Br + I, 14.07), the degree of substitution was estimated as 14.2 mol % (0.94 mmol of V^{2+} in 1 g of polymer).

Reduction of Azobenzene in the Zn-V^{2+} System. To an acetonitrile–pH 4.0 phthalate buffer (9:1) in a three-necked flask equipped with a nitrogen inlet and outlet were added Zn powder (0.916 g, 3 mmol), azobenzene (0.455 g, 2.5 mmol), and viologen (0.125 mmol). The reaction mixture was stirred vigorously with a Teflon-coated magnetic bar (1 cm) at room temperature. After 24 h, insoluble parts were filtered with suction, and to the filtrate was added 10 mL of pH 4.0 buffer. The solution was evaporated under reduced pressure before being extracted with dichloromethane (3 20-mL portions). The extract was washed with 20 mL of water, dried over $MgSO_4$, and evaporated in vacuo. The resulting residue was weighed and a yield of hydrazobenzene was determined by ^1H NMR in CD_3CN; δ 6.60–7.35 (aryl protons of hydrazobenzene), 7.40–8.10 (aryl protons of azobenzene).

Reduction of Azobenzene in the $Na_2S_2O_4$ System. To a 10-mL aqueous solution of sodium dithionite (0.609 g, 3.5 mmol), potassium carbonate (0.483 g, 3.5 mmol), and viologen (0.125 mmol) in a three-necked flask was added a 10-mL solution of azobenzene (0.455 g, 2.5 mmol) in dichloromethane under nitrogen pressure. The reaction mixture was stirred vigorously with a Teflon-coated magnetic bar (1 cm) at room temperature. After 24 h, the dichloromethane layer was separated and the aqueous layer was extracted with 20 mL of the dichloromethane. Two dichloromethane solutions were combined and treated in manner similar to that described above.

Registry No. Zn, 7440-66-6; $Na_2S_2O_4$, 7775-14-6; $BrPrV^{2+}$, 85681-39-6; P4VP, 25232-41-1; azobenzene, 103-33-3.

References and Notes

(1) Okura, I.; Kim-Thuan, N. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1411.

(2) Dounghong, D.; Borgarello, E.; Gratzel, M. *J. Am. Chem. Soc.* **1981**, *77*, 1411.

(3) Matsuo, T.; Sakamoto, T.; Takuma, K.; Sakura, K.; Ohsako, T. *J. Phys. Chem.* **1981**, *85*, 1277.

(4) Ageishi, K.; Endo, T.; Okawara, M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1085.

(5) Ageishi, K.; Endo, T.; Okawara, M. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(6) Okawara, M.; Hirose, T.; Kamiya, N. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 927.

(7) Saotome, Y.; Endo, T.; Okawara, M., unpublished data.

(8) Factor, A.; Heinsohn, G. E. *J. Polym. Sci., Part B* **1971** *9*, 289.

(9) Simon, M. S.; Moore, P. T. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1.

(10) Kamogawa, H.; Mizuno, H.; Todo, Y.; Nanasawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 927.

(11) Tamagaki, S.; Liesner, C. E.; Neckers, D. C. *J. Org. Chem.* **1980**, *45*, 1573.

(12) Card, R. J.; Neckers, D. C. *Inorg. Chem.* **1978**, *17*, 2345.

(13) Shapiro, B. I.; Minin, V. V.; Srykin, Y. K. *Zh. Struct. Khim.* **1973**, *14*, 642.

(14) 4,4′-Bipyridine was dehydrated refluxing benzene in a flask equipped with a Dean–Stark trap; mp 114 °C.

