Swelling Behavior of Chitosan/Poly(acrylic acid) Complex

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ABSTRACT: This study investigates the improved swelling behavior of chitosan/poly(acrylic acid) complex by solvent (methanol, ethanol, and acetone) extraction. The complex is developed by photoinitiated free-radical polymerization of acrylic acid in the presence of chitosan. The swelling ratio of the complexes depends on the cosolvency effect of poly(acrylic acid) to the extracted solvent, which in turn affects the polymer network structure and ionic states characterized by dynamic force microscopy (DFM), Raman, and FT-IR spectroscopy. The DFM investigation displays the improved structural changes of the polymer network structure after solvent extraction and its relation to the improved swelling property of the chosen system in different environmental conditions (pH, solvent, and salt concentration) are discussed. A high swelling ratio of about 600 times its dry weight is observed in water as well as in low salt and solvent concentration after methanol extraction. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2930–2940, 2004

Key words: chitosan; poly(acrylic acid); hydrogels; networks; photopolymerization

INTRODUCTION

With increasing demands of the utilization of naturally occurring biopolymers, chitin [β-1–4-2-actamido-2-deoxy-D-glucose] and one of its derivatives, chitosan [β-(1–4)-2-amino-2-deoxy-D-glucose] (CTS), have drawn attention for their application in the biomedical, pharmaceutical, cosmetic, and agricultural fields.[1,2] The nitrogen present in their structure imparts unique properties to this class of polysaccharide; that is, aqueous chitin suspensions can be prepared by acid hydrolysis,[3] and chitosan can readily dissolve in aqueous acid solution to contribute a unique polycationic character. By taking this advantage, we have developed a polymer complex/composite based on a three-component system—chitin/chitosan, water, and acrylic acid (AA) monomer—by photoinitiated free-radical polymerization in a different approach, that is, liquid crystalline chitin/poly(acrylic acid) composite with unique optical properties,[4–6] and chitosan/poly-(acrylic acid) complex with excellent swelling properties, in this study.

The polyelectrolyte complex and semi-IPN preparation of chitosan/poly(acrylic acid) have been studied by several researchers for pervaporation and a wide range of biomedical applications.[7–11] Chitosan can dissolve in aqueous AA in the same way as acetic acid, formic acid, lactic acid,[12] and citric acid[13] as follows:

$$\text{CTS—NH}_2 + \text{HOOC—CH}{=}\text{CH}_2$$
$$\rightarrow \text{CTS—NH}_3^{+\,-}\text{COO—CH}{=}\text{CH}_2$$
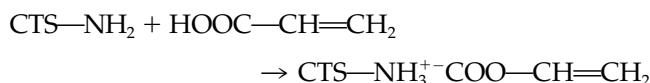
The unsaturated groups of AA in chitosan/AA aqueous mixture underwent photoinitiated free-radical polymerization in the absence of crosslinking agent to form chitosan/poly(acrylic acid) complex, which swelled in water to give a hydrogel in our previous study.[14] The cooperativity of the ionic, hydrogen, and amide bonds between functional groups of two polymers contribute to a three-dimensional network that is able to imbibe water. The swelling property was studied as a function of water content of synthesis component without any posttreatment.

The swelling ability of the absorbent materials depends on the nature of the liquid (swelling medium) and the structure of the polymer network and, in polyelectrolytes, also depends on the degree of dissociation. For polyelectrolyte networks, such as poly-(acrylic acid) (PAA), fixed negatively charged acidic groups on polymer backbones repel each other, which leads to local chain stiffening and long-range excluded volume effects. These effects cause the network to swell tremendously.[15] It is well-known that the commercially important superabsorbent polymers are crosslinked polymers of partially neutralized acrylic acid.[16,17]

An attempt has been made in the present study to enhance the swelling property of synthesized complex with a different approach, by immersing in polar solvents (methanol and ethanol) and nonsolvent (acetone) for PAA after synthesis. AA is well known to exist in different forms depending on the solvent: as a

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TABLE I
Composition of Chitosan/Poly(Acrylic Acid) Complex After Solvent Extraction

Sample ID	Feed ratio (wt/wt %)		Solvent extraction medium	Polymer weight fraction (wt/wt %)	Composition ratio of the complex (wt/wt %)	
	CTS	AA			CTS	PAA
CPA-4	0.99	99.01				
CPA-4(MeOH)	0.99	99.01	Methanol	78.27	1.26	98.74
CPA-4(EtOH)	0.99	99.01	Ethanol	83.34	1.19	98.81
CPA-4(Acetone)	0.99	99.01	Acetone	101.37	0.98	99.02

monomer, as a dimer (self-association), and as a linear oligomer (self-association), associated with a solvent molecule or associated with a carboxylic group of a growing polymer chain. PAA is also soluble to the extent of at least 1–2 pph w/v in water, dioxane, dimethylformamide, ethanol, methanol, and isopropyl alcohol (good polar solvents), whereas acetone, diethyl ether, bezene, and aliphatic hydrocarbon are nonsolvents.[18]

Because of the excess component of AA in the synthesized complex and its cosolvency effect, it is expected that the tendency of PAA is to exhibit associated structure forming ability by solvent treatment. As a consequence, the possibility exists to form some ionized charged groups and redistribution of the network chains to form hydrogen bonds between some of the uncrosslinked temporary entanglements arising from topological interaction during synthesis.

The approach used is to establish the improved network structure of the polymer by simple solvent extraction. We present some observations on the structure of the complex and discuss them in relation to the swelling behavior of the chosen system in different environmental conditions such as pH, organic solvents, and salt concentration.

EXPERIMENTAL

Materials

Chitosan PHS, (degree of deacetylation 85–90%) with an average molecular weight of more than 1,000,000, as reported from the supplier, was kindly provided by Yaizu Suisan Kagaku Kogyo Ltd. (Shizuoka, Japan). Acrylic acid monomer, photoinitiator [2–2′ Azobis (2-amidinopropane dihydrochloride)], and all chemicals used in swelling tests were reagent grade and were purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan). Water used in all the experiments was purified with Millipore (Elix 5), Nihon Millipore Ltd. (Tokyo, Japan).

