

Polyvinylphosphonic Acid Copolymer Hydrogels Prepared with Amide and Ester Type Crosslinkers

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ABSTRACT: Crosslinked hydrogels made of poly(vinylphosphonic acid-*co*-*N,N'*-methylenebisacrylamide) (P(VPA-*co*-MBAA)) and poly(vinylphosphonic acid-*co*-ethyleneglycol diacrylate) (P(VPA-*co*-EGDA)) were prepared by using precipitation polymerization in water medium. A comparison research was made between the resultant hydrogels containing different loads of vinylphosphonic acid segments when *N,N'*-methylenebisacrylamide (MBAA) or ethyleneglycol diacrylate (EGDA) were used as comonomers. Morphological observations indicated that the resultant copolymer appeared as a fine powder at low VPA loadings and strongly aggregated at the high loadings; especially, a copolymer containing 63 mol % of VPA segments in P(VPA-*co*-MBAA) was observed to have a flake-shaped appearance in its aggregated morphology. The resultant copolymer powders were characterized using FTIR spec-

troscopy and titrimetric analysis. Also, monomer reactivity ratios, r_1 and r_2 , of VPA and MBAA or EGDA were estimated as 0.06 and 0.98 for VPA and MBAA and 0.05 and 1.82 for VPA and EGDA, respectively. This suggested that a large distribution of MBAA and EGDA was present in the resultant copolymer powders. Their crosslinked PVPA structure presented hydrogel properties having high water uptakes and an absorption mechanism independent from pH of bulk solution. The evidence showed that high VPA loadings could strongly interacted through hydrogen bonds between neighbor VPA segments even in the presence of water. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3072–3079, 2011

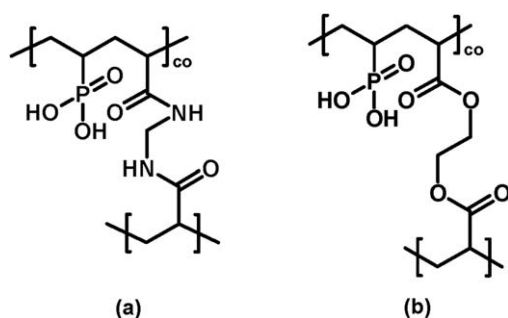
Key words: vinylphosphonic acid; VPA; hydrogel; water uptake; crosslinker

INTRODUCTION

In recent years, polymeric phosphonic acid has been attracting the interest of researchers, because the phosphonic acid segments behave as negative charge functional groups in polymeric chains similar to poly(acrylic acid) and poly(styrene sulfonic acid). Therefore, polyphosphonic acid has been observed to be promising for application in various fields such as fuel cells, ion-exchange, agricultural chemicals, catalyst, and medicine.^{1–5} So far, various types of hydrogels have been developed as for example, poly(ethylene glycol), poly(acrylic acid), and poly(styrene sulfonic acid) to name a few.^{6–10} Among them, polyvinylphosphonic acid (PVPA) has been known to be an excellent hydrophilic polymer material, even though very little has been examined in previous researches. Kaltbeitzel et al. revealed high water absorption of PVPA at wide ranges of temperature.¹¹ Rivas et al. described its ability for metal-ion binding at different pHs values.¹² These results

showed that PVPA was able to retain the metal-ions such as Ni(II), Co(II), and Cu(II). There have been applications where PVPA has shown good biocompatibility and used as adhesion promoters in dental cements.¹³ When utilized with dopants in conductive blends, and furthermore flame retardants, their high water solubility and negative ionicity were excellent properties in those applications.^{14–17} Furthermore, copolymers of VPA with acrylonitrile, styrene, vinylpyrrolidone, and methacrylic acid have been reported to investigate their uses for specific applications. Tan et al. have designed poly(vinylphosphonic acid-acrylamide-tetraethylene glycol dimethacrylate) hydrogels and investigated the protein uptake in such hydrogels.¹⁷ In this report, high protein uptakes were observed in the polymer hydrogels containing 50 mol % of VPA load. However, very little is currently known about the working mechanisms in copolymer hydrogels made of VPA, although they have showed high potentials in several applications as a novel type of hydrogels. Specifically speaking, there have only been reports of crosslinked copolymer hydrogels of VPA with ethyleneglycol diacrylate (EGDA).¹⁶ The VPA hydrogel crosslinked by EGDA was studied to observe the gels behavior at different pH conditions. Therefore, there is a great scientific value in the detailed study

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Scheme 1 Chemical structures of (a) P(VPA-co-MBAA) and (b) P(VPA-co-EGDA) hydrogels.