Electron Transport across Polymeric Membranes Containing the Viologen Structure

Kentaro Ageishi, Takeshi Endo,* and Makoto Okawara

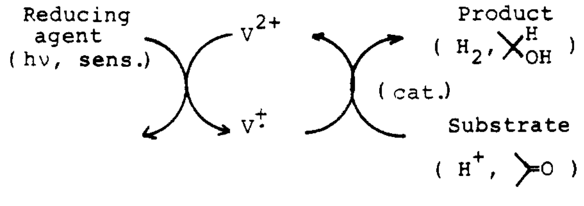
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan. *Received September 22, 1982*

ABSTRACT: Cross-linked membranes containing viologen units were prepared by the reaction of copoly[acrylonitrile–(chloromethyl)styrene] with 4,4′-bipyridyl as a cross-linking agent. Electron transport from $S_2O_4^{2-}$ to $Fe(CN)_6^{3-}$ was achieved with the resultant membranes. Electron transport in the membranes proceeded smoothly by electron diffusion between the viologen units. The rates of diffusion depend on the thickness and degree of cross-linking of the membranes and the concentration and location of the viologen units.

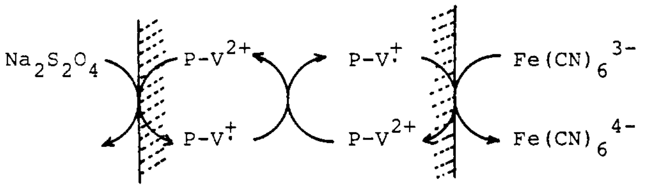
Introduction

Viologen (1,1′-dialkyl-4,4′-bipyridinium, V^{2+}) is known to undergo one-electron reduction to produce the cation radical ($V^{+}\cdot$), which is easily reoxidized to V^{2+}. Recently, viologens have received much attention as an electron-transfer catalyst (ETC) in oxidation–reduction systems,[1-5] especially in hydrogen production by photoreduction of proton (Scheme I). In the oxidation–reduction system containing ETC, the device for charge separation to suppress the back-electron-transfer process must also be effective for electron transport. For this purpose, several redox reactions mediated by liquid membrane,[6-9] micelle,[10-14] bilayer membrane,[15-17] and polymeric membrane[18-23] have been reported. Tabushi et al.[9] have succeeded in this charge separation by the combination of liquid membrane (CH_2Cl_2), and Matsuo et al.[24] have achieved charge separation between Ru^{2+} complex (sensitizer) and $V^{+}\cdot$ for the photoreduction system including viologen–micelle or polysoap. However, the redox reaction using polymeric membrane linked viologen units for charge separation and electron transport has not been reported.

Scheme I



In this article, we describe the preparation of a polymeric membrane with covalently bound viologen units (P-V^{2+}) and the reduction of Fe^{3+} by $S_2O_4^{2-}$ across the solid polymeric membrane.



Experimental Section

Materials. 1-Propyl-4-(4-pyridyl)pyridinium bromide was prepared according to the method previously reported.[25] Other

0024-9297/83/2216-0884$01.50/0

Table I
Rates of Electron Transport across Polymeric Membranes[a]

membrane	viologen content, mol %	thickness, mm	$k \times 10^3$, min^{-1}	yield of Fe^{2+}, %/24 h
1a	4.8	0.046	3.89	100
1b	9.2	0.050	0.30	19
1c	19.6	0.048	0.25	13
1d	5.2	0.095	1.83	55
1e	5.3	0.157	0.20	6
2	5.5	0.042	3.19	100
5	2.4	0.054	0.25	16

[a] $[Na_2S_2O_4]$ = 1000 μmol, $[Fe^{3+}]$ = 125 μmol; 25 °C; under argon.

Table II
Effect of Viologen Concentration on the Rates of Electron Transport by Polymeric Membrane 3[a]

viologen content, mol %	$k \times 10^3$, min^{-1}
0 (membrane 4)	leakage
2.2	0.25
4.8	1.29
8.4	10.89

[a] $[Na_2S_2O_4]$ = 1000 μmol. Membrane 3 was cast by using 1-propyl-4-(4-pyridyl)pyridinium bromide, Dabco (5 mol %), and AN-CMS copolymer (CMS content = 39 mol %). Thickness = 0.05 ± 0.003 mm; 25 °C; under argon.

chemical reagents were of commercial reagent grade. All solvents used in the present paper were purified by accepted procedures.

