

b_k	= covolume parameter, $k=1,2,3$	$[\text{m}^3 \cdot \text{mol}^{-1}]$
ΔH	= heat of vaporization	$[\text{J} \cdot \text{mol}^{-1}]$
m, n	= parameter of proposed function	$[-]$
P	= pressure	$[\text{N} \cdot \text{m}^{-2}]$
R	= universal gas constant	$[\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}]$
T	= temperature	$[\text{K}]$
V	= molar volume	$[\text{m}^3 \cdot \text{mol}^{-1}]$
ΔV	= volume difference, $V^v - V^l$	$[\text{m}^3 \cdot \text{mol}^{-1}]$

Ω_a	= $aP_c/R^2T_c^2$	$[-]$
ω	= acentric factor	$[-]$

<Superscripts>

l	= liquid phase
s	= saturated value
v	= vapor phase

<Subscripts>

c	= critical value
CC	= obtained from Clausius-Clapeyron eq.
dev	= deviation from data

new	= proposed value
PR	= obtained from PR EoS
r	= reduced value

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SWELLING BEHAVIOR AND AN EVALUATION OF NETWORK STRUCTURE OF POLY(ACRYLAMIDE-co-ACRYLIC ACID) GEL

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Key Words: Copolymer Gel, Polymer Network, Volume Change, Equilibrium, Kinetics

Introduction

Several polymer gels are known to undergo a drastic volume change (a phase transition) by infinitesimal changes in solvent compositions, ionic composition, pH, electric field, etc.¹⁻⁵⁾ This phenomenon is brought about by three forces: polymer-polymer affinity, rubber elasticity and hydrogen-ion pressure for ionic gels. Therefore, the degree of volume change depends on the relative magnitude of these forces. When a poly(acrylamide-co-acrylic acid) gel is immersed in a solvent, part of the acrylic acid can be dissociated to carboxyl (R-COO^-) and hydrogen ions (H^+). The hydrogen ions act like molecules to generate positive pressure in a space consisting of a negatively charged polymer network.

Nakano *et al.*²⁾ have reported a preliminary study on the effects of the relative amounts of monomers

(acrylamide, N,N' -methylene-bisacrylamide and acrylic acid) on swelling and shrinking behaviors of polymer gels. In the polymerization, tetramethyl ethylene diamine (TEMED) was used as an accelerator of redox type. Not only the amounts of these monomers but also that of TEMED were found to be an important factor determining the kinetic chain length.

In the present study the concentrations of TEMED were varied in the polymerization. Their effects on structure and swelling behavior of the gels were studied both experimentally and analytically by using the f -values, defined as the number of dissociated counterions per effective polymer chain, and the diffusion coefficients of the gel network related to the kinetics.

1. Sample Preparation and Experimental Procedures

Ionic poly(acrylamide-co-acrylic acid) gels were synthesized from monomers of acrylamide (main

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component), *N,N'*-methylene-bisacrylamide (cross-linking agent) and acrylic acid (ionizable component). These monomers were dissolved in distilled, degassed and nitrogen-saturated water at 303 K. The monomer solutions were mixed fully with tetramethyl ethylene diamine (TEMED: an accelerator) and ammonium persulfate (an initiator) solutions. The polymerization took place in small glass tubes (0.692, 1.05, 1.54, 2.18 mm i.d.) for five minutes at 303 K. Then they were removed from the tubes and cut into rod-shaped pieces having a length about equal to their diameter.

Equilibrium experiments were carried out to measure the equilibrium diameter of the cross-section of the rod-shaped gel in acetone-water mixtures and obtain a critical concentration inducing the phase transition. Subsequently, concentration swing experiments were performed in the vicinity of the critical concentration of acetone, in which the state of the gel became highly sensitive. The time course of the change in diameter of the rod gel was measured under a microscope.

2. Results and Discussion

The compositions of poly(acrylamide-co-acrylic acid) gels used in this study are tabulated in Table 1, in which TEMED concentrations are varied from 1 to 30 mol·m⁻³.

Figure 1 shows, for example, the degree of swelling of the gels having constituents (○ key) shown in Table 1. The abscissa in Fig. 1 shows the ratio of the volume fraction of the network, ϕ/ϕ_0 (ϕ_0 at the preparation and ϕ at equilibrium). The equilibrium volume of the gel, V , can be represented as

$$\frac{V_0}{V} = \frac{\phi}{\phi_0} \quad (1)$$

where V_0 is the volume of the gel at $\phi = \phi_0$. Similar volume changes were obtained for ionic gels of various constituents.

