Articles

Electroconductive Organogel. 3. Preparation and Properties of a Charge-Transfer Complex Gel in an Organic Solvent†

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Received November 15, 1990; Revised Manuscript Received April 25, 1991

ABSTRACT: A novel ionic organogel based on a polymeric charge-transfer (CT) complex was prepared. Cross-linked poly[*N*-[3-(dimethylamino)propyl]acrylamide] (PDMAPAA) gel was synthesized in DMF, followed by subsequent doping of 7,7,8,8-tetracyanoquinodimethane (TCNQ). The PDMAPAA gel showed extensive swelling and exhibited a green color when doped. Spectrophotometric and kinetic studies revealed that swelling and coloration are due to formation of various kinds of ionic species formed by the CT complex between the polymeric network and TCNQ, and the process of complex formation was analyzed. From Flory's theory an equation of swelling of the organogel was derived as a function of charge density of ionic species and compared with experimental results.

Introduction

Polymer hydrogel has attracted considerable attention in recent years. Since polymer gel consists of an elastic cross-linked network and a fluid filling the interstitial space of the network, it can easily change in size and shape in response to environmental change, and this is the one of the intrinsic characteristics of a polymer gel.

For example, an ionized gel changes in volume discontinuously when the solvent composition is continuously varied (phase transition),[1,2] and extensive theoretical and experimental studies have been made on this.[3,4] The phase transition is induced not only by change in the solvent composition but also by change in pH, salt concentration,[3] temperature, and application of an electric field.[4] A theory for the kinetics of the swelling of a polymer hydrogel has also been proposed.[5,6]

The ionizable polymer hydrogel gives rise to important electrochemical swelling and deswelling and this was explained in terms of the electrokinetic process.[7] For example, a polyelectrolyte gel inserted between a pair of electrodes deswells under dc voltage with concomitant water exudation. This phenomenon is associated with the electrophoretic and electroosmotic transport of a highly hydrated macromolecule and its counterions.[8,10]

The shape change observed has potential applications for gel actuators and artificial muscles due to the gel's dramatic dimensional changes caused when the polarity of the electric field is reversibly altered, and some examples of devices have been proposed (chemomechanical system).[7,9]

Dynamic control of protein,[11] drug,[12] and other solute molecules[13] across gel membranes or gel particles[14] has provided a new principle in separation process, and it also has controlled the drug delivery system.

However, the hydrogel has one serious disadvantage when used. That is hydrogen and oxygen gases are produced near the electrodes. The production of gases is due to the decomposition of water and thus the efficiency of the chemomechanical conversion of the system is lowered. It also makes it difficult to set up a "sealed" device. The production of gases also disturbs the contact of the gel with electrodes and results in an unstable electrochemical reaction.

On the basis of these facts we have synthesized a new class of electroconductive organogels swollen in a nonvolatile solvent. This gel consists of an electrodonating polymeric network and a low molecular acceptor subsequently doped to the gel. We used poly[*N*-[3-(dimethylamino)propyl]acrylamide] (PDMAPAA) as a polymeric electron donor and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as an electron acceptor. When TCNQ was doped to PDMAPAA gel in DMF, a significant swelling and coloration due to the formation of a charge-transfer (CT) complex occurred. The gel obtained has a sufficiently high electroconductivity to cause electrodriven shrinkage as a hydrogel.

This paper deals with the preparation, equilibrium, and kinetic studies of a CT organogel. On the basis of Flory's theory,[15] an equation describing the swelling of the gel was derived as a function of the density of ions and was compared with the experimental results.

Material. *N*-[3-(Dimethylamino)propyl]acrylamide (DMAPAA) (from Kohjin Co., Ltd.) was distilled at 120 °C under reduced pressure (532 Pa) before using. *N,N*-Methylenebis(acrylamide) (MBAA) (from Tokyo Kasei Kogyo Co., Ltd.) was used as a cross-linking agent and recrystallized twice from ethanol. Azobis(isobutyronitrile) (AIBN) (from Tokyo Kasei Kogyo Co., Ltd.), which was used as an initiator, was recrystallized from ethanol. 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 distillation in a vacuum after standing overnight in KOH and CaO.[16]

Preparation of the Gel. A cross-linked PDMAPAA gel was prepared by radical polymerization of DMAPAA of 3 M in DMF in the presence of a calculated amount of MBAA and AIBN. The polymerization was carried out

† Previous papers: Osada, Y.; Ohnishi, S. *Macromolecules* 1991, *24*, 3020. Miyano, M.; Osada, Y. *Macromolecules*, in press.

