Korean J. of Chem. Eng., **11**(2), 104-110 (1994)

QUANTITATIVE ANALYSIS ON SWELLING BEHAVIOR OF HSMA/PVA IPN IONIC GELS UNDER ELECTRIC FIELD

Yum Rak Oh, Won Sang Lee, O Ok Park* and Yang-Kyoo Han**

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea
**Polymer Chemistry Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea
(Received 25 June 1993 • accepted 17 November 1993)

Abstract—In order to explain the electric response of HSMA/PVA IPN ionic gel, polyion concentration (f) and/or interaction parameter (χ_{ij}) between gel and water are used, which were previously determined elsewhere by comparing swelling behaviours in the mixed solvents with Tanaka's theory [1]. Ionic polymer gel separated from the electrodes exhibits exponential responses when the electric field is applied or stopped, where the characteristic times for swelling and shrinking and equilibrium swelling ratio are successfully correlated with polyion concentration or interaction parameter. In addition, the strength of field is also an important factor to determine the overall responses. The direction of gel with respect to the electric field is also considered and optimum size was apparent to show maximum swelling.

INTRODUCTION

It is well known that polymer gel with ionic groups in the network swells or shrinks according to the external electric field. It means that chemical energy in the polymer can be transformed into the mechanical energy, so that it is usually called to have 'chemo-mechanical function'. Due to this property, ionic polymer gel has been studied for possible applicability in industrial switching sensor, selective membrane for chemicals, alternative part materials for industrial robot or biomedical materials [2, 3]. Chemo-mechanical gel exhibits more gentle and flexible behaviour like muscle than metalic mechanical part [4].

HSMA/PVA IPN ionic gel in NaOH aqueous solution can be deformed under electric field. It is well known that there are two distinct deformation observed according to the relative position of gels in the electric fields. If gel is touched with electrode, gel shrinks at anode side [5]. On the other hand if gel is located separated from the electrode, anode side swells [6, 7]. It is certainly dependent not only upon gel properties such as polyion concentration, etc., but also upon solution properties such as electrolyte concentration, etc. [8], but it is difficult to measure the concentration of polyions in the gel network.

Therefore in order to explain the electric response of ionic gels, it is necessary to know the gel properties such as effective polyion concentration, interaction parameter between water and gel in the first place. We have reported that a specific IPN type ionic polymer gel can be analyzed based on a proper set of polyion concentration and interaction parameter from Tanaka' s theory in the mixed solvents [1]. Thus here electric responses of such gels will be analyzed based on such parameters.

THEORETICAL BACKGROUND

1. Swelling or Bending, Shrinking Mechanism

Fig. 1 shows a typical swelling behaviours of ionic polymer gels in the electrolyte solution. It is certainly dependent upon electric field, relative position of gels between two platinum electrode plates etc. It is obvious that translation of mobile ions due to the electric field will cause ionic distributions not only inside the gel but also near outside, then there will be an osmotic pressure developed. When the electric field is applied, cations such as Na^+ or K^+ will move from anode to cathode and anion such as OH^- will move in the opposite way. Thus if one consider the cathode side, Na^+ concentration inside the gel will be greater than

*All correspondence should be addressed.

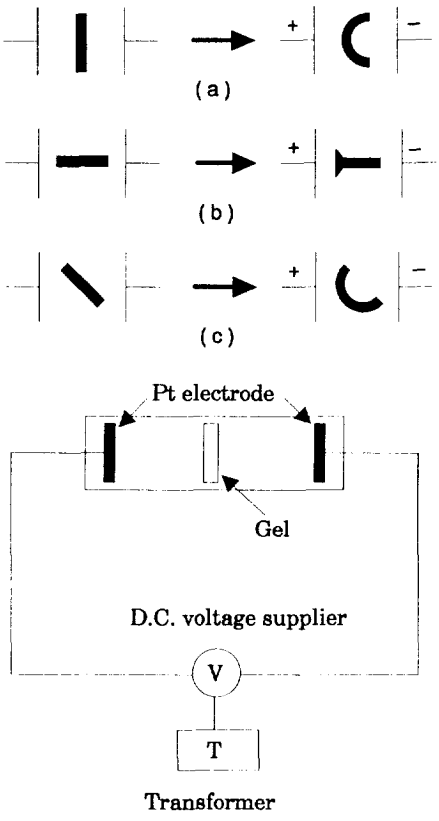

Fig. 1. Experimental apparatus and schematic illustration of the deformation of HSMA/PVA IPN gel without and under the D.C electric field.
(a) Vertical , (b) Horizontal and (c) Diagonal configuration.

