

Studies on Chitosan and Poly(acrylic acid) Interpolymer Complex. I. Preparation, Structure, pH-sensitivity, and Salt Sensitivity of Complex-Forming Poly(acrylic acid): Chitosan Semi-Interpenetrating Polymer Network

HANFU WANG, WENJUN LI, YUHUA LU, ZHILIANG WANG

Department of Macromolecular Science, Fudan University, Shanghai 200433, P.R. China

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ABSTRACT: A novel semi-interpenetrating polymer network (semi-IPN) membrane composed of crosslinked chitosan (cr-CS) and poly(acrylic acid) (PAA) was prepared. Evidence from infrared spectra proved the formation of polyelectrolyte complex through electrostatic interaction between NH_3^+ groups from CS and COO^- groups from PAA. The semi-IPN membrane swelled at high pH and at low pH exhibited a typical pH-sensitivity. Its swelling degrees in different salt solutions with the same ionic valence and equal ionic strength were on similar levels. Under certain ionic strength ($I = 1.5$ mol/L), the degree of swelling increased with increased metal ionic valence. Furthermore, the elongation of the semi-IPN membrane could vary reversibly by immersion into CaCl_2 solution and KCl solution alternately. Reasons for the chemomechanical behavior are discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1445–1450, 1997

Key words: polyelectrolyte complex; interpenetrating polymer network; chitosan; pH sensitivity; salt sensitivity

INTRODUCTION

Recently, interpolymer complexation between polymer pairs through secondary binding forces (such as electrostatic interaction, hydrogen bonding, Van der Waals force, and hydrophobic interaction) has attracted much attention owing to its importance in extensive areas. Up to now, much research interest has concentrated on the biological area because interpolymer interactions play a key role in biological systems. Relevant studies will be helpful in the understanding of a series of important biological phenomena including self-assemblies of proteins and molecular recognition.¹

On the other hand, interpolymer complexes have been the subject of investigations in syn-

thetic polymer field. Special interaction was often introduced into polymer blends to form interpolymer complexes in order to increase or control the compatibility of the components.² These complex-forming blends were disintegrated upon dissociation of interpolymer interaction, which was due to environmental changes. However, introduction of crosslinks into the polymer : polymer complex may result in the formation of an interpenetrating polymer network (IPN) which can prevent the complex-forming blend from collapsing. Therefore, the combination of interpolymer complex and IPN structure lead to a class of novel polymer materials which possess unique structures and properties.³ This kind of polymer materials has attracted many investigators because the materials vary reversibly with changed chemical environments. Such properties are potentially useful in various fields, including controlled drug delivery, chemical valve, chemomechanical system,

Correspondence to: W. Li.

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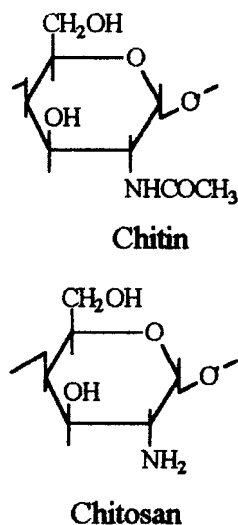


Figure 1 The structure of chitin and chitosan.

and others.⁴ Of course, not only synthetic polymers but also natural biopolymers such as chitosan (CS) and cellulose as well as their derivatives^{5–7} can be used to constitute these responsive polymer materials.

CS is a derivative product obtained by deacetylation of chitin, which distributes widely in invertebrates and the lower forms of plant life (Fig. 1). It is believed to be a promising polymer in chemical and biomedical areas. CS can be considered as a weak polybase due to the large quantities of amino groups on its chains, so it has the possibility of forming polyelectrolyte complex with poly(acrylic acid) (PAA), a weak polyacid, through electrostatic attraction.

This article deals with the preparation of cross-linked CS : PAA complex-forming semi-interpenetrating polymer network (semi-IPN) membrane. The membrane's swelling behavior in pH buffer solutions and salt solutions was also examined.

