

Preparation and characterization of ionic gels prepared from poly(vinyl alcohol) and polyelectrolytes

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For material design of high-performance polymer actuators, it is very important to examine the effect of gel structure on its electrochemical and mechanical properties. In this study, we prepared various kinds of ionic gels based on poly(vinyl alcohol)(PVA), and measured their charge density, water content, ionic conductivity and mechanical strength as a function of the water content and polyelectrolyte content, Cp. Ionic gels were prepared by casting an aqueous solution of mixed PVA and polyelectrolytes, changing Cp. The gels obtained were annealed at various temperatures in order to control the water content of the gels. The water content of the gels increased with increasing Cp, and decreased with increasing annealing temperature. The charge density increased at initial stage and then decreased with increasing Cp, after having a maximum value. The value of the ionic conductivity was in proportion to the square of geometric factors which are a function of the water content.

Key words: gel; charge density; water content; ionic conductivity; mechanical strength

1. INTRODUCTION

Polymer gels are widely applied for eye lenses, sanitary goods and polymer electrolytes for batteries. Recently, there has been a large number of studies on the volume changes of polymers in response to external stimuli, such as pH [1-4], temperature [5-10], electric fields [11-13], and light [14-16]. The volume changes have been expected to be applied to actuating devices of artificial muscle [13] and control release for drugs [5-7]. In order to apply polymer gels to these devices, both high ionic conductivity and high mechanical strength are needed, and it is important to examine relationship between ionic conductivity and mechanical strength and gel structure.

In this study, we prepared many kinds of ionic gels from polymer blend of poly(vinyl alcohol)(PVA) and polyelectrolytes and measured their charge density, water content, ionic conductivity and mechanical strength as a function of the water content and polyelectrolyte content to examine the relationship between the gel properties and their structure.

2. EXPERIMENTAL

2.1. Sample gels

Aqueous solutions of a mixture of PVA[poly(vinyl alcohol), Aldrich] and AP-2[Kuraray CO. Ltd.] were cast for negatively-charged gels (AP-2 gels), and those of PVA and PAAm[poly(allylamine), Nittobo Industries Inc.] were

cast for positively-charged ones (PAAm gels). AP-2 is a kind of PVA which contains 2 mol% of 2-acrylamido-2-methylpropane sulfonic acid groups as a copolymer, and hence provided negatively-charged sites. The weight percent of AP-2 and PAAm in dried gels, Cpa and Cpc, respectively, was changed to control the charge densities of the charged gels. The gels were annealed at various temperatures for 20 min. to control their water content.

2.2. Measurement of the water content

The water content was measured as follows: the gel, weighted in the dry state, was immersed in an ion-exchanged water at a desired temperature for 3 days. The gel was removed from the water, tapped with filter paper to remove excess water on the gel surface, and was weighted in the wet state. The water content is given from the weights in the wet state, W_w , and in the dry state, W_d , as:

$$H = \frac{(W_w - W_d)/1.0}{(W_w - W_d)/1.0 + W_d/1.3} \quad (1)$$

where 1.0 and 1.3 are the densities of water and PVA.

2.3. Determination of the charge density

Membrane potentials $\Delta\phi$ were measured using an apparatus shown in Fig. 1 as a function of the KCl concentration of the chambers. From the measured membrane potential, the charge density C_x was calculated in terms of [17, 18],

$$\Delta\phi = -\frac{RT}{F} \ln \left(r \cdot \frac{\sqrt{C_x^2 + (2C_o)^2} - C_x}{\sqrt{C_x^2 + (2rC_o)^2} - C_x} \right) - \frac{RT}{F} W \ln \left(\frac{\sqrt{C_x^2 + (2rC_o)^2} - C_x W}{\sqrt{C_x^2 + (2C_o)^2} - C_x W} \right) \quad (2)$$

where $W = (\omega_K - \omega_{Cl}) / (\omega_K + \omega_{Cl})$; ω_K and ω_{Cl} are the K^+ and Cl^- ion mobilities in a gel, respectively; F , R and T are the Faraday constant, the gas constant and the absolute temperature, respectively. C_o is the KCl concentration on the low-concentration chamber; r is the concentration ratio between the high- and the low-concentration chambers. Parameters W and C_x were adjusted so that the left-hand side of Eqn. (2) fits the experimental data of $\Delta\phi$ at various KCl concentrations.

