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Ionic conduction in partially phosphorylated poly(vinyl alcohol) as polymer electrolytes

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Abstract

Polymer films of partially phosphorylated poly(vinyl alcohol) (P-PVA) with dipotassium salts have been prepared and characterized, and the effects of phosphorylation on the ionic conduction in the mixed film of P-PVA and polyethylene glycol (PEG: average MW = 200), P-PVA/PEG film, have been investigated. The glass transition temperature (T_g) was significantly decreased by phosphorylation, and it decreased with increasing degree of phosphorylation (DP), indicating an increase in amorphous part on the polymer. For P-PVA/PEG systems, the ionic conductivity increased and activation energy of the ionic conduction decreased with increasing DP, which agreed with the result of T_g. The carrier mobility decreased and carrier density increased with DP. These results indicated that the ionic conductivity of P-PVA/PEG was mainly dominated by the carrier density. Compared with the low molecular weight systems (PVA/K_2HPO_4/PEG systems), the P-PVA/PEG systems had low T_g, low activation energy and high carrier density, although the ionic conductivity was small at 298.15 K.

Keywords: Poly(vinyl alcohol); Phosphorylation; Ionic conduction

1. Introduction

The advantages of polymer solid electrolytes with high ionic conductivities have been recognized. The ion conduction in many polymer electrolytes which consist of poly(acrylronitrile), poly(vinyl pyrrolidone), and poly(ethyleneglycol diacrylate) swollen with a mixed solution of ethylene carbonate and propylene carbonate or other polar solvents containing low molecular inorganic salts such as lithium salts has been investigated [1–3]. The polymers have the mechanical stability and these polymer solid electrolytes containing cations as lithium and alkylammonium ions provide a relatively high ion conductivities. Furthermore, ion-conducting polymers like polyether-based polymer electrolytes are also solid solutions of electrolyte salts in polymers and the ion conductivity range at room temperature is 10^{-4}–10^{-5} S cm^{-1} [4–8].

Partially phosphorylated poly(vinyl alcohol) (P-PVA) has attracted considerable interest because of its nonflammability [9,10], metal complexes [11], anionic polyelectrolyte hydrogels [12], and cation exchange resins [13]. In particular, anionic polyelectrolyte hydrogels can be readily prepared by crosslinking reaction of P-PVA with glutaraldehyde, and the hardness of this gel can be affected by the crosslinking degree [12]. In the present paper, the application of new ion-conducting polymer using P-PVA to polymer solid electrolytes was investigated.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA: $P_n = 2000$) used in these experiments was of an analytical grade from commercial origin, and was completely hydrolyzed by alkali in methanol. Dicyanodiamide was purified by recrystallization from water. *N*,*N*-dimethylformamide (DMF) was purified by double distillation under reduced pressure just before use. Poly(ethylene glycol) (PEG, MW = ca. 200) was used as a plasticizer. All the other reagents were commercially available guaranteed reagents and used without further purification. Partially phosphorylated PVA (P-PVA) with different degree of phosphorylation were prepared as follows. Dicyanodiamide (30 g), urea (45 g), and PVA were dissolved in DMF (150 ml) at 130°C, and then DMF (180 ml) containing 17 wt% of 100%-orthophosphric acid was slowly added at 130°C with stirring. Yellowish-white

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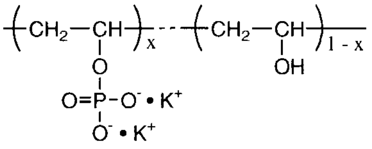


Polymers	DP
P-PVA-1	0.109
P-PVA-2	0.141
P-PVA-3	0.186

Fig. 1. Chemical structure of P-PVA.

precipitate was dissolved in water and the solution was dialyzed in water with cellulose tube in order to remove DMF and phosphoric acid for 3 days. Hydrochloric acid (6 M) was added to the dialyzed solution, and insoluble by-products was removed by filtration. The filtrate was dialyzed in distilled water for 1 week. The solution was adjusted to pH 11 by addition of 1 M potassium hydroxide solution. The white precipitate of potassium salt of P-PVA was obtained by reprecipitation into methanol. The degree of phosphorylation for the P-PVA obtained was determined by pH titration and molybdenum blue method. Chemical structure of P-PVA is shown in Fig. 1. (see Scheme 1)

