

# Synthesis and Characterization of Chitosan/Poly(acrylic Acid) Polyelectrolyte Complex

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**ABSTRACT:** Polyelectrolyte complex based on chitosan and acrylic acid monomer by photoinitiated free-radical polymerization in the absence of crosslinker showed a large transition in swelling in response to changes in pH of surrounding medium. Their ability to swell arises from polyelectrolyte interactions and molecular structure of the complex. The main properties of interest that related to the molecular structure, swelling volumes, glass transition temperature, and elastic modulus of the complex were investigated. The effect of water content, the only variable in the sample component, played an important role in molecular structure of the complex and as a consequence, the extent of intermolecular linkage, especially amide bonds which in turn governed the degree of swelling of the polyelectrolyte complex in this study. The decreased degree of swelling and higher temperature shift of glass transition temperature was found with increased water content, whereas increased modulus of elasticity of dry complex was found in lower water content of synthesis component. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1025–1035, 2002

**Key words:** chitosan; poly(acrylic acid); polyelectrolyte complex; pH-sensitive; photopolymerization

## INTRODUCTION

Complexation of synthetic polymers with naturally occurring macromolecules is a broad area of material sciences and is widely used in potential applications in the form of hydrogels, films, membranes, etc. Polymer complexes are formed by association of two or more complementary polymers and may arise from electrostatic forces, hydrophobic interactions, hydrogen bonding, van der Waal forces, or combinations of these interactions.<sup>1</sup> pH-sensitive hydrogels usually contain pendent acidic or basic groups, such as carboxylic acids and primary amines, or strong acids and

bases, such as sulfonic acids and quaternary ammonium salts, which change ionization in response to changes in pH, thus changing the properties of the gels.<sup>2</sup> pH-sensitive hydrogels can be prepared by covalent crosslinking or by physical crosslinking such as polyelectrolyte complexes where one of the ionic species is in excess.<sup>3</sup> Among the first ionic hydrogels investigated were gels based on acrylic acid and methacrylic acid.<sup>4,5</sup>

Chitosan [ $\beta$ -(1-4)-2-amino-2-deoxy-D-glucose] is a unique basic polysaccharide obtained by deacetylation of chitin, a natural polymer (from exoskeleton of crustacean, cuticle of insects, and cell wall of fungi). Having a primary amino group at C2 and hydroxyl group at C3 and C6 positions, chitosan undergoes a host of chemical reactions under mild conditions rather than chitin. Chitosan has been modified by graft copolymeriza-

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**Table I Composition and Designation of Chitosan/PAA Polyelectrolyte Complexes**

Sample ID	Chitosan (CTS) (g)	Acrylic Acid Monomer (g)	Deionized Water (g)	Photoinitiator (g)
CPA-4	0.05	5.00	4	0.025
CPA-16	0.05	5.00	16	0.025
CPA-24	0.05	5.00	24	0.025

tion and by blending with water-soluble polymers.<sup>6</sup> Chitosan in aqueous acid solution was surface reacted with polyanion aqueous solutions [heparin, sodium alginate, carboxymethylcellulose, poly(acrylic acid)] to give polyelectrolyte complexes.<sup>7</sup>

The use of poly(acrylic acid) and chitosan for blend membrane and semi-interpenetrating polymer network preparations were investigated by several researchers aiming to use them for pervaporation and for a wide range of biomedical applications.<sup>8–15</sup> Because the reaction between two opposite-charged polyelectrolytes always causes precipitation of complexes in aqueous solution, appropriate concentration of acidic solvent (acetic acid or formic acid in this case) is required to get a homogeneous blend solution.<sup>14</sup> However, photopolymerization of acrylic acid monomer in aqueous chitosan solution can overcome the precipitation of the complexes formed.<sup>8–10</sup> We developed this new method (by UV irradiation) in synthesis of complexes with different ratios of chitosan and acrylic acid monomer solutions.<sup>8,9</sup>

Application of photopolymerization is an exciting area of active research because of its unique set of advantages such as solvent-free formulations, very high reaction rates at room temperature, spatial control of the polymerization, low energy input, and chemical versatility. The photoinitiated photopolymerization of monomers and oligomers to form crosslinked higher molecular weight material is the basis for most of the commercial applications. The reactive monomeric materials most commonly used are low-molecular-weight unsaturated acrylate or methacrylate monomers that can be made to crosslink with the use of a radical generating photoinitiator.<sup>16</sup>

All of these factors are taken into account and designed for this study. We selected poly(acrylic acid) and chitosan as anionic and cationic polymer and prepared the polyelectrolyte complex by UV photopolymerization followed by oven curing to induce the development of covalent amide link-

age between two polymers. Our intention is to investigate the relationship of specific interactions between these two polymers in dry state and in swell state as a function of water content of synthesis component.

## EXPERIMENTAL

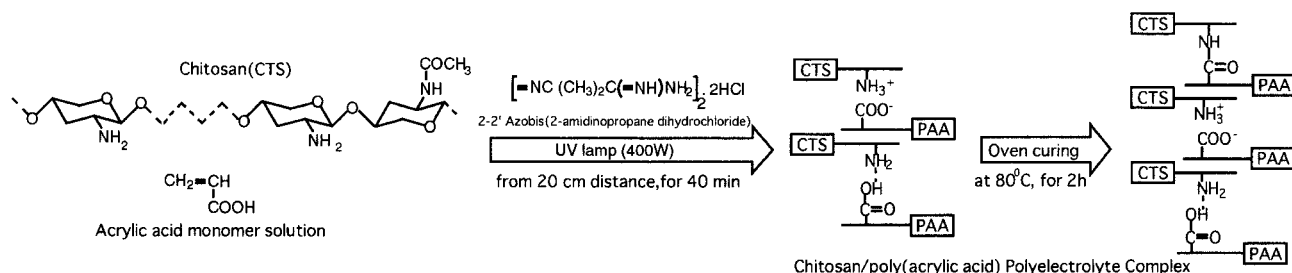
### Materials

Chitosan PSH (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-ken, Japan. Acrylic acid monomer and [2,2'-azobis-(2-amidinopropane) dihydrochloride] as a photoinitiator were purchased from Wako Pure Chemical Industries Ltd., Tokyo, Japan.