of crosslinked VPA hydrogels. For this reason, we aim to prepare and characterize crosslinked VPA hydrogels with crosslinking agents such as MBAA or EGDA having P(VPA-co-MBAA) or P(VPA-co-EGDA) (Scheme 1). As compared to those hydrogels crosslinked by compounds having acrylamide or acrylate segments, VPA hydrogels may also contribute to this overall knowledge. In addition, the crosslinked VPA hydrogels were copolymerized by precipitation technique, to obtain fine powders expected to be used for various application fields such as cation-exchange resin, cosmetics, drug delivery systems, and molecular recognition. Besides that, currently, no reports for crosslinked VPA hydrogels having microsize shape have been published so far, insight into the first attempt at VPA copolymer hydrogels into fine powder shape promises to be of great value. So far, preparation of polymer microbeads was studied by many polymerization techniques; for example, it has been known that emulsion polymerization, surfactant free polymerization and precipitation polymerization are commonly used techniques to prepare hydrophilic copolymer beads.^{18–20} In this work, we focused in precipitation copolymerization as a technique to obtain hydrogel powders of P(VPA-co-MBAA) and P(VPA-co-EGDA) at different VPA loadings. In the resultant VPA hydrogels, important features of the hydrogels were obtained as a function of VPA segment loading in the comonomer segments.

EXPERIMENTAL

Materials

Vinylphosphonic acid (VPA) and acryloyl chloride were purchased from Tokyo Chemical Industry (Tokyo, Japan) (Japan). *N,N'*-methylenebisacrylamide (MBAA), potassium persulfate (KPS), and ethylene glycol were obtained from Nacalai Tesque (Kyoto, Japan). Ethylene glycol diacrylate (EGDA) was synthesized by esterification of acryloyl chloride and ethylene glycol. All reagents were used as received without further purification.

Polymerization and purification

P(VPA-co-MBAA) and P(VPA-co-EGDA) hydrogels (Scheme 1) having various contents of VPA and comonomer (MBAA or EGDA) segments were synthesized by precipitation polymerization in water in the presence of the radical initiator, KPS. The procedure was done as follows: first, both VPA and comonomer, in which total amount of the two monomers was 10 mmol each, were put into a three-necked flask equipped with a mechanical stirrer bar, a N_2 bubbling tube and a condenser. Then, KPS (0.02 g) was added to the monomers as a radical polymerization initiator and all three were dissolved in 25 mL water. After N_2 bubbling for 1 h, precipitation copolymerization was carried out at 80°C for 24 h at 500 rpm stirring. Resultant crosslinked PVPA hydrogel was purified five times by centrifugation with water and then freeze-dried using a FD-5N unit (Kokusan, Tokyo, Japan). The resultant white powders were stored and further dried in a desiccator until they were ready for use. Feeding amounts of monomer in the copolymerization and yields of resultant polymer hydrogels are listed in Table I.

The values of monomer reactivity ratios of VPA and MBAA or EGDA were estimated for when the copolymerization was carried out with a low yield for short reaction times at 80°C.²¹ The VPA loading in the copolymers obtained by different VPA monomer feeds were determined with FTIR spectroscopy.

Observation of crosslinked PVPA hydrogels

Morphologies of resultant VPA hydrogels crosslinked with MBAA or EGDA were observed by scanning electron microscope (SEM) (JEOL JSM-5400, Akishima, Japan). The freeze-dried polymer samples were used after gold-sputtering in vacuum using a quick coater (ULVAC Kiko, VPS-020, Saito, Japan). BET surface areas of the crosslinked copolymers were evaluated by micrometrics Flow Sorb 3 (Shimadzu, Kyoto, Japan) for each polymer hydrogel samples (0.015 g).

The FTIR spectrum of the resultant copolymers was observed using a FTIR spectrophotometer (Shimadzu IR-Prestige-21, Koyto, Japan) with KBr tablet method. To estimate the VPA loading in the hydrogels, the physical mixtures of PVPA and PMBAA or PEGDA homopolymers with different mole contents were used for calibration and estimation of the VPA loading from FTIR spectra. Herein, the IR intensities of the characteristics bands of VPA and MBAA or EGDA were compared using P—O stretching (1000 cm^{-1}) of VPA and C=O stretching of MBAA (1680 cm^{-1}) or EGDA (1740 cm^{-1}), respectively. Moreover, FTIR spectra of each polymer hydrogels mixed with water at pH 5.0 were measured. Herein, the samples were pinched between two CaF_2 windows for

TABLE I
Feed Monomer Amounts in the Copolymerization and Yields, VPA Loading, pK_{a2} and BET Surface Areas of Resultant Polymer Hydrogels

	VPA (mol %)	MBAA (mol %)	EGDA (mol %)	Yield (%)	VPA loading (mol %)		pK_{a2} (-)	BET surface area (m ² /g)
					FTIR	titration		
VPA0-MBAA100	0	100	–	92.2	0	0	–	150 (1.8)
VPA20-MBAA80	20	80	–	88.4	18	21	7.9	88 (4.7)
VPA50-MBAA50	50	50	–	70.9	39	43	7.9	71.1 (0.3)
VPA70-MBAA30	70	30	–	50.9	53	74	7.9	11.3 (0.4)
VPA80-MBAA20	80	20	–	31.6	63	80	8.2	5.7 (0.3)
VPA0-EGDA100	0	–	100	72.0	0	0	–	71.3 (2.0)
VPA20-EGDA80	20	–	80	60.1	10	16	8.1	71.3 (1.4)
VPA50-EGDA50	50	–	50	46.7	30	35	8.1	70.6 (0.6)
VPA70-EGDA30	70	–	30	38.6	45	47	8.1	66.1 (2.0)
VPA80-EGDA20	80	–	20	28.4	54	59	8.1	60.0 (1.1)

The values in parenthesis are standard deviation (σ).

swelled polymer hydrogels having copolymer/water of 2 g/6 g.

