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Preparation and properties of highly phosphorylated poly(vinyl alcohol) hydrogels chemically crosslinked by glutaraldehyde

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New anionic polyelectrolyte gels were prepared by the chemical crosslinking reaction of highly phosphorylated poly(vinyl alcohol) (P-PVA) with glutaraldehyde. The structures of the gels were determined by both i.r. and solid-state ^{13}C n.m.r. spectroscopy. The various types of polyanionic gels having high- or low-swelling characteristics and different degrees of hardness could be prepared by using the crosslinking reaction under different reaction conditions. The gels with low crosslinking densities showed in the order of 500 g g^{-1} of the maximum absorbency value. The thermal properties of the chemically crosslinked P-PVA were also investigated.

(Keywords: phosphorylation; poly(vinyl alcohol); hydrogel)

INTRODUCTION

Poly(vinyl alcohol) (PVA) containing functional groups is useful in practical investigations of functional polymers because of its easy preparation in the form of bulk material, films and fibres. In earlier works, we have reported on the preparation of highly phosphorylated PVA (degree of phosphorylation < 70 mol%) (P-PVA) by phosphorylation in the presence of dicyanodiamide and urea in *N,N'*-dimethylformamide (DMF)[1]. Partially phosphorylated PVA has attracted considerable interest because of its flammability, metal complexes, anionic polyelectrolyte gels, ion conductors, etc. We have reported on the formation and properties of Cu(II)-P-PVA complexes[2], and the thermal stabilities of Ni(II)-P-PVA complex[3,4]. Quite recently, we have investigated the ion conductivities of molecular composites of P-PVA with polyether and metal cations[5,6], such as K^+. In this present work, we have prepared new anionic polyelectrolyte gels by the crosslinking reaction of P-PVA with glutaraldehyde, and report on their swelling and thermal properties.

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EXPERIMENTAL

Materials

The poly(vinyl alcohol) ($DP = 2000$) used in these experiments was of an analytical grade, from commercial origin, and was completely hydrolysed by alkali in methanol[7]. All of the other reagents used here were analytical reagent grade.

Preparation of the highly phosphorylated poly(vinyl alcohol) (P-PVA)

To a solution of dicyandiamide (10 g) and urea (15 g) in 50 ml of DMF, orthophosphoric acid (10 ml) is added. The solution is heated at 140°C, and PVA (6 g) is then added. The reaction solution is stirred for 80 min at 140°C under a stream of nitrogen. The resulting solution is dialysed against distilled water through Visking cellulose tubing for 24 h to remove any surplus reagents. To this solution, 95 ml of aqueous HCl solution (12 N) is added and the solution is again dialysed against distilled water for 1 week in order to remove water-soluble impurities. A powder of P-PVA is obtained by slowly adding, with vigorous agitation, a non-solvent such as acetone to the dialysed P-PVA aqueous solution. The precipitate is filtered, washed with acetone, and then dried at 30°C (in

Table 1 The reaction conditions for the crosslinking reaction of P-PVA with glutaraldehyde[a]

No.	P-PVA (g)	[GA]/[P-PVA]	HCl (ml)	Acetone (ml)	Water absorbency (g g^{-1})	T_g (°C)	T_m (°C)
3a	0.12	0.26	0.1	0	40	6.9	202
3b	0.12	0.52	0.1	0	54	11.2	203
3c	0.12	0.64	0.1	0	53	9.2	203
3d	0.12	1.03	0.1	0	53	7.8	203
3e	0.12	1.28	0.1	0	50	6.0	203
3f	0.12	1.28	0.1	0.5	–	–	206
3g	0.12	1.28	0.1	1.0	–	–	205
3h	0.12	1.28	0.1	2.0	–	–	204
3i[b]	0.12	0.09	0.1	0	104	50.4	221
3j	0.36	0.18	0.1	0	502	57.7	225
3k	0.36	0.36	0.1	0	364	51.7	231
3l	0.36	0.44	0.1	0	307	48.0	230

[a] Reacted at 30°C for 27 h; degree of phosphorylation is 25 mol%; concentration of HCl solution used is 1.0 N
[b] 7.2% aqueous solution (5 ml)

vacuum) for 3 days over phosphorus pentoxide. The degree of phosphorylation determined by pH titration and the molybdovanadophosphoric acid method[1,8], is 25 mol%. A range of P-PVAs having different contents (3.3 to ~35.8 mol%) of phosphoric acid groups is obtained by using the same procedure as described above.

