

## Effect of counter-ions on swelling and shrinkage of polyacrylamide-based ionic gels

P.-Y. Ben Jar\* and Ying Shan Wu

*Department of Engineering, Faculty of Engineering and Information Technology, Australian National University, Canberra, ACT 0200, Australia*  
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The paper presents an experimental study on effect of monovalent and divalent cations on volume change of ionic gels. The results showed that the gel shrank during the hydrolysis in basic solutions with divalent cations, but swelled in solutions with monovalent cations of similar concentration and pH value. The shrunk gel swelled again to a size larger than that before the hydrolysis in a solution of monovalent cations. The behaviour is believed due to the ionic crosslinks that were formed by clustering of ion pairs in the gel. The results suggest that the clusters with divalent cations are much stronger than those with monovalent cations, and that the ionic crosslinking should be considered for analysis of volume transition in the ionic gels.  
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### Introduction

Partially ionized polyacrylamide gels that show a discrete and reversible volume transition have attracted increasing interest in the past decade. Ionization of the gels was proven to be the essential factor for the volume transition<sup>1</sup>. Most of the gels studied in the past were ionized through hydrolysis to convert some of the acrylamide groups into acrylic acid groups ( $-\text{CONH}_2 \rightarrow -\text{COOH}$ )<sup>2</sup>. The hydrolysis was carried out in a basic solution, usually with a pH value of 12. The gel swells during the hydrolysis process due to the change of osmotic pressure difference that was induced by the change of ion content in the gels. In addition to the degree of ionization, the gel swelling can also be varied by changing pH value<sup>1</sup> and salt concentration<sup>3</sup> in the solution, or imposing an electric field to the gel<sup>2</sup>. The widely accepted explanation for the gel swelling is the balance of elastic modulus for the gel and its swelling pressure. The latter is from the osmotic pressure difference of freely mobile ions within the gel and in the outer solution.

Gels may also collapse. Such behaviour was reported occurring in an electric field<sup>2</sup> or in a polymer solution<sup>4</sup>. The former is due to the electric-field-induced changes of ion concentration profile that affects local swelling pressure<sup>5</sup>; and the latter to the polymer solutions being poor for the gel network.

Although most of the gel swelling behaviour was satisfactorily understood using osmotic pressure difference, the explanation can be applied only if the gel network remained unchanged, that is, having the same elastic modulus. Past work on ion-containing polymers (or termed ionomers<sup>6</sup>) has shown that dipole–dipole interaction among the ionic groups induces ionic clusters<sup>7,8</sup> that form ionic crosslinks. The ionic crosslinks

can cause dramatic change in physical properties of the ionomers. With sufficiently high ionic crosslink density, gelation can be introduced by the ionic crosslinks<sup>9</sup>.

In this short communication, we present experimental results that show the effect of the ionic crosslinks on the gel swelling and shrinkage behaviour. We prefer the term ‘shrinkage’ to ‘collapse’ for describing the gel volume decrease. As to be discussed in the paper, the gel shrinkage is due to ionic crosslinking that increases elastic modulus of the gel.

### Experimental

The polyacrylamide gels were prepared using free-radical polymerization, following the method suggested in ref. 1. Acrylamide (5 g, the linear constituent), *N,N'*-methylene-bisacrylamide (0.133 g, the tetrafunctional crosslinking constituent), ammonium persulfate (40 mg, the initiators) and *N,N,N,N'*-tetramethylene diamine (TEMED) (0.16 ml, the accelerator) were dissolved in 100 ml of deionized water for 5 min. Part of the solution was then transferred to plastic tubes of 1.6 mm in diameter. Gelation, based on the remaining solution, occurred within 5 min. After 1 h in the tube, the gel was transferred to deionized water to remove residual monomers and oligomers, such as acrylamide, bisacrylamide, ammonium persulfate and TEMED. The percentage of conversion was not measured, but the polymerization was expected to be nearly completed. The gel was left in the deionized water for 24 h and then cut into sections of 30 mm in length and stored in various basic solutions. The gel length was measured periodically, up to one month in duration. The basic solutions and the range of concentrations used in the study are summarized in *Table 1*. Measurement of the gel length was through a steel ruler assisted with a binocular microscope at a magnification up to 10 times. The gel and solution were stored in an air-conditioned room (around 23°C) in which the gel length was measured.