Polymer and low molecular weight salt samples were prepared as follows. P-PVA was dissolved in distilled water and PEG was added under the conditions in which the molar ratio of oxygen in PEG to phosphoric acid unit equals to 16:1 (polymer salt sample). PVA and K_2HPO_4, in which the molar ratio of phosphoric acid to hydroxyl residue in PVA was equal to the degree of phosphorylation of respective polymer salt samples, were dissolved in distilled water and PEG was added with $[-CH_2CH_2O-]/[PO_4] = 16$ (low molecular weight salt sample).

The standard devices were prepared by casting of sample solution on ITO electrode. Sample solutions were sandwiched between two ITO electrodes, which were coated by acrylic resin, and then slowly dried on P_2O_5.

2.2. Measurements

X-ray diffraction measurements were carried out using a RIGAKU X-ray diffractometer at room temperature. Thermal analyses were performed using SEIKO DSC 15200 instrument systems, consisting of thermogravimetric analysis, differential thermal analysis (TG/DTA 220) and DSC 220 instruments. Thermal experiments were carried out with a heating rate of 20°C min^{-1} at a temperature range of -150 to $+300$°C. Ionic conductivities of the sample films which were sufficiently dried at 50°C in 10^{-5} Torr for 24 h were determined from complex impedance plots obtained using a Hewlett Packard 4192A LF impedance analyzer over the frequency range of 5 Hz–13 MHz. The temperature dependence of the ionic conductivity was carried out in the temperature range from 25 to 60°C. The carrier mobility and density in the films were determined by d.c. polarization measurements using a Yanako polarographic analyzer P-1100 and Watanabe XY-recorder WX4421. After the application of a fixed voltage of $+1.0$ V to the sample films for 1 h, the transient current value, which correlates between current and time was recorded until the current reached a steady state. The carrier mobility (μ_+) and carrier density (N_{0+}) are given from slope and intercept of plotting according to Eq. (1) [14], respectively,

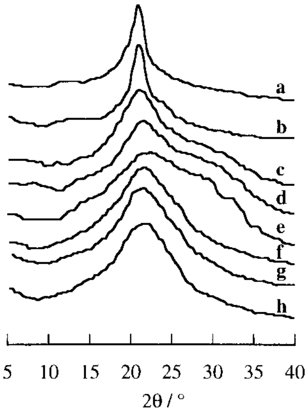
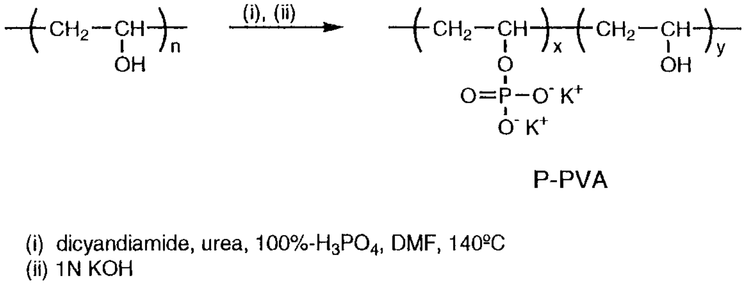


Fig. 2. X-ray diffraction patterns of films: (a) PVA; (b) PVA/PEG, P-PVA/PEG with DP; (c) 10.9; (d) 14.1; (e) 18.6 mol% and PVA/K_2HPO_4/PEG with DP (f) 10.9; (g) 14.1; and (h) 18.6 mol%.

$$\ln I(t) = \ln\left[\frac{SN_0 + q\mu_+ V}{d}\right] - \left[\frac{\mu_+ V}{d^2}\right]t \tag{1}$$

where S is electrode area, q the charge of cation, V an applied voltage, and d the thickness of the film.



