.

0024-9297/91/2224-4755$02.50/0

amounts of TCNQ in DMF solutions whose concentration was the same as the degree of swelling of the gels. Mixing of TBAPC was made in order to study the effect of neutral salt and was made by immersing PDMAPAA gel into a solution of 0.1 M DMF with TBAPC. The concentration of TBAPC in PDMAPAA gel was calculated by measuring the change in conductivity of the solution before and after immersing the gel.

Measurements. A piece of TCNQ-doped PDMAPAA gel, 20 mm long, 10 mm wide, and 10 mm thick, was placed in a closed-type Pyrex vessel where dry N_2 gas was constantly flushed (Figure 1). The temperature of the cell was kept constant by circulating thermostated water or cold ethanol. A pair of platinum wire electrodes, 0.2 mm diameter, 5 mm long, was inserted in the gel at a 10-mm distance, and a constant voltage (10 V) was applied across the gel from a dc source by using the Hokuto 501 potentiometer. The gel sizes were 10 × 10 × 20 mm. The oscillative response of the gel was recorded on a personal computer (NEC Model PC 9800 F) and/or a Y-T recorder (Riken Denshi Model F-45). The oscillation was simultaneously sampled at 200-ms intervals.

Gas evolution analysis was made at 25 ± 0.2 °C by using a microgas meter (Nikko Kagaku), which is able to measure within 0.1-μL accuracy. Control experiments were performed by using uncross-linked PDMAPAA solutions containing TCNQ or TBAPC. Water-swollen poly(2-(acrylamido)-*N*,*N*-dimethylpropanesulfonic acid) (PAMPS) gel was also used as a hydrogel sample and compared with DMF-swollen PDMAPAA gel.

Results

The polymer gel consists of an elastic cross-linked polymer network and a fluid filling the interstitial space of the network. We recently synthesized a new class of electroconductive organogels swollen in nonvolatile organic solvent: DMF.[12] This gel is composed of an electrodonating polymeric network and a low molecular electron acceptor, subsequently doped to the polymer network. For example, PDMAPAA gel obtained in DMF is slightly yellow and transparent. However, significant swelling and coloration takes place by subsequent TCNQ doping, i.e., by immersing the PDMAPAA gel in a large amount of DMF solution of TCNQ.

The maximum swelling observed at TCNQ/PDMAPAA is 0.25. Increasing the concentration of TCNQ resulted in a decrease in the swelling equilibrium, and it is speculated that the reason for this deswelling could be associated with the formation of $TCNQ^{2-}$.[2] The degree of swelling is related to the degree of cross-linking of the gel. An attempt to associate the swelling of charge-transfer (CT) polymer gels as a function of the degree of cross-linking and the ionic density of the network was made by using Flory's theory.[2]

The color change and the swelling phenomena of the PDMAPAA gel by TCNQ doping is attributed to the formation of a charge-transfer complex. TCNQ is a strong electron acceptor and forms CT complexes with a variety of electron donors[13-15] as follows:

$$TCNQ^0 + \text{amine} \rightleftharpoons (TCNQ^{\bullet -}\cdot \text{amine}^+) \rightleftharpoons TCNQ^{\bullet -} + \text{amine}^+ \quad (1)$$

$$2TCNQ^{\bullet -} \rightleftharpoons TCNQ^{2-} + TCNQ^0 \quad (2)$$

The anion radical of $TCNQ^-$ is stable in nonaqueous polar solvents and forms ion-radical salts. In polar solvents, they also dissociate to give corresponding cation and anion radicals[14] and show electric conductivities as high as 10^{-3} S cm^{-1}. However, according to our spectral investigation and analysis of swelling on the basis of Flory's equation, it was found that more than 98% of CT complexes have been dissociated and behave as free ions in such polar solvents as DMF.[2] Therefore, the reaction is practically irreversibly shifted to the right side of eq 1. This high conductivity of the organogel led us to consider the possibility that application of the dc electric field may give rise to periodic current oscillation, as the polyelectrolyte gels showed in water.[10,11]

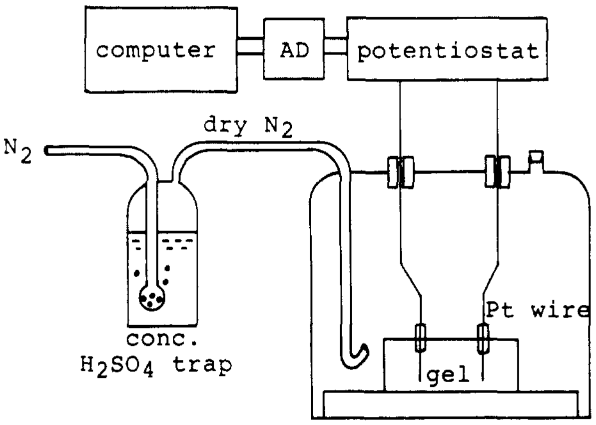

Figure 1. Apparatus for measuring current oscillation in closed-type vessel.