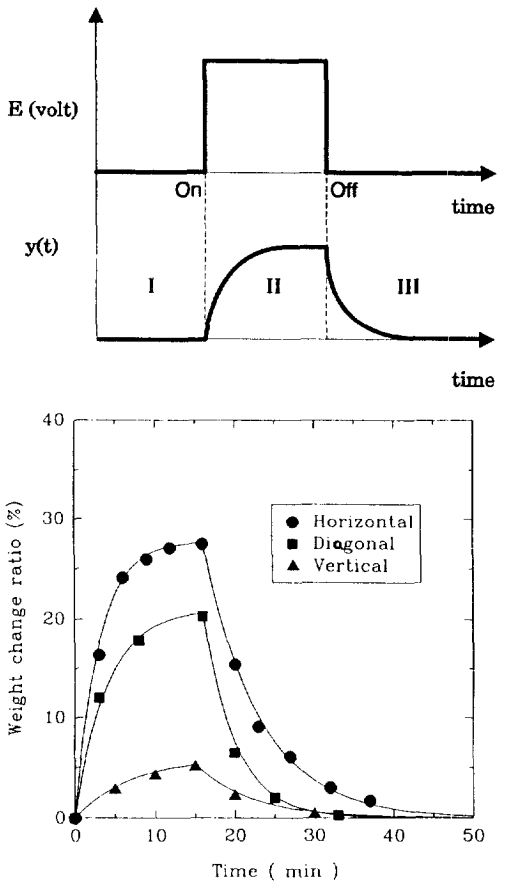

Fig. 2. Transient behaviours of gel's (sample 2) swelling-shrinking resulting from switching on-off of D.C electric field (10V) in the 0.04 N NaOH aqueous solution.

outside, which make water penetrate into the gel to maintain Donnan equilibrium resulting in swelling of that part. As shown in Fig. 1, relative area for such swelling makes different shape of bending deformation. In order to analyze the overall deformation picture, it is necessary to consider the constitutive relation for the gel in detail, but here we are mainly concerning the degree of deformation only for quantitative analysis.

2. Swelling under Electric Field

Fig. 2 shows a typical electric response of ionic gel after electric field is applied or stopped. Apparent exponential response can be analyzed by using three parameters such as equilibrium swelling ratio y (∞), characteristic swelling time (τ_s) and characteristic shrinking time (τ_h).

$$y(t) = y(\infty)\left\{1 - \exp\left(-\frac{t}{\tau_s}\right)\right\} \quad (1)$$

where $$y(t) = \frac{\{w(t) - w_s\}}{w_s} \quad (2)$$

$$y(\infty) = \frac{\{w_\infty - w_s\}}{w_s} \quad (3)$$

w_∞ and w (t) are weights of gel at long time after electric field is applied and at time t respectively. w_s is the equilibrium weight of gel in NaOH aqueous solution.

After the electric field is stopped, gel shrinks exponentially like

$$y(t) = y(\text{off})\ \exp\left(-\frac{t}{\tau_h}\right) \quad (4)$$

Here τ_h is charateristic shrinking time, and y (off) is relative swelling ratio before electric field is stopped.

Table 1. Relative composition and characteristic parameters of HSMA/PVA IPN gels

Sample	1	2	3	4
HSMA[a] (mol*)	1	1	1	1
CA[b] (mol*)	0.1	0.1	0.1	0.1
H-PVA[c] (mol*)	0	0.1	0.2	0.3
f**	0.4	0.83	0.95	1.1
χ_{ij}**	−0.7	−1.28	−2.0	−2.3

a: Hydrolyzed styrene-maleic anhydride alternating copolymer has molecular weight of 50,000, b: Poly (ethylene glycol 600 diglycidyl ether) was used as a crosslinking agent, c: 80%-hydrolyzed poly(vinyl alcohol) has molecular weight of 9,000-10,000, f: The number of dissociated counter ions per effective chain, χ_{ij}: Interaction paramater between HSMA/PVA IPN Gel and water, *denotes the number of mole per repeating unit, **obtained from Park et al. [1].

