

Studies on Chitosan and Poly(acrylic acid) Interpolymer Complex. II. Solution Behaviors of the Mixture of Water-Soluble Chitosan and Poly(acrylic acid)

HANFU WANG, WENJUN LI,* YUHUA LU, ZHILIANG WANG, and WEI ZHONG

Department of Macromolecular Science, Fudan University, Shanghai 200433, People's Republic of China

SYNOPSIS

Water-soluble chitosan with a 50% deacetylation degree was prepared according to the literature. The mixtures of water-soluble chitosan and poly(acrylic acid) (PAA) in water was studied by various experimental techniques, such as viscometry, potentiometry, and transmittance measurements. The results showed that water-soluble chitosan may complex with PAA through electrostatic attraction. This polyelectrolyte complex exists steadily at about an equimolar unit composition. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Interpolymer complexes have some unique characteristics due to the specific interactions between the constituent polymers, such as hydrogen bonds, electrostatic attractions, and hydrophobic interactions.¹ The electrostatic attraction between anionic and cationic polyelectrolytes results in the formation of a polyelectrolyte complex (PEC). Poly(acrylic acid) (PAA) is a kind of synthetic anionic electrolyte which has been thoroughly studied. However, chitosan (CS) belongs to a class of biomacromolecules obtained by deacetylation of chitin, which has attracted much attention because of its potential uses in medical and industrial areas. Because the deacetylation reaction proceeded incompletely, common CS consists of *N*-acetylglucosamine units and glucosamine units (Fig. 1). It should be noted that CS possesses basic amino groups which can interact with the carboxylic acid groups of PAA through electrostatic attractions. According to this property, matrix polymerization of methacrylic acid on the CS has been carried out.²

The investigation of solution behaviors is an ordinary method to study the interpolymer complex.³⁻⁶ Unfortunately, chitosan is only soluble in some specific

solvents such as trichloroacetic acid/dichloroethane, dimethylacetamide/lithium chloride, and hexafluoro-2-propanol, so it was difficult to determine the common solvent for both chitosan and PAA. However, several efficient procedures for the preparation of water-soluble CS have been established.⁷⁻⁹ It was found that acetylated CSs obtained under homogeneous conditions with about a 50% deacetylation degree exhibited high water solubility because of the random distribution of two kinds of units on the chain.^{10,11} This CS can be regarded as a kind of copolymer in which glucosamine units with amino groups are "active" units which can interact with the carboxylic acid groups from PAA through electrostatic forces.

In our previous work, the preparation and structure as well as the pH and salt sensitivity of the CS : PAA complex-forming semi-IPN were discussed. In this article, a water-soluble chitosan (w-CS) with a 50% deacetylation degree was prepared according to the method suggested by Kurita et al.¹¹ The mixture of w-CS and PAA in a water solution was studied by various experimental techniques, such as viscometry, transmittance measurements, and potentiometry.

EXPERIMENTAL

Materials

PAA was synthesized in a 10% water solution of AA using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the initiator at 60°C. The re-

* To whom correspondence should be addressed.

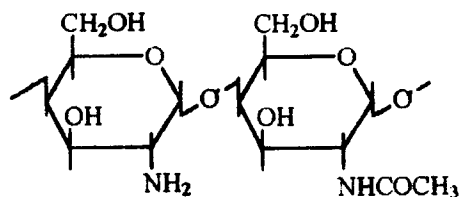


Figure 1 Chitosan.

action mixture was evaporated and dissolved in ethanol. This solution was purified by filtration and dried at room temperature. Its molecular mass was determined viscometrically in dioxane at 30°C and was found equal to 2.3×10^5 .

w-CS was prepared according to the following process: CS with a 90% deacetylation degree was dissolved in 5 wt % acetic acid. After filtration, the solution was neutralized with ammonia water. The white precipitate of CS was washed to pH 7 with distilled water and deionized water and dried under an infrared lamp. Then, 1 g purified CS was dissolved in 20 mL 10 wt % acetic acid. This solution was dropped into a flask which contained 200 mL pyridine, 2.8 mL acetic anhydride, and 16 mL methanol. The reaction was maintained 5 h under magnetic stirring at room temperature. After the solvent was leached, the product was washed with ethanol and methanol and dried under a vacuum for 24 h at 25°C.

Preparation of the Stock Solutions

A preweighted amount of w-CS was dissolved in deionized water. After filtration, the insoluble residue was dried and weighted precisely, thereby determining the amount of w-CS dissolved in the water. This solution was further diluted with deionized water. The $[\eta]_{w-CS}$ obtained from a viscosity measurement in deionized water at 25°C was 315 mL/g. A predetermined amount of PAA was dissolved in the deionized water to prepare a stock solution of PAA.

Preparation of the Mixtures

Mixtures with the desired composition were prepared by mixing certain quantities of stock solutions and diluting them with deionized water. Mixtures with desired pH values were prepared by the following methods: Certain quantities of w-CS and PAA stock solutions were mixed together and diluted with Britton-Robinson buffer solutions. The precise pH values were determined by a pH meter.