Sample preparation

The sample preparation was described in detail in the previous study.[14] Briefly, chitosan (0.05 g) was dis-

solved in aqueous AA monomer solution (5.00 g) at different water contents (4.0–40.00 g). AA was added into suspended chitosan powder in water and was mixed together with stirring for 24 h to get a homogeneous casting solution. After addition of water-soluble photoinitiator (0.5% of the monomer), the mixture was cast onto a Teflon plate. UV irradiation (400 W UV lamp) was conducted from a distance of 20 cm for 40 min followed by oven curing at 80°C for 2 h to enhance the reaction between amino groups of chitosan and carboxyl groups of PAA.

The dried films obtained were further immersed in different solvents, such as methanol (CPA4–40), ethanol (CPA-4), and acetone (CPA-4), for 24 h. The purpose was twofold: (a) to remove the soluble fractions (monomer or oligomer) incorporated into the network and (b) to induce the possible formation of charged density variation (although the sites of ionization are not fixed but may distribute along the chains as they adopt different configurations) and reorganization of PAA chains to form new junction zones. The solubility and/or association property of PAA decreased as following order: MeOH > EtOH > acetone (Table I). After 24 h immersion, the sample showed a considerable extent of swelling depending on the type of solvent (swelling in methanol was greater than that in ethanol) and no change was observed in acetone. It is expected that the higher swelling in methanol during extraction will produce a relatively looser polymer network structure than in ethanol, whereas a relatively more compact structure will be observed in sample of acetone extraction. The polymer fractions were vacuum dried at 60°C for 48 h. The polymer network weight fractions were calculated from the relation:

$$(W_d/W_0) \times 100$$

where W_0 and W_d are dry weight of the sample before and after solvent extraction, respectively. The sample as-synthesis was denoted as CPA, whereas posttreatment samples were denoted as CPA(MeOH), CPA(EtOH), and CPA(Acetone) for methanol, ethanol, and acetone extraction, respectively. The numerical number indicated the water content of the synthesis com-
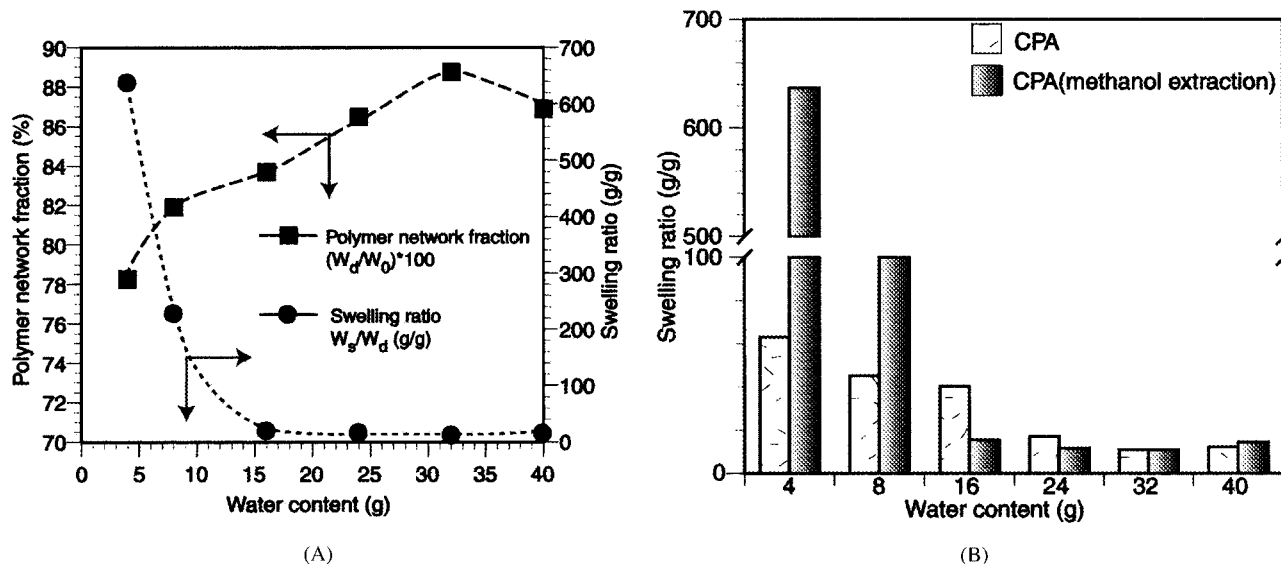
Figure 1   (a) Polymer network fraction and weight-swelling ratio of chitosan/poly(acrylic acid) complex after extraction with methanol. (b) Weight-swelling ratio for chitosan/poly(acrylic acid) (from CPA-4 to CPA-40) complexes before and after methanol extraction as a function of water content of synthesis component.

ponent (e.g., CPA-4 indicated water 4.00 g was used at the time of synthesis).

Measurements

FT-IR Nicolet Model Magna IR 860 with Raman module was used to obtain Raman spectra of all samples. Samples for FT-IR spectra were prepared by grinding the vacuum-dried sample with KBr and compressing the mixture to form disks.

Noncontact mode AFM (Dynamic Force Microscopy) images were obtained at ambient condition using an Atomic Force Microscope (Seiko Instrument Inc., Tokyo, Japan). A standard silicon tip with a resonance frequency of approximately 338 kHz and a spring constant of approximately 38 Nm^{-1} were used. The scan rate was (1.0–2.0 Hz). The cross-section surface and air-surface of the solvent-extracted specimens were mounted on copper disks with an adhesive tape and were directly imaged without special preparation. For the cross-section image, freshly cleaved samples (the exposed surface) were assembled between two sides of copper disks with adhesive tape.

Dynamic mechanical analysis (DMA) was performed by using a Rheovibron Dynamic Viscoelastometer model DDV-II-C (Toyo Baldwin Co., Ltd, Japan) with a heating rate of 10°C min^{-1} and at a frequency of 110 Hz. The specimen dimensions were approximately 25 × 5 × 0.5 mm. The dynamic storage modulus E' and loss modulus E'' were analyzed at the temperature range of 25 to 180°C.

The swelling ratio was measured by immersing a preweighed dry sample (ca. 1 cm^2) in appropriate swelling medium at a given time interval. Excess sur-

face water was blotted out with filter paper before weighing. Highly swollen samples were placed like a sandwich between two sieves and then blotted with filter paper. The weight-swelling ratio, W, was calculated by using the following equation:

$$W(g/g) = W_s/W_d$$

where W_s and W_d denote the weight of the swollen and dry sample, respectively. Experiments were carried out in triplicate and the swelling ratio reported was an average swelling value after 24 h. The swelling mediums are as follows: (a) water, (b) pH 3 and pH 11 solution using 0.01N HCl and 0.01N NaOH, (c) pH buffer solutions (prepared by mixing 0.2M disodium hydrogenphosphate, 0.1M citric acid, 0.05M borax, and 0.2M boric acid and 0.1N NaOH solution),[19] (d) water-organic solvent mixture (methanol, ethanol, or acetone), and (e) NaCl and $CaCl_2$ solution (10^{-8} to 10^{-1} M).