### Synthesis of Chitosan/Poly(Acrylic Acid) Polyelectrolyte Complexes

It was expected that the chitosan/poly(acrylic acid) polyelectrolyte complexes were formed via intermolecular association between amino groups on chitosan and carboxyl groups on poly(acrylic acid) (PAA) in addition to other secondary intermolecular bonding forces. UV irradiation was used to create free radicals from 2,2'-azobis-(2-amidinopropane) dihydrochloride, which in turn initiate to polymerize acrylic acid monomers.

Based on our preliminary experiments at different UV irradiation times (20, 40, and 60 min), different oven curing times (2, 4, and 6 h), and our previous works,<sup>8,9</sup> 40-min UV irradiation time, 2-h oven curing time, and water content of 4, 16, and 24 g (from 4 to 40 g) were designed for the present study. Chitosan (0.05 g) dissolved in aqueous acrylic acid monomer solution (5 g) at different water contents were listed in Table I. Chitosan powder was first suspended in an appro-



**Figure 1** Schematic description of chitosan/poly(acrylic acid) polyelectrolyte complex.

appropriate amount of deionized water for preswelling for 24 h and then solutions of aqueous acrylic acid monomer and chitosan were mixed together (molar ratio  $\text{COOH} : \text{NH}_2 = 99.68 : 0.32$ ) with stirring for another 24 h to form a homogenous casting solution. After addition of water-soluble photoinitiator 2,2'-azobis-(2-amidinopropane) dihydrochloride 0.025 g, the mixture was cast onto a Teflon plate. UV irradiation (400 W UV lamp) was conducted for 40 min from a distance of 20 cm followed by oven curing at  $80^\circ\text{C}$  for 2 h to enhance the reaction between amino groups of chitosan and carboxyl groups of PAA. The dried films obtained were further subjected under vacuum drying at room temperature for 3 days to remove any unreacted residues and acrylic acid monomers. The schematic description of complex preparation was shown in Figure 1.

### Measurements

Fourier transform infrared (FTIR; Nicolet Model Magna IR 860) with a Raman module was used to obtain Raman spectra of all the samples (dried samples before and after treated with deionized water and swollen samples). Samples for FTIR spectra were prepared by grinding the dry complex with KBr and compressing the mixture to form disks.

The swelling behavior was measured by immersing preweighted dry samples in deionized water, pH 3, and pH 11 solutions at a given time interval. Samples were cut into strips and were swollen at  $25^\circ\text{C}$ . Excess surface water was blotted out with filter paper before weighing. The degree of swelling (DSW) was calculated by using the following equation:

$$\text{DSW}(\%) = [(W_s - W_d)/W_d] \times 100$$

where  $W_s$  and  $W_d$  denote the weight of the swollen and dry samples, respectively. Differential scanning calorimetry (DSC) thermograms were re-

corded with a Perkin-Elmer DSC-1 (Perkin-Elmer, U.S.A.). In the tests, about 8–10 mg of samples were used and sealed in aluminum pans. All measurements were conducted under a constant flow of nitrogen at a  $10^\circ\text{C}/\text{min}^{-1}$  heating rate in a temperature range of  $25$ – $200^\circ\text{C}$ .

Dynamic mechanical analysis (DMA) was performed by using Rheovibron Dynamic Viscoelastometer model DDV-II-C (Toyo Baldwin Co., Ltd., Japan) with a heating rate of  $1^\circ\text{C}/\text{min}$  and at a frequency of 110 Hz. All the specimen dimensions were approximately  $25 \times 5 \times 0.5$  mm and were dried again at  $25^\circ\text{C}$  under vacuum for 2 days before testing. The dynamic storage modulus,  $E'$ , loss modulus,  $E''$ , and mechanical loss tangent, ( $\tan \delta = E''/E'$ ), were analyzed at the temperature range of  $25$ – $180^\circ\text{C}$ ; a temperature of the rubbery state was attained.

## RESULTS AND DISCUSSION

We focused our interest in the range of  $1400$ – $1800$   $\text{cm}^{-1}$  in all spectra, because it is a suitable region to investigate the influence on the vibration modes of carbonyl groups and carboxylate groups of possible hydrogen bonding interactions in the complex.

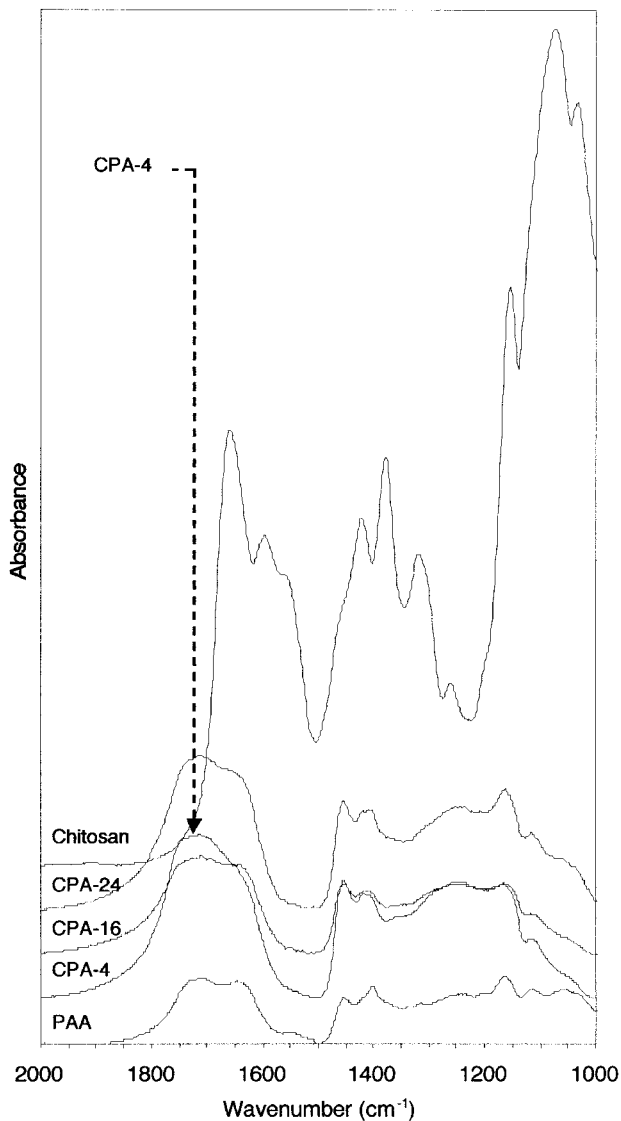
### FTIR Analysis

FTIR spectra of chitosan/poly(acrylic acid) polyelectrolyte complex can be seen in Figure 2-4. The characteristic peaks of chitosan are located at  $3416$   $\text{cm}^{-1}$  of hydroxyl group (not shown) and at  $1658$ ,  $1561$   $\text{cm}^{-1}$  of amide I and amide II, respectively, whereas absorption bands of PAA appeared around  $3432$   $\text{cm}^{-1}$  (not shown),  $1716$   $\text{cm}^{-1}$ , and  $1454$   $\text{cm}^{-1}$ .