EXPERIMENTAL

Materials

PAA was synthesized in a 10% water solution of AA using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as initiator at 60°C. The reaction time for AA polymerization was about 4 h. Its molecular mass has been determined viscometrically as 2.3×10^5 in dioxane at 30°C.⁸

CS was produced by the following process: Chitin (commercial product) was soaked in 47 wt % alkali solution at 70°C for 4 h under N_2 atmosphere. The obtained product was washed with

water and dried. The viscosity-average weight was determined using 0.1M CH_3COONa and 0.2M CH_3COOH as solvent at 30°C and calculated to be 3.0×10^5 according to the Mark–Houwink equation: $[\eta] = K \cdot M^\alpha$, where $K = 1.424 \times 10^{-3}$ and $\alpha = 0.96$.⁹ Deacetylation degree was 86%. The method for the determination of deacetylation degree has been described in our previous work.¹⁰

Preparation of CS : PAA Semi-IPN and Blend Membrane

One gram of CS was dissolved in 25 mL 36 wt % acetic acid and was mixed with a certain amount of water solution of PAA (6 wt %). The unit ratio between CS and PAA was maintained equal. As a white gel-like precipitate was formed, excess acetic acid was added to dissolve the precipitate. It was necessary to use a high concentration of acetic acid in order to dissociate the precipitate. An appropriate quantity of water solution of glutaraldehyde (2×10^{-5} mol/mL) was then added to the mixture with stirring. The molar ratio of glutaraldehyde and deacetylation unit of CS ($[\text{GA}] : [\text{CS}-\text{NH}_2]$) was kept at 0.01 : 1. After filtration, the transparent yellow solution was cast onto a glass plate and maintained at 30°C for membrane forming.

If no crosslinking agent was added during solution casting, CS : PAA blend membrane was obtained.

To evaluate swelling, the membranes were dried at 25°C in vacuum to constant weight.

Infrared Spectra

CS : PAA semi-IPN and CS : PAA blend membranes for the determination of infrared (IR) spectra (thickness $< 10 \mu\text{m}$) were prepared according to the methods described above. The semi-IPN membranes were treated with deionized water and 0.1N HCl solution, respectively. Their IR spectra as well as the spectra of PAA, CS, cross-linked CS ($[\text{GA}] : [\text{CS}-\text{NH}_2] = 0.01 : 1$) were obtained with a Fourier transform infrared spectrophotometer (Magna 550).

Swelling Tests

The preweighted semi-IPN or blend membranes were immersed in Britton–Robinson buffer solutions or salt solutions and maintained for 24 h at 30°C until equilibrium swelling was reached. The swollen samples were then removed from the solu-

tion, quickly wiped with filter paper to remove droplets on the surface, and weighed. The degree of swelling (SW) was calculated from the following expression: $SW \text{ (wt \%)} = (W - W_0)/W_0 \times 100\%$, where W and W_0 are the weights of the sample at the equilibrium swelling state and dry state, respectively.

The reversibility of swelling has been observed by the following method. Semi-IPN membrane cut into strips (63 mm long, 13.5 mm wide, 40 μm thick) was suspended in a graduated tube with a constant load of 1.5 g. CaCl_2 solution (0.5M) was first poured into the tube and the elongation of the sample strip was measured versus time. Once the equilibrium elongation was reached, CaCl_2 solution was discharged from the tube through the outlet on the bottom of the tube. Consequently, KCl solution (1.5M) was added and the contraction versus time was then measured.

RESULTS AND DISCUSSION

Structure of CS : PAA Interpolymer Complex

CS crosslinking via glutaraldehyde has been investigated by many researchers.¹⁰⁻¹³ The crosslinking mechanism probably involved the formation of imine bonds between amino groups on CS and aldehyde groups on glutaraldehyde.¹² However, in our experiment obvious differences between CS and crosslinked CS, CS : PAA blend, and CS : PAA semi-IPN could not be found from the IR spectra because the glutaraldehyde content in samples was low. This article deals only with the IR spectra of crosslinked CS and CS : PAA semi-IPN.