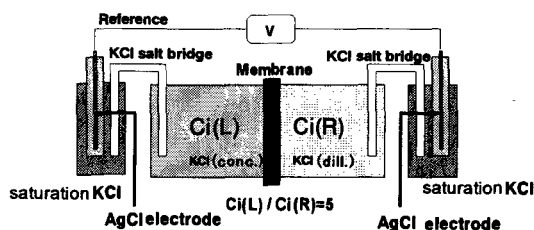


Fig. 1 Apparatus for membrane potential measurement.

2.3. Measurement of the ionic conductivity

The resistance in the gels was measured in 0.5 N salt solution using an apparatus shown in Fig. 2 with a LCR meter at 1K Hz AC [Hewlett Packard LCR-4263A]. The ionic conductivity was obtained from the resistance, the area and thickness of the gels.

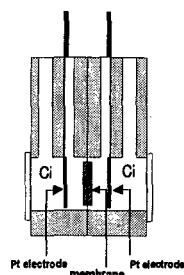


Fig. 2 Apparatus for the resistance measurement.

3. RESULTS AND DISCUSSION

Fig. 3(a) and 3(b) shows the water content of the negatively- and positively-charged gels, respectively, as a function of AP-2 and PAAm content. The water content of the gels increased with the polymer content because osmotic pressure in a gel increases with increasing the number of the charged groups in the gels.

Fig. 4 shows the water content of AP-2 gels and PAAm gels as a function of annealing temperature. The water content decreased with increasing annealing temperature because the degree of crystallinity in the PVA matrix increase with increasing annealing temperature. The positively charged gels have higher water content than the negatively charged ones. The relationship between water content and annealing temperature was the same in the case of the other polyelectrolyte contents.

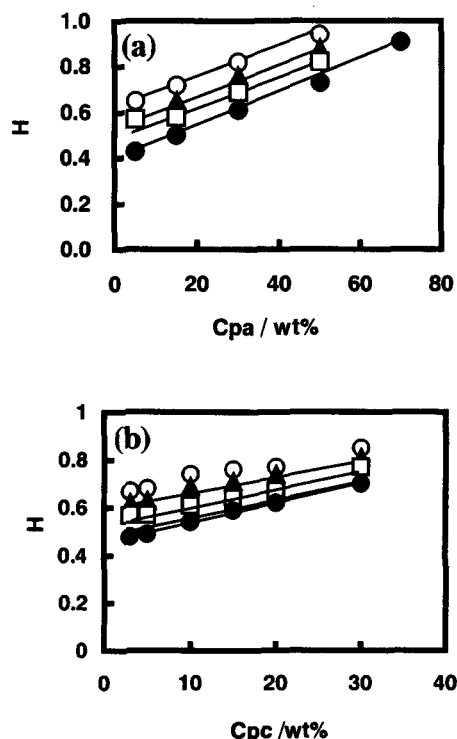


Fig. 3 Water content of the gels as a function of polyelectrolyte content. (a) the data for negatively-charged gel, (b) for positively-charged one. Annealing temperature; $\bullet$:160°C, $\square$:140°C, $\blacktriangle$: 120°C, $\circ$: 100°C.