RESULTS AND DISCUSSION

The polymer network fractions and the relative swelling ratio after extraction with methanol is shown in Figure 1(a) as a function of water content of synthesis component. The amount of polymer network fractions increased and the swelling ratio decreased with increased water content of the synthesis component. No appreciable change in swelling ratio was observed from CPA-24 to CPA-40 before and after methanol extraction. [Fig. 1(b)]. The results indicated that there was a strong interaction such as covalent bonds between chitosan and PAA arising from better compat-
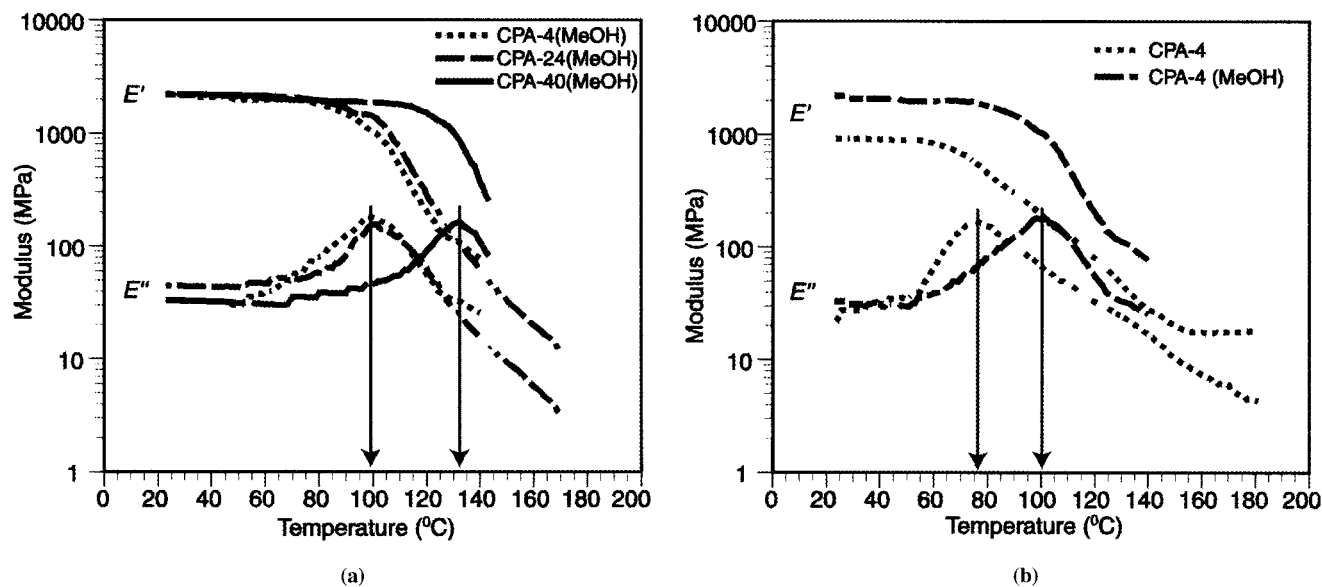
Figure 2 (a) Temperature dependence of dynamic storage modulus (E') and loss modulus (E'') for CPA-4, CPA-24, and CPA-40 after methanol extraction (at 110 Hz). (b) Temperature dependence of dynamic storage modulus (E') and loss modulus (E'') for CPA-4 (as-synthesis) and CPA-4(MeOH) (at 110 Hz).

ibility of the two polymers, in addition to hydrogen bonds and ionic bonds, as water content increased in the synthesis component.

On the other hand, the lowest water content CPA-4 complex shows an excellent swelling ratio of about 600 times its dry weight, which was about 10 times higher than that of the as-synthesis sample. The PAA chains in the as-synthesis CPA-4 might be a tightly coiled structure, which results in a low degree of swelling (see MORPHOLOGY). After solvent treatment, dissociation and association of redistributed carboxyl groups as well as ionized charges contribute to changes in the original tight-coiled structure of PAA chains and the expected result was obtained.

The improved network structure was then determined by DMA [Fig. 2(a)]. The temperature dependence of the storage modulus E' and the loss modulus E'' of the complex as a function of water content of synthesis component was observed. The transition temperature was determined as being where E'' was a maximum. A higher glass transition temperature [from 75 to 101°C in CPA-4(MeOH)] was found compared to that of CPA-4 [Fig. 2(b)]. The glass transition temperatures of CPA-4 to CPA-24 were found nearly at the same temperature after methanol extraction. The higher temperature shift with increased water content (101°C for CPA-4 to 134°C for CPA-40) confirmed the compatibility of the two polymers with increased water content, which agreed with the swelling ratio as shown in Figure 1(a). The elastic modulus property of solid state was maintained when the system underwent swelling to become a hydrogel, that is, the highly swollen hydrogels [CPA-4(MeOH)] upon drying did reswell to the original swollen condi-

tion within an experimental range of three cycles (data not shown). The drying was done at room temperature for 24 h.

From DMA and swelling results, CPA-4(MeOH) was selected to further investigate its swelling behavior in different environmental swelling conditions affected by solvent extraction.

Morphology

The dynamic force microscopy images of cross-section surfaces of CPA-4, CPA-4(MeOH), and CPA-4(acetone) are shown in Figures 3(a–f). The color density for height images in Figure 3 shows the vertical profile of the samples with the light regions being the highest points and the darkest regions being the lowest points (voids). The area of chitosan/PAA appeared white compared to the embedding PAA polymer. For phase images, the light regions (not the white) and the dark regions represent the soft (PAA rich phase) and hard (CTS-PAA rich phase) phases.