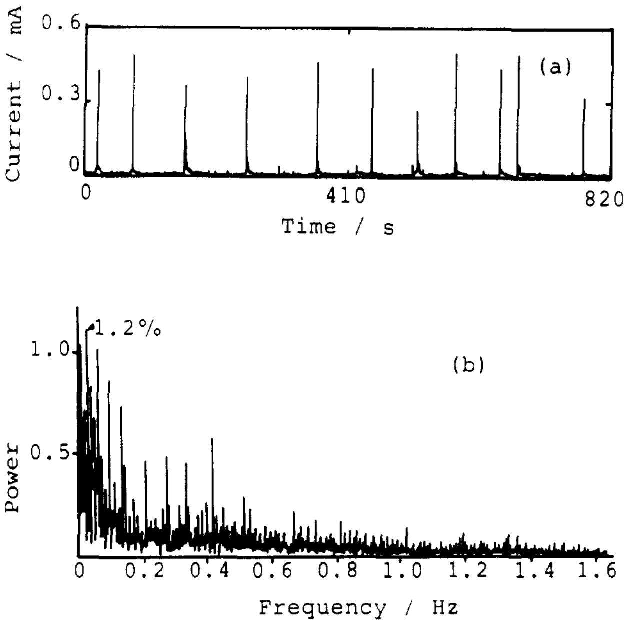

Figure 2. (a) Typical current fluctuation of TCNQ-doped PDMAPAA gel. Conditions: electrode distance, 10 mm; DR = 1.0; DCL = 1.0 mol %; DS = 52. (b) Power spectra of current oscillation of TCNQ-doped PDMAPAA gel shown in a.

Figure 2a shows part of the typical current oscillation curve of PDMAPAA gel containing TCNQ (DR = 1.0), the degree of cross-linking (DCL), and MBAA/PDMAPAA × 100 = 1.0 mol %. The oscillatory current appeared after a certain introduction period, and during the induction period, a breakdown of the current often occurred. The value of the base current under this condition was relatively low in the range 1–3 μA; however, a peak current as large as 0.4–0.5 mA appeared periodically upon the base current. The power spectrum had a peak with many higher harmonics at a frequency of 0.032 Hz as shown in Figure 2b. The magnitude of the oscillation with a frequency of 0.032 Hz was about 1.2% of the total magnitude within the range around 1.8 Hz. It was found that the amplitude of the signal with a frequency of 0.032 Hz gradually increased with time, suggesting that the oscillation transfers to a more stable state. The Lorentz plot of the current of the gel obtained by plotting each amplitude against the preceding gel current resulted in a convergent set around a point on the line of slope 1, indicating that the frequency of the repetitive oscillation fluctuates around this peak and any irregular oscillation can be attributed to a quasi-periodic motion.

Similar oscillations can be obtained by using another PDMAPAA/TCNQ gel with different DCL and different DR. In some cases, the oscillation went on for over 10 days. However, no oscillation appeared at all in the PDMAPAA gel unless it was doped with TCNQ (see Figure 4). As described later, in the polymer solution (4 wt % solution of DMF with PDMAPAA containing an equimolar amount of TCNQ) there were no periodic peaks (Figure 7a) and DMF solution of linear PDMAPAA showed no oscillation.

Previously, we reported on the current oscillation of water-swollen hydrogels.[10] The oscillation appeared only in cross-linked polyelectrolyte gels, and no waves appeared either in the polyelectrolyte or in the low molecular weight electrolyte solution. The obtained result is the same as in the case of the oscillation of hydrogel. However, different from the case of the hydrogel, in the given system, no gas production occurred due to electrode reaction. Figure 3 shows profiles of the gas evolution of water-swollen PAMPS gel and TCNQ-doped PDMAPAA gel when 0.3 mA of dc was applied for a period of 30 min. In the case of hydrogel, a significant amount of gas evolution is observed throughout the whole experimental period. Gas evolution is obviously associated with the electrolysis of water to give hydrogen and oxygen expressed as the following reactions:

cathode

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O \quad (3)$$

anode

$$4OH^- \rightarrow O_2 + 2H_2O + 2e^- \quad (4)$$

However, there has been no gas evolution at all in the organogel. No gas was produced in the PDMAPAA/TCNQ solution with the same concentration as well. Gas production makes incomplete contact of the gel with electrodes, possibly giving rise to any unnecessary noise of the oscillation. Therefore, electroconductive organogel is more suitable for quantitative analysis of the oscillation behavior in the polymer gel.

The nature of the oscillation is closely related to the electric field. Oscillative experiments applying 3 and 10 V were carried out. At 3 V, we obtained an oscillation with an amplitude of 22 μA and a base current of 3 μA using CT gel with 0.5 mol % DCL and 148 DS. At 10 V, similar oscillation was obtained, but with an amplitude of 303 μA and the same base current, 3 μA. Thus, the amplitude of the oscillation increased 150 times by increasing the electric field from 3 to 10 V with no base current increase. We have also investigated the amplitude of current oscillation on electric field using polymer hydrogel, PAMPS, and found that the amplitude of the current oscillation increases in proportion to the electric field.[16]

Effect of Doping. It is expected that the oscillative behavior is closely related to the charge density in the electroconductive polymer gel, and an experiment was carried out using gels with different DR's.

