

# The Flocculating Properties of Chitosan-graft-Polyacrylamide Flocculants (I)—Effect of the Grafting Ratio

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**ABSTRACT:** A series of chitosan-graft-polyacrylamide copolymers have been prepared as flocculants for waste water treatment. The results indicated that the grafting ratio was one of the key factors for the flocculating effects. The copolymers with various grafting ratios showed different flocculating properties. To observe every detail of this effect, the specific refractive index increment measurement (SRIIM) method was used to determine the grafting ratio at the beginning of this study. Interestingly, it was found that as the grafting ratio increased, the flocculating effect increased until

it reached its maximum point. At that point, it decreased. This result was discussed in terms of the cooperative effects of the charge neutralization and bridging flocculating mechanisms. A structure model of chitosan-g-polyacrylamide copolymer flocculants has been proposed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1876–1882, 2010

**Key words:** chitosan-g-polyacrylamide copolymer flocculants; the grafting ratio; specific refractive index increment measurement; flocculating effects

## INTRODUCTION

It is well known that water is essential for human life. However, with the rapid development of modern industries, the problem of water pollution has become increasingly serious. Therefore, one of the hottest research projects in the field of the waste water treatment is to create new technology that is highly efficient, relatively inexpensive, and nontoxic.<sup>1,2</sup>

Recently, natural polymers have received considerable attention in the field of water purification because they are believed to be nontoxic and environmental-friendly.<sup>3,4</sup> Chitosan (poly- $\beta$ -(1 $\rightarrow$ 4)-2-amino-2-deoxy-D-glucose) is one of the high-performance natural polysaccharide materials. It is derived from the deacetylation of natural chitin, the second most abundant natural polymer in the world. In terms of its novel characteristics, chitosan has al-

ready been widely applied in many fields.<sup>5–8</sup> Chitosan contains abundant free amino groups along the chain backbone that are cationically charged in acidic media. It has a prominent flocculating effect in water purification. Chitosan also has an excellent chelating effect because it has abundant free  $-\text{OH}$  and  $-\text{NH}_2$  groups on the chain, enabling the efficient removal of metal ions, humic acids, and synthetic surfactants. In addition, chitosan can also be used as an adsorbent to absorb impurities from water. Thus, it is believed that chitosan is very useful in the field of waste water treatment.<sup>9,10</sup>

However, disadvantages such as its low molecular weight and poor solubility has limited the practical application of chitosan. To improve its performance, modified chitosan materials have been manufactured. Graft polymerization has been a conventional and useful method for chemical modification,<sup>11</sup> and this reaction would introduce synthetic functional polymers as side chains to polymer backbone. Polyacrylamide (PAM) materials have already proved useful in water purification. However, materials with a super-high molecular weight are necessary for high flocculating efficiency. Obviously, grafting PAM onto chitosan would improve the properties and increase the potential application of both materials. Based on previous research reports related to chitosan-g-PAM flocculants, the influence of external factors such as pH and dose has already been investigated.<sup>12,13</sup> However, there is little research about the effects of structure factors, such as the grafting

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ratio, on flocculating properties. In fact, structure factors are the most important factors for the performances of materials. In this article, a series of PAM-grafted chitosan samples with various grafting ratios have been prepared, using Ce(IV) as the initiator. The graft copolymers show different flocculating effects for their different structures, and the grafting ratio of the copolymers is believed to be one of the key factors for the flocculating effects. At the beginning of this study, the grafting ratio of the copolymers is first measured using the specific refractive index increment measurement (SRIIM) method. This will be discussed in detail later. The results have been confirmed by  $^1\text{H}$  HR-MAS NMR technique, and measuring the PAM/chitosan weight percents of the chitosan and PAM mixtures, with a known weight mixed ratio, using SRIIM method. Based on the actual flocculating effects of the chitosan-g-PAM copolymers, the effects of the grafting ratio on their flocculating properties have been investigated in this article.

## EXPERIMENTAL PART

### Chemicals

Chitosan has been purchased from Shangdong Aokang Biological Co. Ltd., and the degree of deacetylation is 85.2%, and its viscosity average molecular weight is  $83.4 \times 10^4$  g/mol, calculated from the intrinsic viscosity.<sup>14</sup> Acrylamide (C.P. grade) from Nanjing Chemical Reagent Co. Ltd. and ceric ammonium nitrate (A.R. grade) from Sinopharm Chemical Reagent Co. Ltd. are used without further purification.

### Instruments

A Bruker Vector-22 FTIR spectrometer was used in this work, and a BI-DNDC differential refractometer from Brookhaven Instruments was applied to measure the  $dn/dc$  values of various samples.  $^1\text{H}$ -NMR experiments were performed with a Bruker DSX spectrometer operating at 300.13 MHz  $^1\text{H}$  Larmor frequency. A 4-mm  $^1\text{H}$  HR-MAS double-resonance probe was used in the experiments. A model 722s spectrophotometer from Shanghai Lengguang Technology Co. Ltd. was used to determine the effects of flocculants on the flocculating properties.