There was a marked difference in the microphase conformation before and after solvent extraction. The irregular voids with a diameter of 30–90 nm were observed in CPA-4 [Fig. 3(a and b)], but a rather fine phase contrast observed in solvent extracted samples [Fig. 3(d and f)] indicated that the posttreatment may result in an advantageous structural change in the complex. The air-surface images of the solvent extracted samples after swelling in water are shown in Figure 3(g-j). The height images show the fibrillar and networklike structures [Fig. 3(g and i)]. We can thus imagine that solvent-
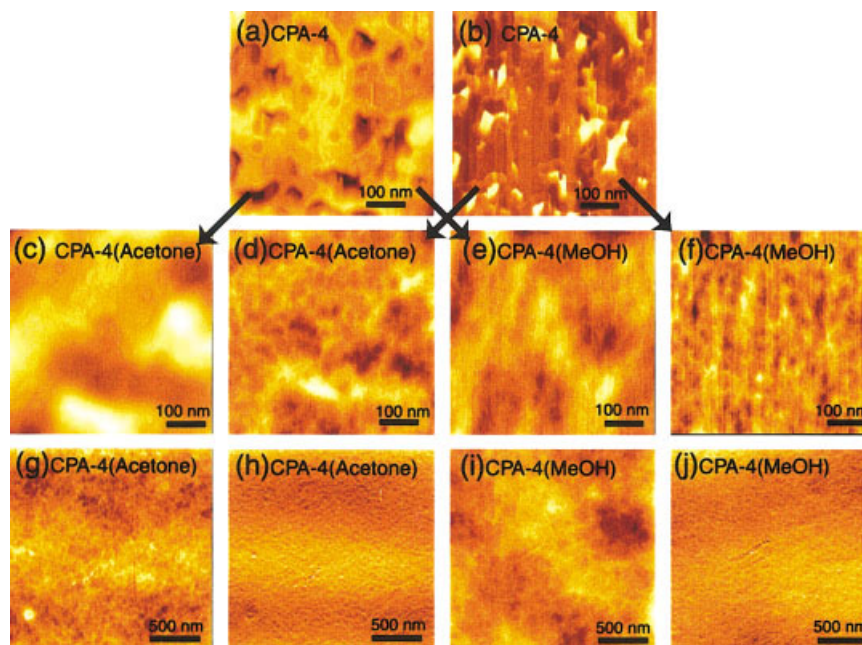
Figure 3 Topograph and phase images of CPA-4, CPA-4(MeOH), and CPA-4(Acetone) obtained by DFM. (a, c, and e) Topographic images of the cross-section surface of CPA-4 before (a) and after extraction with acetone (c) and methanol (e). Image size is 0.5 × 0.5 μm, Z scale (a) 10 nm, (c and e) 5 nm. (b, d, and f) Phase images of the cross-section surface of CPA-4 before (b) and after extraction with acetone (d) and methanol (f). Image size is 0.5 × 0.5 μm, Z scale (b) 100°, (d) 75°, and (f) 68°. (g and i) Topographic images of the surface of (g) CPA-4(Acetone) and (i) CPA-4(MeOH) after swelling in water (vacuum-dried sample). Image size is 2.0 × 2.0 μm, Z scale 5 nm. (h and j) Phase images of the surface of (h) CPA-4(Acetone) and (j) CPA-4(MeOH) after swelling in water. Image size is 2.0 × 2.0 μm, Z scale (h) 60°, (j) 65°.

extracted complexes have a more improved network structure than as-synthesis complex.

The appearance of irregular voids in CPA-4 with its lower swelling ability than CPA-4(MeOH) might be a kind of proliferous polymerization of acrylic acid in aqueous solution encountered in free-radical polymerization.[20,21] In such a case of pure PAA, a low crosslink density with voluminous structure due to many included voids and a white opaque appearance was observed when the mole fraction of water was around 0.6 and 0.7.[21,22] It also showed a low swelling ability despite its low crosslink density. The authors have indicated that the entanglements of macromolecules make an important contribution to the low swelling ability in this kind of polymerization. In our study of CPA-4, the mole fraction of water was 0.76 (if only water and AA are assumed) and the irregular voids in the image indicated a somewhat similar type of polymerization, hence lower swelling ability was observed in the as-synthesis complex.

In considering the substrate effect, it was reported[23] that, when an aqueous solution of vinyl monomers (including AA) was polymerized on hydrophobic substrate, like Teflon plate, obvious heterogeneity occurred in the region of the interface. The resulting hydrogels exhibited a larger degree of swelling, which was related to the loosely crosslinked architecture on the Teflon surface. Because of its extremely low sur-

face tension, polymerization on the Teflon surface was suppressed to some extent and the polymer concentration in the interface region was lower than that in the neighboring region. The migration of monomers from the interface region to the neighboring region and a faster rate of polymerization in the neighboring region caused a concentration difference between the two regions. This continuous process led to formation of a heterogeneous surface structure of hydrogels synthesized on hydrophobic substrates.

In our study of the CPA-4 complex, the chitosan macromolecules migrated along with migration of AA/growing PAA from interface region to neighboring region. Therefore, the resulting complex film exhibited was opaque in air-surface with a lower swelling degree and transparent in Teflon-surface with a higher swelling degree while swelling.