Preparation of Copolymers. The copolymerization of acrylonitrile (AN) with (chloromethyl)styrene (CMS; 60% meta, 40% para) (mole ratio, [AN]:[CMS] 9:1, 4:1, and 3:2) in DMF (concentrated; 3 mol/L) was carried out at 60 °C for 72 h by using 2,2′-azobis(isobutyronitrile) (AIBN) (1 mol %) as an initiator. After the reaction, the reaction mixture was poured into a large amount of MeOH. The isolated copolymers were filtered off and dried in vacuo. The concentration of CMS units in the polymers was determined from chlorine analysis (% Cl = 6.57, 8.98, and 14.92, corresponding to CMS concentrations of 12, 19, and 39 mol %, respectively). An AN-CMS-2-vinyl-2-pyrrolidone (VPy)-terpolymer (mole ratio, [AN]:[CMS]:[VPy] 7:1:2) was prepared by the same procedure. The terpolymer composition was estimated by chlorine and nitrogen analysis [% Cl = 8.98; % N = 16.66; [AN]:[CMS]:[VPy] 34:18:48 (mol %)].

Preparation of Membranes. Membranes **1**–**3** were prepared as follows. AN-CMS copolymer (0.5 g) was added to dimethylformamide (DMF) solution (10 mL) containing specific amounts (5–20 mol % vs. CMS units in the copolymer) of 4,4′-bipyridyl or 1-propyl-4-4-pyridyl)pyridinium bromide and 1,4-diazabicyclo[2.2.2]octane (Dabco). The solution was cast on a Teflon plate and heated at 60 °C to form membranes. The membranes were washed with 1:1 methanol–DMF. Blank membrane **4** was prepared in the same manner except Dabco was used as a cross-linking agent instead of 4,4′-bipyridyl. Membrane **5** was prepared by the reaction of membrane **4** (cross-linked with 2 mol% Dabco) with 1-propyl-4-(4-pyridyl)pyridinium bromide at 60 °C in DMF (50 mL) for 48 h. The concentration of viologen units in the membranes is given in Tables I–IV.

Measurement. The polymeric membranes were set in the apparatus shown in Figure 1. The reaction system consisting of sodium dithionite ($Na_2S_2O_4$) (1000 μmol)/0.1 M phosphate buffer (pH 7, 50 mL) and $K_3Fe(CN)_6$ (125 μmol)/0.1 M phosphate buffer (pH 7, 50 mL) was separated by polymeric membranes **1**–**6** (diameter = 1.5 cm, reaction area = 1.76 cm^2, thickness measured by micrometer). Poth sides were stirred at 25 °C under an atmosphere of argon, as shown in Figure 1.

The rates of electron transport from $S_2O_4^{2-}$ to $Fe(CN)_6^{3-}$ were estimated spectrophotometrically by monitoring the decrease in the absorbance of $Fe(CN)_6^{3-}$ at 420 nm. Leakage of $S_2O_4^{2-}$ through polymeric membranes **1**–**6** was checked by a spot test using *o*-dinitrobenzene in methanol/aqueous ammonia solution (limit of detection = 3 μg; limit of dilutions *o*-dinitrobenzene/solvent = 1/16600)[26].

Table III
Effect of Cross-Linking Degree on the Rates of Electron Transport by Polymeric Membrane 3[a]

[Dabco], mol %	$k \times 10^3$, min^{-1}
0	3.19
2.1	2.83
4.2	1.29
9.4	0.16
8.3[b]	0.93

[a] $[Na_2S_2O_4]$ = 1000 μmol, $[Fe^{3+}]$ = 125 μmol; membrane 3 was cast by using Dabco, 1-propyl-4-(4-pyridyl)-pyridinium bromide (5 mol %), and AN-CMS copolymer (CMS content = 39 mol %). Thickness = 0.05 ± 0.03 mm; 25 °C; under argon. [b] [1-Propyl-4-(4-pyridyl)pyridinium bromide] = 5 mol %.