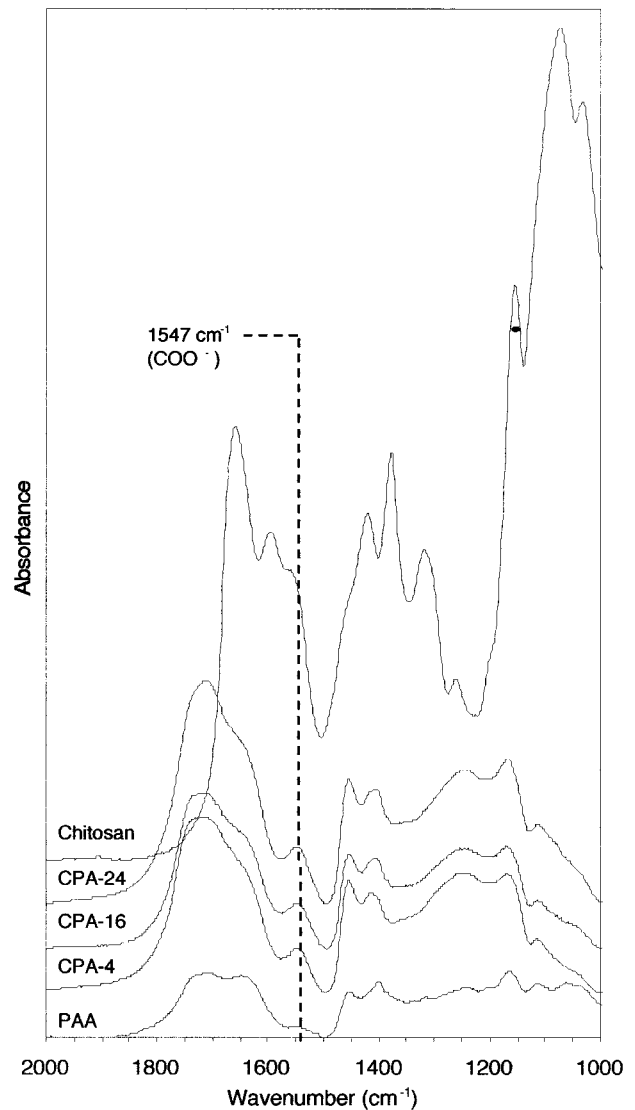
A slightly lower frequency shift of carbonyl band (with a prominent shoulder) of CPA-16 and

CPA-24 in Figure 2 indicated that more carbonyl groups of PAA were covalently interacted with amino groups of chitosan than in CPA-4, leading to compatibility of the complexes.

In contrast with Figure 2, a significant new peak appeared at about  $1547\text{ cm}^{-1}$  in the spectra of all three CPA after swelling in deionized water ( $\sim\text{pH } 7$ ), as shown in Figure 3. It can be assigned as asymmetric deformation of  $\text{COO}^-$ . A more pronounced higher frequency shift ( $\sim 1575\text{ cm}^{-1}$ ) of  $\text{COO}^-$  was found in the spectra after swelling at pH 11, whereas the carbonyl and carbonyl amide region appeared only as a shoulder (Fig. 4). Because this polyelectrolyte complex behaved as