EXPERIMENTS

1. Experimental Apparatus

HSMA/PVA (hydrolized styrene-maleic anhydride alternating copolymer/polyvinyl alcohol) IPN ionic gel used in this study was synthesized according to the method explained previously [1, 10]. Characteristic properties of the gels obtained separately are tabulated in Table 1 with relative compositions of the gels [1]. Experiments were carried out in the electrolyte bath shown in Fig. 1. Dimensions of the bath are 8 cm×6.5 cm×1.5 cm to which D.C power supplier with transformer is connected.

2. Experimental Procedure

Each gel (1-4) is put in the 0.02 N or 0.04 N NaOH aqueous solution for at least one day in order to reach its equilibrium state. 2 cm sample is cut from the equilibrium gel obtained and the weight is measured after wiping with filter paper. After placing it into the electrolyte cell filled with 0.02 N or 0.04 N NaOH aqueous solution and then electric field is applied. The weight is measured every 3 min or 5 min until the weight is unchanged. After the electric field is off, the weight is measured every 3 min or 5 min until unchanged. The whole experiment is repeated with other sample, different field strength, different relative position of the gel.

RESULT AND DISCUSSION

1. Effect of Gel Direction

As shown in Fig. 2, gel direction has a great influence on the swelling and shrinking of gel after on and off of the electric field. When gel is placed horizontally

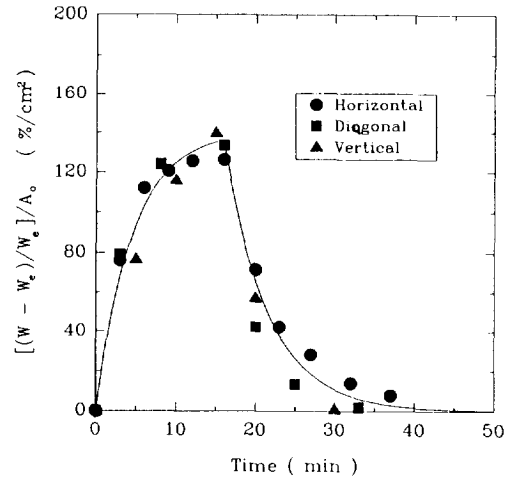

Fig. 3. The weight change ratio scaled by projectional area for different orientations of HSMA/PVA IPN gel under the D.C electric fields.

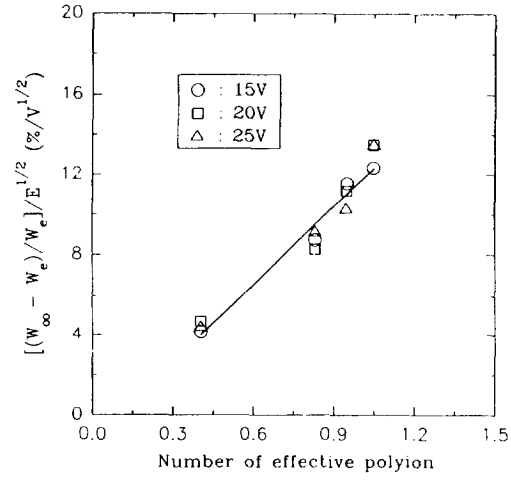

Fig. 4. The weight change ratio reduced by root square of the D.C electric field vs. number of effective polyion.

(Fig. 1a), the change was greater than other cases, so that the weight change ratio can be normalized by the projectional area of the gel on the electrode as shown in Fig. 3. Thus it gives us fairly well fitted master curve using

$$\frac{\{w(t) - w_i\}}{w_i} \propto A_r \tag{5}$$

2. Effect of Gel Properties f and $|\chi_{ij}|$

Fig. 4 shows a linear relationship between relative swelling due to the electric field normalized by square