\* To whom correspondence should be addressed

## Results and discussion

Hydrolysis of the gels started when the gel was transferred to the basic solution, and was estimated<sup>10</sup> to convert ultimately around 20% of the acrylamide groups into acrylic acid groups. Using Donnan's theory<sup>11</sup>, Flory showed that the greater concentration of the mobile ions in the gel than outside solution creates a higher osmotic pressure of the solution in the gel. The difference in osmotic pressure results in an expansive force that swells the gel until the force is balanced by the elastic force of the gel network. Therefore, gels with greater hydrolysis conversion swell more. Figure 1a shows the extent of gel swelling as a function of time. The gels for Figure 1a were in the solutions of NaOH and KOH, each of 0.001 M. The results suggest that balance between the swelling pressure and the elastic force in the gel was reached within 20 days.

Final gel length, defined as the plateau value in Figure 1a, for those in solutions with monovalent cations is plotted in Figure 1b as a function of ion concentration in the solution. The figure supports the prediction by Doi *et al.*<sup>5</sup> that based on the osmotic pressure difference, the extent of swelling for an ionic gel is a function of ion concentration in the solution. Their calculation suggests that by increasing the ion concentration from a very small value, say  $1 \times 10^{-7}$  M, the osmotic pressure difference firstly increases, but then decreases. The increase is due to the increasing number of the dissociated COOH groups that effectively increase electric charges of the gel, thus increasing its osmotic pressure difference from the outside solution. However, at a certain ion concentration,  $1 \times 10^{-2}$  M for Figure 1b, nearly all of the COOH groups are dissociated. Above that ion concentration, the osmotic pressure difference is inversely proportional to the ion concentration in the solution. As a result, further increase of ion concentration causes the decrease of the gel swelling. Results in Figure 1b are consistent with the prediction in ref. 5.

Similar investigation was also conducted on gels with divalent cations,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ . With a low ion concentration in the solution (below or equal to  $3 \times 10^{-3}$  M), the gel swelled with time, due to progressive reaction of the hydrolysis. When the ion concentration was above a certain level,  $1.5 \times 10^{-2}$  M in our study, the gel swelled in the first few days, but then shrank. For the gels in ion solutions of above  $3 \times 10^{-2}$  M, the final gel length was shorter than the gel length before the hydrolysis. Typical behaviour is presented by two curves in Figure 2a in which the gel length is plotted as a function of time. Concentrations of  $\text{OH}^-$  in the solutions for Figure 2a are  $3 \times 10^{-3}$  and  $6.2 \times 10^{-2}$  M, respectively.

Final gel length as a function of cation concentration in solution with divalent cations,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ , is plotted in Figure 2b. The data in Figure 1b are also presented here by a dash line for comparison. Both sets of data, from solutions with mono- or divalent cations,