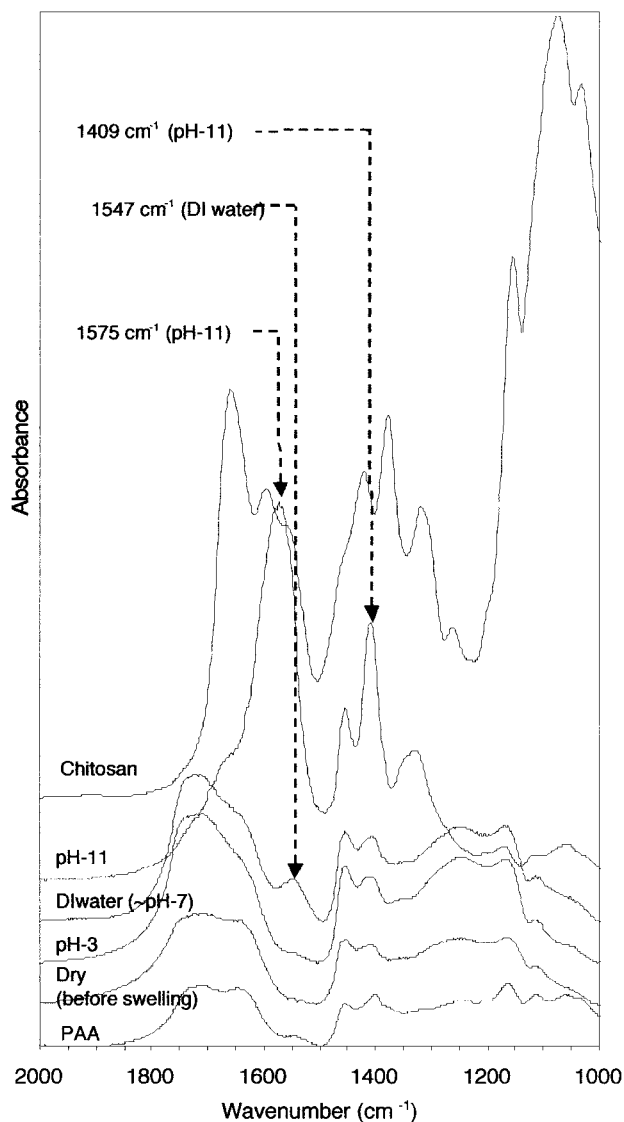


**Figure 2** FTIR spectra of dry chitosan/poly(acrylic acid) polyelectrolyte complex (before swelling in DI water).



**Figure 3** FTIR spectra of chitosan/poly(acrylic acid) polyelectrolyte complex (after swelling in DI water).

acidic hydrogels while swelling, increased pH of the swelling medium favored increased ionization of  $\text{COOH}$  in PAA. Thus, a significant development of carboxylate ion absorption band was found as increasing pH of the swelling medium. A slightly higher frequency shift of carbonyl region was found from dry state to after swelling at pH 3 and deionized (DI) water and was drastically diminished after swelling at pH 11 solution medium because of increasing ionization of  $\text{COOH}$  groups and dissociation of hydrogen bonding. Because of very low chitosan content (mole ratio of  $\text{NH}_2 : \text{COOH} = 0.32 : 99.68$ ), the peak with respect to  $\text{NH}_3^+$  deformation peak cannot be found in the spectra after swelling at pH 3.



**Figure 4** FTIR spectra of CPA-16 at dry state and, after swelling at pH 3, DI water ( $\sim$  pH 7), and pH 11 solution medium.

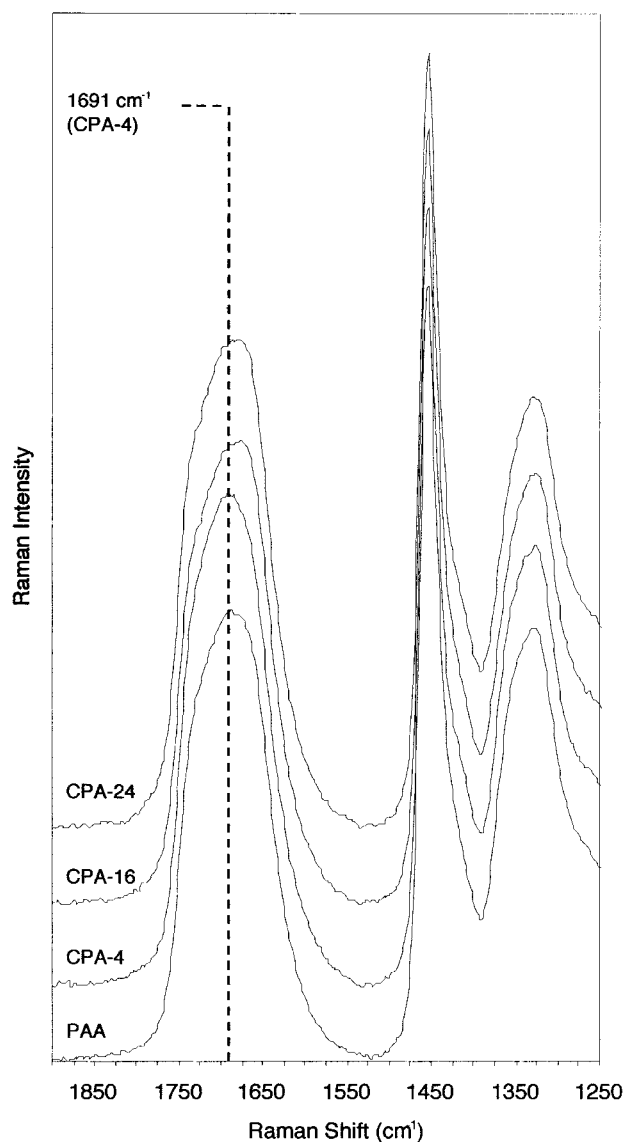
### Raman Analysis

Because water is a highly polar molecule and strong IR absorber, the structural determination of the complex while swelling in water could not be detected by IR spectroscopy. Compared to IR spectroscopy, the advantage of working with Raman spectroscopy was that Raman spectra could be recorded in great detail for substances in aqueous solution with little interference arising from water, and samples of any size and shape without modification could also be analyzed.<sup>17</sup> Hence, we used Raman spectroscopy to detect the wet state of the samples.

Raman spectra of CPA-4, CPA-16, and CPA-24 are shown in Figures 5-8. The peaks of chitosan are located at  $1659$ ,  $1594$ , and  $1263$   $\text{cm}^{-1}$  of amide I, II, and III, respectively (not shown), whereas the peaks of PAA appeared at about  $2933$   $\text{cm}^{-1}$  (not shown),  $1689$   $\text{cm}^{-1}$ , and  $1454$   $\text{cm}^{-1}$ .

A low frequency shift of carbonyl absorption band ( $1691$ ,  $1675$ ,  $1678$   $\text{cm}^{-1}$  in Fig. 5) in the spectra of dry state CPA-24 and CPA-16 indicated that there was an increased tendency of amide bond formation in CPA-16 and CPA 24 than in CPA-4.

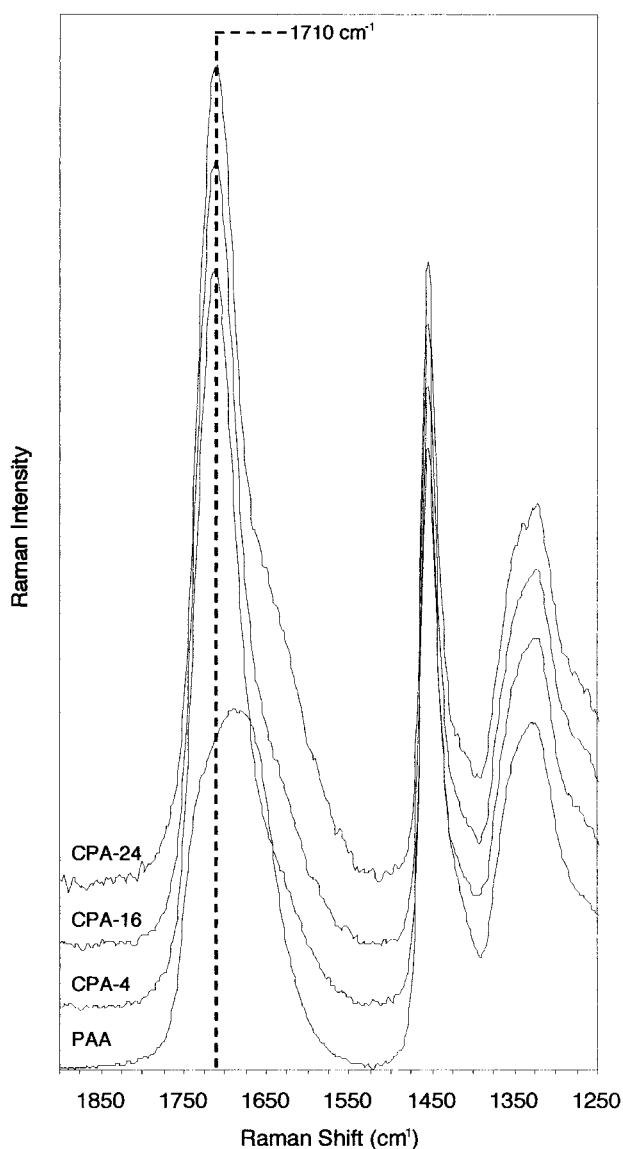
Figure 6 showed the wet state of CPA-4, CPA-16, and CPA-24. It was found that a higher fre-