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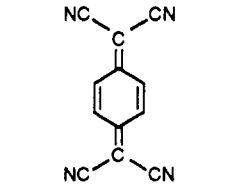
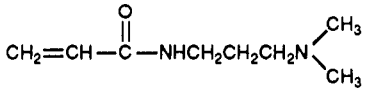


tetracyanoquinodimethane
(TCNQ)



N-[3-(dimethylamino)propyl]acrylamide
(DMAPAA)

in an ampule (1 cm in diameter, 10 cm in length) at 60 °C for 10 h under nitrogen atmosphere.

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; this usually took approximately 1 week. During this procedure, DMF was repeatedly changed to remove unreacted monomer and other chemicals.

Doping of TCNQ was made by immersing PDMAPAA gel in a large amount of DMF solution of TCNQ. Significant swelling of the gel occurred. The degree of swelling q was calculated by measuring the diameters of the equilibrated and original dry gels:

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

where D, V and D_0, V_0 are the diameters and volumes of equilibrated and original gels, respectively.

The diameter of the gel was measured by a microscope with calibrated scale.

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

Results and Discussion

PDMAPAA gel obtained in DMF was transparent and slightly yellow in color. When the PDMAPAA gel was immersed in a large amount of the DMF solution containing TCNQ, a thin green border initially appeared on the surface of the gel, which gradually moved into the inner part of the polymer network. At the same time the PDMAPAA gel swelled considerably. The volume change depended on the concentration of TCNQ. Figure 1 shows the time dependence of the change in gel volume when immersed in various concentrations of TCNQ. A higher concentration of TCNQ solution brought about deswelling of the gel with prolonged doping. Figure 2 shows the dependence of the equilibrated gel swelling on the TCNQ concentration. The maximum swelling observed at TCNQ/PDMAPAA is 0.25. Increased 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 $TCNQ^{2-}$, which is described later. The degree of swelling is related to the degree of cross-linking of the gel and Figure 3 shows the dependence of the final equilibrated volume on the degree of cross-linking of PDMAPAA gel. The gel exhibited a significant swelling with reduction in the degree of crosslinking when doped by TCNQ, while with no doping it showed much less swelling.

The color change and the swelling phenomenon of PDMAPAA gel by TCNQ doping are likely to be associated with the formation of a CT complex. TCNQ is a strong electron acceptor and forms CT complexes with a variety of electron donors.[17-19] According to the literature,[17-19] TCNQ forms a CT complex with various kinds of aliphatic amines that are strong electrolytes and fully ionized in

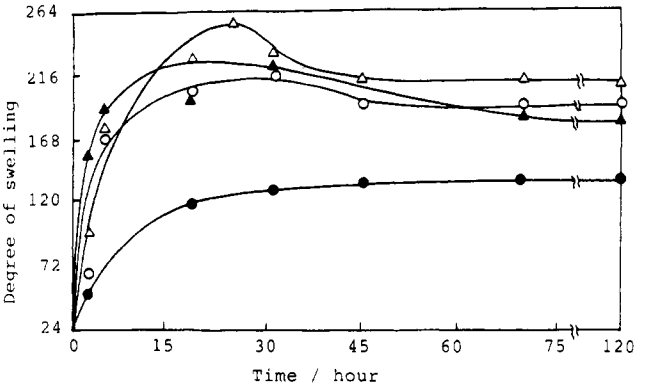


Figure 1. Time dependence of volume change of PDMAPAA gel immersed in TCNQ solution of various concentrations. TCNQ concentration per DMAPAA unit: (●) 0.2, (○) 0.5, (△) 1.0, (▲) 3.0; degree of crosslinking: 0.5 mol %.