Raman and FT-IR analysis

The Raman spectra of the vacuum-dried CPA-4(MeOH) samples after swelling at pH 3, water, and pH 11 are shown in Figure 4(a). A higher frequency shift of carbonyl band was observed after swelling at pH 3 and water similar to CPA-4.[14] The main difference was that a COO$^-$ asymmetric stretching band appeared not only at pH 11 but also in spectra of pH 3 and water medium due to the presence of
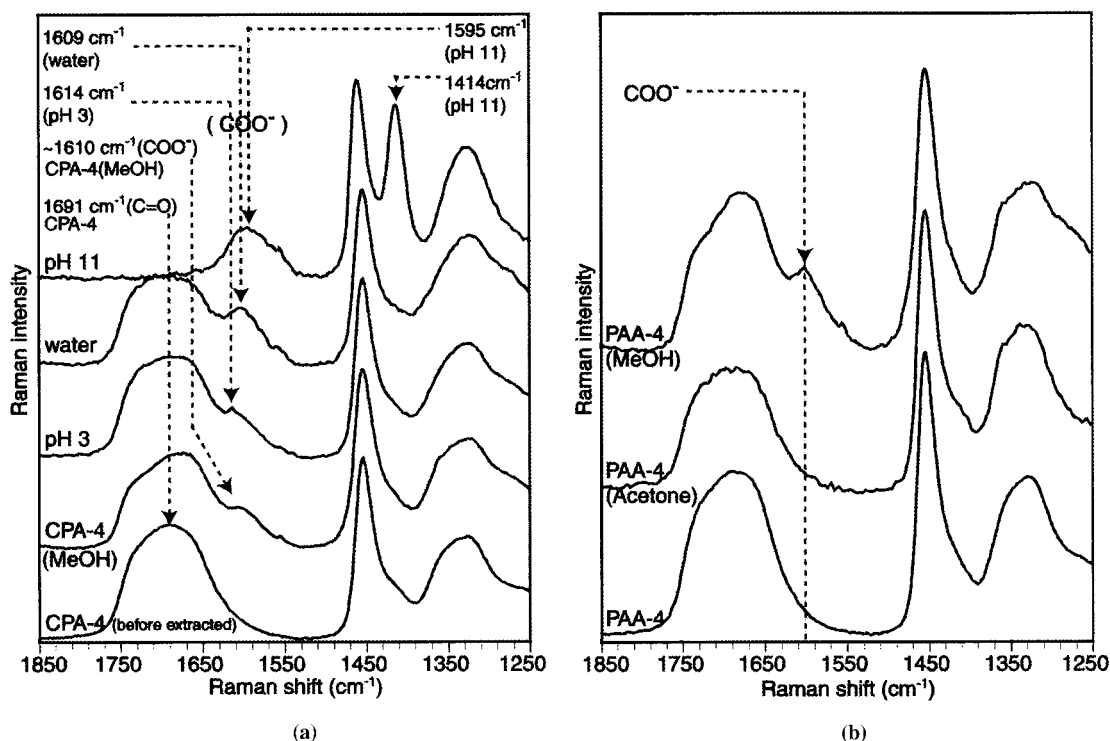
Figure 4 (a) Raman spectra of CPA-4(MeOH) after swelling at pH 3, water, and pH 11 mediums (vacuum-dried samples). (b) Raman spectra of poly(acrylic acid) (PAA-4) after extraction with methanol and acetone (vacuum-dried sample).

some network-fixed carboxylate groups of PAA after solvent extraction [Fig. 4(b)]. This will register the increase swelling degree of CPA-4(MeOH).

FT-IR spectra (1,900–1,500 cm^{-1} range) of vacuum-dried CPA-(MeOH) complex after swelling in different pH buffer solutions for 24 h are shown in Figure 5(a) to estimate the degree of dissociation of the carboxylate group of PAA as a function of pH. The absorption bands of C=O(COOH) and COO$^-$ appeared approximately at the same wavenumber over the whole pH range, which was also reported by Tamura et al.[24] The absorbance ratio of COO$^-$/ [COO$^-$ + C = O(COOH)] as a function of pH of the mediums is shown in Figure 5(b). The absorbance ratio increased with increased pH of the medium and maximum absorbance ratio of dissociation reached at pH 6 and then showed saturation with further increases in pH. The relative insensitivity to the absorbance ratio above pH 6 is due to nearly complete dissociation of carboxylate groups, which will be described in detail in the pH-dependent swelling behavior of CPA-4(MeOH).

Swelling behavior

The three osmotic pressures that determine the equilibrium volume are positive pressure of counterions, negative pressure due to the affinity among polymers,

and the so-called rubber elasticity, which keeps the network in a moderate expansion. Temperature, pH, and salt ions affect both positive and negative pressure, whereas solvent composition influences only the negative pressure.[25,26]

The swelling property is proposed to be caused by ion swelling pressure, the difference between the osmotic pressure of mobile ions in the gel and in the surrounding solution, described by the Donnan theory.[25,27] Within this theory, the ionic forces depend only on the ionic composition of the solvent and on the concentration of fixed ionizable groups in the hydrogel. The higher ion concentration will increase water flow into the gel due to osmosis, resulting in an increase in swelling. Another factor contributing to an increase in swelling is the repulsion of charges along the polymer chains.[28,29] In our case, however, this interaction does not significantly affect on swelling because solvent extraction produced a very low charged density of PAA. The pK_a of the gel, a parameter that has been incorporated into degree of swelling, depends on the degree of ionization and also changes in pH. It is well known that the pK_a of PAA is about 4[30], thus, at a pK_a of about 5, ionization of carboxylic acid sites along the network backbone results in a high pH sensitivity of the acidic gel.[28,30]
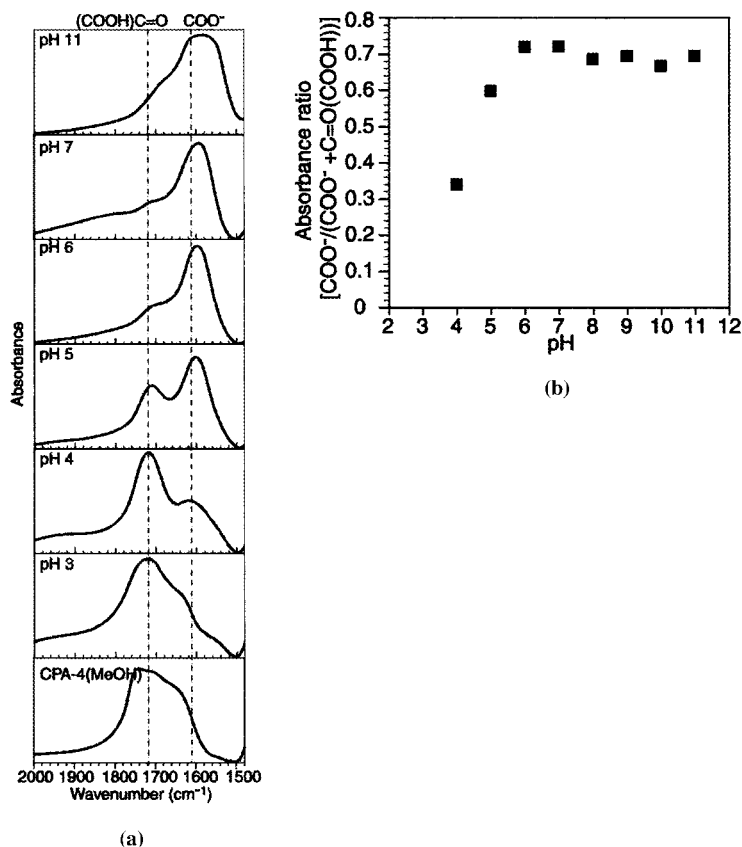
Figure 5 (a) FT-IR spectra of CPA-4(MeOH) after swelling in different pH buffer mediums (vacuum-dried samples). (b) Plot of absorbance ratio of COO⁻ to C=O(COOH) groups for CPA-4(MeOH) against pH of the buffer solution.