As shown in Figure 4a, PDMAPAA gel showed no oscillation unless it was doped with TCNQ. Figure 4b shows that a polymer gel with a DR of 0.25 has an extremely weak oscillation with a long induction period, but a polymer gel with a DR of 1.0 has a constant and periodical oscillation and the peak current is very high. If the amplitude (which is defined as the peak current minus the base current) is plotted against DR, one gets Figure 5. It is interesting that the base currents of the gel are constant and remain very low throughout all DR, whereas the peak current increased markedly with an increase in DR. Previously, we attempted to associate the swelling behavior with the ionic density of the network by using Flory's theory[17] and found that the degree of ionization of the gel calculated in this way coincides well with the DR. From this result as well as spectral analysis, we estimate that all TCNQ added reacts with PDMAPAA to give a CT complex consisting of cation radicals of polymer network and TCNQ anions radicals according to eq 1. Therefore, it is reasonable that the doping of TCNQ results in enhanced ionization and enhanced current of the gel. However, the results obtained showing very low and constant values of the base current despite an increase in DR suggest the presence of any specific ionic conduction process. In connection with this, a current–voltage characteristic was obtained for the gel shown in Figure 6, which is quite different from the current–voltage characteristics of hydrogels.[10]

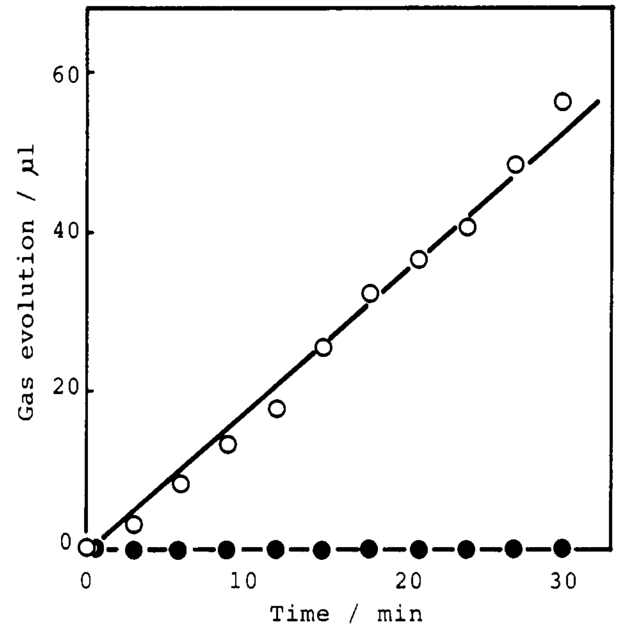

Figure 3. Gas evolutions of water-swollen PAMPS gel (○) and TCNQ-doped PDMAPAA organogel (●). Conditions: electrode distance, 10 mm; current, 0.3 mA; temperature, 25 + 0.2 °C. PAMPS gel: DCL = 0.5 mol %; DS = 165. PDMAPAA gel: DCL = 1.0 mol %; DS = 148; DR = 1.0.

Effect of Cross-Linking. As described, the PDMAPAA gel DMF solution of either TCNQ or DMAPAAA/TCNQ did not exhibit oscillation at all. This fact suggests that the network structure of charged molecules is important to the periodic oscillations. Therefore, we studied the effect of the density of cross-linking on the oscillation. PDMAPAA/TCNQ gels, with DCL of 0.5, 0.75, 1.0, 1.5, and 2.0 mol % per monomer unit, were synthesized, keeping DR and DS constant as 1.0 and 6.0.

Figure 7 shows the current fluctuation of organic gels with different DCL's. Besides solvated PDMAPAA/TCNQ, the DCL = 0.5 mol % gel showed no peaks throughout the experiment period (2.5 h). However, a