The IR spectrum of chitosan (Fig. 2c) showed the characteristic peak of amino groups at 1589 cm^{-1} , and amide I and amide III bands at 1651 cm^{-1} and 1329 cm^{-1} , respectively.¹³ The strongest peak, at 1709 cm^{-1} in the IR spectrum of PAA (Fig. 2a), has been assigned to C=O stretching vibration of carboxylic acid groups. In the spectrum of CS : PAA semi-IPN (Fig. 2b), two strong peaks at 1552 cm^{-1} and 1404 cm^{-1} were observed due to the asymmetrical and symmetrical stretching of COO^- groups, respectively, while the peak at 1630 cm^{-1} was attributed to the formation of NH_3^+ groups.¹³ These facts confirmed that the carboxylic groups of PAA were dissociated to COO^- groups which complexed with protonated amino groups from CS through electrostatic interaction during the formation of the semi-IPN.

During the membrane-forming process of the CS : PAA blend or semi-IPN, an interesting phenomenon was observed. After casting, certain areas of the solution turned from transparent yellow to opaque white with volatilization of solvents (water and acetic acid). With further devolatilization the entire casting region appeared milky white. Finally, the milky white gradually disappeared and a dry golden-yellow membrane was obtained. This phenomenon does not occur during the membrane-forming process of pure CS. The color-changing phenomenon should be related to the aggregative state of two polymers in the solution. The concentration of the casting solution increased with the volatilization of the solvents. When the concentration reached a critical value, the CS chains were close to the PAA chains and the carboxylic acid groups of PAA were dissociated to form NH_3^+ groups, which led to the complexation of PAA and CS chains. The orientated chains probably caused the refraction change of the light, so the casting solution turned milky-white. Meanwhile, it should be noted that CS is a polymer with rigid chains which make it possible to form liquid crystal-like cellulose or its derivatives.^{14,15} This suggests that a liquid crystal state was probably involved during the membrane-forming process. Studies concerning the essence of this problem are being conducted.

Swelling Behavior of CS : PAA Semi-IPN and Blend Membranes in pH Buffer Solutions

Figure 3 shows the equilibrium SW of CS : PAA blend and semi-IPN as a function of pH. The results indicate that the semi-IPN swells strongly at low pH ($\text{pH} < 2$); as the pH value increases, the degree of swelling drops sharply. In the range of $3 < \text{pH} < 8$, the degree of swelling is smaller than 100%. With increasing pH value, SW increases again at $\text{pH} = 8$ and reaches a maximum at about $\text{pH} = 11$. In comparison with the semi-IPN, the complexed CS : PAA blend exhibits a higher SW in the basic medium and dissolves at $\text{pH} < 2$. We have also found that PAA cannot be crosslinked by glutaraldehyde under this membrane-forming condition. This finding suggests that the finally formed polymer network was a semi-IPN and the crosslinked CS network prevented the semi-IPN from collapse. It was useful in retaining complex insolubility at low pH but limited swelling at high pH.

IR spectrum of semi-IPN treated with 0.1N HCl (Fig. 4b) shows a strong peak at 1716 cm^{-1} due