To know the dissociation of phosphonic acid segments of the crosslinked hydrogels, acid–base titration was carried out. It was known that phosphonic acid showed two steps acid–base equilibrium.²² The VPA loading and pK_a in each crosslinked PVPA hydrogel were determined as follows: 0.01M-HCl aqueous solution was added dropwise in to 0.01M-NaOH aqueous solution (50 mL) containing the polymer hydrogels (0.05 g) and agitated with magnetic stirring. Then, the pH values of the polymer solutions were sequentially measured using a pH meter (HORIBA F-21, Kyoto, Japan) against the HCl amounts that were added dropwise. The titrimetric curves were plotted with the pH values and the added HCl amounts.

Water uptakes for crosslinked PVPA hydrogels were measured in the following manner: each freeze-dried hydrogel (0.02 g) was used as a dried weight, W_{dry} , and the powders were immersed in the water. The swelled polymers were precisely weighed. The equation of water uptakes for each hydrogels was calculated as follows:

$$\text{Water uptake(\%)} = \frac{W_{\text{swell}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

To obtain copolymer powders, precipitation copolymerization of VPA and MBAA or EGDA was carried out at different monomer feed (Table I). The values of r_1 and r_2 were estimated from the copolymers obtained at 4–8% yields. As a result, the monomer–copolymer composition curves are presented in Figure 1 for P(VPA-co-MBAA) and P(VPA-co-EGDA) systems. The crosslinked copolymers were able to

become tiny particles after the freeze-drying process. Figure 2 shows SEM images for each resultant copolymer. From Figure 2(a–e), the copolymer had powder like particles having 0.2–0.4 μm in size. It was very interesting to note that strong indication of aggregation were observed in Figure 2(i,j) for the P(VPA-co-MBAA) with 63 mol % of the VPA loading. The copolymer morphology of VPA80-MBAA20 for P(VPA-co-MBAA) system contained high VPA segments and looked as an aggregated morphology resembling like flat flaked particles. Then, to make more observations to this flat flaked morphology, we carried out SEM measurements where samples were prepared by freeze-drying VPA80-MBAA20 after keeping the solution at pH 2.2 and 9.6 for 24 h

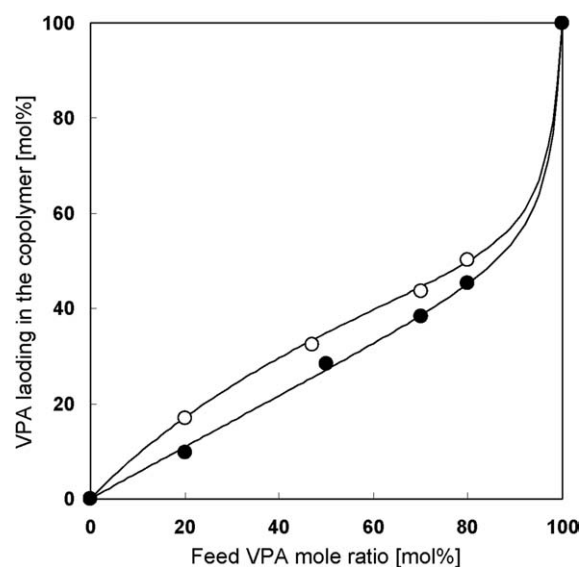


Figure 1 Monomer–copolymer composition curves for the radical copolymerization of VPA with comonomer at the low yields. (○) and (●) were experimental values for MBAA and EGDA, respectively. Solid lines were calculated values.