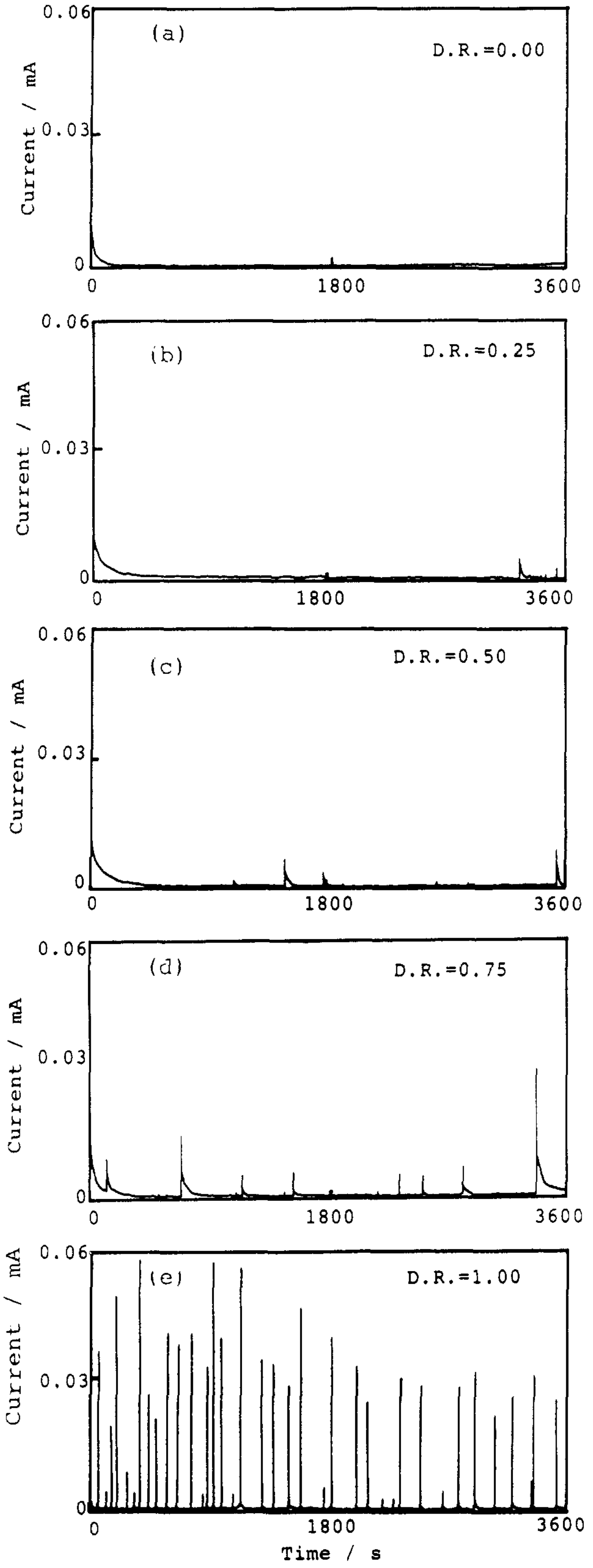

Figure 4. Typical current fluctuations of organogels with different DR's. Conditions: electrode distance, 10 mm; voltage, 10 V.

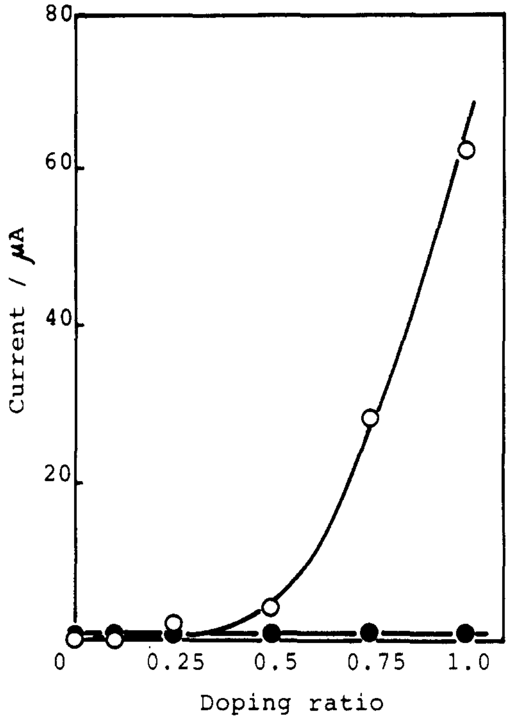

Figure 5. Current amplitude (○) and base current (●) dependences on DR.

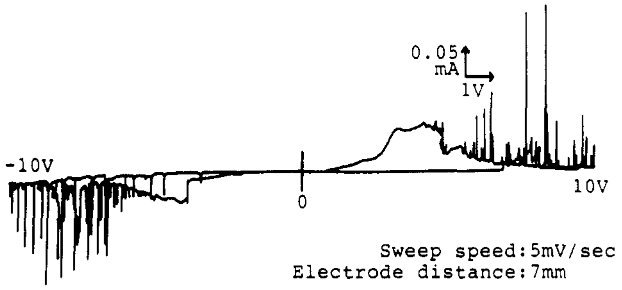

Figure 6. Current–voltage characteristic of the TCNQ-doped PDMAPAA gel. The current–voltage curve was obtained by applying triangular voltage. Gel: DR = 1.0; DCL = 0.5 mol %; DS = 148.

polymer gel with a DCL = 1.0 mol % exhibited periodic oscillation but the amplitude of the peak was only 0.05 mA. More intensive current peaks appeared with DCL more than 0.75 mol %. If the current amplitude is plotted against the DCL of the gel, one can get a straight line intersecting at DCL = 0.05 mol % (Figure 8). It is clearly seen that amplitude of the oscillation increased in proportion to the DCL of the gel. DCL of 0.5 mol % corresponds to the presence of one cross-linking joint per 200 monomer units on average, and this indicates a critical point of the DCL to make current oscillation with given conditions.

An increase in the DCL increased not only the amplitude of oscillation but the frequency of the oscillation. Figure 9 shows the frequency dependence on DCL. The frequency increased in proportion to DCL. However, the induction period of the oscillation decreased with an increase in DCL. For example, a polymer gel with a DCL of 1 mol % or less shows oscillations with an induction period of 5–15 min, but those with a DCL higher than 1.5 mol % showed the oscillation with no induction period. These results indicate that an increase in cross-linkage makes it more favorable to induce current oscillation.