Crosslinking reaction of P-PVA with glutaraldehyde

Homogeneous crosslinking in aqueous solution. 0.12 g of P-PVA is dissolved in 1.0 ml of glutaraldehyde aqueous solution (25%) and 0.1 ml of an aqueous solution of HCl (1 N) is added, as a catalyst, to the solution with stirring. The reaction mixture is kept at 30°C for 27 h. The resulting precipitation is washed repeatedly with water, and the solution is then added to excess ethanol, filtered, washed with ethanol, and dried at 40°C in vacuum.

To 5.0 ml of a solution of P-PVA (7.2%), 0.5 ml of an aqueous solution of HCl (1 N) is added, as a catalyst, with stirring. The reaction mixture is kept at 30°C for 27 h. The crosslinked P-PVA is obtained by the same procedure as described above.

Heterogeneous crosslinking in acetone–water mixed solution. 0.12 g of P-PVA is suspended in 2 ml of acetone and 0.1 ml of an aqueous solution of HCl (1 N) as a catalyst, is added to the mixture. The suspension is kept at 30°C for 27 h. The reaction product is then obtained by the same procedure as described above. The reaction conditions are shown in *Table 1*.

Measurement of water absorbency of crosslinked P-PVA[9]

An accurately weighed sample (15–20 mg) of crosslinked P-PVA was allowed to stand for 24 h in deionized water or NaCl aqueous solution (0.9%). The swollen polymer was separated from the unabsorbed material by screening through a tared 280 mesh sieve (diameter = 7.5 cm). The polymer remaining on the sieve was allowed to drain for 20 min, and the sieve was then weighed to determine the weight of the water-swollen gel. The absorbency was calculated as the number of grams of water per gram of dry polymer, also taking into account the initial moisture content of the polymer. No correction was made for the percentage of polymer that was soluble in water, and the absorbency values would therefore be higher if based only on the amount of insoluble polymer.

Measurements

The infra-red (i.r.) spectra of the polymers were recorded on a JASCO FT-IR 7300 Fourier transform spectrophotometer. Samples for i.r. analysis were prepared as dispersions in spectroscopic grade KBr. The ^{13}C n.m.r. spectra of the P-PVA samples were recorded in the solid state at room temperature by means of a JEOL A-400 FT-NMR Fourier transform spectrophotometer. Thermal characterization was carried out by using a SEIKO DSC 15200 instrument system, consisting of thermogravimetric analysis, differential thermal analysis (TG/DTA 220) and differential scanning calorimetry (DSC 220), at a rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Preparation and characterization of P-PVA crosslinked by glutaraldehyde

Chemically crosslinked P-PVAs were prepared by the homogeneous crosslinking reaction of the residual vinyl alcohol units in P-PVA with glutaraldehyde, in aqueous solution at 30°C for 27 h. By stirring the mixed aqueous solutions of P-PVA and glutaraldehyde, the total amount of P-PVA in the feed solution formed hydrogel immediately. The crosslinked P-PVAs were also prepared by the heterogeneous crosslinking reaction of the residual vinyl alcohol units in P-PVA with glutaraldehyde in acetone–water mixed solutions, also at 30°C for 27 h. Water-insoluble hydrogels were also obtained in this way. The ratio of the molar concentrations of glutaraldehyde to the residual vinyl alcohol units in P-PVA in the reaction feed ([GA]/[P-PVA]) varied over the range from 0.09 to 0.40. In this way, hydrogels of P-PVA of various degrees of hardness can be prepared. *Figure 1* shows the *FT*i.r. spectra of crosslinked P-PVAs obtained in both an aqueous solution (b) and in an acetone–water mixture (c), compared with that of P-PVA (a). As seen in (b) and (c) in this figure, new absorption peaks at 1000 cm^{-1} have appeared. This absorption peak at 1000 cm^{-1} was the characteristic absorption of the