(i) dicyandiamide, urea, 100%-H_3PO_4, DMF, 140ºC
(ii) 1N KOH

Scheme 1.

Table 1
Thermal data obtained from DSC measurements

Sample	DP (mol%)	T_g (°C)	T_m (°C)[a]
PVA	0	35	219
PVA/PEG	0	32	209
Low molecular weight salt			
PVA/K_2HPO_4-1	10.9	53	218
PVA/K_2HPO_4-2	14.1	54	212
PVA/K_2HPO_4-3	18.6	66	221
PVA/K_2HPO_4/PEG-1	10.9	23	210
PVA/K_2HPO_4/PEG-2	14.1	33	212
PVA/K_2HPO_4/PEG-3	18.6	40	213
Polymer salt			
P-PVA-1	10.9	−44	206
P-PVA-2	14.1	−45	212
P-PVA-3	18.9	−62	218
P-PVA/PEG-1	10.9	−34	-[b]
P-PVA/PEG-2	14.1	−42	-[b]
P-PVA/PEG-3	18.9	−51	-[b]

[a] Melting point.
[b] Not detected.

3. Results and discussion

3.1. X-ray diffraction measurements

Fig. 2 shows the X-ray diffraction pattern of PVA film, P-PVA films and P-PVA/PEG films. For all polymer films, the peaks around $2\theta = 20°$, arising from PVA crystalline, were observed. The diffraction pattern of PVA/PEG film was similar to that of PVA film, indicating that the crystallinity of PVA crystalline was hardly affected by PEG due to weak interaction of PEG with PVA. Compared with PVA and PVA/PEG films, the peaks around $2\theta = 20°$ of P-PVA and P-PVA/PEG films broaden. In particular, the P-PVA films have broad peaks around $2\theta = 30°$ depending on DP; namely, the intensity increases with increasing DP. In contrast, the P-PVA/PEG films have broad peak around $2\theta = 20°$, but not broad peaks around $2\theta = 30°$. Furthermore, the X-ray diffraction patterns of P-PVA/PEG films are independent of DP. These results indicate that conformation of the polymer is varied by the introduction of phosphorylate ester groups. The phosphorylate ester groups with dipotassium, which are highly polarized, restrict the crystallization of PVA parts induced by hydrogen bonding between hydroxyl segments, thus leading to the change in the conformation. By addition of PEG, the PEG may complex with potassium ions like crown ethers, and the polarity becomes small.

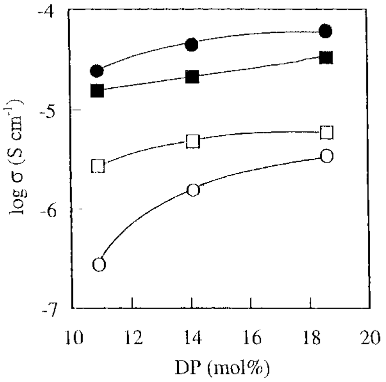


Fig. 3. DP dependence of ionic conductivity for P-PVA/PEG systems (circle symbols) and PVA/K_2HPO_4/PEG (square symbols) at 298.15 K (○, □), and 333.15 K (●, ■).

On the contrary, for low molecular weight samples, the X-ray diffraction patterns of the PVA films containing 10.9 and 14.1 mol% of K_2HPO_4 showed a peak only around $2\theta =$ 20°, while those of the PVA film containing 18.9 mol% of K_2HPO_4 and all PVA films adding PEG showed the sharp peaks, arising from crystalline K_2HPO_4 as well as PVA crystalline and the peak increases with increasing concentration of K_2HPO_4. The facts indicate that PVA can dissolve a low concentration of the potassium salt and the solubility of the potassium salt is decreased by the addition of PEG. Probably, the solubility of the potassium salt into PEG is low.

3.2. DSC measurements

Glass transition temperatures (T_g) and melting points (T_m) of all the samples obtained from DSC measurements are summarized in Table 1. In PVA and PVA/PEG systems, the T_g and T_m values almost resemble, which indicates that the PVA barely interacts with the PEG. This result agrees with that obtained from the X-ray diffraction patterns.