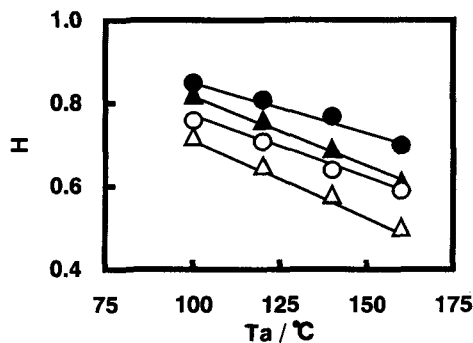


Fig. 4 Water content as a function of annealing temperature. $\circ, \bullet$: the data for positively charged gels at $C_{pc}=5\text{wt}\%$ and $C_{pc}=30\text{wt}\%$, respectively; $\triangle, \blacktriangle$: for negatively charged ones at $C_{pa}=5\text{wt}\%$ and $C_{pa}=30\text{wt}\%$, respectively.

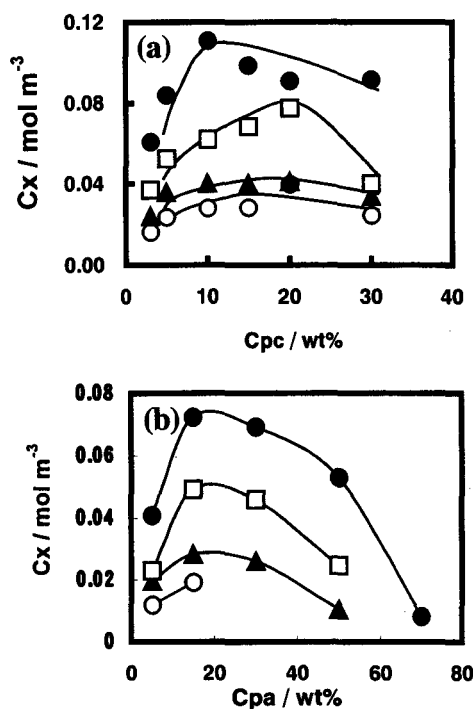


Fig. 5. The charge density as a function of polyelectrolyte content. (a) the data for positively charged gels, (b) for negatively charged ones.

Annealing temperature; ●:160°C, □:140°C, ▲:120°C, ○:100°C.

Figs. 5(a) and 5(b) show the charge density of the positively and negatively charged gels as a function of the polyelectrolyte content. The charge density increased as the number of the charged groups, Cpc and Cpa, increased. The charge density is defined as the division of the number of the charged groups by the water content. Since the water content increased with increasing the polyelectrolyte content, the charge density decreased as the content increased after the charge density has a maximum value around Cpa=15% for the negatively-charged gel. The higher is the annealing temperature, the higher maximum charged density the gels have because the water content decreases with increasing annealing temperature as shown in Fig. 4.

Fig. 6 shows the conductivity of Li⁺ ions in AP-2 gels as a function of AP-2 content. The conductivity increased with Cpa, and decreased with increasing annealing temperature because the water content increased with Cpa as shown in Fig. 3, and decreased with increasing annealing temperature as shown in Fig. 4. To examine the ionic mobility in gels, many authors have replaced the ionic mobility, σ_i , in eqn (3) with the apparent one, $\bar{\sigma}_i$, which is a function of both σ_i and factors such as gel geometry. The factors due to gel geometry are related to the mobility ratio as [19,20]

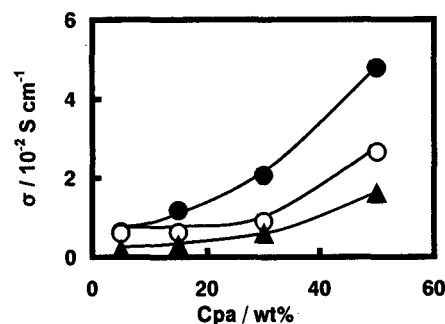


Fig. 6 The conductivity of Li⁺ ions in AP-2 gels. Annealing temperature; ●:120°C, ○:140°C, ▲:160°C.