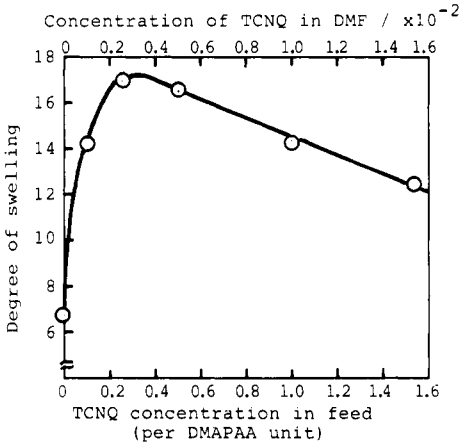


Figure 2. Dependence of the final equilibrated swelling of PDMAPAA gel on TCNQ concentration. Degree of crosslinking: 2 mol %.

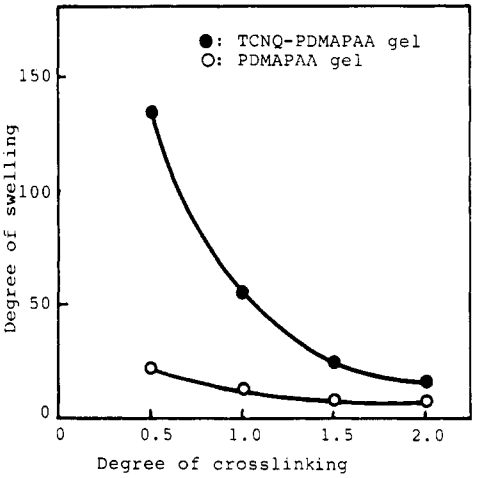


Figure 3. Dependence of the final equilibrated swelling on the degree of crosslinking of PDMAPAA gel. (○) PDMAPAA gel, (●) TCNQ-PDMAPAA gel, TCNQ concentration per DMAPAA unit: 0.25.

DMF.[18] The reaction can be expressed as

$$TCNQ^0 + \text{amine} \rightleftharpoons (TCNQ^{\bullet-}\text{amine}^{\bullet+}) \rightarrow TCNQ^{\bullet-} + \text{amine}^{\bullet+}$$

The anion radical of $TCNQ^{\bullet-}$ is stable in nonaqueous polar solvents and forms ion radical salts. In polar solvents it also dissociates to give corresponding cation and anion radicals.[18]

Thus, the swelling of the gel in a DMF solution containing TCNQ may be associated with the formation

of a CT complex between PDMAPAA gel and TCNQ, since cation and anion radicals formed in the gel would create excess osmotic pressure inside the polymer network and result in significant swelling. In order to confirm this, electronic spectra of the TCNQ–PDMAPAA solution as well as those of the gel were measured under nitrogen. As shown in Figure 4, a strong absorption of neutral TCNQ at 392 nm (ϵ = 85 000) became weaker in the presence of PDMAPAA and, instead, new absorptions at 420 nm (ϵ = 24 300) and 842 nm (ϵ = 43 500) and weak absorption bands at 744, 760, 680, and 665 nm probably assignable to $TCNQ^{\bullet-}$ [18,20] appeared. A new absorption appeared at 330 nm and this was assigned to $TCNQ^{2-}$ (ϵ = 33 000).[21] Absorption at 480 nm (ϵ = 39 200)[21] is due to the oxidized product of $TCNQ^{2-}$ with an oxygen molecule, giving α,α-dicyano-*p*-toluoylcyanide anion ($DCTC^-$). The presence of oxygen may be associated with residual moisture due to the extremely hygroscopic character of ammonium polymers. Essentially the same absorption spectra based on the CT complex were obtained for the TCNQ–PDMAPAA gel as shown in Figure 4d and it can be assumed that the same reaction takes place in the gel as in solution. Shoulder peaks appearing at 330 and 480 nm are due to $TCNQ^{2-}$ and $DCTC^-$ and can also be observed in the TCNQ–PDMAPAA solution (Figure 6). This will be explained in detail later.