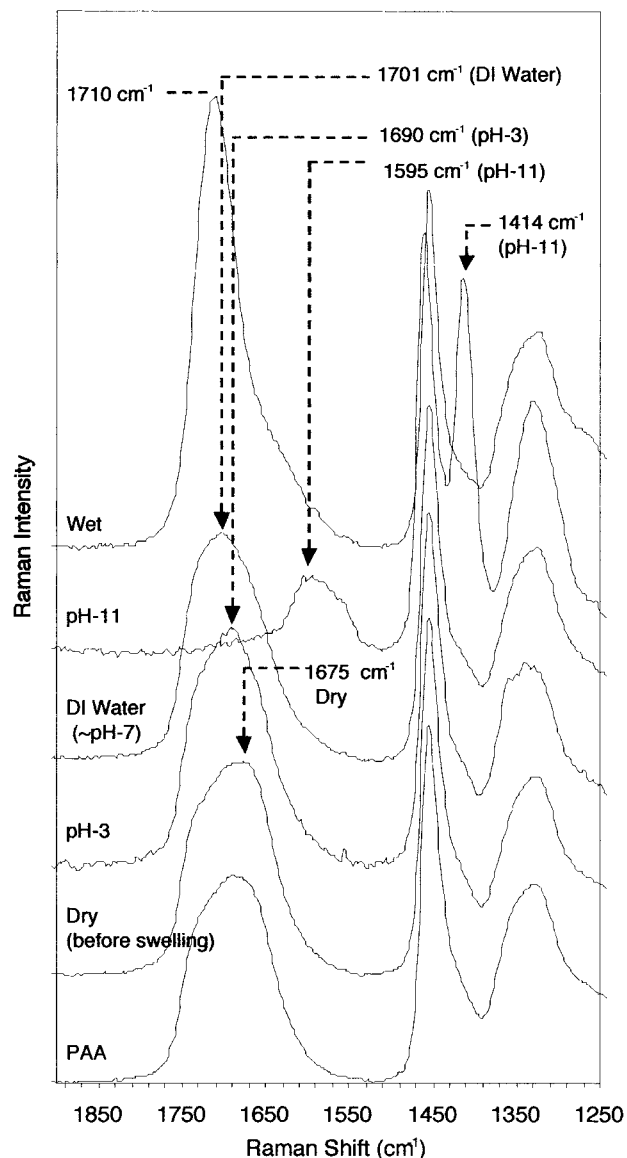
**Figure 5** Raman spectra of dry chitosan/poly(acrylic acid) polyelectrolyte complex (before swelling).

quency shift of carbonyl absorption band ( $\sim 1710 \text{ cm}^{-1}$ ) with a sharp peak indicated dissociation of hydrogen-bonding interactions while swelling. However, the increasing tendency of carbonyl amide region was found in increased water content of the complex, confirming that more amide bonds were formed in CPA-16 and CPA-24 than in CPA-4.

Similar to FTIR spectra, higher frequency shift of carbonyl region from dry state to after swelling at pH 3 and DI water ( $1675\text{--}1690\text{--}1701 \text{ cm}^{-1}$ ) was found in the spectra of CPA-16 (Fig. 7). After swelling at pH 11 solution medium, the peak at carbonyl region significantly diminished and two



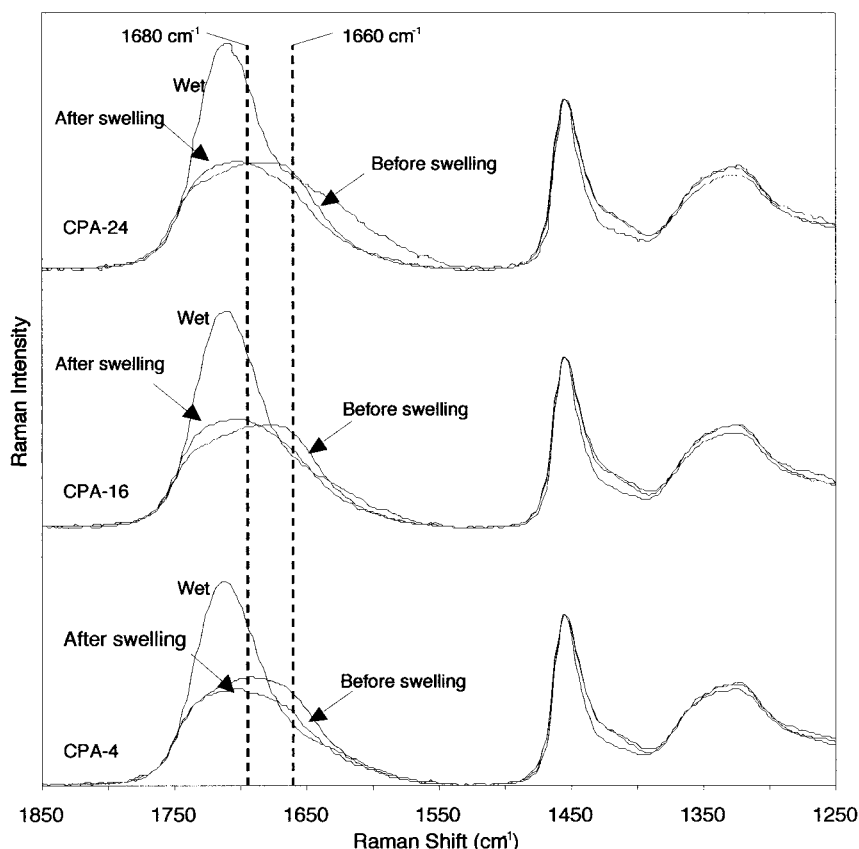
**Figure 6** Raman spectra of wet chitosan/poly(acrylic acid) polyelectrolyte complex.