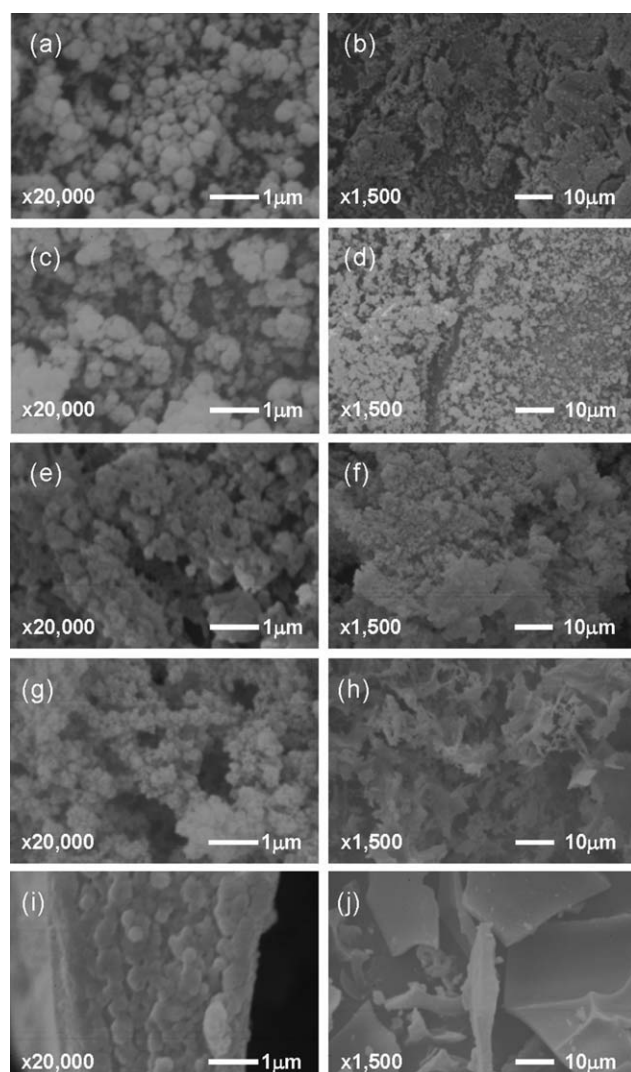


Figure 2 SEM images of P(VPA-*co*-MBAA) hydrogels. (a) and (b) VPA0-MBAA100, (c) and (d) VPA20-MBAA80, (e) and (f) VPA50-MBAA50, (g) and (h) VPA70-MBAA30, and (i) and (j) VPA80-MBAA20.

and also by oven-drying VPA80-MBAA20 at 50°C for 24 h *in vacuo*. As shown in Figures 2(j) and 3, all VPA80-MBAA20 samples showed flat flake morphology with no depending on their drying conditions. In the case of P(VPA-*co*-EGDA), SEM images indicated a powder like morphology and the size distributions were in the range of 0.1–0.3 μm (Figure

4). In addition, no indication of such flat flaked particles was observed in the P(VPA-*co*-EGDA) system. Therefore, the appearance of such aggregation suggested that the copolymer segments of MBAA influenced in the formation of such morphology in the fine powders. As shown in Table I, we also measured the BET surface areas of the crosslinked copolymer. The surface areas of the P(VPA-*co*-MBAA) tended to significantly decrease with the increasing of the VPA loading. For example, the value of surface areas of VPA80-MBAA20 and MBAA homopolymer was 5.7 m²/g and 150 m²/g, respectively. This tendency indicated that each copolymer contained with high VPA loadings could become to aggregate with the neighboring particles. As a result, this meant that the surface area values of the copolymer depended upon the VPA loading. Therefore, it was considered that the morphology became dense as seen in the SEM picture [Fig. 2(i,j)], resulting in low surface area at high VPA loadings. However, in the cases of surface areas for the P(VPA-*co*-EGDA), the values were in the range of 71.3 m²/g to 60.0 m²/g and slightly decreased when the VPA loading in the copolymer was increased. This suggested that the VPA segments introduced to the EGDA segments showed no dense morphology even at high VPA loadings for the VPA80-EGDA20 system. Therefore, apparently, such type of copolymer segments having amide or ester groups did have an influenced in the powder morphology and their properties.

To obtain further information of the reason of why the different aggregations appear in the cross-linked VPA copolymers, the FTIR spectrum measurements and titrations were performed in each sample. Figure 5 shows the FTIR spectra for the resultant copolymers of [Fig. 5(A)] P(VPA-*co*-MBAA) and [Fig. 5(B)] P(VPA-*co*-EGDA). When the VPA feed increased in the precipitation polymerization, the obtained P(VPA-*co*-MBAA) and P(VPA-*co*-EGDA) clearly exhibited in FTIR spectra that their copolymers had both IR peaks of P–O stretching band of VPA and C=O stretching bands of MBAA (a)–(f) or EGDA (g)–(l) at around 1000 cm⁻¹ and 1680 or 1740 cm⁻¹, respectively. The IR intensity of the P–O stretching bands of VPA segments in the both of P(VPA-*co*-MBAA) and P(VPA-*co*-EGDA)

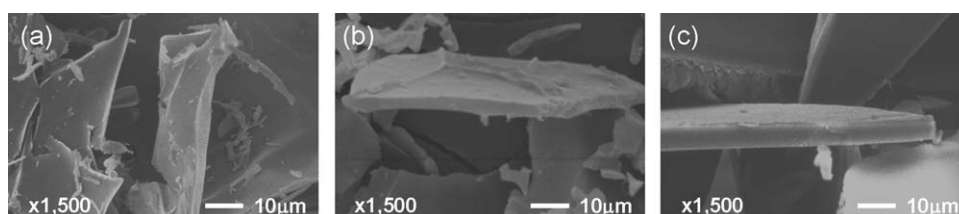


Figure 3 SEM images of VPA80-MBAA20 freeze-dried at (a) pH 2.2, (b) pH 9.6, and (c) oven-dried at 50°C for 24 h *in vacuo*.