Table IV
Dependence of Rate of Electron Transport by Polymeric Membrane 1a[a] on Sodium Dithionite Concentration

$[Na_2S_2O_4]$, μmol	$k \times 10^3$, min^{-1}	$[Na_2S_2O_4]$, μmol	$k \times 10^3$, min^{-1}
500	1.04	2000	15.42
1000	3.89	2500	25.37
1500	7.72		

[a] $[Fe^{3+}]$ = 125 μmol; 25 °C; under argon.

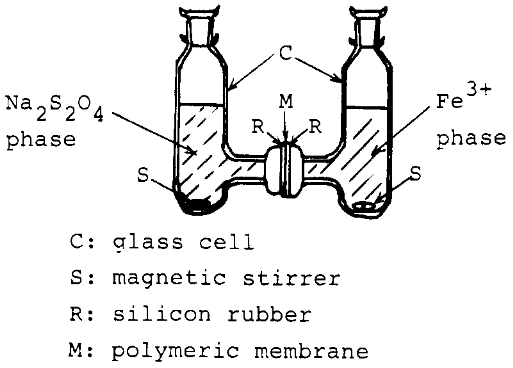


Figure 1. Reaction apparatus.

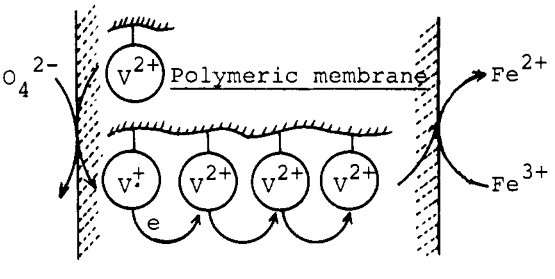


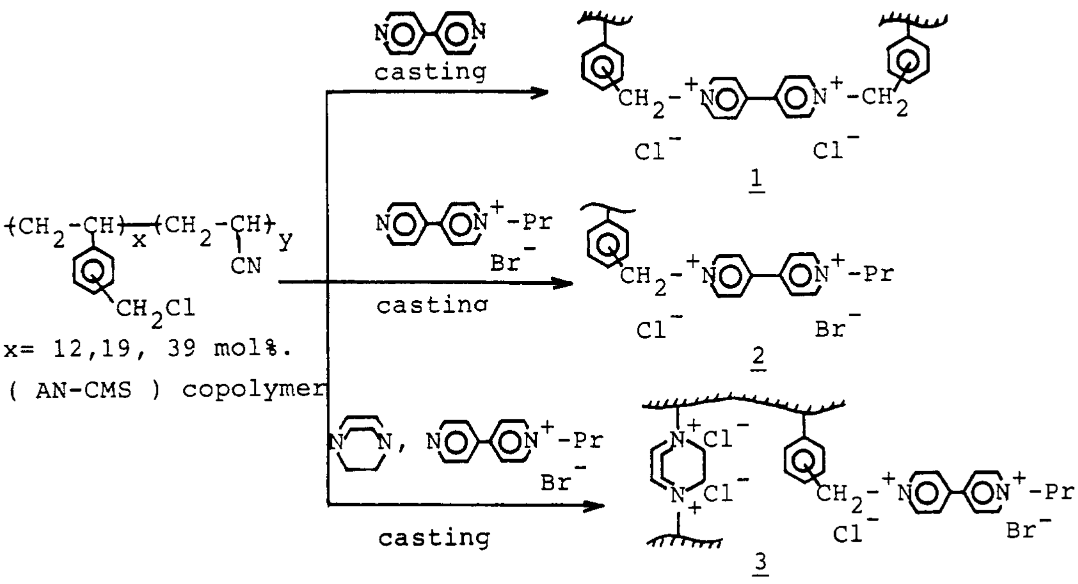
Figure 2. Polymeric membrane.