The effects of the degree of swelling on the oscillation were made using a CT gel with a constant degree of cross-linking: 0.75 mol %. It was found that the swelling of the gel results in enhanced oscillation. For example, oscillation with a 0.43-mA amplitude and 0.011-Hz frequency is obtained when CT gel with a DS of 28 are used. However, oscillation with an amplitude of 0.18 mA and a frequency of 0.0025 Hz is obtained or the gel with a DS of 15.

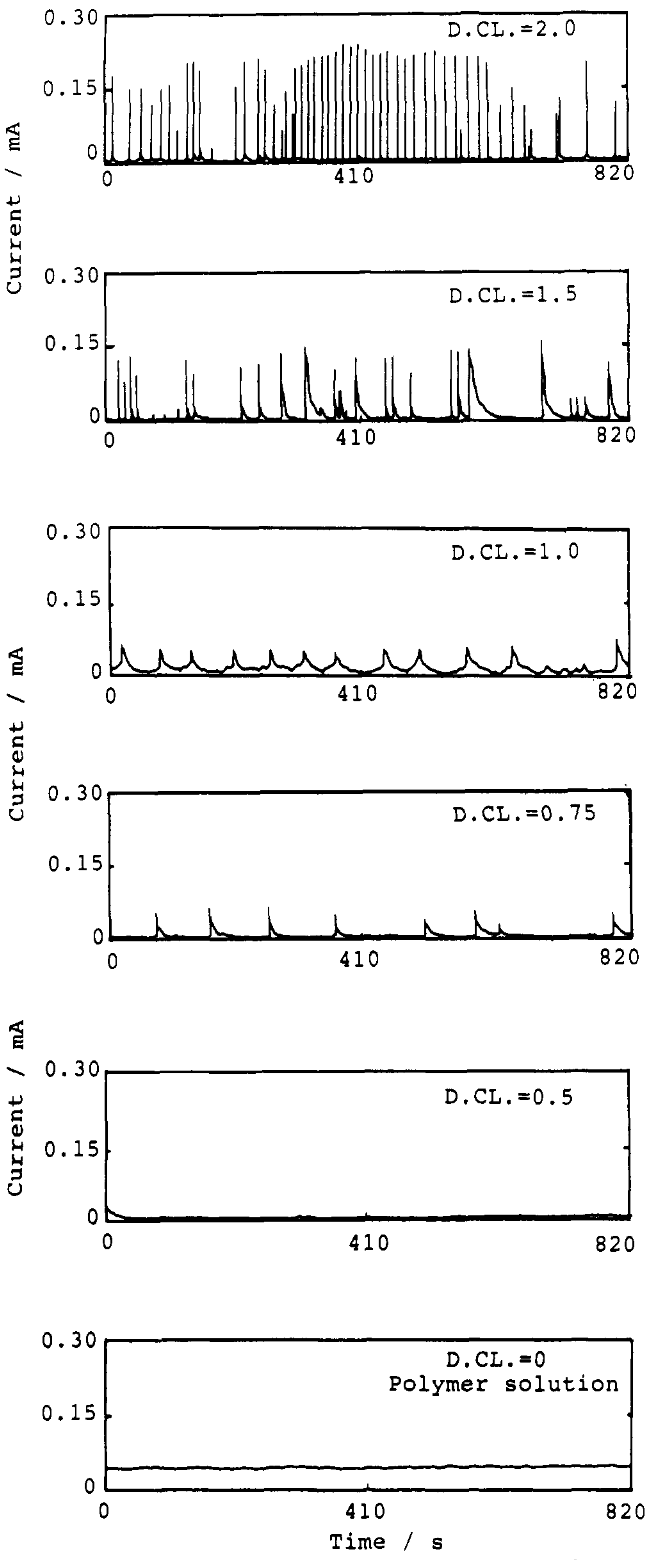

Figure 7. Typical current fluctuations of organogels with different DCL's (DCL = 0 mol % indicates the polymer solution). Conditions: electrode distance, 10 mm; voltage, 10 V; DR = 1.0; DS = 6.

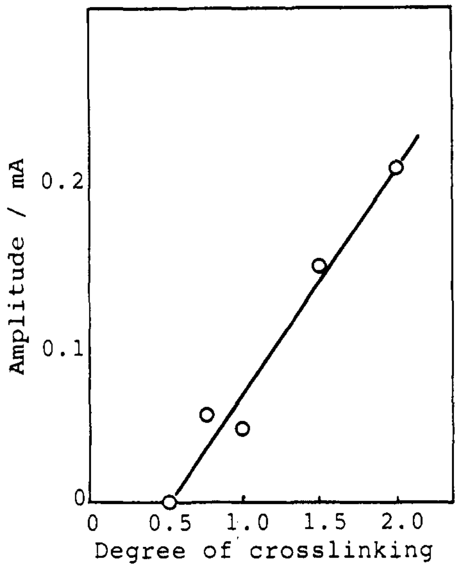

Figure 8. Amplitude of current oscillation as a function of DCL.