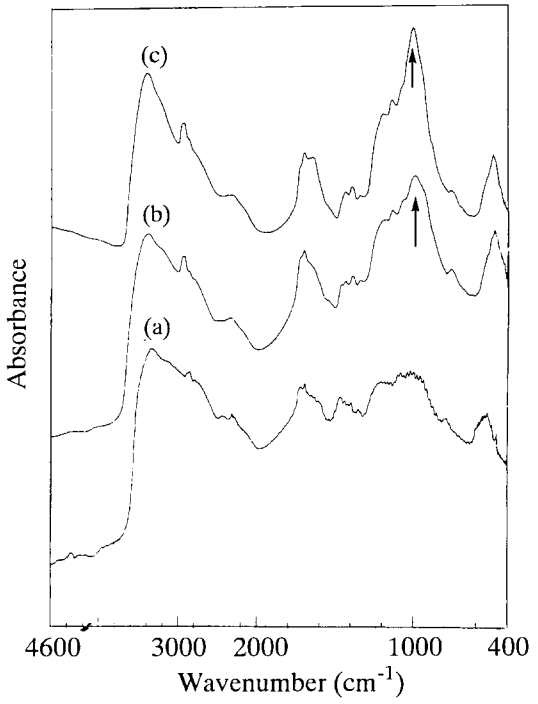

Figure 1 The *FT*i.r. spectra of: (a) P-PVA; (b) crosslinked P-PVA (3e); (c) crosslinked P-PVA (3h)

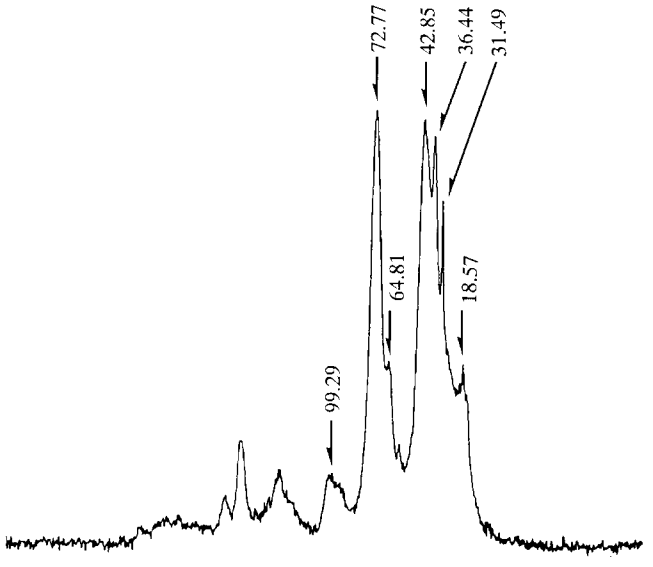

Figure 2 ^{13}C n.m.r. spectrum of crosslinked P-PVA (3h) measured in the solid state by the cross polarization/magic angle spinning (CP/MAS) method at room temperature

C–O–C group in crosslinked P-PVA. *Figure 2* shows the solid-state ^{13}C n.m.r. spectrum of crosslinked P-PVA obtained in acetone–water mixture. In the ^{13}C n.m.r. spectra one peak found at 99.3 ppm was assigned to the acetal carbon formed by the crosslinking reaction of the nonphosphorylated vinyl alcohol unit in P-PVA with glutaraldehyde. The signal at 72 ppm was assigned to the main-chain α-carbon in crosslinked P-PVA, while the signal at 18.6 ppm was assigned to the β-carbon in the crosslinked chain. These results indicate that reaction of the residual vinyl alcohol units in P-PVA with glutaraldehyde had taken place. *Figure 3* shows the relationship between the ratio of molar concentrations of glutaraldehyde to the residual vinyl alcohol units in P-PVA, [GA]/[P-PVA] in the feed solutions and the ratio of the absorbances at 1000 cm^{-1} (C–O–C) to 1700 cm^{-1} (P=O), A_{1000}/A_{1700}, in the corresponding *FT*i.r. spectra. It can be seen that an increase in the ratio of A_{1000}/A_{1700} was observed with increases in the [GA]/[P-PVA] ratio in the feed solutions to ~ 1.0, while above this ratio the A_{1000}/A_{1700} values remained constant. Several studies of the crosslinking reaction of PVA with glutaraldehyde have been carried out[10,11]. However, there has been no solid-state ^{13}C n.m.r. or *FT*i.r. analyses of crosslinked PVA, or, in particular crosslinked P-PVA.