### Preparation of chitosan-graft-PAM<sup>15,16</sup>

Chitosan was used as the backbone for all graft copolymerizations. The desired amount of solid chitosan powder was dissolved in 150 mL of 1% acetic acid aqueous solution by agitation. After 30 min stirring under  $\text{N}_2$ , the Ce(IV) initiator and acrylamide

were added to the solution. The amount of chitosan was kept a constant, but the amount of acrylamide was changed for each synthesizing experiment to prepare a series of PAM-grafted chitosan samples with various grafting ratios. The mass ratio of chitosan and acrylamide (AM) was 1 : 1, 1 : 3, 1 : 5 and 1 : 8, respectively. After 3 h for reaction, the polymerization was stopped and the samples were precipitated in acetone. The white products were purified three times by repeated dissolving-precipitating treatment, then by Soxhlet extraction using acetone as solvent further, and finally dried at 50°C in a vacuum oven for 48 h. In addition, the four final graft samples were named chitosan11, chitosan13, chitosan15, and chitosan18, respectively, based on the mass ratio of chitosan and AM before reaction as mentioned earlier.

The homopolymer of PAM was synthesized according to the reported method.<sup>17</sup> The PAM sample was purified by Soxhlet extraction using acetone as solvent, and dried at 50°C in a vacuum oven for 48 h. Its weight-average molecular weight was  $1.8 \times 10^5$  g/mol, and the ratio of weight- to number-average molecular weight was about 2.45, as determined by size exclusion chromatography.

### Specific refractive index increment measurement

For SRIIM, a series of solutions with different concentrations for each sample, including chitosan, PAM, each graft copolymer, and five mixtures of chitosan and PAM (with known weight mixed ratios of 4 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 4, respectively) were prepared by being weighed, and the acetic acid/sodium acetate buffer solution of pH = 4.4 was used as solvent. All solutions were kept immobile for at least 24 h at room temperature. They were then filtered using a millipore filter with a pore diameter of 0.45  $\mu\text{m}$  to remove any dust before measurements were taken. Deionized water was used in all experiments. The weight concentration was converted to volume concentration (in g/mL) by applying the density correction for the latter calculation.

The refractive index increment was measured with a BI-DNDC differential refractometer by Brookhaven Instruments, using a wavelength of 535 nm. Before measuring, the instrument was calibrated using a KCl aqueous solution, and the value of the constant ( $k$ ) was  $2.757 \times 10^{-4} \text{ V}^{-1}$ . All experiments were measured at 30°C.

### $^1\text{H}$ -NMR

A 4-mm  $^1\text{H}$  HR-MAS double-resonance probe was used to obtain the  $^1\text{H}$ -NMR spectra of various samples. In these experiments, the swollen samples with a sample to solvent ratio of  $\sim 20\%$  in weight were

spun at 3 kHz. When compared with the usual solution  $^1\text{H-NMR}$  spectra of chitosan derives the signal-to-noise ratio in the  $^1\text{H}$  HR-MAS spectra increased significantly, which facilitated to calculate the grafting ratio of samples. The difference in the solution and HR-MAS  $^1\text{H-NMR}$  spectra could be attributed to the poor solubility of the samples. Comparison of the solution and HR-MAS  $^1\text{H-NMR}$  spectra was the subject of ongoing studies. The signal assignment in the spectra of chitosan and the derives followed the literatures.<sup>18,19</sup> Based on the integral ratio of characteristic peaks corresponding to grafting PAM and chitosan, the grafting ratio of samples were calculated.

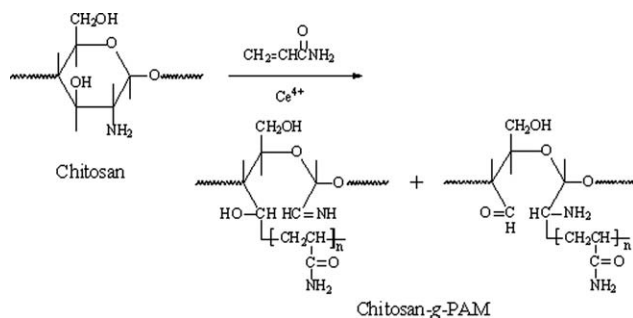
### Flocculating experiment

Kaolin suspension (700 mg/L), with particles a diameter of 74  $\mu\text{m}$ , was used as simulated waste water. The preparation method of this simulated waste water was described in detail as follows. A certain amount of kaolin was added to water and was mixed using a magnetic force stirrer for 20 min, resulting in a dynamic homogenous kaolin solution that could be used as simulated waste water. The flocculants of chitosan or chitosan-g-PAM were dissolved in acetic acid aqueous solutions. A known amount of flocculant solution was added to the simulated waste water. After being stirred at 200 r/min for 10 min, the kaolin suspension was kept immobile. The turbidity was measured using a model 722s spectrophotometer at a wavelength of 550 nm after 5, 10, 20, 40, and 60 min to determine the time dependence of the flocculating properties.