Effect of solvent extraction on swelling ratio of CPA-4 in water

The CPA-4(MeOH), CPA-4(EtOH), and CPA-4(Acetone) maintained their shapes while swelling and exhibited different swelling ratios as shown in Figure 6. CPA-4(MeOH) and CPA-4(EtOH) showed a sharp increased swelling in the first 2 h, whereas CPA-4(Acetone) showed a gradual increase of the swelling ratio. After 5 h, the degree of swelling of CPA-4(EtOH) began to drop, whereas that of CPA-4(MeOH) and CPA-4(Acetone) continued to increase slowly for up to 8 h. After 8 h, both hydrogels began to drop to an equilibrium value. The reason for the difference in maximum and equilibrium swelling ratios was the cosolvency effect of PAA in water. The significant weight loss of the dried samples after swelling compared to initial dry weight confirmed this result. The degree of dissolution was 28, 34, and 24% for CPA-4(MeOH), CPA-4(EtOH), and CPA-4(Acetone), respectively, defined by the following equation:

$$\text{Degree of dissolution} = ((W_d - W_d')/W_d) \times 100$$

where W_d and W_d' were dry weight of the samples before and after swelling, respectively.

The initial swelling rate is mainly affected by the ionic states of the complex, but the maximum swelling ratio is controlled by network structure (looser or denser) of the complex. Therefore, the maximum
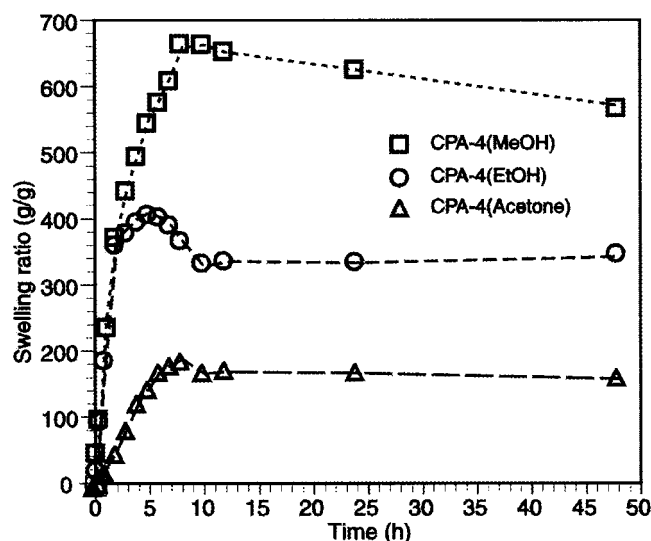

Figure 6 Effect of solvent extraction on weight-swelling ratio of CPA-4 complex in water as a function of time.
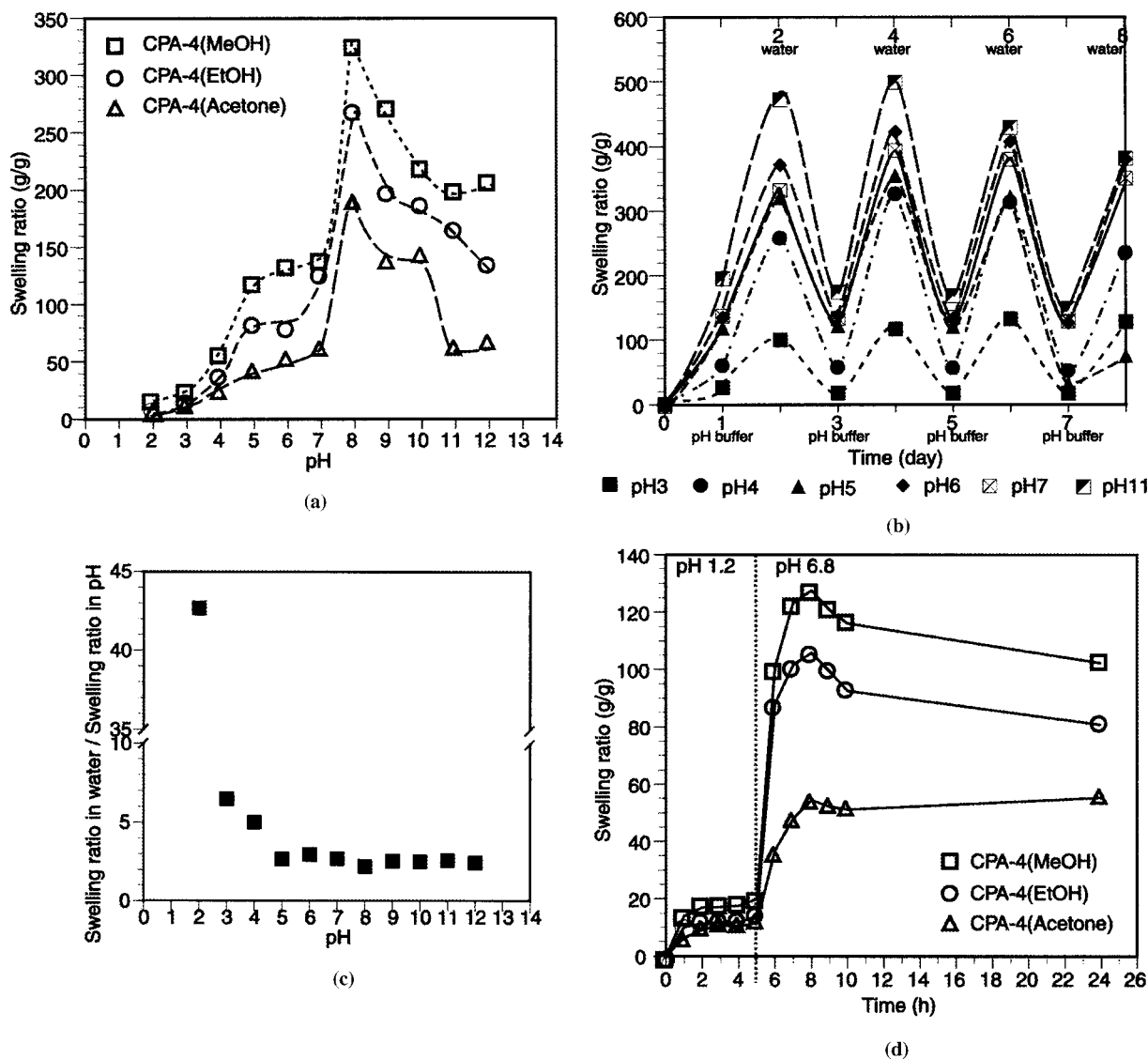
(a)