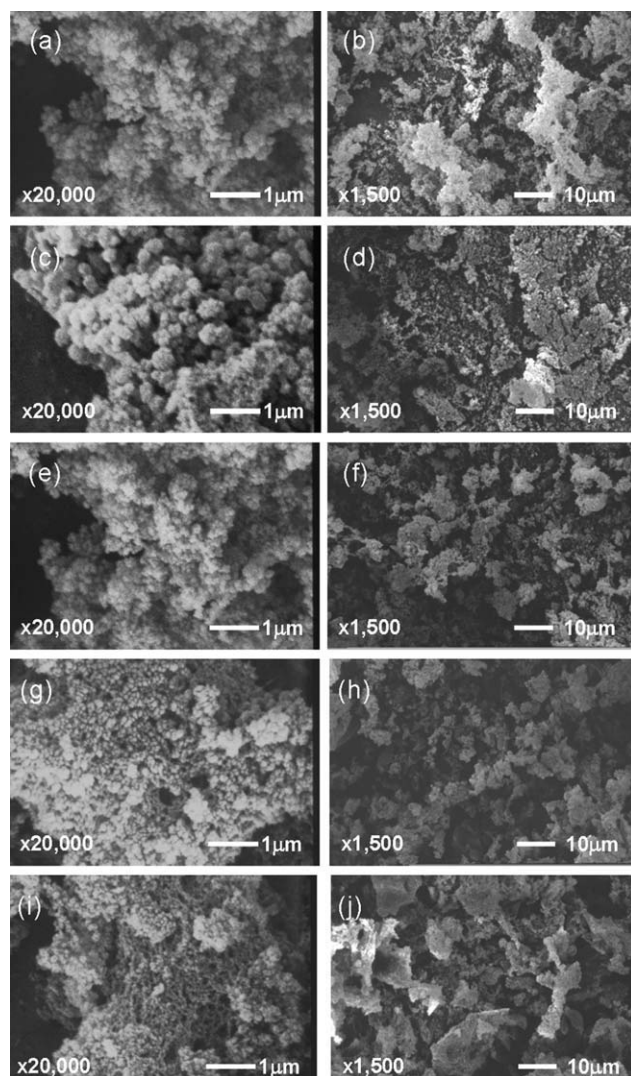


Figure 4 SEM images of P(VPA-co-EGDA) hydrogels. (a) and (b) VPA0-EGDA100, (c) and (d) VPA20-EGDA80, (e) and (f) VPA50-EGDA50, (g) and (h) VPA70-EGDA30, and (i) and (j) VPA80-EGDA20.

increased as the VPA loading increased. As comparing FTIR spectra observed in different VPA loadings, VPA homopolymer (PVPA) apparently showed the characteristic anhydride —P—O—P— bands in 775 cm^{-1} and 705 cm^{-1} . This indicated that the PVPA was condensed from its —P—OH groups to be anhydride form.^{23,24} However, in this work, no IR peaks corresponding to the —P—O—P— bands at around 775 cm^{-1} and 705 cm^{-1} were observed in the case of P(VPA-co-MBAA), or even in VPA80-MBAA20. Namely, this meant that the —P—O—P— segments might be absent in the obtained P(VPA-co-MBAA). In the case of P(VPA-co-EGDA), a similar tendency was observed in which no appearance of the —P—O—P— bands occurred. Thus, the phosphonic acid groups were present in —P—OH form in their copolymers. It was noted in the FTIR spectra of copolymers that the broad peaks of associated O—H

groups could be clearly observed at $2500\text{--}3700\text{ cm}^{-1}$ (Fig. 5) for —P—OH groups. It was clear that the VPA homopolymer showed a broad band near $2800\text{--}2900\text{ cm}^{-1}$ for each —P—OH group. Apparently, P(VPA-co-MBAA)'s band became broad in these wavenumber regions, indicating that MBAA segment promoted the hydrogen bond formation. Figure 6 shows titrimetric results for [Fig. 6(A)] P(VPA-co-MBAA) and [Fig. 6(B)] P(VPA-co-EGDA) obtained with different VPA loadings. In this work, the titration was carried out from base condition at pH 12 to pH 3. The data of titrimetric curves of P(VPA-co-MBAA) and P(VPA-co-EGDA) indicated two step dissociations of $\text{—PO}_3\text{H}_2$ group.