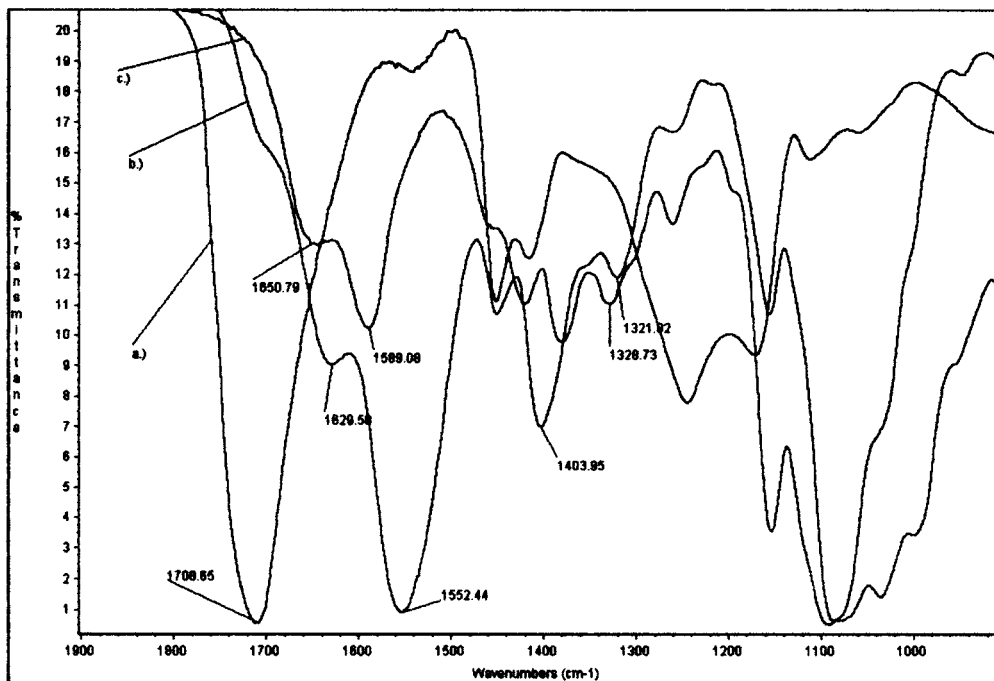


Figure 2 IR spectra of PAA (a), CS : PAA semi-IPN (b), and crosslinked CS (c).

to the C=O stretching vibration of carboxylic acid groups, which confirms that the complexation of COOH and amino groups was inhibited under strongly acidic conditions. On the other hand, the characteristic peaks at 1628 and 1520 cm⁻¹ indicate the formation of NH₃⁺ groups.¹³ According to the IR spectra analysis, the swelling of semi-IPN or the collapse of CS : PAA blend at low pH can be explained by the dissociation of ionic cross-

links. The swelling of the CS : PAA blend or the semi-IPN at high pH can be similarly explained by the following equation:

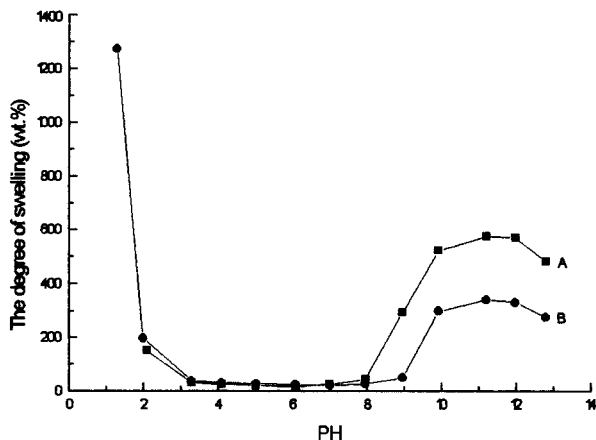
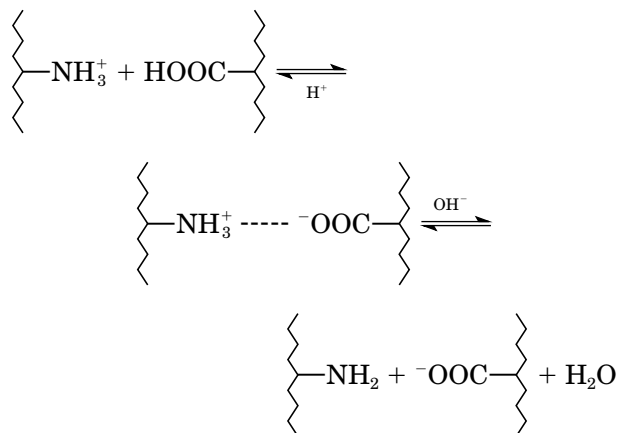


Figure 3 The degree of swelling as a function of pH for CS : PAA alloy membrane (A) and CS : PAA semi-IPN membrane (B). Temperature: 30°C; thickness of membrane: 50 μm.