Determination of Average Unit Molecular Mass of Water-Soluble Chitosan

A predetermined amount of the stock solution of w-CS was acidified to pH 2.5 with 0.1N HCl. This solution was then titrated with a standard solution of 0.1N NaOH using a pH meter. The deacetylation degree, calculated from the consumed amount of the base by the protonated amino groups in the solution,¹² was found to be 50.6%. The average unit molecular mass (*AM*) was determined as follows:

$$AM = 161 \times D + 203 \times (1 - D)$$

where *D* is the deacetylation degree and 161 and 203 are the molecular masses of glucoamine and *N*-acetylglucoamine units, respectively. It was equal to 181.7.

Viscosity Measurement

The viscosity measurements for mixtures of w-CS and PAA with various unit molar fractions were performed with an Ubbelohde viscometer for which the kinetic energy correction was negligible. The total concentration of mixtures were maintained at 2.75×10^{-3} unit mol/L.

Transmittance Measurement

The percentage transmittance in mixed solutions was measured at a 480 nm wavelength with a spectrophotometer (Model 72) made by the Shanghai Analytical Instrument Factory.

pH Measurement

The pH values of the mixtures were determined with a digital pH meter (PHS-3C) with an appropriate electrode.

RESULTS AND DISCUSSION

Figure 2 shows the variation of the specific viscosity, η_{sp} , for the PAA/w-CS mixtures as a function of the unit mol fraction *r* of w-CS ($r = [w-CS]/([w-CS] + [PAA])$). When $r < 0.5$, the addition of PAA in the solution of w-CS results in a decrease of the specific viscosity. Further addition of the PAA leads to a steady increase in η_{sp} again. The minimum of the curve exists around $r = 0.5$. The above-mentioned behavior has been considered as a typical phenomenon of systems forming polymer complexes.

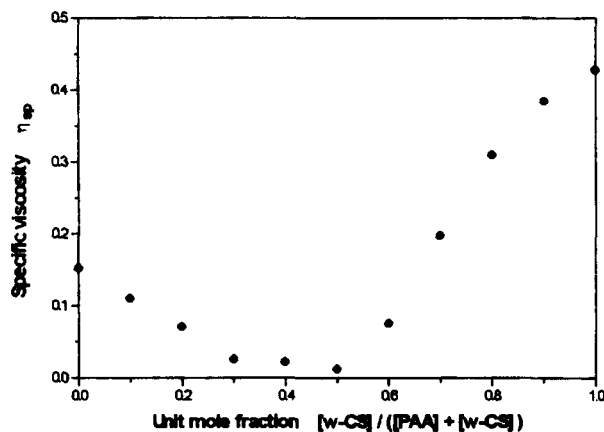


Figure 2 Variation of η_{sp} of mixture as a function of its composition. Temperature: 25°C; $[w\text{-CS}] + [PAA] = 2.75 \times 10^{-3}$ unit mol/L.

The decrease viscosity for $r < 0.5$ may be attributed to the formation of the compact structure of the complex: The total hydrodynamic volume of the complexed chains is smaller than the hydrodynamic volume of the free chains.

In Figure 3, the variation of the transmittance as a function of r is presented. Its trend is consistent with the viscosity measurements, which confirm the formation of the interpolymer complex. The curve shows a minimum transmittance around $r = 0.5$. As the complex formation is complete beyond $r > 0.5$, the transmittance is increased due to the dilution of the complex.

The variation of transmittance vs. pH was also observed (Fig. 4). The transmittance of the w-CS : PAA mixture reached nearly 100% at low pH (pH < 2), which indicates that the complex dissociates

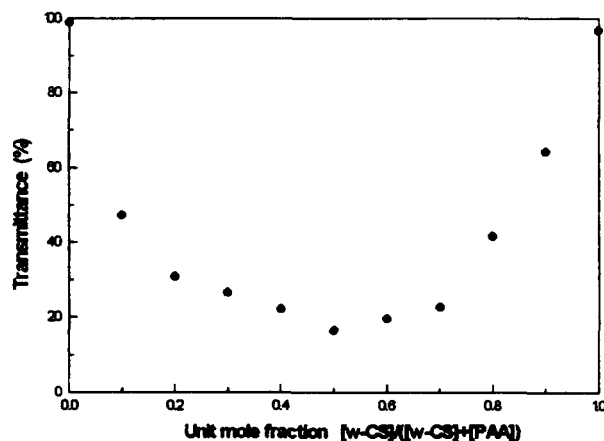


Figure 3 Variation of transmittance of mixture as a function of its composition. Temperature: 15°C; $[w\text{-CS}] + [PAA] = 2.75 \times 10^{-3}$ unit mol/L.