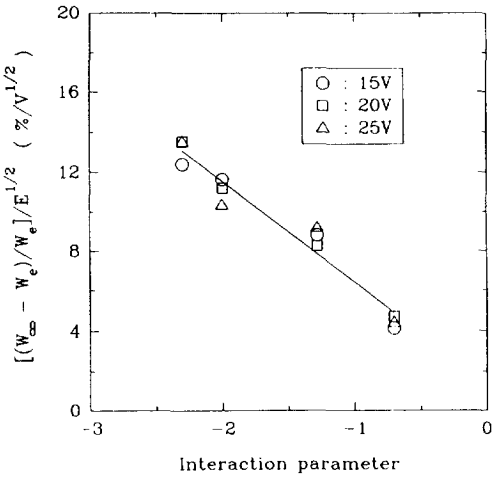

Fig. 5. The weight change ratio reduced by root square of the D.C electric field vs. interaction parameter.

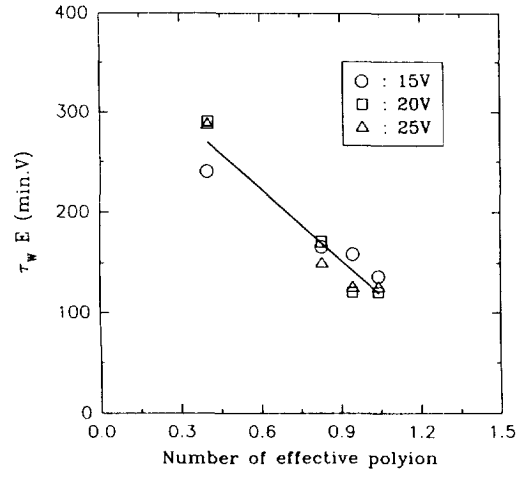

Fig. 6. The characteristic swelling time multiplied by electric field vs. number of effective polyion of HSMA/PVA IPN gel in the 0.02 N NaOH aqueous solution. Sample dimension: diameter-0.215 mm, length-2 cm.

root of electric field and the effective polyion concentration in HSMA/PVC IPN gel network. Apparent linearity holds for fairly wide range of experiments for 3 different electric field and four gels having different effective polyion concentration. Interaction parameter (χ_{ij}) between gel and water can be used in similar way as shown in Fig. 5. It is necessary to review the essence of previous report [1] in order to understand how these values are obtained.

According to Tanaka's theory the ionic polymer gel swells and shrinks according to the following equation of state [11].

$$\frac{\Delta F}{kT} = \frac{S_u\phi^3}{\phi^2}\left\{(2f+1)\left(\frac{\phi}{\phi_u}\right) - 2\left(\frac{\phi}{\phi_u}\right)^{1/3}\right\} - \frac{2}{\phi} - 2\ln\frac{(1-\phi)}{\phi^2} \quad (6)$$

Here, S_u is $(v\upsilon/\phi^3 N)$, and ΔF is merely excess free energy. f is effective polyion concentration between crosslinking points in the gel, and N is nothing but the Avogadro number. This equation of state can be applied for mixed solvent system by using following type of free energy [12, 13]

$$\Delta F = x_1\Delta F_{13} + x_2\Delta F_{23} - x_1x_2\Delta F_{12} \quad (7)$$

Here x_1 and x_2 $(=1-x_1)$ are mole fractions of each solvent 1 and 2 respectively. And ΔF_{13} and ΔF_{23} are from the interaction between solvent 1 and gel (3) and solvent 2 and gel (3) respectively. Interaction parameter (χ_{ij}) can be used instead of free energy change (ΔF_{ij}).

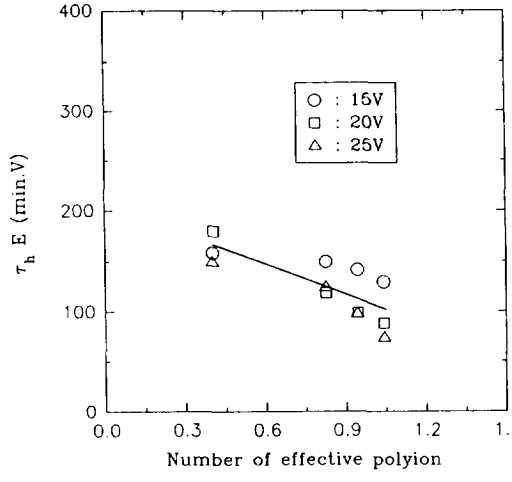

Fig. 7. The characteristic shrinking time multiplied by electric field vs. number of effective polyion of HSMA/PVA IPN gel in the 0.02 N NaOH aqueous solution. Sample dimension: diameter-0.215 mm, length-2 cm.