The above knowledge can also be used to explain the preparing process of the casting solution. As the water solution of PAA was added into the acetic acid solution of CS, a gel-like precipitate appeared to indicate complex-formation between CS and PAA. However, addition of high-concentration acetic acid reduced the pH value of the mixture which caused the dissociation of the complex, so the gel-like precipitate was dissolved once again.

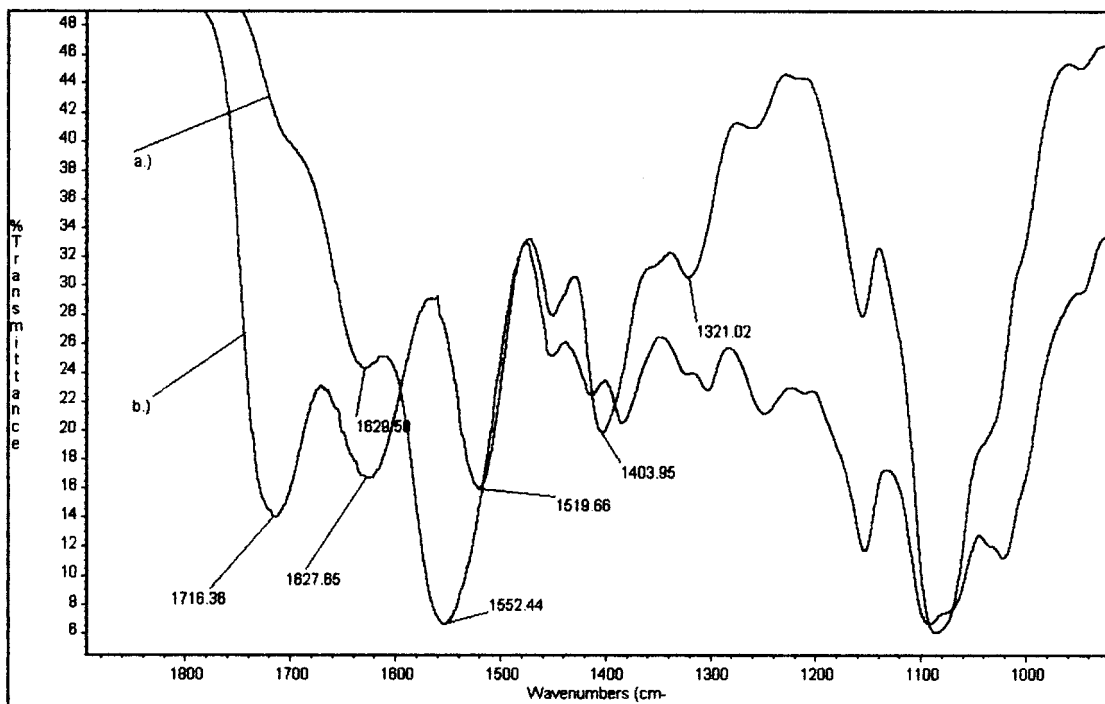


Figure 4 IR spectra of CS : PAA semi-IPN swollen in deionized water (a) and in 0.1N HCl (b).

Swelling in Salt Solutions

The degrees of swelling of the semi-IPN in various salt solutions were investigated (Table I). It was noted that SW in different salt solutions with both

Table I Degree of Swelling of Semi-IPN Membrane in Salt Solutions

Salt	Concentrations (mol/L)	Degree of Swelling (wt %)
LiCl	0.5	58.7
NaCl	0.5	54.4
KCl	0.5	76.8
KBr	0.5	75.2
KI	0.5	85.3
KCl	1.5	76.7 ^a
MgCl ₂	0.5	248.6 ^a
CaCl ₂	0.5	250.7 ^a
CaCl ₂	1.5	122.7
SrCl ₂	0.5	268.3 ^a
BaCl ₂	0.5	287.6 ^a
CuCl ₂	0.5	254.9 ^a
AlCl ₃	0.25	318.7 ^a
FeCl ₃	0.5	133.6
AlCl ₃	0.5	151.1

Thickness of membrane: 30 μ m; temperature: 30°C.