Swelling and solubility of crosslinked P-PVA

All of the P-PVAs, chemically crosslinked by glutaraldehyde, that are shown in *Table 1* are insoluble in water. The water absorbencies of the crosslinked P-PVAs at 30°C are also listed in *Table 1*. None of the crosslinked P-PVA samples are soluble in water at room temperature. The crosslinked P-PVAs obtained by homogeneous reaction in aqueous solution (3a–3e) have absorbency values ranging from about 40 to 53 g g^{-1}. The crosslinked P-PVAs prepared by heterogeneous reaction in acetone–water mixtures (3f–3h), however, have absorbency values of the order of about 19 to 24 g g^{-1}. These values are about one half of those found for samples 3a to 3e. The water absorbability depends directly on the crosslinking density and degree of crystallinity in the hydrogel. The crosslinking density on the surface of the P-PVA hydrogels prepared using the acetone–water dispersion systems are much higher than those prepared in the homogeneous aqueous systems. Therefore, the water absorbency values for samples 3a to 3e are lower than those of samples 3f to 3h. P-PVAs having lower crosslinking densities were also obtained by the crosslinking reaction with glutaraldehyde using lower concentrations (0.0857 mol l^{-1}) of P-PVA in homogeneous aqueous solutions, at 30°C for 27 h (3i–3l). The relationship between the ratio of the molar concentrations of the vinyl alcohol units in P-PVA to glutaraldehyde, [GA]/[P-PVA], in the feed solution and

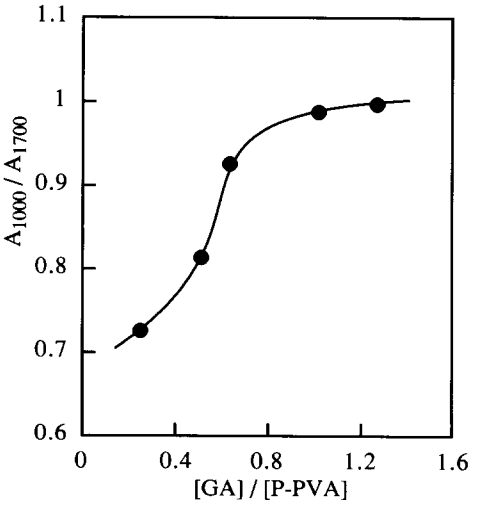

Figure 3 The relationship between [GA]/[P-PVA] and A_{1000}/A_{1700} in the *FT*i.r. spectra of the crosslinked P-PVAs

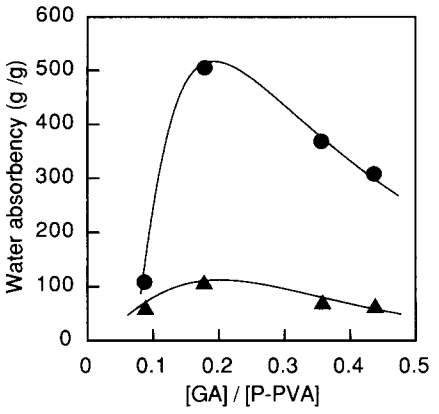

Figure 4 The relationship between [GA]/[P-PVA] in the reaction mixture and water absorbency of the crosslinked P-PVAs: (●) in water; (▲) in NaCl aqueous solution (0.9%)

the water absorbency of these crosslinked P-PVAs is shown in *Figure 4*. The water absorbencies of these crosslinked P-PVAs increase initially with an increase in the ratio of [GA]/[P-PVA], and then decrease after passing through a maximum. The maximum absorbency value is of the order of 500 g g^{-1}, a value which is more than 50 times that of crosslinked PVA prepared under the same crosslinking conditions. It is generally known that the water absorbency of 'superabsorbent' resins decreases when increasing the degree of crosslinking, due to inhibition of the penetration of water into polymer networks of high crosslinking density. For ratios of [GA]/[P-PVA] > 0.18 in *Figure 4*, the penetration of water into the crosslinked P-PVA may be decreased when increasing the crosslinking density. In cases where the ratio of [GA]/[P-PVA] < 0.18, the water absorbencies of the crosslinked P-PVAs also decreased. The crosslinked P-PVAs obtained with lower ratios than were partially soluble in water. The non- or low-crosslinked P-PVA material may be removed from the crosslinked P-PVAs by dissolving the polymers in water, as described in the purification procedure for the resin. The crosslinked P-PVA which remains can have a high crosslinking density. Therefore, the crosslinked P-PVA prepared under conditions where [GA]/[P-PVA] < 0.18 may show a low water absorbency. The water absorbencies of these hydrogels in NaCl aqueous solutions (0.015 M) as a function of [GA]/[P-PVA] are shown in *Figure 4b*. It can be seen that the water absorbency values of the hydrogels prepared in NaCl aqueous solutions were significantly lower. Therefore, the swelling behaviour of these hydrogels may be related to the change of phosphate groups in the side chains of the crosslinked P-PVA. Many resins containing carboxyl and sulfonic acid groups have been reported as anionic gels. However, the resin containing the phosphoric acid group have been hardly reported in this connection as far as we are aware[12].