Thus, the overall reaction scheme between PDMAPAA and TCNQ may be written as

(a) PDMAPAA + $TCNQ^0$ →

$$PDMAPAAH^+ + TCNQ^{\bullet-}$$

(b) $$2TCNQ^{\bullet-} \rightarrow TCNQ^{2-} + TCNQ^0$$

(c) $$TCNQ^{2-} + O_2 \rightarrow {}^-O{-}C{\equiv}N + DCTC^-$$

It should be noted that DMF behaves as a weak electron donor and is able to form a CT complex with TCNQ. Figure 4c shows the spectrum of DMF solution of TCNQ. Very weak but similar absorptions of $TCNQ^{\bullet-}$ of TCNQ–PDMAPAA were observed and these are apparently characterized by the formation of a CT complex in the form of $DMF^+TCNQ^{\bullet-}$.

The relative intensity and shape change of spectra over time were investigated. If absorption maxima of the peaks $TCNQ^0$, $TCNQ^{\bullet-}$, $TCNQ^{2-}$, and $DCTC^-$ are plotted with time, the kinetic profiles of these species are obtained as shown in Figure 5.

As seen from the figure, the concentration of $TCNQ^0$ rapidly decreases with time and if the second-order reaction plot (reciprocal of TCNQ with time) is made, one can get a linear relation (Figure 6). Thus, this process can be expressed as

$$d[TCNQ^0]/dt = -k_1[TCNQ^0]_0[P^0] + k'_1[TCNQ^{\bullet-}][PH^+]$$

Since the reverse reaction can be neglected in the same sense as the reverse reaction of dissociation of strong electrolytes can be neglected in aqueous media and the concentration of $TCNQ^0$ is equal to that of PDMAPAA in the given case, this equation can be written as

$$d[TCNQ^0]/dt = -k_1\{[TCNQ^0]_0 - [TCNQ^{\bullet-}]\}^2$$

From the slope of Figure 6 the rate constant of the complex formation k_1 is 0.18 L/(mol min).

As the figure shows, after 17 h the amount of $TCNQ^{\bullet-}$ reaches a maximum and the decay of $TCNQ^{\bullet-}$ is also a second-order reaction. The rate of this reaction can

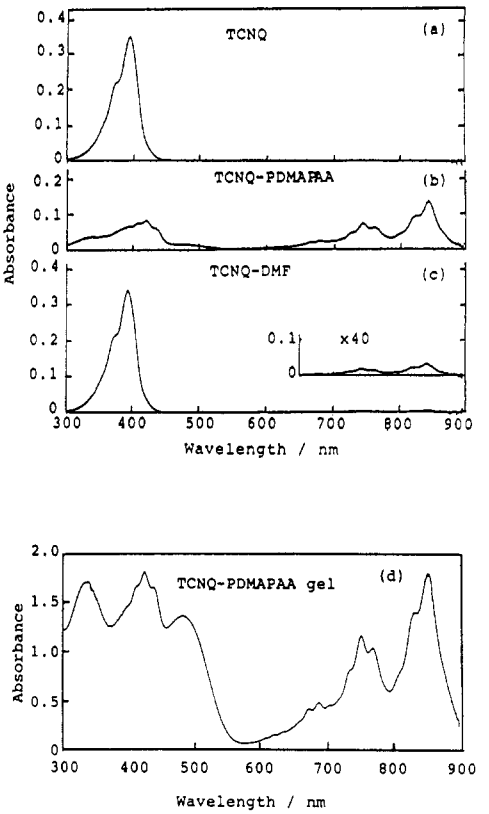


Figure 4. Electronic spectra of (a) TCNQ; (b) TCNQ–PDMAPAA; (c) TCNQ–DMF and (d) PDMAPAA gel doped by TCNQ. Concentration: TCNQ 5×10^{-6}M, PDMAPAA 5×10^{-5}M, DMF 5×10^{-5}M. All spectra were measured in acetonitrile except that of gel.