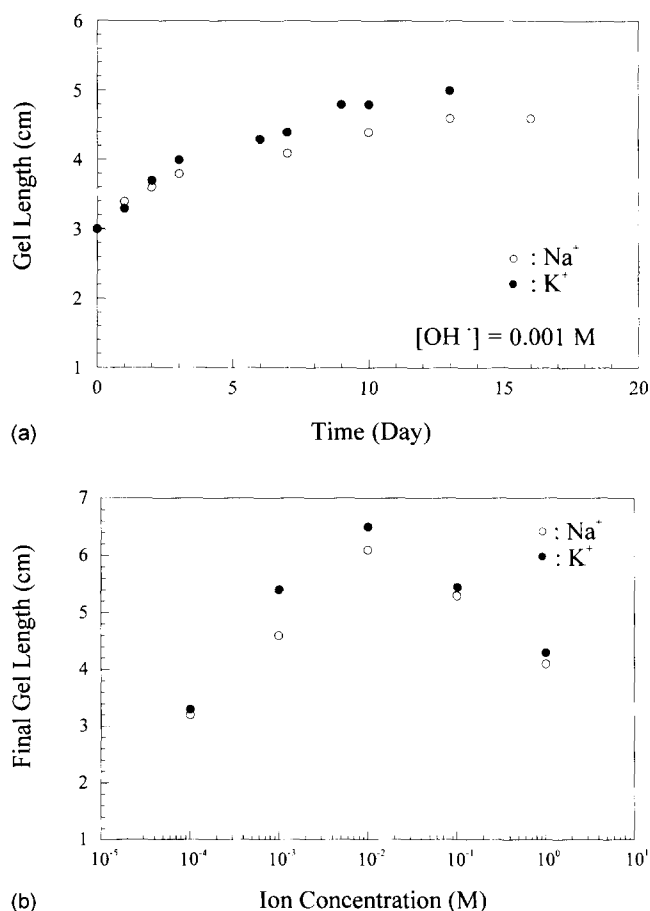


Figure 1 (a) Gel length as a function of time in NaOH and KOH solutions. Concentration of the solute was 0.001 M. (b) Final gel length as a function of ion concentration in the solutions of NaOH and KOH

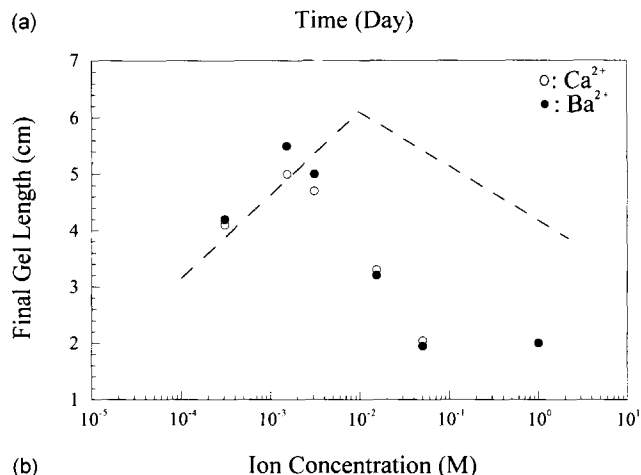
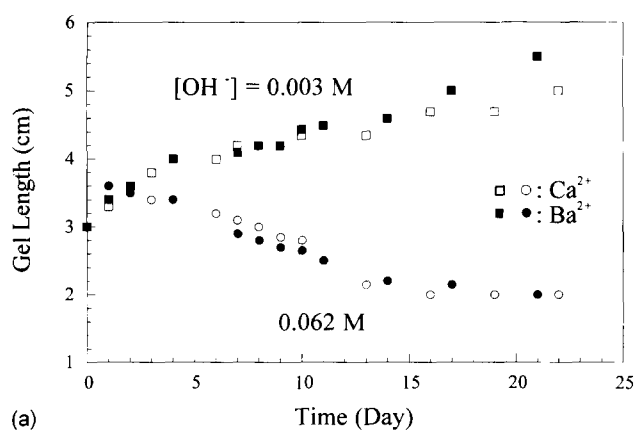
show that the final gel length firstly increases with the increase of ion concentration, but then decreases. For the left part of Figure 2b where the final gel length increases with ion concentration, the two sets of data coincide. However, for the right part of Figure 2b where final gel length decreases with increase of ion concentration, the one for gels with divalent cations decreased much faster than that for gels with monovalent cations. When the ion concentration is high enough, Figure 2b shows that the gels with divalent cations shrank to a length even shorter than the length before the hydrolysis, 3 cm. Since osmotic pressure in the gel is always higher than or equal to that in the outside solution<sup>11</sup>, the gel shrinkage cannot be explained solely by the osmotic pressure difference being reversely proportional to the ion concentration in the solution.