The poly(vinyl alcohol-*co*-acrylic acid) (PVA-*co*-AA) resin is well known as an anionic hydrogel with good absorbency and maintenance of water[13]. This PVA-*co*-AA resin has a maximum absorbency value of ~570 g g^{-1}, which is approximately the same as that of the crosslinked P-PVA hydrogel.

Crosslinked P-PVA samples with various degrees of phosphorylation were also prepared by the same procedure as sample 3b in *Table 1*. The effects of the degree of phosphorylation on the water absorbency is shown in *Figure 5*. The water absorbencies of these crosslinked P-PVAs increase with an increase in the degree of phosphorylation, remaining constant above a value of ~25 mol% of degree of phorphorylation.

Thermal properties of P-PVA chemically crosslinked by glutaraldehyde

The glass transition temperatures (T_gs) of the chemically crosslinked P-PVAs were determined on the basis of analysis of their d.s.c. curves. The T_g values of all of the crosslinked P-PVAs are listed in *Table 1*. The crosslinked P-PVAs obtained by the homogeneous crosslinking in aqueous solution (3a–3e) showed glass temperature temperatures over the range from 6.0–11.2°C. These T_g values are the same as those of noncrosslinked P-PVA. The melting points (T_ms) of the crosslinked P-PVAs were measured by differential thermal analysis (d.t.a.). The T_m values of all the crosslinked P-PVAs are also listed in *Table 1*. The T_m values of samples 3a–3e were in the range from 202–203°C. The T_g and T_m values of poly(vinyl alcohol) have been reported in the ranges 70–80°C and 207–220°C, respectively[14]. The T_g and T_m values of the P-PVAs were lower than those of unphosphorylated PVA. These results show that the bulky phosphoric ester groups in the side chains of the P-PVAs distort the orientation of the polymer chains and prevent the crystallization of unreacted vinyl alcohol units. The heterogeneous crosslinked P-PVAs from the acetone–water mixed solvent system do not have glass transition temperatures: this may further prevent the crystallization of vinyl alcohol units by the crosslinking reaction.

The flame retardation of partially phosphorylated PVA (degree of phosphorylation = 5.2 mol%) has been reported by Inagaki *et al.*[15]. We have also reported on the flame retardation of the complexes of Co(II), Ni(II), Cu(II) and Zn(II) with P-PVA with the same degree of phosphorylation (25 mol%). The Ni(II)-P-PVA complex showed the high weight residue, i.e. 73.8 wt% at 1000°C. Recently, a detailed study on the influence of covalently bound phosphorus-containing groups on the flammability of PVA and poly(ethylene-*co*-vinyl alcohol) has been reported by Mavis *et al.*[8]. *Figure 6* shows t.g.a.

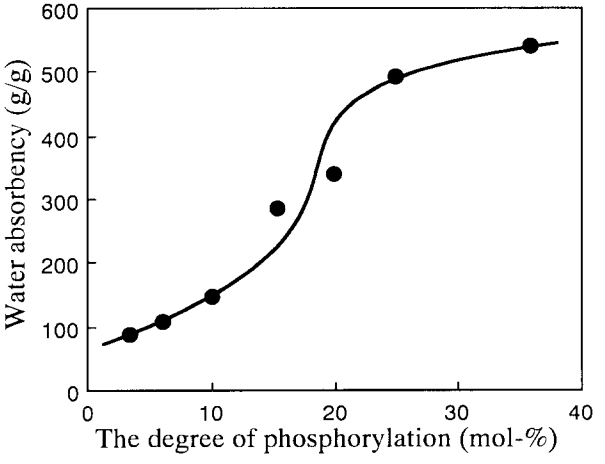

Figure 5 The effect of degree of phosphorylation on the water absorbency of the crosslinked P-PVAs