By phosphorylation, the T_g significantly decreases with increasing DP. For PVA/K_2HPO_4 systems, the T_g values are increased by the addition of K_2HPO_4 and increase with increasing K_2HPO_4. For polymer salt systems, an amorphous part in P-PVA is extended by a decrease in the crystallinity of PVA induced by introducing phosphorylate groups, therefore, leading to the decrease in T_g. In contrast, PVA/K_2HPO_4, occurs the phase separation between PVA and K_2HPO_4, and the phase separation may accelerate the crystallization of PVA. Furthermore, the PEG barely affects the T_g values in the P-PVA systems, while it decreases the T_g in the PVA/K_2HPO_4 systems. This is attributable to the interaction between PVA and complex of PEG and K_2HPO_4.

In general, the ionic conducting polymer materials require a low T_g, which is one of the important factors. It is clear that the polymer salt films adding PEG have a low T_g compared with those non adding PEG. Therefore, we investigate on ionic conductivity of films containing PEG.

3.3. Ionic conductivity

3.3.1. DP effects on ionic conductivity

Fig. 3 shows the DP dependence of ionic conductivity for P-PVA/PEG and PVA/K_2HPO_4/PEG systems at 298.15 and 333.15 K. For both the systems, the ionic conductivity increased with increasing DP; particularly, the DP dependence for P-PVA/PEG systems was remarkable at low

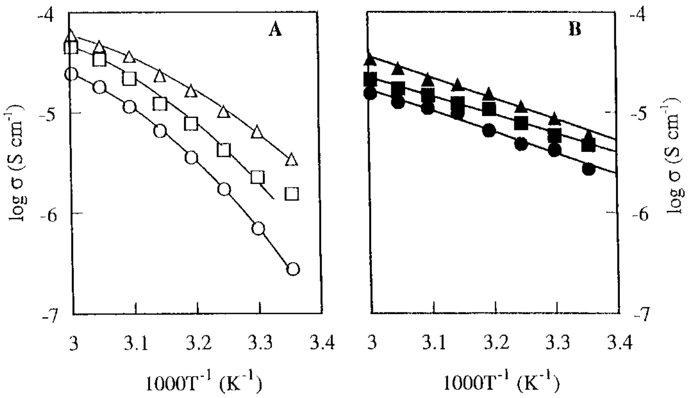


Fig. 4. Temperature dependence of ionic conductivity for P-PVA/PEG systems (A) and PVA/K_2HPO_4/PEG (B) at DP = 10.9 (○, ●), 14.1 (□, ■) and 18.9 (△, ▲).

temperature. The ionic conduction in a P-PVA/PEG matrix would be mainly affected by segment motion of the polymer because the anion groups in the P-PVA are fixed on the polymer backbone. The segment motion more readily occurs in amorphous polymer backbone. The ionic conductivity at low temperature increases with increasing amorphous part induced by an increase in DP. At high temperature, the segment motion of the polymer is active; consequently, the DP dependence of the ionic conductivity is small. In contrast, the DP dependence of ionic conductivity for PVA/K_2HPO_4/PEG systems is small. This is attributable to the fact that the ionic conduction in PVA is hardly affected by the segment motion of PVA because of phase separation between PVA and K_2HPO_4–PEG complex. Furthermore, it is noteworthy that the P-PVA/PEG systems have larger ionic conductivity than the PVA/K_2HPO_4/PEG systems.

3.3.2. Temperature dependence of ionic conductivity

Fig. 4 shows temperature dependence of the ionic conductivity for polymer salt systems (A) and low molecular weight salt system (B). The ionic conductivities depended on temperature with downward deviating curves for the polymer salt systems and straight lines for low molecular salt systems, respectively. This result indicates that the ionic conduction is Williams–Landel–Ferry [15] (WLF) type for P-PVA/PEG systems and Arrhenius type for PVA/K_2HPO_4/PEG systems. It is well known that the ionic conduction in the polymer matrix is WLF type as it is affected by the motion of the polymer segment. In contrast, the ionic conduction in solution is Arrhenius type. Considering the facts, it is clear that the ionic conduction for the PVA/K_2HPO_4/PEG systems is hardly affected by the motion of PVA segments.