Namely, in Figure 6(A), central and right side plateau regions of the added HCl for over 0.3–0.48 mol and 0.55 mol were due to the equilibrium for eqs. (2) and (3), respectively. In the dissociation step (2), the $\text{p}K_{a2}$ values could be determined from the titration data. The obtained values of $\text{p}K_{a2}$ are listed in Table I. In the titrimetric results, the values of $\text{p}K_{a2}$ for P(VPA-co-MBAA) and P(VPA-co-EGDA) were determined as 7.9 and 8.1, respectively. Obviously, a comparison let us observed that P(VPA-co-MBAA) showed a clear difference at lower loadings of the VPA segments as compared with that of P(VPA-co-EGDA). It is to note that the monomer reactivity of VPA (r_1) and comonomer (r_2) in the FTIR spectroscopy were estimated by fitting the experimental values (Fig. 1) to be $r_1 = 0.06$ and $r_2 = 0.98$ for the P(VPA-co-MBAA) and $r_1 = 0.05$ and $r_2 = 1.82$ for the P(VPA-co-EGDA). The values suggested that the MBAA comonomer showed higher polymerization rates relative to that of VPA. Therefore, P(VPA-co-MBAA) formed MBAA segments first and then VPA segments in the copolymerization process. Because of this, there was the possibility for the MBAA monomers of being predominantly homopolymerized, as a little amount of VPA monomers were copolymerized with MBAA. On the other hand, the values of r_1 and r_2 for the P(VPA-co-EGDA) indicated that the polymerization ability of EGDA was much higher than that of MBAA when VPA was present. Therefore, these demonstrated that VPA segments appeared around EGDA homopolymer parts in the copolymer powders. It seems that such VPA segments might be set on surface of the MBAA and EGDA segments in the copolymers. As a result, aggregation might occur with the hydrogen bond interaction of phosphonic acid segments in the copolymers.

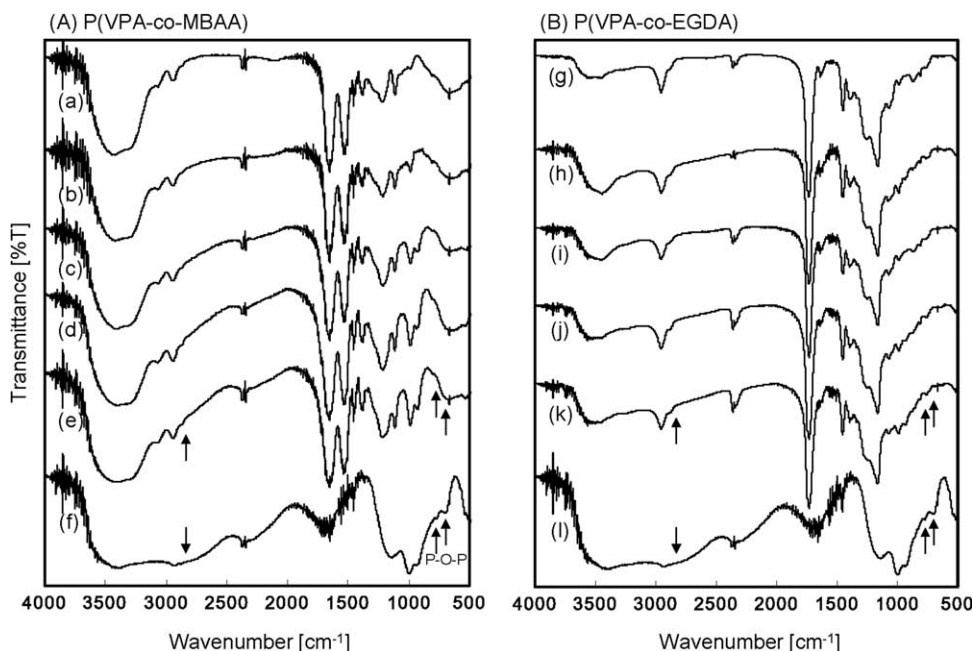


Figure 5 FTIR spectra of (A) P(VPA-co-MBAA) and (B) P(VPA-co-EGDA). (a) VPA0-MBAA100, (b) VPA20-MBAA80, (c) VPA50-MBAA50, (d) VPA70-MBAA30, (e) VPA80-MBAA20, (f) VPA100-MBAA0, (g) VPA0-EGDA100, (h) VPA20-EGDA80, (i) VPA50-EGDA50, (j) VPA70-EGDA30, (k) VPA80-EGDA20, and (l) VPA100-EGDA0.

As Bingöl et al. reported, phosphonic acid segments showed high swelling capacity for the cross-linked hydrogels in water.¹⁶ Namely, the resultant copolymers behaved dominant driving force for water uptake. Therefore, swelling behavior in water absorption experiments was examined at different pH values in the present copolymers. The results of water absorption experiments for the P(VPA-co-MBAA) and P(VPA-co-EGDA) are presented in Figure 7. Here, the nonbuffered aqueous solutions adjusted with dilute HCl or NaOH solution to be pH 2.2, 5.0, and 9.0, and 0.1M buffered aqueous solutions were prepared with HCl and KCl, CH₃COOH

and CH₃COONa, and NH₃ and NH₄Cl at similar pHs for buffered system. The results demonstrated that the copolymers absorbed large amounts water in both systems. As noted in the reference that the values of pK_{a1} and pK_{a2} for phosphonic acid were about 2.0 and 8.0, respectively.²² Namely, the dissociation of O–H groups of phosphonic acid occurred in 50% at pH 2.2 and 100% at pH 5.0. At pH 9.0, the second dissociation of O–H groups would be occurred in 90%. It was apparent in Figure 7 that water absorbency in a wide range of bulk pH values could be observed. For example, 1280–1370% for VPA70-MBAA30 and 1170–1230% for VPA70-