Results and Discussion

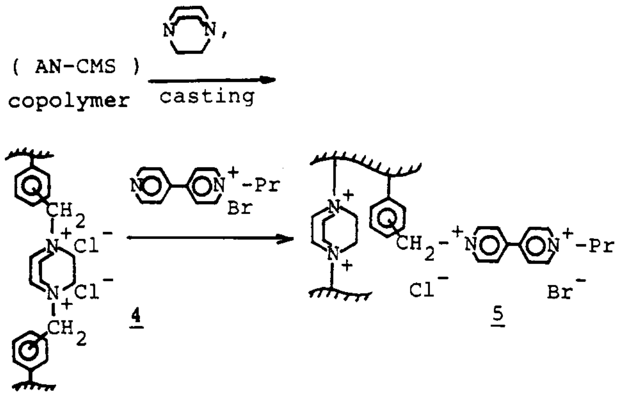
Preparation of Polymeric Membranes. The polymeric membranes used in this study were prepared by the methods shown in Scheme II.

The insoluble membrane **1** with the viologen structure as a cross-linking unit was prepared by casting a DMF solution containing the AN-CMS copolymer and 4,4′-bipyridyl. The non-cross-linked membrane **2** was prepared by using AN-CMS copolymer and 1-propyl-4-(4-pyridyl)pyridinium bromide and was soluble in DMF, Me_2SO, etc. The insoluble membrane **3** was prepared by use of 1-propyl-4-(4-pyridyl)pyridinium bromide and 1,4-

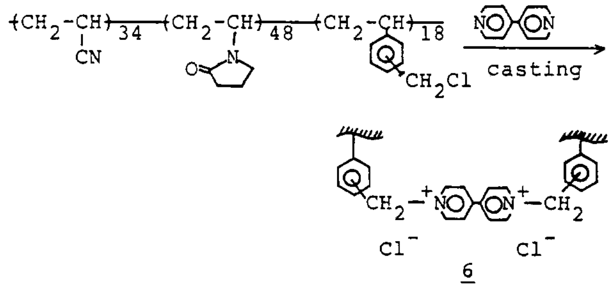
Scheme II



diazabicyclo[2.2.2]octane. The blank membrane 4 without the viologen moiety was obtained by using Dabco instead of 4,4′-bipyridyl. Membrane 5 with attached viologen structure on its surface was prepared from membrane 4 and 1-propyl-4-(4-pyridyl)pyridinium bromide.



The preparation of the more hydrophilic membrane 6 was carried out by reaction of AN–CMS–1-vinyl-2-pyrrolidone terpolymer with 4,4′-bipyridyl.



Electron Transport through the Membranes. Electron transport through the membrane from $S_2O_4^{2-}$ to Fe^{3+} has been examined, with the expectation that the interaction between a viologen cation radical ($V^{+}\cdot$) and other viologen units (V^{2+}) is as shown in Figure 2. The electron transport process in the reduction of ferricyanide with dithionite was followed by monitoring the decrease of UV absorption at 420 nm due to the ferricyanide.

It was confirmed by a spot test that $S_2O_4^{2-}$ did not leak or diffuse through polymeric membranes 1, 2, 3, and 5. On the other hand, in the case of membranes 4 and 6, $S_2O_4^{2-}$ passed through the membranes.