WLF equation

$$\log\left[\frac{\sigma(T)}{\sigma(T_g)}\right]=\left[\frac{C_1(T-T_g)}{C_2(T-T_g)}\right] \tag{2}$$

$$y=\left\{\log\left[\frac{\sigma(T)}{\sigma(T_g)}\right]\right\}^{-1}=\frac{C_2x}{C_1}+\frac{1}{C_1} \qquad x=(T-T_g)^{-1} \tag{3}$$

VTF equation

$$\sigma=A'\exp\left[\frac{-E'_a}{(T-T'_0)}\right] \tag{4}$$

$$\log\sigma=\left[\frac{-E'_a}{2.303(T-T'_0)}\right]+\log A' \qquad T'_0=T_g-C_2 \tag{5}$$

In order to obtain activation energy of ionic conduction for the polymer salt systems, WLF plot (Eqs. (2) and (3)] and then VTF plot (Eqs. (4) and (5)) (Vogel–Tamman–Fulcher [16]) were carried out. Furthermore, the activation energy for PVA/K_2HPO_4/PEG systems can be obtained from the slope of Arrhenius plots. The parameters obtained

Table 2
WLF and VTF parameters for P-PVA/PEG systems and activation energy for PVA/K_2HPO_4/PEG systems

	C_1	C_2	T'_0	log A/10^{-2}	E_a' (eV)/10^{-1}
P-PVA/PEG-1	18.06	32.65	206.50	73.36	1.33
P-PVA/PEG-2	16.90	34.82	196.33	47.41	1.27
P-PVA/PEG-3	15.44	41.66	180.49	1.66	1.24
PVA/K_2HPO_4/PEG-1	–	–	–	–	4.05
PVA/K_2HPO_4/PEG-2	–	–	–	–	3.88
PVA/K_2HPO_4/PEG-3	–	–	–		4.93

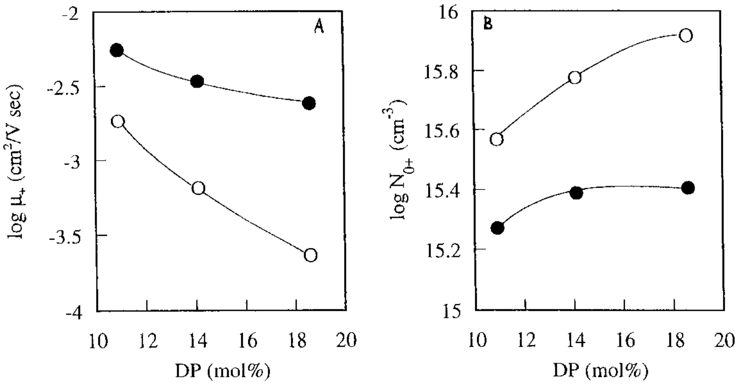


Fig. 5. DP effects on carrier mobility (A) and carrier density (B) for P-PVA/PEG systems (○) and PVA/K_2HPO_4/PEG (●).

from WLF and VTF plots of P-PVA/PEG systems and activation energy of PVA/K_2HPO_4/PEG systems are summarized in Table 2. The activation energy of the P-PVA/PEG systems was smaller than that of the PVA/K_2HPO_4/PEG systems. With increasing DP, the activation energy slightly decreased for P-PVA/PEGs, while it increased for PVA/K_2HPO_4/PEGs. These results are similar to those of T_g. As mentioned above, the amorphous part in the polymer salt films increases with increasing DP, while that in PVA/K_2HPO_4/PEG films decrease. Because the ionic conduction in polymer matrix more readily occurs in amorphous part, the activation energy for ionic conduction of P-PVA/PEG films having more amorphous area is small. For the PVA/K_2HPO_4/PEG films, the ionic conduction is more difficult to occur in the PVA/PEG matrix because the crystallinity of PVA increases with increasing DP, leading to high activation energy.