(b)

(c)

(d)

Figure 7 (a) pH dependence weight-swelling ratio for CPA-4(MeOH), CPA-4(EtOH), and CPA-4(Acetone). (b) Reversible swelling behavior of CPA-4(MeOH) in different pH buffer mediums and water medium. (c) Ratio of weight-swelling ratios in water medium and pH medium for CPA-4(MeOH) as a function of pH level of the pretreating solution (pH 2 = 0.01N HCl, pH 3–12 = pH buffer) (data based on swelling ratio from b). (d) Sequential swelling ratio for CPA-4(MeOH), CPA-4(EtOH), CPA-4(Acetone) as a function of time with abrupt change in pH from 1.2 to 6.8.

swelling degree was observed in the order CPA-(MeOH) > CPA-4(EtOH) > CPA-4(Acetone) if we compare the effect of solvent extraction. For each sample, the swelling behavior depends on the availability of the fixed ionizable groups and the affinity of the hydogels network to the solvent medium.

Effect of swelling medium (pH, salts, and solvents)

pH dependence swelling behavior

Changes in pH or ionic strength varied the degree of dissociation of the carboxyl groups, which contribute the pH dependence swelling behavior of the CPA-4 complexes [Fig. 7(a)]. All three CPA-4s showed a sim-

ilar trend with different degrees of swelling. In general, the hydrogels do not swell significantly at low pH (< pH 3) where the acidic groups are unionized form, but highly swell at high pH due to the osmotic swelling pressure of the counterions associated with ionized acidic groups. The major changes occurred over the range of pH 3–8. First, a gradual increase in swelling from pH 3 to pH 5 followed by a slight increase to pH 7, then a sharp gel-phase transition was observed from pH 7 to pH 8. The swelling ratio decreased upon further increases in pH of the swelling medium.

At the regime of pH 5–7, the swelling ratio was roughly maintained to some extent. This may be at-

tributed to the buffer action of the carboxylate groups with an acid or base around its pK_a.[18] In the range of pH 7–8, the system turns into basic pH and the concentration of base cations in the outer solution also increases. These ions are attracted into the hydrogel and replace the mobile H^+ ions. As a consequence, new H^+ ions are supplied by undissociated acrylic acid and the mobile ions concentration increase more rapidly than in the outer solution. Thus, a sharp transition was observed in this pH range.[27] The counterions involved in protonated chitosan in acid pH range also enhanced this sharp transition.

The decrease in swelling after pH 8 can be explained by a complete dissociation of acidic groups and further increases in the amount of mobile ions leads only to a decrease in osmotic pressure, which can also be seen in the absorbance ratio of FT-IR spectra [Fig. 5(b)].

Reversible swelling behavior in response to pH

The pH dependence swelling behavior was found to be completely reversible as shown in Figure 7(b) with periodic swelling and shrinking cycles in water and different pH buffer mediums for CPA-4(MeOH). The samples first swelled in different pH buffer mediums for each 24 h were transferred to water mediums for another 24 h and were going on repeated cycles for 1 week. The swelling and shrinking cycle remained constant up to three rounds in all pH mediums. This behavior is particularly useful for the intended application to speed up the swelling by using a material that is already preswollen in an appropriate pH medium because reswelling behavior is influenced by the pH level of the medium used for preswelling. Ratios of the swelling in water medium to respective pH buffer medium [Fig. 7(c)] provided further information about the dissociation state of the carboxylate ions and state of the mobile ions in acidic and basic solutions, which contribute to ion swelling pressure in cyclic swelling. The higher water uptake ratio was found approximately six times and approximately five times in pH 3/water and pH 4/water mediums, respectively. The rest of medium pairs showed a nearly constant water uptake ratio regardless of the pH of the preswelling medium. However, the highest water uptake ratio was observed in pH 2/water mediums ($\sim$ 42 times), which was not a buffer solution. This observation clearly demonstrates the effect of buffer action on ion swelling pressure of the CPA-4(MeOH).

Sequential swelling study

Sequential swelling studies in pH 1.2 and pH 6.8 buffer mediums were also investigated as these pH mediums represent the pH of gastric and intestinal fluids. The samples were first swollen in pH 1.2 for 5 h, followed by swelling in pH 6.8 for additional 5 h [Fig. 7(d)]. Because the CPA complex behaved as acidic hydrogels, the swelling ratio in pH 1.2 medium was roughly maintained at a constant value throughout the 5-h interval. When the hydrogels were transferred to pH 6.8, a higher swelling ratio was observed within 1 h and the maximum swelling ratio was reached after 3 h. At later time points in pH 6.8, the swelling ratio decreased to some extent (upto 10 h from the initial swelling) and approached the equilibrium value. All three samples showed a similar trend with specific swelling degree with respect to type of extracted solvent. Such swelling behavior is attractive for the formulation of a controlled release device for the gastrointestinal tract.

Swelling behavior in salt solution

Because the complex contained some network-fixed charges, counterion H^+ will be exchanged for the salt cations. New free H^+ counterions will be produced by dissociation of free COOH groups of PAA and hence the ion swelling pressure within the hydrogel will increase. This will lead to a greater osmotic pressure inside the hydrogel compared to outside, which causes it to swell first. When the PAA is completely dissociated, the difference in the ionic osmotic pressure between the gel and the external solution will decrease upon further increase in salt concentration. This will lead to the hydrogel shrinkage.

According to the pH-dependence swelling study, free COOH groups of PAA were completely dissociated at pH 8. The swelling study performed in aqueous salt solution had no pH adjustment (assumed at pH 7). In this condition, few COOH groups will available for dissociation. Therefore, the swelling maximum was observed in very low NaCl concentrations (10^{-6} to 10^{-7}M) in CPA-4(MeOH) and CPA-(EtOH), whereas continuous shrinkage was observed in $CaCl_2$ solution with increased salt concentration [Fig. 8(a and b)]. Along with the concentration, the nature of the salt (monovalent and divalent) also affects the swelling degree.