To analyze the effects of the concentration of TEMED on structure and swelling behavior of the gels, two approaches are employed in this study.

One is the use of the Flory-Huggins, mean field theory which is applied to evaluate the f -value in Eq. (2). The f -value is defined as the number of dissociated hydrogen ions per effective polymer chain.

$$\tau = 1 - \frac{\Delta F}{kT} = -\frac{vv}{N\phi^2} \left[(2f+1) \left(\frac{\phi}{\phi_0} \right) - 2 \left(\frac{\phi}{\phi_0} \right)^{1/3} \right] + 1 + \frac{2}{\phi} + \frac{2 \ln(1-\phi)}{\phi^2} \quad (2)$$

The f -value can be obtained by fitting the width of the volume change plotted in Fig. 1 with Eq. (2), in which v is the number of constituent chains per unit volume at $\phi = \phi_0$ and the number is represented by the

Table 1. Compositions of poly(acrylamide-co-acrylic acid) gels.

Key	Ac [*] [mol·m ⁻³]	Am ^{**} [mol·m ⁻³]	B ^{***} [mol·m ⁻³]
○	20.42	689.4	9.081
①	0.00	689.4	9.081
③	10.21		
⑤	61.26		
⑦	122.5		
⑨	204.2		
□	20.42	590.9	9.081
■		984.8	
■		1379	
△	20.42	689.4	6.811
▲			13.62
▲			22.70
TEMED conc. 1~30 [mol·m ⁻³]			
* : Acrylic Acid			
** : Acrylamide			
*** : Bisacrylamide			

amount of TEMED.

The other approach is the use of the diffusion coefficient, D , of the gel network during swelling, which can be obtained from both the time course of the volume change observed in the concentration swing experiment and Eqs. (3) and (4), reported in the previous paper.²⁾ Two kinds of experiments are performed in the concentration swing, as shown by the segments of each line with an arrowhead in Fig. 1. One is where the high concentration side of acetone is fixed and the lower ones are varied as ①, ③, ⑤, ⑦ and ⑨ (case I). The other is the reverse case as ②, ④, ⑥ and ⑧ (case II).

First, these ways were evaluated by using the diffusion coefficient of the gel network obtained by analyzing the time course of change in radius of the rod gel with Eqs. (3) and (4).

$$\frac{\Delta a(t)}{\Delta a_0} = (6/\pi^2) \sum n^{-2} \exp(-n^2 t/t_s) \quad (3)$$

$$t_s = a^2/D$$

Equation (3) is derived from a diffusion equation of the gel network in a solvent.²⁾ It can be rewritten in a simpler form when t/t_s is larger than unity:

$$\frac{\Delta a(t)}{\Delta a_0} = (6/\pi^2) \exp(-t/t_s) \quad (4)$$

The swelling time is scaled by the characteristic time

of swelling t_s .

The swelling ratios $\Delta a(t)/\Delta a_0$ are plotted as a function of t in a semilog scale in Fig. 2, as an example. The characteristic time t_s could be determined from the slope of the straight line calculated by using Eq. (4). The diffusion coefficient D is obtained from $t_s = a^2/D$ in Eq. (3). In addition, the validity of $t_s = a^2/D$ was experimentally verified for the gels used in this study.

Figure 3 shows the relationships between the diffusion coefficient of the gel network and the width in the concentration swing. In case I, the diffusion coefficient was found to be directly proportional to the width of concentration. In case II, it was almost constant. Therefore, the width within 5% across a critical concentration of acetone-water mixture was chosen as the width of concentration swing in this study. Such phenomena are also notable from the medical engineering viewpoint. For example, they will be useful in studying the kinetics of the swelling and shrinking cycle of an artificial muscle by changes in solvent compositions.

Using the above approaches, the effects of TEMED concentration on structure and swelling behaviors of the gels were studied in more detail.

The f -value is also estimated from Eq. (5) based on the concept of a polymerization process, which has been already reported in detail in a previous paper.²⁾

$$f = \frac{2A_c}{B[(A_c + A_m)V_{\text{reac}}]^2} \quad (5)$$

where the symbols of A_m , B , A_c are the concentrations of acrylamide, N,N' -methylene-bisacrylamide and acrylic acid, respectively.