^a Equal ionic strength.

the same metal ionic valence and equal ionic strength are basically on a similar level. Under certain ionic strength ($I = 1.5$ mol/L), SW increased substantially with increased ionic valence. Semi-IPN exhibits maximum SW in the solutions of trivalent salts (Al^{3+}), lower SW in the solutions of divalent salts (Ca^{2+} , Mg^{2+} , etc.), and minimum SW in the solutions of monovalent salts (K^+ , Na^+).

These swelling behaviors can be attributed principally to the different dissociation degrees of electrostatic attraction between CS and PAA when the semi-IPN was swollen in various valent salt solutions. Although CS exhibits strong chelating ability for heavy-metal ions (Hg^{2+} , Ni^{2+} , Au^{3+} , etc.), it cannot chelate with the alkali and alkaline earth-metal ions such as K^+ and Ca^{2+} .¹⁶ PAA may thus play an important role in interacting with the ions from the solutions. In fact, as the ionic valence increased, the bond strength between PAA and metallic ions became stronger,¹⁷ which brought about a greater dissociation degree of CS : PAA complex. Consequently, distinct dissociation degrees within the complex led to the different osmotic pressures which cause the varying swelling degrees of the semi-IPN. Therefore, under certain ionic strength, the semi-IPN showed various swelling degrees upon changing ionic valence of the salts.

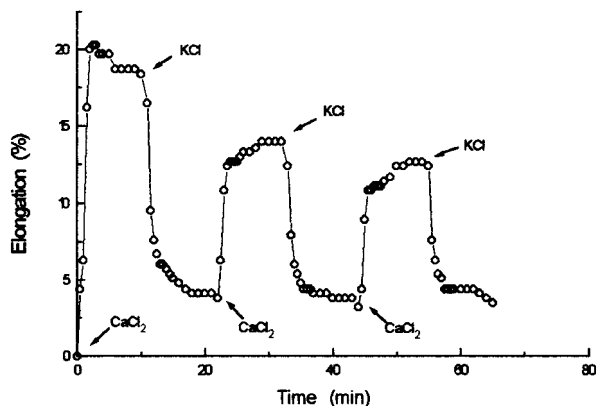


Figure 5 Chemomechanical elongation and contraction of semi-IPN induced on alternating addition of CaCl_2 solution ($0.5M$) and KCl solution ($1.5M$).

When the semi-IPN was treated alternately by KCl solution and CaCl_2 solution with equal ionic strength, the reversible chemomechanical elongation and contraction curve was obtained (Fig. 5). The semi-IPN was first elongated in CaCl_2 solution, then contracted in KCl solution. This chemomechanical property resulted from the ion exchange ability of polycarboxylic acid.¹⁸ When the semi-IPN was swollen by the CaCl_2 solution, PAA chains within the semi-IPN bonded with Ca^{2+} ions. As the swollen semi-IPN was treated with the KCl solutions, the Ca^{2+} ions bonded to PAA chains were exchanged by K^+ ions. This led to variations in dissociation degree and osmotic pressure, which brought about the dimensional changes.

On the other hand, if the semi-IPN was first swollen by AlCl_3 ($0.25M$), it was not contracted by KCl ($1.5M$) because trivalent ions may bond with PAA strongly and K^+ ions cannot exchange with them. Likewise, if the semi-IPN was first swollen by CuCl_2 ($0.5M$), KCl ($1.5M$) solution could not make it contract because Cu^{2+} can complex not only with PAA but also with CS, but K^+ cannot replace them yet.

CONCLUSIONS

A novel complex-forming CS : PAA semi-IPN has been synthesized via crosslinking CS with glutar-

aldehyde. Electrostatic attraction forms between protonated amino groups on CS and acrylate groups on PAA. CS : PAA semi-IPN shows not only pH sensitivity but also salt sensitivity. In addition, it exhibits reversible response to valent variation of salts due to the ion-exchange ability of PAA.

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