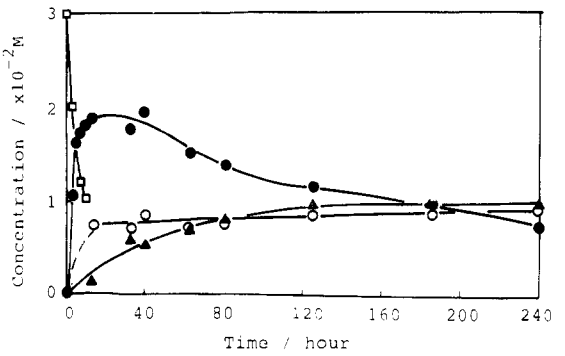


Figure 5. Time dependence of $TCNQ^0$ (□); $TCNQ^{\bullet-}$ (●); $TCNQ^{2-}$ (○); $DCTC^-$ (▲) concentrations. Molar ratio of TCNQ to PDMAPAA r = 1.0, initial TCNQ concentration: 3.0×10^{-2}M. The spectra were measured at 25 °C in DMF.

therefore be written as

$$d[TCNQ^{\bullet-}]/dt = -k_2\{[TCNQ^{\bullet-}]_0 - [TCNQ^{\bullet-}]\}^2$$

The value of the second-order rate constant k_2 was obtained as 0.009 L/(mol min). The rate constant of the $TCNQ^{\bullet-}$ (k_1) formation is much larger than that of $TCNQ^{2-}$ (k_2). This fact indicates that doping of TCNQ is initially predominated by reaction a, which results in a swelling in the gel. However, when the concentration of $TCNQ^{\bullet-}$ increases and reaction b becomes more important, the gel starts to shrink because $TCNQ^{2-}$ is the real cross-linking agent binding two adjacent ammonium cations of the polymer network.

Thus, an attempt to associate the swelling of CT polymer gels as a function of the degree of cross-linking and the ionic density of the network was made using Flory's theory.[15]

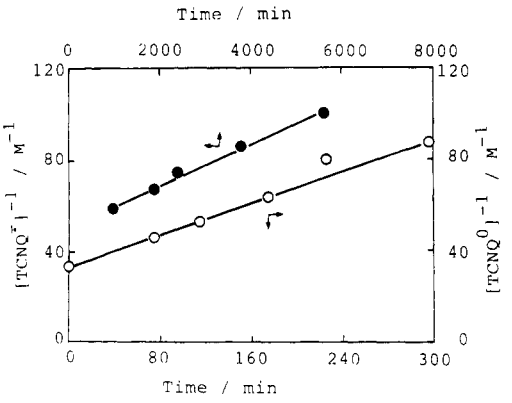


Figure 6. Reciprocal plots of $1/[TCNQ^0]$ and $1/[TCNQ^{\cdot-}]$ with time, initial concentration of TCNQ and PDMAPAA: 3.0×10^{-2}M, molar ratio of TCNQ to PDMAPAA: r = 1.0, solvent: DMF, temperature: 25 °C.

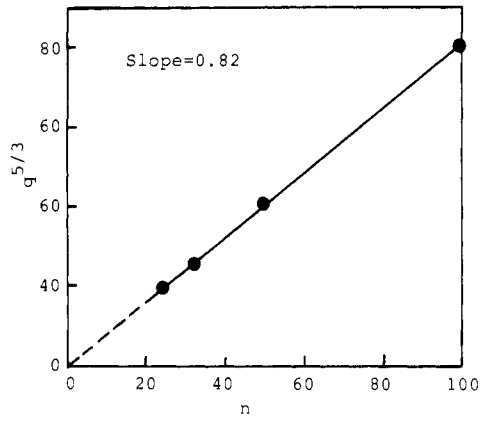


Figure 7. Degree of swelling as a function of number of monomer units between two crosslinking points.

When the gel is equilibrated with the surrounding solvent the osmotic pressure inside and outside the gel is assumed to be equal. Under this condition, the degree of swelling q of a neutral (noncharged) gel equilibrated in a good solvent is expressed as

$$q^{5/3} = (V_0/v_e)(1/2 - \chi)/v_1 \quad (1)$$

where v_e is the effective number of chains in the network in a molar unit, χ Flory's interaction parameter between polymer and solvent, v_1 the molar volume of solvent, V_0 the dried gel volume, and V the swollen gel volume.