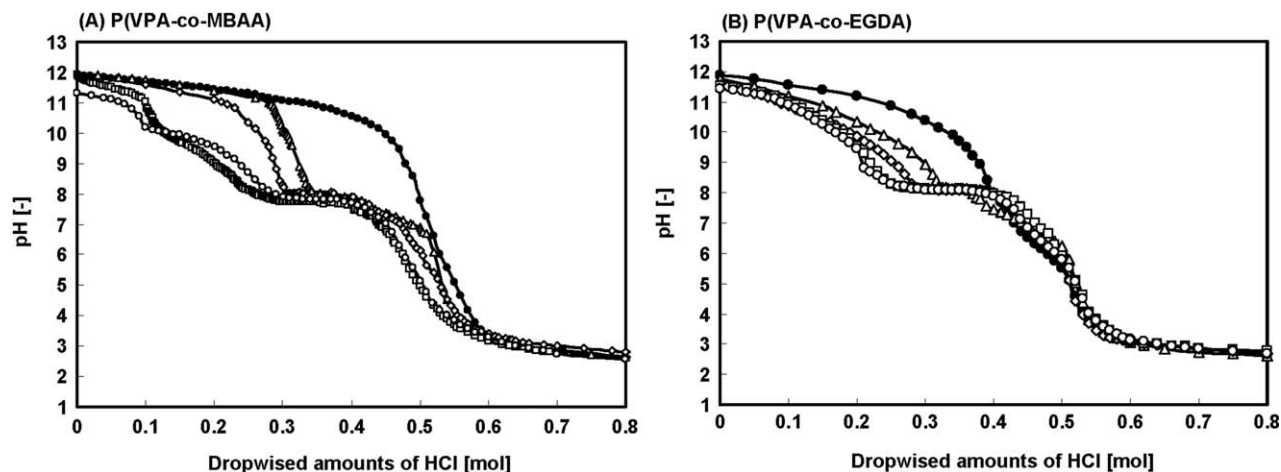


Figure 6 Titration curves of (A) P(VPA-co-MBAA) and (B) P(VPA-co-EGDA). (A) (●) VPA0-MBAA100, (△) VPA20-MBAA80, (◇) VPA50-MBAA50, (□) VPA70-MBAA30, and (○) VPA80-MBAA20. (B) (●) VPA0-EGDA100, (△) VPA20-EGDA80, (◇) VPA50-EGDA50, (□) VPA70-EGDA30, and (○) VPA80-EGDA20.

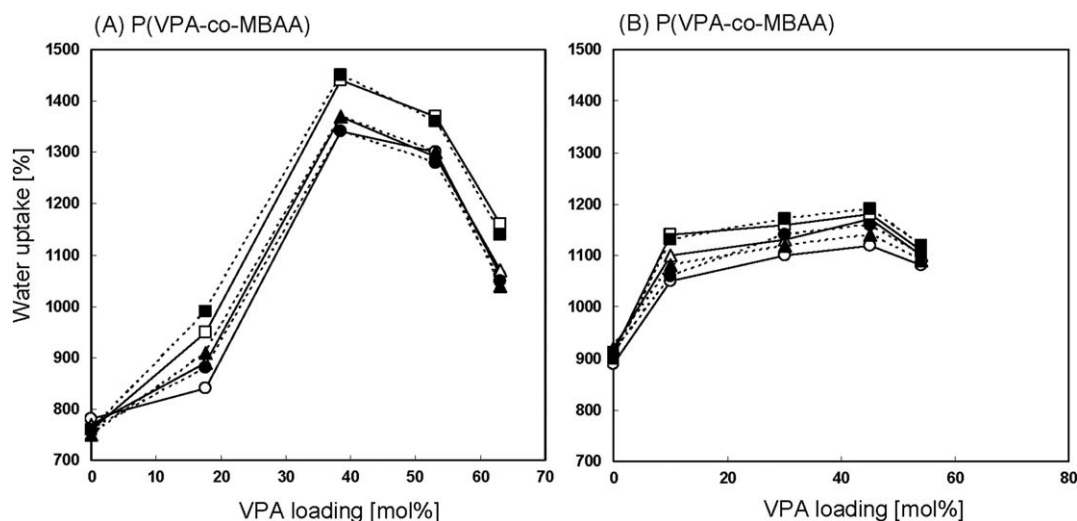


Figure 7 Water uptakes of (A) P(VPA-co-MBAA) and (B) P(VPA-co-EGDA). Nonbuffered aqueous solution at (○) pH 2.2, (△) pH 5.0, and (□) pH 9.0. Buffered aqueous solution at (●) pH 2.2, (▲) pH 5.0, and (■) pH 9.0.