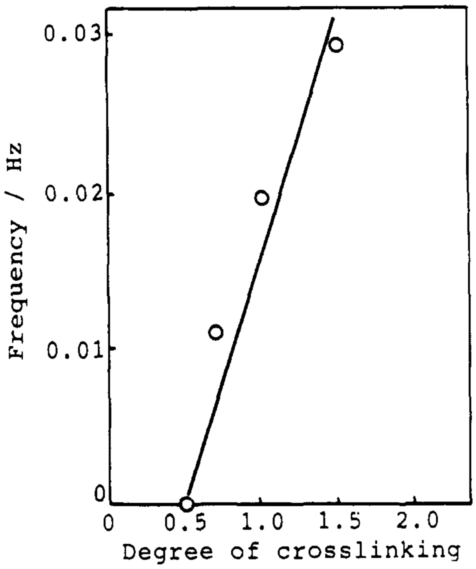

Figure 9. Frequency of current oscillation as a function of DCL.

Effect of Temperature. The oscillation of a polyelectrolyte gel under electric field is associated with the transfer process of micro- and macroions and with also the dynamic segmentational motion of the charged network in the solvent. Thus, it is important to associate the oscillation with the thermal segmental motion of the charged network in the gel.

Current oscillation experiments of an organic gel under a wide temperature range were carried out. Figure 10 shows the current oscillation of an organic gel of DCL = 0.75 mol % and DR = 1.0 at −45, 0, 30, and 60 °C when 10 V of dc was applied. At −45 °C, there was no peak and the base current was 7 μA throughout the experimented period. Small peaks appeared at 0 °C soon after the electric field was applied but these peaks were unstable and disappeared later. The base current in this case increased to 10 μA. At 60 °C, many peaks appeared immediately after applying the dc voltage and continued for a long period of time while the base current remained constant as 10 μA. If the amplitude of oscillation is plotted against temperature, one can get a curve increasing exponentially with increasing temperature (Figure 11), and from this figure, an apparent activation energy of current oscillation was calculated as 292.5 J/mol or 3×10^{-3} eV/mol. The frequency of the oscillation also exponentially increased with increasing temperature as shown in Figure 12, while the induction periods became less with increasing temperature. Thus, the elevated temperature results in enhanced amplitude and a higher frequency of oscillation.

There are several factors where temperature may influence the oscillation. They are (1) mobility of microions, (2) segmental molecular motion of charged network, (3) kinetic of electrode reactions, and (4) dissociation constant of ions. A rise in the temperature results

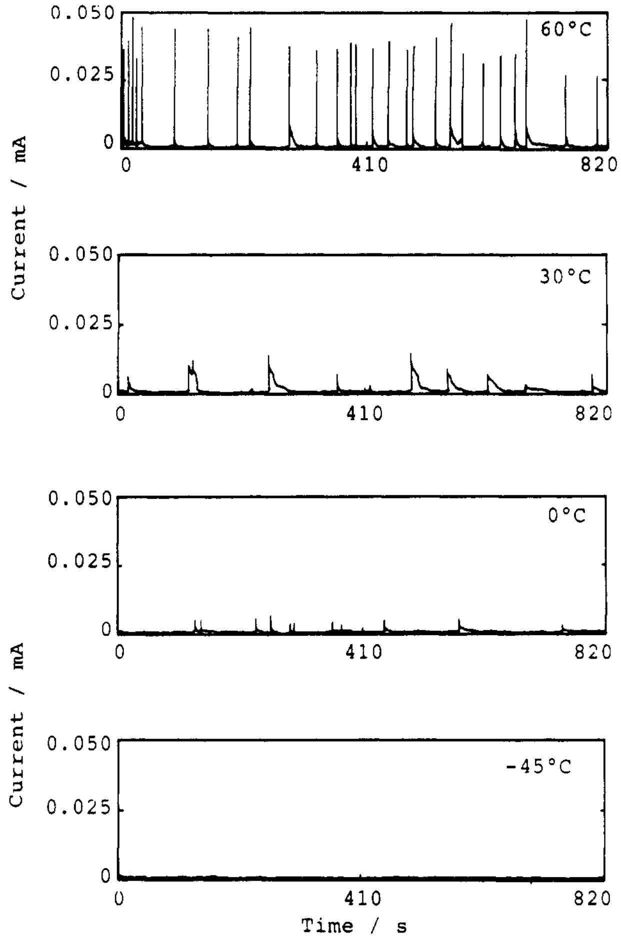

Figure 10. Current fluctuations under various temperatures. Conditions: electrode distance, 10 mm; voltage, 10 V; DR = 1.0; DCL = 0.75; DS = 25.