$$\chi_{ij} = \frac{\Delta F_{ij}}{2kT} \quad (8)$$

Thus if interaction parameter between mixed solvent is known in advance, interaction parameter between gel and water and f can be obtained from best fitting of swelling experiments. Details are found in the pre-

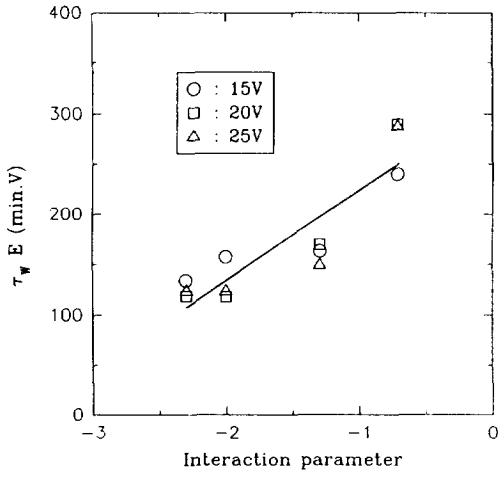

Fig. 8. The characteristic swelling time multiplied by electric field vs. interaction parameter of HSMA/PVA IPN gel in the 0.02 N NaOH aqueous solution. Sample dimension: diameter-0.215 mm, length-2 cm.

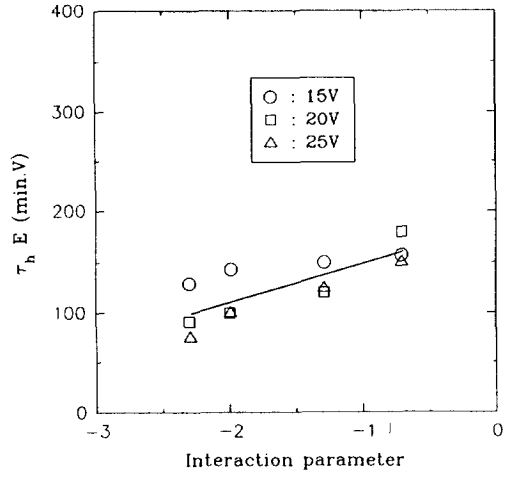

Fig. 9. The characteristic shrinking time multiplied by electric field vs. interaction parameter of HSMA/PVA IPN gel in the 0.02 N NaOH aqueous solution. Sample dimension: diameter-0.215 mm, length-2 cm.

vious paper [1]. Thus using these parameters it may be concluded that swelling of ionic HSMA/PVC IPN gel due to the electric field is proportional to $\sqrt{E}$.

3. Characteristic Times

In order to explain the electric response of ionic gel two characteristic times τ_w, and τ_h were determined according to Eq. (1)-(4). As shown in Fig. 6 and

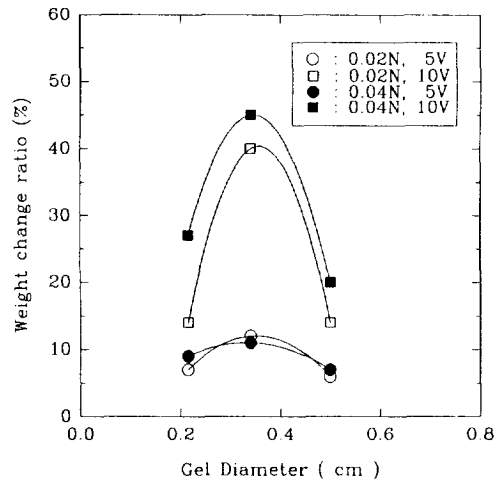

Fig. 10. The weight change ratio of HSMA/PVA IPN gel vs. gel diameter (sample 2) at different NaOH concentrations and electric fields.