For the network with very low/no ionic groups, CPA-4(Acetone), the swelling ratio could be divided into three stages: the initial rapid decrease of the swelling ratio, then a constant swelling ratio for some extent, followed by a continuous shrinkage with increased salt concentration [Fig. 8(c)]. The first rapid decrease in the swelling ratio could be explained by the decreased osmotic pressure of counterions in the gel phase due to the addition of salt to the system.[31]

Swelling behavior in organic solvents–water mixture

In general, the swelling ratios of less than 20% solvent concentration were comparable to their respective swelling ratio in water and the weight-swelling ratio
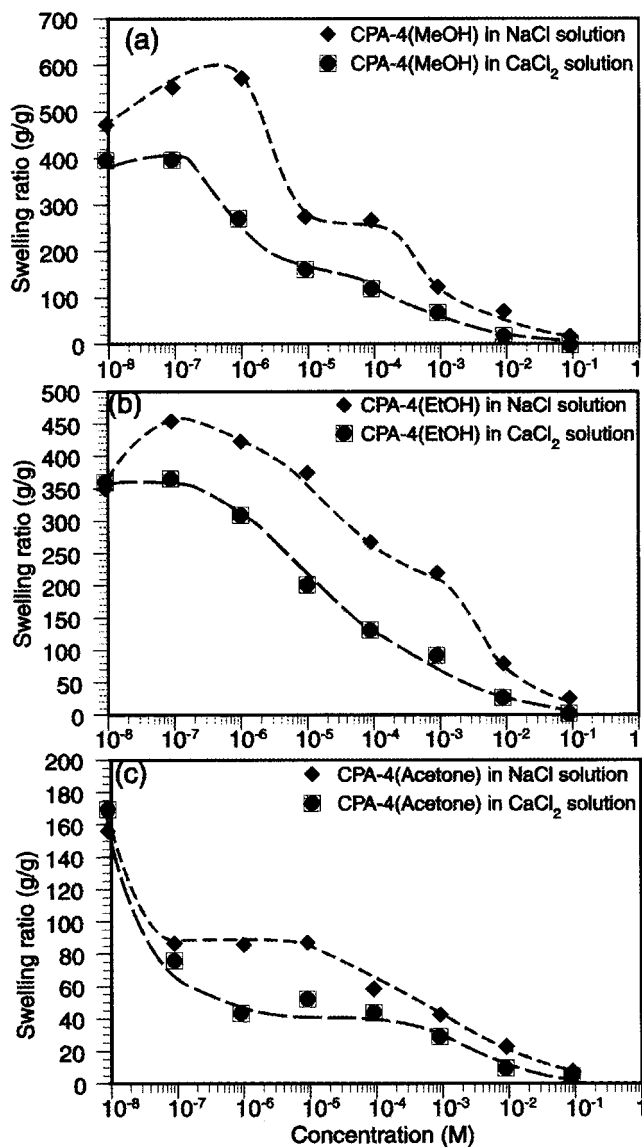
Figure 8 Swelling ratio for CPA-4(MeOH), CPA-4(EtOH), and CPA-4(Acetone) as a function of NaCl and CaCl$_2$ concentration.

decreased with increased solvent composition and no significant difference was observed above 70% solvent concentration [Figs. 9 (a–c)]. CPA-4(EtOH) and CPA-4(Acetone) showed continuous phase transition (de-swelling) with increased solvent concentration, whereas the swelling ratio of CPA-4(MeOH) was somewhat sensitive to solvent concentration and exhibited a distinct phase transition between 20 and 70% solvent concentration. It was noted that the swelling ratio of each solvent-extracted sample in three different solvent mediums showed a similar trend as shown in Figure 9(d); for example, CPA-4(EtOH) and CPA-4(Acetone) also showed a similar trend. This accounts for the negative osmotic pressure due to affinity among polymers[26] and also demonstrates the specific polymer network structure of each sample affected by

type of extracted solvent. The high swelling ratio of the CPA complex in the water–organic mixture is useful to enhance the performance of pervaporation separation of the water–alcohol mixture in which highly water permselective performance is needed.[8]

CONCLUSION

Chitosan/poly(acrylic acid) complex was prepared by photoinitiated free-radical polymerization. An im-
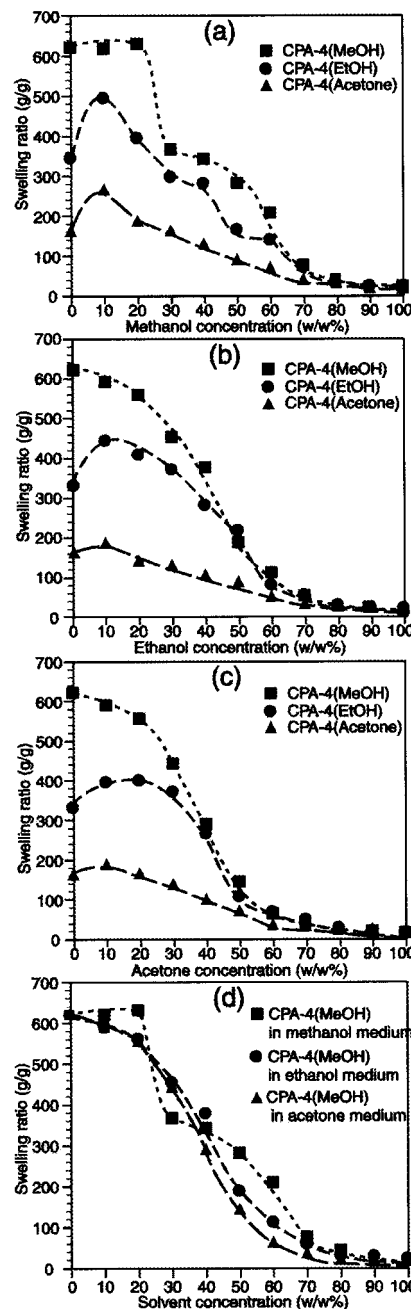

Figure 9 Weight-swelling ratio of CPA-4(MeOH), CPA-4(EtOH), and CPA-4(Acetone) in (a) methanol medium, (b) ethanol medium, (c) acetone medium, and (d) comparison of weight-swelling ratio of CPA-4(MeOH) in different organic solvent mediums.

proved polymer network structure then was evaluated by simple solvent extraction. FT-IR, Raman, and DFM images confirmed the structure of the complex, which related to its swelling behavior. Consistency of the swelling ratio with specific network structure affected by type of solvent extraction was observed. The CPA-4 (MeOH) showed an excellent swelling property (about 600 times its dry weight) not only in water but also in low salt (10^{-6} to 10^{-7}M NaCl) and organic solvent (10–20% w/w methanol, ethanol, and acetone) concentration. The swelling ratio was sensitive to pH and reversible swelling behavior in response to pH of the swelling medium was observed.

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