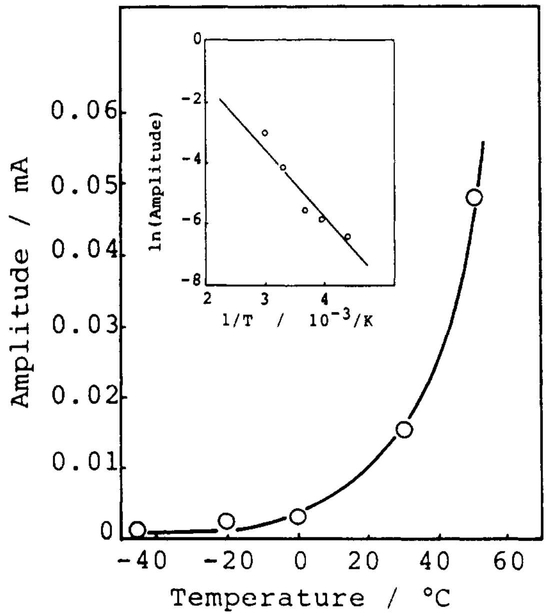

Figure 11. Amplitude of current oscillation as a function of temperature. (Inserted) Logarithmic dependence of amplitude on the reciprocal temperature (Arrhenius-type plot).

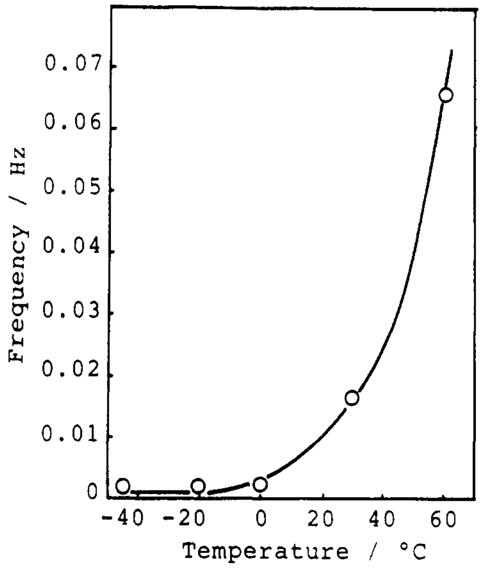

Figure 12. Frequency of current oscillation as a function of temperature.

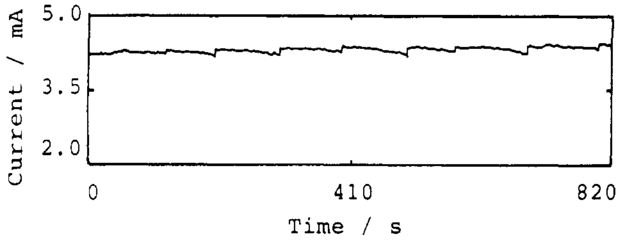

Figure 13. Current fluctuation of the PDMAPAA gel containing TBAPC. Conditions: electrode distance, 10 mm; voltage, 10 V; TBAPC/PDMAPAA = 1.0; concentration of TBAPC = 0.1 M.

in enhanced mobility and probably increased concentration of ions due to enhanced dissociation of the complex. The rate of electrode reaction must be increased with the rise in temperature. As a result, the increase in temperature should increase the current flow. However, in our case, practically constant current of 7–10 μA was observed in all the temperature range. The amplitude and frequency meantime increase so much and indicate a specific conduction process of ions in the gel.

Discussion

TBAPC is a strong electrolyte and fully ionized in DMF. Instead of TCNQ, we "doped" TBAPC in PDMAPAA gel as the supporting electrolyte and the oscillation experiment was carried out in the same manner. As shown in Figure 13, PDMAPAA gel containing TBAPC showed a base current as high as 4.3 mA, and this value exceeded more than 2 orders of magnitude that of PDMAPAA/TCNQ gel (10 μA). However, PDMAPAA/TBAPC gel showed only weak and unstable current fluctuation through the experiment. In addition, if the amplitude/base current (A/B) is plotted against TBAPC concentration, extremely low and almost constant values are obtained, whereas A/B values of TCNQ exponentially increase with an increase of TCNQ concentration (Figure 14). This experimental fact indicates that the ionization of the polymer network is substantial in order to exhibit stable oscillation.

Now, it is necessary to consider the transport process of macro- and microion carriers and their nature, whose motion could give rise oscillative behavior. First, it is supposed that the microions make electrophoretic travel faster than the charged network and the electroconduction is largely dominated by the microions. Since the microions have to travel through an oppositely signed three-dimensional network, they permeate through the sinusoidal potential barriers, coupled with segmental motions of network. Thus, the mobility of microions can be associated with the energy gap of the amorphous network, being attracted by the electrostatic force of the charged network

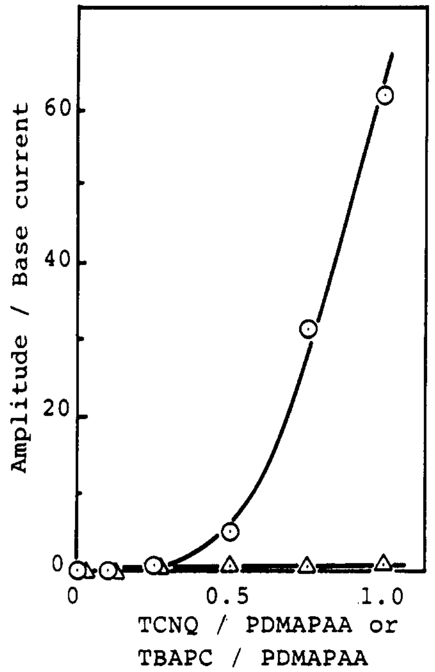

Figure 14. Dependence of amplitude/base current (*A*/*B*) on DR. (○) TCNQ-doped PDMAPAA gel; (△) PDMAPAA gel containing TBAPC.

with an associated activation energy *W*. Thus,

$$\mu = \mu_0 e^{-W/kT}$$

where μ_0 is the intrinsic mobility and *W* is a factor involving the energy barriers of network, which will probably depend on the charge density and cross-linking density. The logarithmic dependence of the amplitude on the reciprocal temperature (Arrhenius-type plot) gave a straight line as shown in Figure 11 (inserted), and *W* was computed as 292.5 J/mol or 3×10^{-3} eV/mol.