As mentioned before, deformation of ionic gels is also controlled by their elastic modulus which in previous studies<sup>12</sup> was assumed to be constant during the swelling process. Our results suggest that the assumption of a constant elastic modulus may not be correct, especially for gels containing divalent cations. If crosslinks were introduced through clustering of the ion pairs<sup>6</sup>, the resultant increase of elastic modulus decreases the extent of gel swelling. When the effect of osmotic pressure difference is superseded by the ionic-cluster-induced increase in elastic modulus, the gel shrinks instead of swelling.

Although evidence to support the above speculation is

Table 1 Basic solutions and the concentration range used in the study

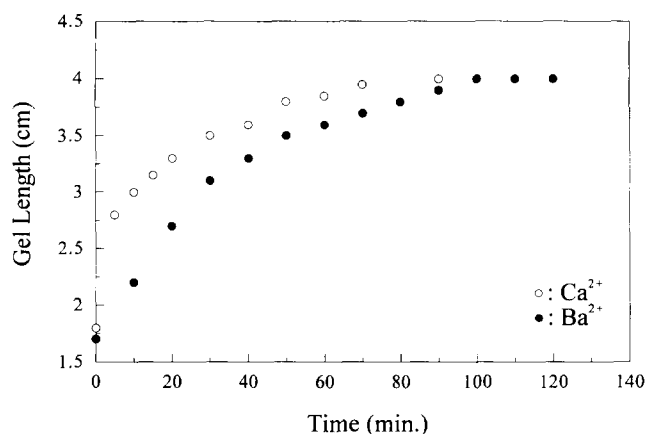
Solute in deionized water	$\text{OH}^-$ Content (M)
NaOH	$1 \times 10^{-4}$ - $1 \times 10^0$
KOH	$1 \times 10^{-4}$ - $1 \times 10^0$
$\text{Ca}(\text{OH})_2$	$6.2 \times 10^{-4}$ - $6.2 \times 10^{-2}$
$\text{Ba}(\text{OH})_2$	$6.2 \times 10^{-4}$ - $6.2 \times 10^{-2}$



**Figure 2** (a) Gel length as a function of time in  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  solutions. Concentrations for the solute are 0.003 M for the top two curves, and 0.062 M for the bottom two curves. (b) Final gel length as a function of ion concentration in the solution of  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ . The dash line represents data from Figure 1b

yet to be produced, several publications have suggested that ion pairs with divalent cations have a much stronger tendency than those with monovalent cations in forming clusters. Otocka's<sup>13</sup> experimental results suggested that in molten phase of sulfonated polystyrene ionomers, clusters formed by divalent cations ( $\text{Ca}^{2+}$ ) are much stronger than those by monovalent cations ( $\text{Na}^+$ ). Jar<sup>14</sup> showed that in the solid state, the former resisted temperature to nearly  $280^\circ\text{C}$ ; while the latter were disintegrated below  $220^\circ\text{C}$ . Although the structure of ionic clusters in gel might be different from that in a molten ionomer, their effect on the enhancement of elastic modulus should be similar.

The study on ionomers in polar solvents<sup>9</sup> showed evidence supporting that the effect of divalent cations is different from that of monovalent cations on solution viscosity. The characteristic viscosity behaviour of ionomers in a polar solvent is that a critical ionomer concentration ( $c^*$ ) exists for their reduced viscosity ( $\eta_{sp}/c$ ), where  $\eta_{sp}$  is specific viscosity and  $c$  solution concentration. Above  $c^*$ , decrease of ionomer concentration in the solution causes decrease of  $\eta_{sp}$ ; but below  $c^*$ ,  $\eta_{sp}/c$  increases. Though with some controversy, difference in the trend was explained by the inter- and intra-molecular interaction between the ion pairs<sup>6</sup>. Hara *et al.*<sup>9</sup> observed that the  $c^*$  for solutions with divalent cations is always lower than that for solutions with monovalent cations, and that above  $c^*$ ,  $\eta_{sp}/c$  for the former is lower than that for the latter. We believe that