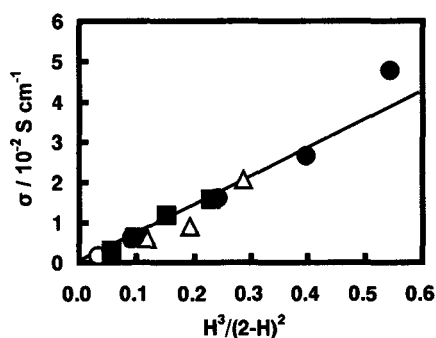


Fig. 7 The conductivity of Li⁺ ions in AP-2 gels as a function of the geometric factor, $H^3/(2-H)^2$. AP-2 content (Cpa); ●:50wt%, △:30wt%, ■:15wt%, ○:5wt%.

$$\frac{\bar{\sigma}_i}{\sigma_i} = \varepsilon \frac{1}{\theta^2} \quad (3)$$

where θ is the tortuosity defined as a mean increase in path length due to the obstruction of gel matrix; ε is the void fraction defined as the ratio of the sum of the cross sectional area of the paths to the gel area. Mackie and Meares [20] derived stochastically the factor as a function of the water content, H , of a swollen gel:

$$\varepsilon = H, \quad \theta = \frac{2-H}{H} \quad (4)$$

Equations (3) and (4) give the ionic mobility in the gel as a function of the ionic mobility in water and gel water content as:

$$\bar{\sigma}_i = \frac{H^3}{(2-H)^2} \sigma_i \quad (5)$$

The conductivity of Li⁺ ions shown in Fig. 7 were re-plotted as a function of $H^3/(2-H)^2$. The conductivity of all the gel treated with different annealing temperature decrease with decreasing the geometric factor, $H^3/(2-H)^2$ and are in proportion to the factor. This means that the ionic conductivity in the gel can estimate using the value of the water content.

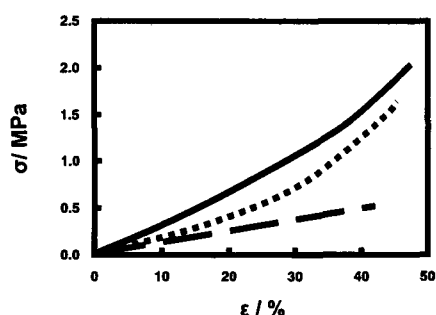


Fig. 8 Stress-strain curves of AP-2 gels. Solid, dotted and dashed curves are the data for gels whose water content is 0.73, 0.74 and 0.90, respectively.

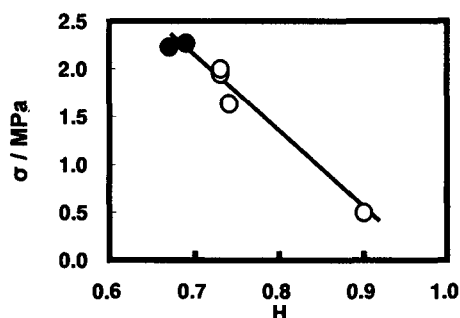


Fig. 9 Maximum strength of the gels as a function of their water content. ●:PAAm, ○:AP-2.

Fig. 8 shows stress-strain curves of AP-2 gels. Both the maximum strength and the elastic modulus of the gels, which is calculated from the slope of the curves, increases with decreasing water content.

Fig. 9 shows maximum strength of AP-2 gels as well as PAAm gels obtained from their stress-strain curves as a function of their water content. The relation between the maximum strength and water content for both AP-2 and PAAm gels becomes a straight line. This means that the maximum strength of charged gels can be estimated using the water content.

4. CONCLUSION

In this study, we prepared many kinds of ionic gels from polymer blend of poly(vinyl alcohol)(PVA) and polyelectrolytes and measured their charge density, water content, ionic conductivity and mechanical strength as a function of the water content and polyelectrolyte content. The ionic conductivity in the gels increased with increasing water content, H , and was in proportion to the geometric factor of the gels, $H^3/(2-H)^2$. The mechanical strength decreased with increasing H and was in proportion to H . Therefore, the value of the ionic conductivity and mechanical strength of ionic gels can be estimated using the water content.

5. ACKNOWLEDGMENT

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