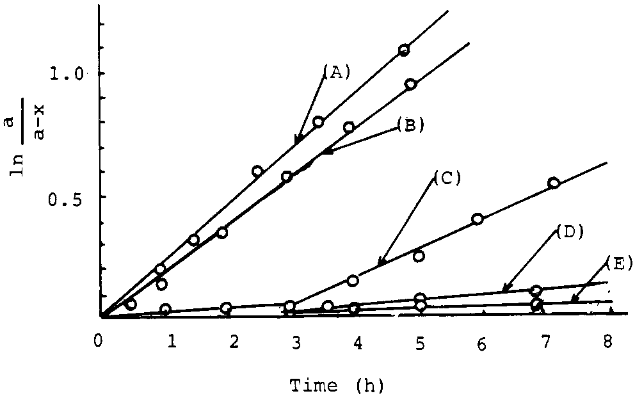


Figure 3. First-order plots in the reduction of ferricyanide to ferrocyanide with the use of polymeric membranes: (A) membrane 1a; (B) membrane 2; (C) membrane 1d; (D) membrane 5; (E) membrane 1e. $[Na_2S_2O_4]$ = 1000 μmol, $[Fe^{3+}]$ = 125 μmol; for thickness and V^{2+} content, see Table I; 25 °C; under argon.

Figure 3 presents first-order plots for the reduction of ferricyanide to ferrocyanide with the use of membranes 1, 2, and 5. In all cases, leakage of $S_2O_4^{2-}$ was not detected for 48 h without Fe^{3+} phase. Rate enhancement was observed in the case of thinner membrane 1a (line A). However, in the thicker membranes 1d and 1e, the rates were slower and exhibited an induction period (lines C and D). In addition, electron transport was also observed through the non-cross-linked membrane 2 without leakage (line B). In membrane 5 with attached viologen on its surface, electron transport was very slow (line D). The rates of electron transport by membranes 1, 2, and 5 are summarized in Table I. Membrane 1 containing the viologen structure was prepared by using 4,4′-bipyridyl as a cross-linking agent, and an increase in viologen concentration led to an increasing in degree of cross-linking. In membranes 1a, 1b, and 1c with similar thickness the rates decreased as viologen content increased. This may be due to reduced mobility of viologen in the membrane and the rigid viologen structure resulting from cross-linking. In non-cross-linked membrane 2, electron transport was also observed. With membrane 5 viologen units that were supported on the surface of the membrane inhibited electron migration due to the lower mobility and the large distance between the viologen units. Each membrane seems to be hydrophobic by change of ionic (cation) to neutral structure (radical) with the reduction of viologen units, and thereby the coulombic repulsion in the membrane would decrease. As shown in Table II, when the viologen content of membrane **3** with constant degree of cross-linking increased, a rate enhancement was observed. However, when the degree of cross-linking in memrane **3** with constant viologen concentration increased, the rates dropped dramatically, as indicated in Table III. This is presumably due to the decrease of mobility of the polymer chain with increasing degree of cross-linking, which interferes with access between $V^{+\cdot}$ and Fe^{3+}.

The rate of electron transport through membrane **1a** was observed to be markedly faster when the concentration of $Na_2S_2O_4$ as reducing agent was increased, as shown in Table IV.

In conclusion, we have succeeded in showing that electron transport through polymeric membranes containing viologen moieties occurs. As described above, the rates of electron transport depend on the thickness, the degree of cross-linking of the membranes, the concentration of viologen units, and the location of electron carriers. These oxidation–reduction systems mediated by polymeric membrane provide a new charge separation model, and their application to the decomposition of water in photoirradiation systems can be expected.

Registry No. $Na_2S_2O_4$, 7775-14-6; $K_3Fe(CN)_6$, 13746-66-2; D, 280-57-9; [AN]:[CMS], 9080-68-6; [AN]:[CMS]:[VPy], 85613-97-4; 4,4′-bipyridyl, 553-26-4.