**Figure 3** Variation of gel length as a function of time after being transferred to 0.06 M NaOH solution. The gel for open circles was in  $\text{Ca}(\text{OH})_2$  solution, and for solid circles in  $\text{Ba}(\text{OH})_2$ , each of 0.03 M

the results gave an indication of strength for the dipole-dipole interaction. Those with divalent cations have a stronger dipole-dipole interaction than those with monovalent cations.

By applying the above concept to ionic gels, the clusters formed in solutions with divalent cations should be stronger than those formed in solutions with monovalent cations, resulting in stronger crosslinks in the former. In solutions with the high ion concentration, the resultant low osmotic pressure difference makes it easier to be superseded by the increase of elastic modulus, thus leading to shrinkage of the gel.

An additional experiment was carried out to support the above conclusion. In the experiment, the shrunk gels in solutions of  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ , of 0.03 M respectively, were transferred to NaOH solution of 0.06 M, that is, to a solution with the same  $\text{OH}^-$  concentration but containing monovalent cations. In the NaOH solution, the  $\text{Na}^+$  ions were expected to diffuse into the gel and replace the divalent cations as the counter-ion for  $\text{COO}^-$  groups. This has two effects on the gel deformation, that is, increasing osmotic pressure in the gel by increase of the cation concentration, and decreasing elastic modulus of the gel by decrease of the crosslink density. Both will prompt the gel to swell. Indeed, as shown in Figure 3, the gel started swelling immediately after the transfer and reached a new equilibrium length within 2 h. The new equilibrium length was longer than the gel length before the hydrolysis.

Study of the salt effect on the gel swelling has been conducted by Tanaka and his co-workers. Ricka and Tanaka<sup>12</sup>, based on Donnan's Theory, successfully described the gel swelling behaviour as a function of ion composition in the solvent. Their results showed a quantitative agreement between theoretical prediction and experimental results for gels with monovalent cations, but only to a qualitative agreement for gels with divalent cations. The discrepancy for divalent-cation systems was attributed to the ignorance of ionic crosslinks. Ohmine and Tanaka<sup>3</sup>, using the concept of phase transition, described how the presence of salt affects the discrete volume transition of the gel in a water/acetone mixture. Difference of the monovalent and divalent cations on the volume transition was attributed to difference in ion concentration required to

neutralise the gel network, resulting in difference of the osmotic pressure in the gel. Since the osmotic pressure difference was sufficient to explain the observed gel swelling behaviour, effect of ionic crosslinking was not discussed. For the gel shrinkage that is presented in the current study, the ion-clustering-induced crosslinks need to be considered in order to provide a satisfactory explanation.

### Conclusions

Effect of monovalent and divalent cations on volume variation of ionic gels in water solution was studied. The results confirmed the reported theoretical prediction on how ion concentration affects the gel swelling behaviour. In addition to the gel swelling, gel shrinkage was observed during the hydrolysis in solutions with divalent cations. The gel shrinkage was attributed to the formation of ionic crosslinks that change elastic modulus of the gel. Replacing the divalent cations by monovalent cations, the shrunk gel swelled to a size larger than that before the hydrolysis. The results suggest that gel swelling and shrinkage can be controlled by valency for the cations in the solution. The valency for the cations affects density of ionic crosslinks, resulting in variation of elastic modulus for the gel. The balance between the osmotic pressure difference and the elastic modulus of the gel provides a way to control the gel deformation behaviour.

As the study suggests that the ionic crosslinks, due to

ionic clusters, affect the elastic modulus of the gel, further study using small angle X-ray scattering will be carried out to provide evidence of the ionic clustering, especially for the gels with divalent cations.

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