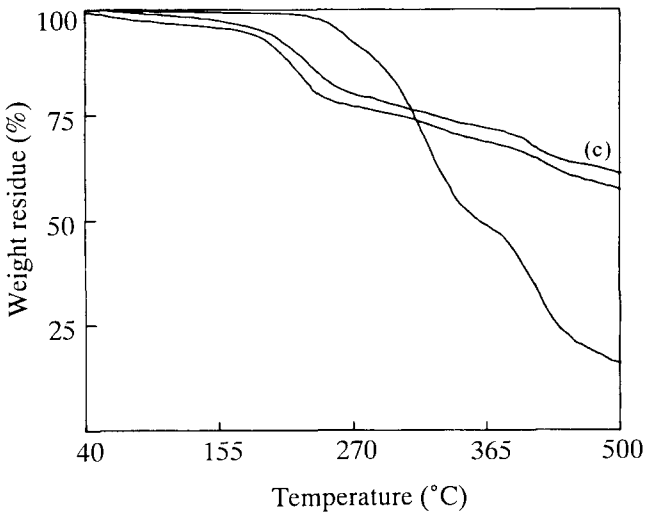

Figure 6 T.g.a. curves of: (a) PVA; (b) P-PVA; (c) crosslinked P-PVA

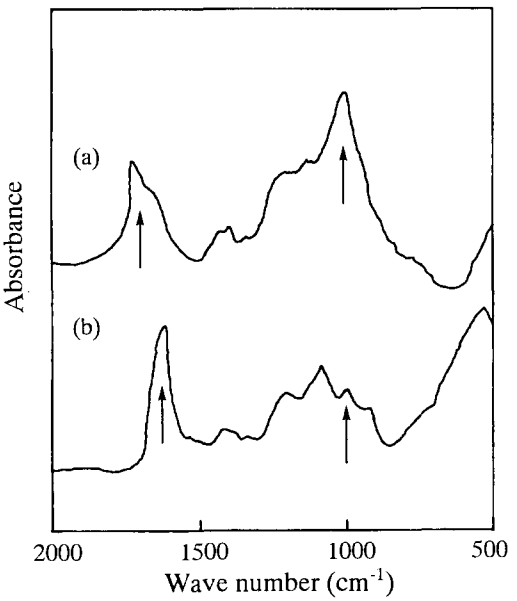

Figure 7 The *FT*i.r. spectra of (a) crosslinked P-PVA and (b) crosslinked P-PVA containing adsorbed calcium ions

curves for P-PVA crosslinked by glutaraldehyde (c), compared with P-PVA (b) and PVA (a). Although the thermal stability of crosslinked P-PVA is reduced, compared with virgin PVA, in the initial decomposition step, the crosslinked P-PVA showed the highest weight residue after thermal decomposition in air. The thermal stabilities of P-PVA and crosslinked P-PVA was much higher than that of the virgin PVA.

Adsorption of calcium ions

20 mg of crosslinked P-PVA is suspended in 10 ml of distilled water and 10 ml of $CaCl_2$ aqueous solution (0.01 M) is added to the solution, and stirred at 30°C for 1 h. The precipitation is filtered, washed with water, and dried at 40°C in vacuum. White coloured, hard resin was obtained. *Figure 7* shows the *FT*i.r. spectrum of crosslinked P-PVA resin containing adsorbed calcium ion (b), along with that of virgin crosslinked P-PVA (a). As can be seen in this figure, the absorption band at 1700 cm^{-1}, characteristic of the P=O stretching of the phosphate group in the crosslinked P-PVA was shifted to a lower wave number, i.e. 1632 cm^{-1}, as a result of the calcium adsorption. In addition, the strong absorbance at 1013 cm^{-1}, arising from the P-O stretching and P-O-H bending modes, is decreased in intensity in the spectrum of the calcium-adsorbed resin. This latter fact indicated $[-O-PO_3]Ca^{2+}$ to be the absorption site. To summarize, highly phosphorylated poly(vinyl alcohol) hydrogels were prepared by the crosslinking reaction of P-PVA with glutaraldehyde. The gels with low crosslinking densities show much higher swelling than the highly crosslinked species. Many types of polyanionic gels having both high- or low-swelling characteristics and different degrees of hardness can be prepared. These polyionic hydrogels may be useful in the form of films or fibres, as artificial teeth (as the calcium complex) and as metal adsorbents. More detailed studies of these aspects are now in progress.

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