For an ionic polymer gel placed in a solvent with low ionic concentration the degree of swelling is expressed as

$$q^{2/3} = (i/V_u)V_0/(v_e) + (V_0/v_e)(1/2 - \chi)/(qv_1) \quad (2)$$

where i is the degree of ionization between two cross-linked points and V_u the molar volume of a monomer unit.

If we suppose that the polymer network swells homogeneously and no physical entanglement occurs and if we consider $TCNQ^{\cdot-}$ as the only counterions that can contribute to gel swelling (i.e., there is no contribution of $TCNQ^{2-}$ to gel swelling), we obtain the effective number of chains as $v_e = M/n$, where M is the moles of the gel and n is the number of monomer units between two cross-linking points. Since the molar volume of a monomer unit V_u can be expressed as V_0/M, eqs 1 and 2 can be written as follows

$$q^{5/3} = n(V_u/v_1)(1/2 - \chi) \quad (3)$$

$$q^{2/3} = ni + n(V_u/v_1)(1/2 - \chi)/q \quad (4)$$

Table I
Data of the Degree of Ionization i Calculated from Equation 5 for the Gels with Various Degrees of Cross-Linking with Different Doping Ratios of TCNQ[a]

degree of cross-linking	degree of swelling	degree of ionization
	TCNQ/DMAPAA = 0[b]	
0.5	14	0
1.0	9	0
1.5	7	0
2.0	6	0
	TCNQ/DMAPAA = 0.1	
0.5	51	0.12
1.0		
1.5	33	0.11
2.0	11	0.12
	TCNQ/DMAPAA = 0.25	
0.5	134	0.26
1.0	56	0.28
1.5	27	0.24
2.0	17	0.22

[a] $r = 0, 0.1, 0.25$. [b] In this case degree of cross-linking was calculated the same as the molar ratio of cross-linking agent to monomer.

Thus, it is seen from eq 3 that the logarithmic plot of the degree of swelling q against n for noncharged polymer gel should have a $^3/_5$ slope. The experimental data obtained for PDMAPAA gel swollen in DMF (no doping) gives a straight line with a slope of 0.625, which is in good agreement with the theoretical value of $^3/_5$ in eq 3. Here, the number of monomer units between two cross-linking points n was estimated from the molar ratio of the cross-linking agent to the monomer. Thus, it is clearly demonstrated from the swelling behavior that PDMAPAA gel before doping has no charge in the polymer network. From eq 3 one can obtain χ, Flory's parameter expressing the first neighbor interaction free energy, divided by kT, for solvent with polymer. Since in the present case the ratio $(V_u/v_1)(1/2 - \chi)$ can be calculated from the slope of the straight line in Figure 7, we obtain $(V_u/v_1)(1/2 - \chi) = 0.82$. Equation 4 can now be expressed in the following very simple form:

$$i = q^{2/3}/n - 0.82/q \quad (5)$$

Table I contains data showing the degrees of ionization i calculated from eq 5 for the gels with various degrees of cross-linking and for two doping ratios of TCNQ: $r = 0.1$ and 0.25.

It can be seen that the values showing the degree of ionization calculated in this way are almost the same as those of r (the molar ratio of added TCNQ to PDMAPAA gel) for the gels with different degrees of cross-linking. From these results, we can estimate that practically all of the TCNQ has reacted with PDMAPAA according to eq 1 to give a CT complex consisting of cation radicals of a polymer network and TCNQ anion radicals.

When r is larger than 0.25, it is difficult to calculate i since the formation of $TCNQ^{2-}$, which behaves as a cross-linking agent and induces deswelling of the gel, must be taken into account.

Conclusion

1. A polymer network containing an amino group stoichiometrically formed a charge-transfer complex with TCNQ to give the corresponding cation and anion radicals, which fully ionized in DMF.

2. Using Flory's theory, swelling of TCNQ–PDMAPAA gels was quantitatively expressed as a function of ion density and degree of cross-linking of the polymer network.

Acknowledgment. We are indebted to Osaka Organic Chemical Industry, Ltd., for its kindness in providing TCNQ.

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Registry No. TCNQ, 1518-16-7; (DMAPAA)(MBAA) (copolymer), 132460-82-3.