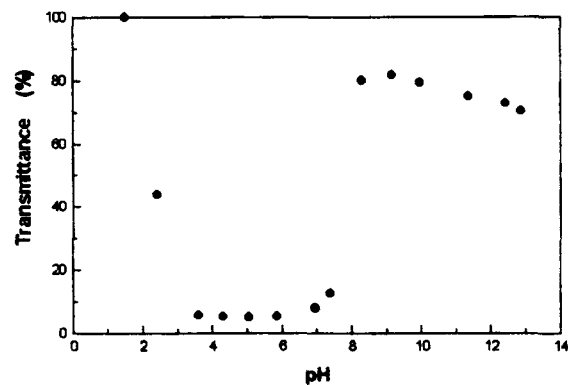


Figure 4 pH dependence of the complexation ability of water-soluble CS with PAA. Temperature: 25°C; $[w\text{-CS}] = [PAA] = 2.55 \times 10^{-3}$ unit mol/L.

very completely in a strong acid condition. In basic medium (pH > 8), the transmittance was about 70%. The mixture was not completely transparent in the basic medium, probably due to the precipitation of w-CS under a high pH value. This behavior is considered to be the characteristic property of a polyelectrolyte complex.¹³ The electrostatic attraction in the form of $-\text{NH}_3^+ \cdots \text{OOC}-$ would be destroyed either in acid or basic regions.

The curve in Figure 5 shows a gradual decrease in the pH on the addition of PAA to the w-CS solution. A turning point appears at around a 1.0 : 1.0 unit mol ratio. A further increase of the PAA concentration does not reduce the pH obviously. This fact is coincident with the viscosity and transmittance measurements which prove the formation of complex at about an equimolar composition. Mixtures shows weak acidity, probably due to the dissociation of PAA within the complex.

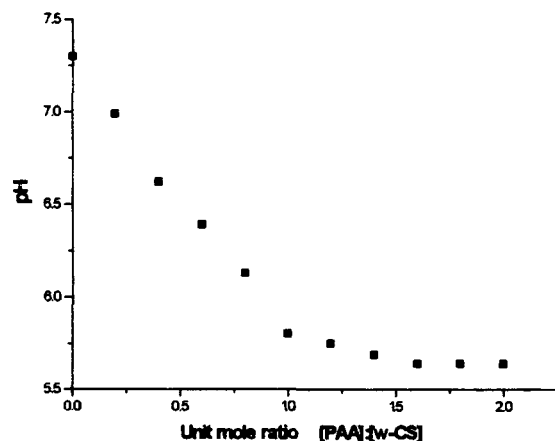


Figure 5 Variation of pH with the unit mol ratio. Temperature: 15°C; $[w\text{-CS}] = 1.2 \times 10^{-3}$ unit mol/L.

Although there are several kinds of groups in the CS chains including amino groups, hydroxyl groups, acetamido groups, etc., the electrostatic attraction between acrylate groups and protonated amino groups are the strongest interaction among all the possible secondary bonds between w-CS and PAA.¹⁴ So, the electrostatic attraction plays a predominant role during the formation of complex. But this does not mean that other interactions such as hydrogen bonding will not exist definitely; on the contrary, they may be beneficial to the stabilization of the complex.

CONCLUSION

Complex formation between water-soluble CS and PAA was studied by viscometry, transmittance measurement, as well as potentiometry. The studies on solution behaviors show that a steady polyelectrolyte complex with an equimolar composition may form between PAA and water-soluble CS, a copolymer with two kinds of units distributed randomly in the chains. It was also found that the complex may exist steadily from a weak acid region to a neutral region, but dissociate in lower pH or higher pH regions.

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REFERENCES

1. E. Tsuchida and K. Abe, *Advances in Polymer Science*, Springer-Verlag, Berlin, 1982, Vol. 45.
2. S. Kataoka and T. Ando, *Kobunshi Ronbunshu*, **37**, 185 (1980).
3. S. K. Chatterjee, J. B. Yadav, K. R. Sethi, and A. M. Khan, *J. Macromol. Sci.-Chem. A*, **26**, 1489 (1989).
4. G. Staikos and C. Tsitsilianis, *J. Appl. Polym. Sci.*, **42**, 867 (1991).
5. G. Staikos, G. Bokias, and Tsitsilianis, *J. Appl. Polym. Sci.*, **48**, 215 (1993).
6. I. Iliopoulos and R. Audebert, *Macromolecules*, **24**, 2566 (1991).
7. E. Loubaki, S. Sicsic, and F. Le Goffic, *Eur. Polym. J.*, **25**, 379 (1989).
8. M. Yalpani and L. D. Hall, *Macromolecules*, **17**, 272 (1984).
9. L. A. Berkovich, M. P. Tsyurupa, and V. A. Darvan-kov, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 1281 (1983).
10. T. Sannan, K. Kurita, and Y. Iwakura, *Makromol. Chem.*, **177**, 3589 (1976).
11. K. Kurita, Y. Koyama, S. Nishimura, and M. Kamiya, *Chem. Lett.*, 1597 (1989).
12. W. J. Li, W. S. Pan, and Y. Tang, *Chem. J. Chin. Univ.*, **13**, 415 (1992).
13. K. Abe, M. Koide, and E. Tschida, *Macromolecules*, **10**, 1259 (1977).
14. E. Tsuchida and K. Abe, *Advances in Polymer Science*, Springer-Verlag, Berlin, (1982), Vol. 45, p. 82.

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