**Figure 7** Raman spectra of CPA-16 at dry state, wet state, and after swelling at pH 3, DI water ( $\sim \text{pH } 7$ ), and pH 11 solution medium.

new peaks appeared at about  $1595$  and  $1414 \text{ cm}^{-1}$ , which can be assigned as asymmetric and symmetric stretching vibration of  $\text{COO}^-$  groups, whereas the carbonyl amide region appeared as a shoulder. Most of the hydrogen bonding interactions believed to be interrupted while swelling and the stable covalent amide bonds remained consistent.

The spectra of difference in peak shift and peak shape of CPA-4, CPA-16, and CPA-24 before and after swelling in deionized water were shown in Figure 8. It obviously can be seen that a more increased tendency of amide region was found in



**Figure 8** Raman spectra of CPA-4, CPA-16, and CPA-24 (wet state, before, and after swelling in DI water).

CPA-16 and CPA-24 than CPA-4. Moreover, one can conclude that inner oligomeric form ( $1660\text{ cm}^{-1}$ ) and cyclic dimer form ( $1680\text{ cm}^{-1}$ ) of PAA segments<sup>18</sup> were dominant in CPA-4 than in CPA-16 and CPA-24 because formation of such structures required some segments of two polymer chains be paralleled and this probability was more favorable in lower water content CPA-4.

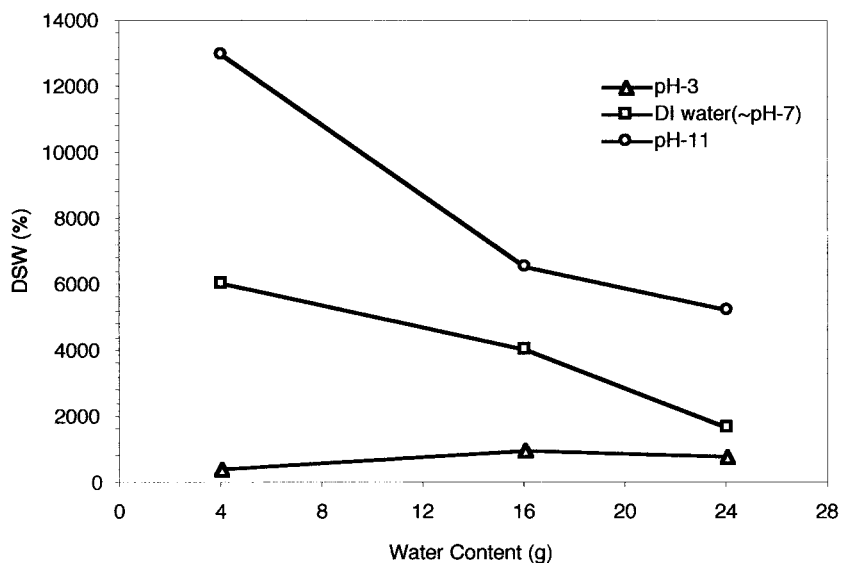
According to the FTIR and Raman spectra, it can be concluded that covalent interaction was dominant in CPA-16 and CPA-24, whereas hydrogen-bonding interaction was pronounced in CPA-4. The peak represented to the carboxylate ion was found to be still fixed at the dry state even once it was swollen.

### Swelling Behaviors

Amide bonds and interactions between macromolecular chains including entanglements, the extent of which depends on the composition of the complexes, take part in swelling properties. As an acrylic acid monomer ratio is in excess composi-

tion, it behaved similar to acidic hydrogels. The swelling is proposed to be caused by the difference between the osmotic pressure of mobile ions in the gel and in the surrounding solution, described by the Donnan theory.<sup>19,20</sup> The higher ion concentration will increase water flow into the gel because of osmosis, resulting in an increase in swelling. Another factor contributing to increase in swelling is the interaction and repulsion of charges along the polymer chains,<sup>3,21</sup> which is pronounced in high pH.<sup>3</sup>

The degree of swelling is expressed as the amount of absorbed water per gram dry polymer during a definite time interval. Figures 9 and 10 illustrated swelling behaviors of chitosan/poly(acrylic acid) polyelectrolyte complex in deionized water and different pH at room temperature. A decreased degree of swelling with increased water content in the complex has been observed. The degree of swelling increased with increasing pH of the swelling medium and a very limited extent of swelling kinetics in acidic pH was found because of the inherent hydrophobicity of the gel dominat-



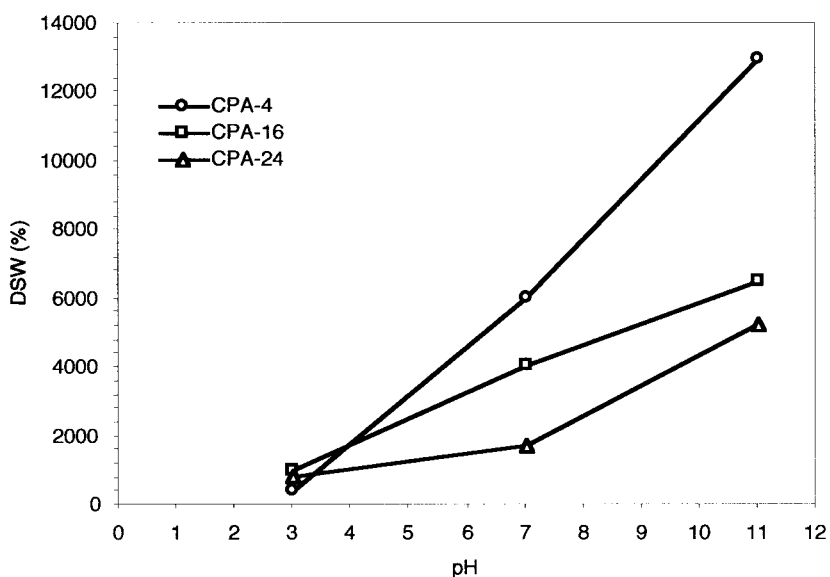
**Figure 9** Swelling behavior of chitosan/poly(acrylic acid) polyelectrolyte complex as a function of water content of synthesis component.