Figure 4 shows the relationship between the f -values explained above and the right-hand term of Eq. (5). All the results are on a straight line except for those of the gel having higher concentrations of A_c (keys: \odot , \bullet , \bullet). The TEMED concentrations are, of course, varied in the range of 1 to 30 mol·m⁻³ for the results on the straight line. At higher concentrations of A_c , the f -values decreased monotonically with the concentration of TEMED. This means that hydrogen ions produced by dissociation of acrylic acid do not act effectively as ion pressure inside gels.

Figure 5 shows the relationship between the diffusion coefficients of the gel network D and the f -values for gels having various constituents. The diffusion coefficients correlated well with f -values in the form of $D = \exp(\alpha f + \beta)$; $\alpha = 0.833, 0.484, 0.292$ and $\beta = -15.2, -13.9, -13.0$ for TEMED concentrations of 10.0, 20.0, 30.0, respectively. The results mean that the diffusion coefficients increase exponentially with the number of dissociated counterions per effective polymer chain. Both f -values (the number of dissociated counterions per effective polymer chain)

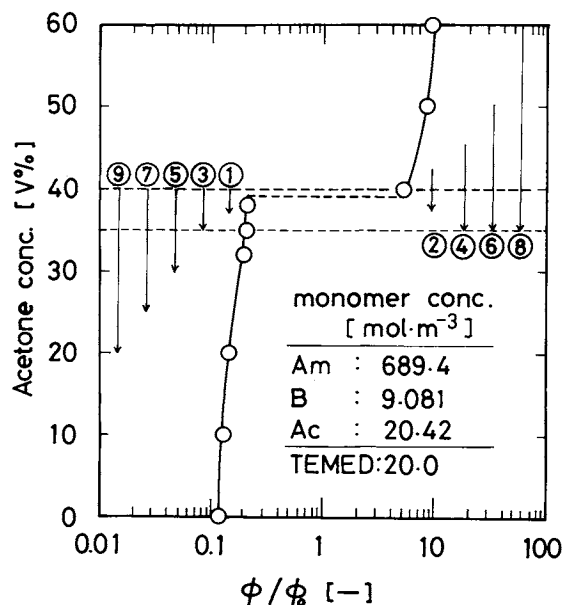


Fig. 1. Equilibrium degree of swelling of poly(acrylamide-co-acrylic acid) gels and two kinds of experimental procedures in concentration swing.

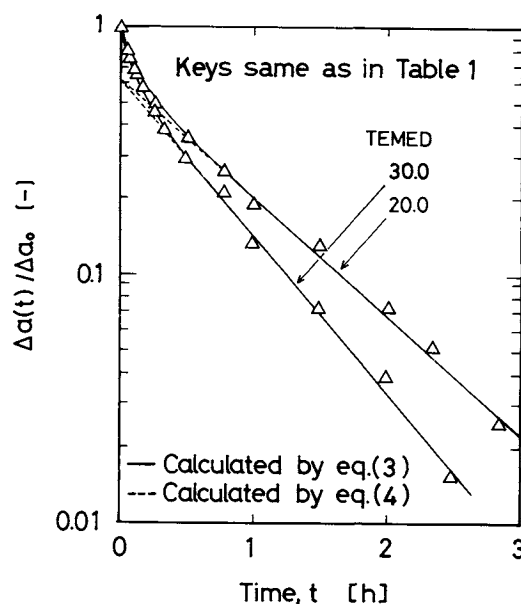


Fig. 2. Time courses of radius of cross-section in the gels during swelling when the concentrations of TEMED are varied.

and diffusion coefficients of gel network increased with decrease of acrylamide (main component) or N,N' -methylene-bisacrylamide (cross-linking agent) as well as increase of acrylic acid. As the TEMED concentration became higher, the dependency of diffusion coefficients of gel network on the f -values became less sensitive.