EGDA30 were observed, meaning that extremely large absorbency values of both copolymers powders are present. The data showed that the loading of VPA segments enhanced this ability, since the degree of water uptake gradually became high with the increasing of VPA loading in the copolymers up to about 40 mol %. However, as it increased to be about 60 mol % of VPA loading, the values of the absorbency decreased. A similar tendency was observed in the case of P(VPA-co-EGDA). These meant that the swelling of the hydrogels slightly restricted at in higher VPA loadings. As indicated in the SEM images and surface areas, this seemed to be

due to strong networks of hydrogen bonds with phosphonic acid segments. As shown in Figure 8, for the case of P(VPA-co-MBAA) the strongly stretching bands of hydrogen bond for PO-H...H₂O appeared at around 3000 cm⁻¹ when water was present in the copolymer. Specifically, the spectral shape of VPA80-MBAA20 became broad near 2200–3300 cm⁻¹. This tendency was also observed for the case of P(VPA-co-EGDA). However, when water molecules were present, the wavenumber of the O-H band appeared somewhat different for P(VPA-co-EGDA). With the increase of the VPA loading, the band shifted from 3400 cm⁻¹ to 3300 cm⁻¹. In

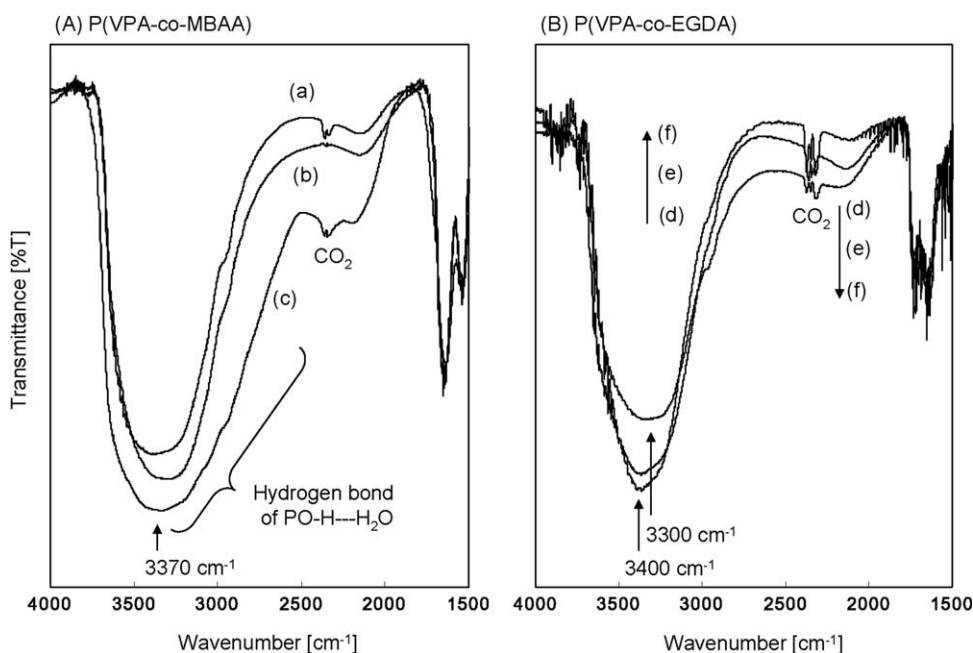


Figure 8 FTIR spectra of (A) P(VPA-co-MBAA) and (B) P(VPA-co-EGDA) with adding water at pH 5.0. (a) VPA20-MBAA80, (b) VPA50-MBAA50, (c) VPA80-MBAA20, (d) VPA20-EGDA80, (e) VPA50-EGDA50, and (f) VPA80-EGDA20.

contrary, the P(VPA-*co*-MBAA) had almost same band remaining at around 3370 cm^{-1} at low and high loading cases. This indicated that the presence of the amide influenced the hydrogen band of $\text{PO}-\text{H}\cdots\text{H}_2\text{O}$. The data for the P(VPA-*co*-EGDA) suggested that, at higher VPA loadings, the copolymers had hydrogen bond formation in crosslinked copolymer, which changed depending on amounts of phosphonic acid groups.

CONCLUSIONS

It is concluded that VPA copolymers crosslinked with MBAA and EGDA displayed excellent water absorbency having about over 1000%. This work could provide meaningful data as novel VPA hydrogels, especially in P(VPA-*co*-MBAA). In the resultant copolymers having higher VPA loadings, the copolymer powder formed as flat flake particles. In addition, the copolymer showed lower surface area of the P(VPA-*co*-MBAA) in the case of high loadings. Comparison of the P(VPA-*co*-MBAA) and P(VPA-*co*-EGDA) suggested that the VPA segments connected with MBAA segments could be affected giving hydrogen bonding formation of $-\text{PO}_3\text{H}_2$ groups and influenced on that of $-\text{PO}_3\text{H}_2\cdots\text{H}_2\text{O}$.

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