ing at low pH value. This reflects the character of acidic hydrogels which will be ionized at high pH but unionized at low pH, thus the equilibrium degree of swelling will increase at high pH where the gel is ionized.<sup>3</sup>

The pKa of the gel, a parameter that has to be incorporated into degree of swelling, depends on the degree of ionization and also changes with pH. It is well known that the pKa of poly(acrylic acid) is about 4,<sup>10,22</sup> and above the pKa of about 5, ionization of carboxylic acid sites along the net-

work backbone results a high pH sensitivity of the acidic gel.<sup>3,22</sup>

Crosslinking density also influences pH-dependent swelling. An increasing in crosslinking density restricts the equilibrium degree of swelling. However, the swelling result was not parallel to the values of elastic modulus (at dry state) of appropriate specimens. According to Kou et al.,<sup>23</sup> investigating the swelling of poly(metacrylic acid-co-2-hydroxyethyl methacrylate) hydrogel with different crosslinking density, the effect of crosslinking den-



**Figure 10** pH dependence of chitosan/poly(acrylic acid) polyelectrolyte complex.



sity was found to be more pronounced at high pH than at low pH. At high pH, the gel was ionized and hydrophobic interactions and hydrogen bonding inside the gel present at low pH were interrupted.

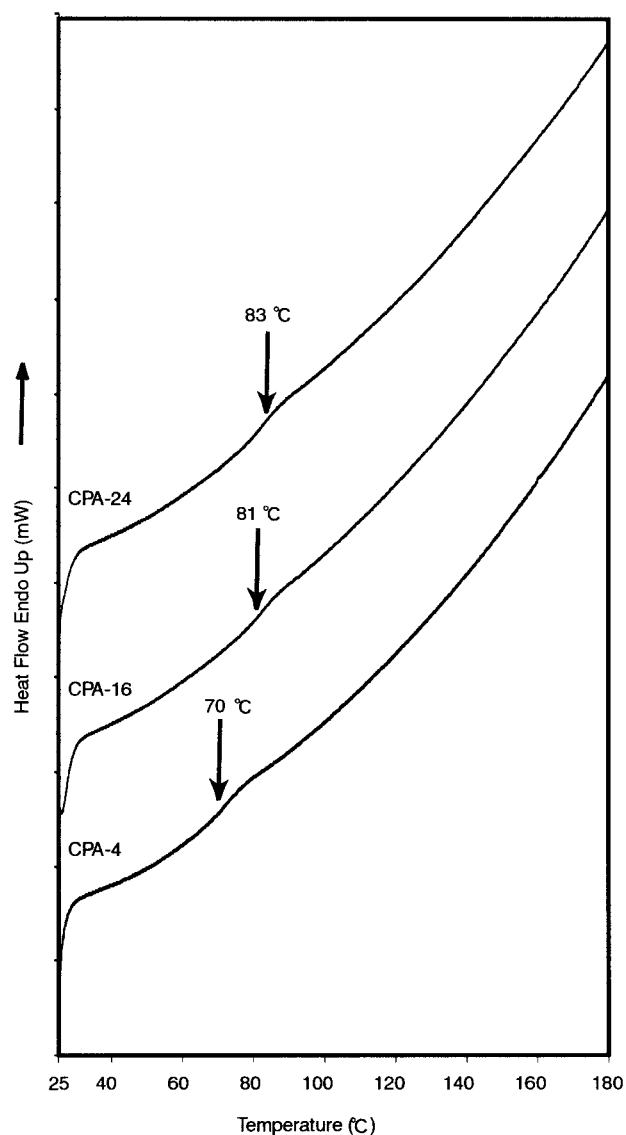
Because the elastic modulus at dry state was a cooperative function of all types of intermolecular bonding forces of attraction, lightly crosslinked and unstable hydrogen bonds appeared to be dissociated while swelling. According to FTIR and Raman spectra, more amide bond formations were observed in spectra of increased water content (i.e., CPA-16 and CPA-24) than spectra of lower water content, CPA-4. Therefore, the degree of swelling of CPA-4 was higher than degree of swelling of CPA-16 and CPA-24 at high pH (pH 7 and pH 11, which are higher pHs for acidic hydrogels), whereas an opposite result was found at pH 3, parallel to the elastic modulus value. It was found that the degree of swelling was significantly dependent on the extent of amide bond formations.

### DSC Analysis

DSC thermograms of chitosan/poly(acrylic acid) polyelectrolyte complex are shown in Figure 11. The glass transition temperature ( $T_g$ ) was determined by the midpoint of the transition region (inflection point) and was taken from the second DSC trace following an initial run. It was found that the higher temperature shift of DSC curves with increased water content of synthesis component (70, 81, and 83°C for CPA-4, CPA-16, and CPA-24, respectively). In general, higher transition temperatures are favored by high-intermolecular bonding forces of attraction because more thermal energy is required to separate strongly bonded chains than weakly bonded chains. Hence, the higher  $T_g$  with increased water content in this study attributed to the compatibility of the two polymers in the complex.