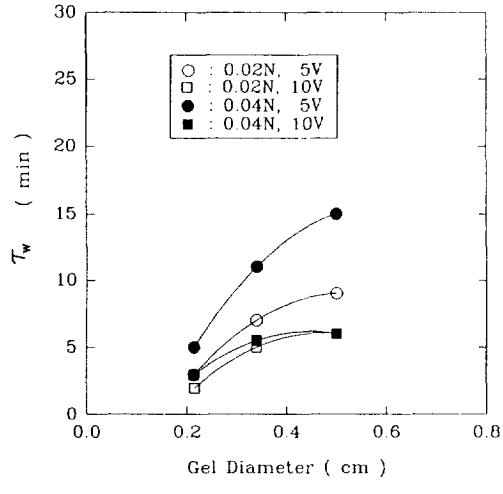

Fig. 11. The characteristic swelling time of HSMA/PVA IPN gel (sample 2) vs. gel diameter at different NaOH concentrations and electric fields.

7, these relaxation time decreases as the effective polyion concentration increases. It is notable that those times are scaled approximately by 1/E. Similar correlationships can be found reversely if we choose the interaction parameters between gel and water as shown in Fig. 8 and 9.

4. Effect of Gel Size

Swelling behavoiurs of ionic gel with different diameters are shown in Fig. 10. According to this plot, an optimum diameter is apparent and it is clear for a specific combination of electric field and ionic concen-

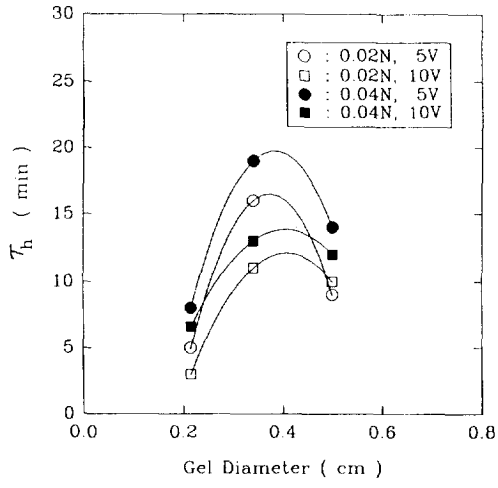

Fig. 12. The characteristic shrinking time of HSMA/PVA IPN gel (sample 2) vs. gel diameter at different NaOH concentrations and electric fields.

tration. Electric field strength affects more than ionic concentration. As far as characteristic time for swelling is concerned, there is no such optimum size as shown in Fig. 11, but characteristic time for shrinking shows some optimum size as shown in Fig. 12. In order to explain these effect quantitatively one should consider more detailed mathematical model to include every aspect of the system, which will be remained for further study.

CONCLUSION

It was confirmed that electric response of ionic polymer gel is governed by effective polyion concentration in the gel network or interaction parameter between gel and water. Swelling ratio due to electric field is proportional to square root of electrical field strength, and characteristic time is inversely correlated with electric field strength. In order to have better performance of gels it is necessary to have high concentration of polyion in the gel network or large negative value of interaction parameter as long as its mechanical strength is acceptable. Gel size effect and relative position are also important to determine the overall swelling behaviours, so that it is definitely necessary to build an equation of deformation along with a proper constitutive equation in order to expain the deformational behaviour of the ionic gel.

ACKNOWLEDGEMENT

It is supported partially by Korean government research fund, of which authors are appreciative (MOST Grant NO9580).

NOMENCLATURE

A_0 : cross sectional area
f : the number of dissociated counter ions per effective chain
E : the strength of electric field applied
ΔF : the excess free energy
ΔF_{ij} : the free energy of the association between component i and j
k : Boltzmann's constant
N : Avogadro number
S_0 : $=\nu\ \upsilon/\phi_0^{1/3}N$
T : absolute temperature
W_e : weight of gel in NaOH aqueous solution at equilibrium
W(t) : weight of gel at time t
W_∞ : weight of gel fully swollen
x_i : mole fraction of component i
y(t) : weight change ratio of gel at time t
$y(\infty)$: weight change ratio of gel fully swollen

Greek Letters

ν : the number of constituent chains per unit volume at $\Phi=\phi_0$
υ : the molar volume
ϕ, ϕ_0 : the volume fraction of the network and at random-work configurations respectively
χ_{ij} : interaction parameter between component i and j
τ_w : characteristic swelling time
τ_h : characteristic shrinking time

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