References and Notes

(1) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720.
(2) Okura, I.; Kim-Thuan, N. *J. Mol. Catal.* **1979**, *5*, 311.
(3) Kawai, T.; Tanimura, K.; Sakata, T. *Chem. Lett.* **1979**, 137.
(4) Okawara, M.; Hirose, T.; Kamiya, N. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 927.
(5) Ageishi, K.; Endo, T.; Okawara, M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1085.
(6) Grimadi, J. J.; Boileau, S.; Lehn, J. M. *Nature (London)* **1977**, *265*, 229.
(7) Anderson, S. S.; Lyle, I. G.; Paterson, P. *Nature (London)* **1976**, *259*, 147.
(8) Tabushi, I.; Yazaki, A.; Koga, N.; Iwasaki, K. *Tetrahedron Lett.* **1980**, *21*, 373.
(9) Sugimoto, T.; Miyazaki, J.; Kokubo, T.; Tanimoto, S. *Tetrahedron Lett.* **1981**, *22*, 373.
(10) Katagi, T.; Yamamura, T.; Sauto, T.; Sasaki, Y. *Chem. Lett.* **1981**, 503.
(11) Takuma, K.; Sakamoto, T.; Matsuo, T. *Chem. Lett.* **1981**, 815.
(12) Takuma, K.; Sakamoto, T.; Nagamura, T.; Matsuo, T. *J. Phys. Chem.* **1981**, *85*, 619.
(13) Takuma, K.; Sakamoto, T.; Nagamura, T.; Matsuo, T. *Chem. Lett.* **1981**, 815.
(14) Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.
(15) Tabushi, I.; Nishiya, T. *Tetrahedron Lett.* **1982**, *23*, 2661.
(16) Tunuli, M. S.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2507.
(17) Tien, H. T.; Verma, S. P. *Nature (London)* **1970**, *227*, 1232.
(18) Takeishi, M.; Inomata, N.; Hayama, S. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 374.
(19) Kaneko, M.; Yamada, A. *Makromol. Chem.* **1981**, *182*, 1111.
(20) Kaneko, M.; Yamada, A. *Inorg. Chim. Acta* **1980**, *45*, L73.
(21) Oyama, N.; Anson, F. C. *J. Electroanal. Chem.* **1980**, *112*, 271.
(22) Facci, J.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 2870.
(23) Shigehara, K.; Oyama, N.; Anson, F. C. *Inorg. Chem.* **1981**, *20*, 518.
(24) Takuma, K.; Sakamoto, T.; Nagamura, M. *J. Phys. Chem.* **1981**, *85*, 1277.
(25) Kamogawa, K.; Mizuno, H.; Todo, Y.; Nanazawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3149.
(26) Kuhr, R.; Weyand, F. *Ber.* **1935**, *69*, 1967.

Chemical Modification of Acrylamide Gels: Verification of the Role of Ionization in Phase Transitions

David Nicoli*

Department of Physics, University of California at Santa Barbara, Santa Barbara, California 93106

Carl Young and Toyoichi Tanaka

Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Alfred Pollak and George Whitesides[†]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received April 1, 1982*

ABSTRACT: We prepared "doped" acrylamide gels containing the ester *N*-acryloxysuccinimide; subsequent hydrolysis of the ester alone yielded gels of varying network ionization. After incubation in acetone–water mixtures, these gels displayed a swelling behavior qualitatively similar to that obtained from time-dependent hydrolysis of pure acrylamide gels. These results confirm that the network ionization plays a crucial role in the phase transition of these ionic gels.

Introduction

Cross-linked polymer gels of acrylamide/bis(acrylamide) that have been equilibrated in acetone–water mixtures have been observed to undergo dramatic decreases in volume with increasing acetone concentration or decreasing temperature.[1,2] This reversible volume behavior ranges from continuous shrinkage to a discontinuous collapse of the network, depending on the length of time (measured in days) that the gel is incubated in a basic solution (e.g., pH 12) prior to being equilibrated in the acetone–water mixture.

Tanaka et al.[2] were able to explain the principal qualitative features of the unusual nonlinear dependence of the gel "swelling ratio" on solvent composition by postulating a variable degree of ionization of the polymer network due to time-dependent hydrolysis of the acrylamide groups into

---

[†] Present address: Department of Chemistry, Harvard University, Cambridge, MA 02138.

0024-9297/83/2216-0887$01.50/0 © 1983 American Chemical Society