3.3.3. Carrier mobility and carrier density

All the systems gave good linear relationships for plotting according to Eq. (1). Fig. 5 shows the DP dependence of carrier mobility (A) and carrier density (B) at 298.15 K. The carrier mobility decreased with increasing DP for P-PVA/PEG and PVA/K_2HPO_4/PEG systems, while the carrier density increased for both the systems. In particular, the DP dependence was large for P-PVA/PEG system. For PVA/K_2HPO_4/PEG film systems, the DP dependence of the carrier mobility is similar to that of T_g. In contrast, the carrier mobility for P-PVA/PEG film systems significantly decreases with increasing DP even when the amorphous part increases, indicating that the carrier mobility is hardly affected by the amorphous part in this case.

The carrier density for P-PVA/PEG film systems is larger than that for PVA/K_2HPO_4/PEG film systems. That is to say, the polymer salt can form more carriers under the same conditions of potassium concentration. For PVA/K_2HPO_4/PEG, the amount of K_2HPO_4, which dissolves in PVA/PEG, has a limitation, and excess of K_2HPO_4 added is crystallized; consequently, K_2HPO_4 is heterogeneously distributed into the PVA/PEG matrix. Furthermore, the degree of dissociation of K_2HPO_4 may become small in K_2HPO_4-saturated PVA/PEG, resulting in a decrease in the carriers. For P-PVA/PEG, the phosphate groups with dipotassium cations are homogeneously distributed into the polymer matrix because anion groups (phosphate) are fixed on the polymer backbone; the phosphate salts do not saturate in the polymer matrix. Therefore, the P-PVA/PEG can form many carriers. In the present experimental conditions, however, the concentration ratio of phosphorylate groups and PEG is constant, and the concentration of PEG increases when DP increases. This fact suggests a contribution of PEG to the carrier mobility. The ionic conduction would occur, hopping of potassium cations, probably forming complex with PEG, between phosphate groups. It is likely that the carrier mobility is decreased by PEG. Considering these facts, the increase in ionic conductivity with DP, as shown in Fig. 3, is mainly caused by an increase in the carrier density.

4. Conclusions

We demonstrated the preparation of ionic conducting polymer materials based on poly(vinyl alcohol) (PVA) and the effects of phosphorylation of PVA on the ionic conductivity. The phosphorylation of PVA decreases the T_g values and the activation energy of ionic conduction, and increases the ionic conductivity, which depend on DP. These results are attributable to the fact that amorphous area is extended. For the low molecular weight systems, addition of K_2HPO_4 to PVA/PEG increases the T_g and accelerates the crystallization of PVA. Although the ionic conductivity slightly increases with addition of K_2HPO_4, the activation energy of ionic conduction increases, resulting in the crystallization of K_2HPO_4 in addition to PVA.

On the contrary, with increasing DP, the carrier mobility decreases and carrier density increases for both the systems; particularly, the P-PVA/PEG systems have large DP dependence. For PVA/K_2HPO_4/PEG film systems, the excess of K_2HPO_4 and the part of PVA are crystallized in the film, and K_2HPO_4, which can generate the ionic carrier, is heterogeneous and small. Therefore, the carrier mobility is large and the carrier density is relatively small. In contrast, most of the phosphate groups can generate the ionic carrier and are homogeneously distributed in the P-PVA/PEG films. The carrier density is relatively large because the polymer salt system has many phosphate groups being able to generate the carriers. However, the carrier mobility decreases with increasing DP because the PEG concentration also increases at the same time. Consequently, the ionic conductivity is mainly increased by the increase in the carrier density, which counterbalances the decrease in the carrier mobility induced by increasing PEG.

Such P-PVA/PEG films are very effective for application to ionic conducting materials containing salts with high lattice energy, such as potassium phosphate. Furthermore, it is suggested that these films can be sufficiently applied to polymer ionics materials.

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