The above phenomena probably result from the structure of the gel network and the degree of ionic pressure generated inside the gels. Polymerization of the gel proceeds by way of the chain reaction.⁴⁾ First,

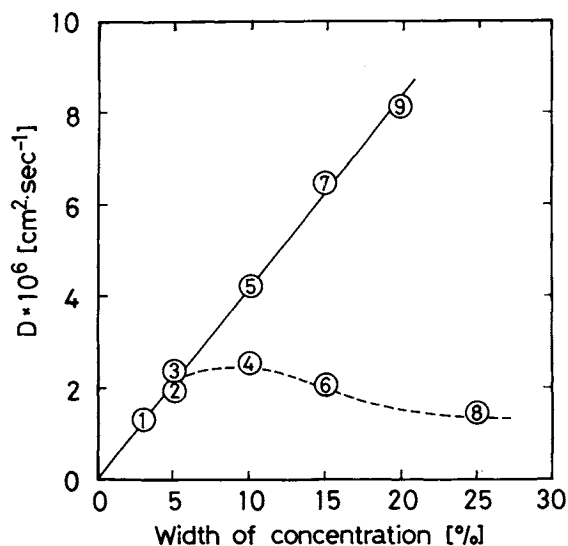


Fig. 3. Relationship between diffusion coefficients of network in poly(acrylamide-co-acrylic acid) gels and width of concentration swing.

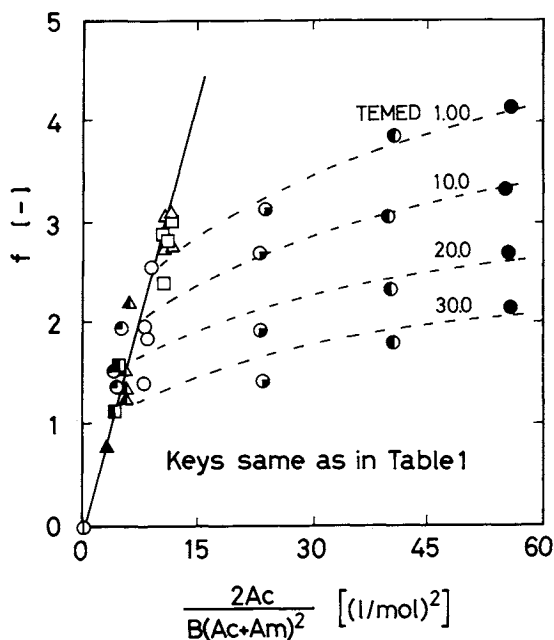


Fig. 4. Relationship between f -values of poly(acrylamide-co-acrylic acid) gels determined from equilibrium degree of swelling and compositions of gel at preparation.

ammonium persulfate decomposes to produce radicals in the presence of TEMED, resulting in all TEMED with reactive unpaired electron because 1.5 times as much ammonium persulfate as TEMED by concentration is used. Then, the TEMED combines with either acrylamide or acrylic acid and the chain units grow by shifting the activated site to the end. Bisacrylamide is incorporated into growing chains to form the gel network. Therefore, when the amount of acrylamide or N,N' -methylene-bisacrylamide was small compared with other monomers, the length of polymer chains between adjacent cross-linking points

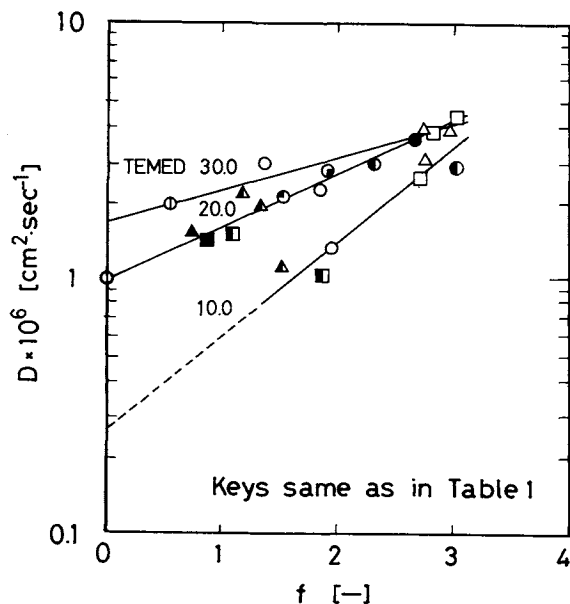


Fig. 5. Relationship between diffusion coefficients of network and f -values in poly(acrylamide-co-acrylic acid) gels.

would become large and the probability of involving acrylic acid units in the effective polymer chain would increase. This leads increases of both f -values and diffusion coefficients of the gel network, as shown in Fig. 5. Furthermore, when the gel is formed under higher concentration of TEMED, it has a configuration consisting of many free ends in the polymerization process so that the gel network tends to be more flexible, giving large diffusion coefficients. On the other hand, the force of hydrogen ion pressure cannot act effectively on the gel network because the structure has many free ends even if the amount of acrylic acid increased in the polymerization. Consequently, the diffusion coefficient of the gel network is hardly affected by the f -values.