W could be associated with the counterion influence of the "field" in the gel lowering of activation barrier when "approaching" and increasing when "drifting apart" from the network. Thus, the microion possesses a sinusoidal nature of energy gap in the process of electrophoretic migration, making harmonized coupling with the network. Here, the three-dimensional polymer structure may be essential to maintain segmental motion and make harmonized coupling with microions as indicated in Figure 8; otherwise, they may deplete interaction with the solvent molecules.

Since there are many possible elementary kinetic processes in such systems, there is no need to make particular assumptions; one simply supposes that propagating waves of ions can occur provided certain constraints are satisfied. One condition that should be satisfied is that the density of charges in the network is reasonably large, the value of which is determined by such factors as the electric field, degree of cross-linking of the gel, and the temperature.

Thus, propagation is brought about by a local transportation process of charges caused by local gradients of driving forces, in this particular case, the gradient of the electric field, as it is independent of the existence of closed circuit and occurs in the continuous system as polymer gel.

There are two distinct classes of oscillatory systems; those in which the fluxes are the result of driving force and those in which the forces are the result of fluxes.[18] Most of the known oscillations, in particular those of chemical, electrochemical, and biological systems, are classified to force-dependent oscillations, and such characteristics arise frequently in the systems where high field strength of forces can occur such as in the membrane and at interfaces. Different from the membranes described, the oscillation of our gels is induced neither by change in gradient of the transmembrane concentration of the ions nor by the periodical response of specific chemical reagents like liquids[19,20] but is induced by the amorphous and homogeneously swollen polyelectrolyte gels. The application of constant electric potential, higher than a certain threshold value, is the only requirement for the generation of periodical oscillations.

Nonlinear oscillations occurring in chemical, biological, electrochemical, and other systems look remarkably similar in their general shape despite their different physicochemical nature and suggest that there may exist a common kinetic principle for their occurrence. However, the difficulties of elucidating oscillation mechanism in the molecular level seem to arise from the fact that the systems are multivariable with nonlinear kinetic relation and complicated coupling mechanism.

Much more experiment is required to confirm these ideas conclusively.

Acknowledgment. We are indebted to Osaka Organic Chemical Industry Ltd. for the courtesy of providing TCNQ.

References and Notes

(1) Matsumoto, G.; Kim, K.; Uehara, K.; Shimada, J. *J. Phys. Soc. Jpn.* **1980**, *49*, 906.
(2) Depoy, P. E.; Mason, D. M. *Symp. Faraday Soc.* **1974**, *No. 9*, 47.
(3) Prigogine, I.; Nocolis, C. T. *Q. Rev. Biophys.* **1971**, *4*, 107.
(4) Teorell, T. *Gen. J. Physiol.* **1958**, *42*, 831.
(5) Seno, M.; Yamabe, T. *Physiol.* **1963**, *36*, 877.
(6) Shashoua, V. E. *Nature (London)* **1967**, *215*, 847.
(7) Katchalsky, A.; Spangler, R. *Q. Rev. Biophys.* **1968**, *1*, 127.
(8) Rosenberg, B.; Pant, H. C. *Biochim. Biophys. Acta* **1971**, *225*, 379.
(9) Osada, Y.; Hasebe, M. *Chem. Lett.* **1985**, 1285.
(10) Osada, Y.; Umezawa, K.; Yamauchi, A. *Makromol. Chem.* **1988**, *189*, 597.
(11) Osada, Y.; Umezawa, K.; Yamauchi, A. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3238.
(12) Gong, J. P.; Kawakami, I.; Sergeyev, V. G.; Osada, Y. *Macromolecules*, in press.
(13) Asker, D. S.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Melby, L. R.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1960**, *82*, 6408.
(14) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374.
(15) Hertler, W. R.; Hartzler, H. D.; Asker, D. S.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3387.
(16) Unpublished data.
(17) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(18) Frank, F. *Symp. Faraday Soc.* **1974**, *No. 9*, 137.
(19) Toko, K.; Tsukiji, M.; Ezaki, S.; Yamafuji, K. *Biophys. Chem.* **1984**, *20*, 39.
(20) Bassingnana, I. C.; Reiss, H. *J. Membrane Sci.* **1983**, *15*, 27.

Registry No. DMAPAA/MBAA (copolymer), 132460-82-3; DMAPAA (homopolymer), 27754-92-3; TCNQ, 1518-16-7; TBAPC, 1923-70-2.