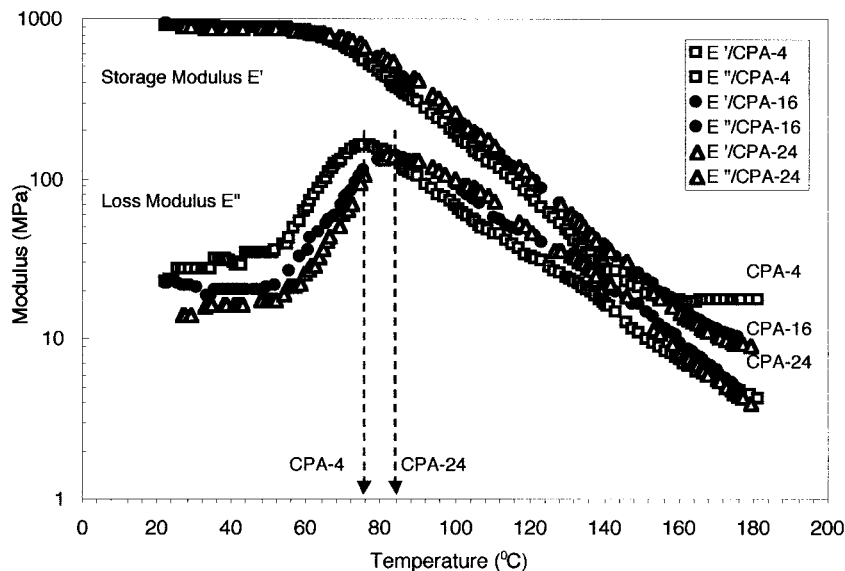
### DMA

The use of a Rheovibron, the storage modulus  $E'$ , and the loss modulus  $E''$  as a function of temperature for CPA-4, 16, and 24 obtained are shown in Figure 12. The transition temperature as determined by the dynamic mechanical analysis was used for most consideration of composition effects. All the transition temperatures were determined as being where  $E''$  was a maximum. As acrylic acids were excess components in the complex, the peak with respect to PAA was found distinctly



**Figure 11** DSC thermograms of chitosan/poly(acrylic acid) polyelectrolyte complex.

and that related to chitosan was seen as a shoulder on the main transition. The peak of PAA was found at about 75, 83, and 85°C, whereas peaks related to chitosan were found at about 124, 117, and 105°C for CPA-4, CPA-16, and CPA-24, respectively. A low-amplitude transition of chitosan centered at 90°C was tentatively assigned by Ratto et al.<sup>24</sup> because of local chain motions, which may originate within the acetamide and amine regions. On the other hand, Pizzoli et al.<sup>25</sup> reported from dielectric and dynamic mechanical spectra that a low-amplitude relaxation of chitosan was found in the vicinity of 130°C (at 3 Hz) because of local chain motions of dry polysaccha-



**Figure 12** Temperature dependence of dynamic storage modulus  $E'$  and loss modulus  $E''$  of chitosan/poly(acrylic acid) polyelectrolyte complex (at 110 Hz).

rides. The transition temperatures of chitosan obtained were in agreement with their tentative assignments.<sup>24,25</sup>

It was found that the peak shifted to a higher transition temperature as water content increased, indicating the increased compatibility of the complex and excellent agreement with DSC analysis. A covalent crosslinking (amide bond) appeared to be related to the inward shifting of the transition temperature. The extent of inward shifting of the transition temperature of PAA and chitosan was found to be closer in CPA-24, and, in CPA-16, than CPA-4, which agreed with the FTIR and Raman spectra. However, at constant polymer compositions and applied frequency (110 Hz), the storage modulus  $E'$  decreased with increasing water content in the rubbery region at dry state. Perhaps decreased compatibility and increased modulus in CPA-4 may be the effect of water composition during polymerization and state of water-preswollen chitosan networks.

Generally, a nonreactive diluent, such as water, is added to a monomer to decrease the glass transitions of a growing polymer during polymerization, thus helping drive the polymerization to completion at a lower temperature.<sup>26</sup> High-molecular-weight chitosan in lower water content aqueous AA monomers, CPA-4 (because composition ratio of chitosan and AA monomers were the same in all three samples), was dissolved to form high-viscous solution and to bring about the inhomogeneity of forming PAA distribution in the matrix

while photopolymerization occurs. Some segments of the preformed PAA polymers might prefer to associate themselves and enhanced further increased viscosity of the matrix. Probably the mobility of growing polymer was restricted and probability of amide bond formations with amino group of chitosan was also interrupted in CPA-4. However, relatively higher water content more likely helped to align more acrylic acid monomers. This alignment may speed up the attack of a double bond of acrylic acid molecules by a neighboring acrylic propagating radical leading to a faster rate of polymerization on one hand and increased mobility leading more likely to form amide bonds with amino groups of chitosan on the other hand.

Indeed, all intermolecular bonds (ranging from the van der Waal force through the relatively stronger hydrogen bonds to the strongest type of bonds provided by chemical crosslinks) can be considered as crosslinks, either physical or chemical. So, a complete spectrum of bond strength can be controlled through manipulation of both the nature and the density of the interchain connection.<sup>27</sup> The increased modulus in CPA-4 seemed to be the character of the physical networks of interactions (mainly due to hydrogen bonding interactions rather than covalent amide bonds) and also its behaviors were primarily determined by the conditions of the preparation of the polymer complex. Thus, it showed high swelling, although it possessed high modulus of elasticity in dry state. Strong electrostatic repulsion also limited

the number of elastically effective strands while swelling at higher pH medium. This observation demonstrated that the elastic modulus at dry state depends on the nature of the polymer components in the complex, and that the water-sorbing capacity does not necessarily parallel to the modulus of elasticity.

## CONCLUSION

Polyelectrolyte complexes based on chitosan and acrylic acid monomers were prepared by UV irradiation to photopolymerize acrylic acid monomers followed by oven curing to promote crosslinking networks between resulting polymer and existing chitosan polymer. FTIR and Raman spectroscopy confirmed the structure of chitosan/poly(acrylic acid) polyelectrolyte complex. More amide bonds have been found in CPA-16 and CPA-24, and more hydrogen bonds in CPA-4, whereas ionic bonds appear to be equally effective in this respect. The degree of swelling was sensitive to pH of the medium and is contradictory to elastic modulus at dry state. The extent of amide bond formations played an important role in swelling behavior of the complex. The DSC analysis and DMA confirmed the compatibility of the complex as increased water content of synthesis component. It was found that the leatherlike behavior of the complex was extended over a wide temperature range. This extension of leatherlike properties of polymeric systems to a practical temperature range illustrated the importance of this material. A pH-sensitive properties and improved mechanical stability make these new materials, leading to open the door to industrial and biomedical applications. Understanding the relationship of mechanical property, swelling behavior, and their dependence on chemical compositions during polymerization allows the development of optimum complex compositions for specific uses.

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