Conclusion

The effects of the concentrations of tetramethyl ethylene diamine (TEMED) (an accelerator) as well as the other constituents (A_m : acrylamide; B : N,N' -methylene-bisacrylamide; A_c : acrylic acid) on the ionic poly(acrylamide-co-acrylic acid) gel network and its kinetics were investigated by using f -values, defined as the number of counterions per effective polymer chain, and the diffusion coefficients of gel network related to the kinetics.

Over the range of TEMED concentrations, both f -values and diffusion coefficients of the gel network increased with decrease in concentrations of A_m and B , or increase of A_c , which were closely related to the kinetic chain length between adjacent cross-linking points. The diffusion coefficients correlated well with the f -values in the form of $D = \exp(\alpha f + \beta)$ (both α and β depend on the concentrations of TEMED).

At lower concentrations of TEMED, the diffusion coefficient of the gel network became smaller. At higher ones, however, it became larger because the gels were more flexible due to the increase of free ends. The diffusion coefficient of the gel network was remarkably dependent on the f -values as the TEMED concentration became lower.

Nomenclature

A_c	= molar concentration of acrylic acid	[mol/l]
A_m	= molar concentration of acrylamide	[mol/l]
$\Delta a(t)$	= increment in radius at t	[cm, m]
Δa_0	= total increment in radius in entire process of swelling	[cm, m]
B	= molar concentration of bisacrylamide	[mol/l]
ΔF	= free-energy decrease associated with formation of contact between polymer segments	[N·m]
f	= number of dissociated counterions per effective polymer chain	[—]
k	= Boltzman constant	[J/K]
N	= Avogadro's number	[1/mol]

t	= time	[s, h]
t_s	= characteristic time	[s, h]
V	= volume of gel	[l]
V_{reac}	= reaction volume around a cross-linking molecule	[l]
v	= molar volume of solvent	[l/mol]
ν	= number of constituent chains per unit volume at $\phi = \phi_0$	[1/l]
τ	= reduced temperature	[—]
ϕ	= volume fraction of network at equilibrium	[—]
ϕ_0	= volume fraction of network at preparation	[—]

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EFFECTS OF PREPARATION CONDITIONS ON RADIAL COMPRESSIVE STRENGTH OF La_2O_3 PELLETS

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Key Words: Chemical Reaction, Lanthanum Oxide, Pellet, Compressive Strength, Hydration, Dehydration, X Ray Diffraction, Thermogravimetry

Recently it has become possible to obtain high-purity rare earth oxides, and demand for them has been stimulated by the need for new materials for lasers, sensors and fluorescent substances.³⁾ In addition, considerable attention has been paid to the high catalytic activity of rare earth oxides.²⁾

Catalysts are generally pelletized for actual use, but when preparation is accompanied by chemical reactions its effect on the mechanical strength of the pellets is not fully understood. The present work examines the effect on radial compressive strength of various factors by varying water content and molding pressure, using lanthanum oxide as the starting material.

Weight was measured by a thermogravimeter and by X-ray diffraction analysis to verify the transformation of lanthanum compounds, and the depen-

dence of chemical or physical properties on the compressive strength of La_2O_3 pellets under different conditions of preparation was examined to obtain more definite information on molding accompanied by hydration/dehydration.

1. Experimental

1.1 Procedure for preparation of pelletized catalyst

1) Parameters at the preparation stage As shown in Fig. 1, preparation was carried out in two steps—pre-granulation and molding. The objective of pre-granulation was preparation of pellet intermediate as an agglomerate, because this was found to provide advantages of smooth operation by preventing powdered samples from intruding into the gap between piston and cylinder during molding, and by producing high-density pellets.⁷⁾

Molding samples were prepared by wetting of pellet intermediate. In molding, three parameters were em-

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