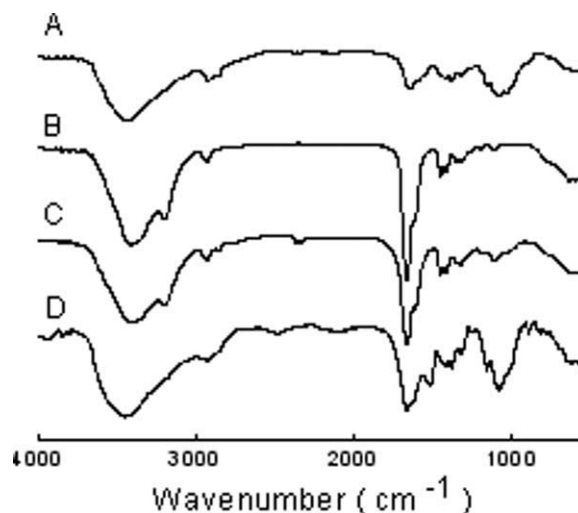
## RESULTS AND DISCUSSIONS

### Characterization of chitosan-g-PAM samples by FTIR and $^1\text{H-NMR}$

A series of the chitosan-g-PAM samples with various grafting ratios were successfully prepared according to the reported methods<sup>15,16</sup> by adjusting the mass ratio of chitosan and AM before reaction. The poly-



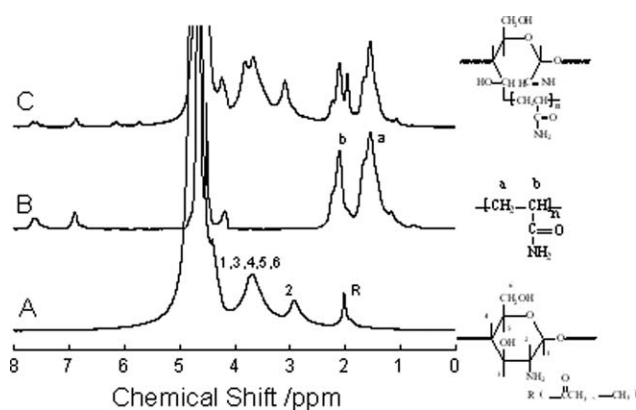
**Scheme 1** The polymerization mechanism of acrylamide grafted onto chitosan.



**Figure 1** Infrared (IR) Spectra of (A) Chitosan; (B) PAM; (C) Mixture of Chitosan and PAM (mass ratio of chitosan/PAM is 1:1); (D) Chitosan11.

merization mechanism of acrylamide grafted onto chitosan was shown in Scheme 1. The infrared (IR) spectra of various samples were shown in Figure 1. From Figure 1(A), the IR spectrum of chitosan showed a characteristic peak of  $\text{C}=\text{O}$  around  $1650\text{ cm}^{-1}$  due to partial deacetylation, and characteristic peaks of amino group appeared around  $3400$ ,  $1650$ , and  $1320\text{ cm}^{-1}$ . For the PAM, the overlapped peaks around  $1665$  and  $1550\text{ cm}^{-1}$  were assigned to the amide I and II bands, respectively, which were shown in Figure 1(B). Furthermore, comparison of the IR spectrum of graft copolymer to the simple mixture of chitosan and PAM, the peak occurred around  $1430\text{ cm}^{-1}$ , due to the  $\text{C}-\text{N}$  stretching in graft copolymer, as shown in Figure 1(D), which further supported that graft reaction occurred; But the IR spectrum of the mixture of chitosan and PAM, as shown in Figure 1(C), was just a simple summation of that of chitosan and PAM.

$^1\text{H}$  HR-MAS NMR has been applied to investigate the structures of copolymers also. Figure 2(A,B) showed the  $^1\text{H-NMR}$  spectra of chitosan and PAM. The assignment of the peaks in the  $^1\text{H-NMR}$  spectra were made according to the previous work.<sup>18,19</sup> The signal of the H2 proton in chitosan was at  $\sim 2.92$  ppm, and those of H1 and H3-6 protons superposed together around  $3.14\text{--}4.06$  ppm, and R was the resonance of acetyl-protons around  $2.01$  ppm as shown in Figure 2(A). The peaks at  $\sim 1.55$  and  $2.10$  ppm in Figure 2(B), which corresponded to the methylene and methine protons in the main chain, respectively, were the characteristic signals of PAM. The  $^1\text{H-NMR}$  spectrum of Chitosan-g-PAM, as showed in Figure 2(C), consisted of the characteristic signals of chitosan and PAM, which supported that graft reaction occurred further. However, from the Figure 2(C),



**Figure 2**  $^1\text{H}$  HR-MAS NMR spectra of (A) Chitosan, (B) PAM, and (C) Chitosan-g-PAM.

there were still several weak signals observed at low magnetic field, which might be related to the fine structures of chitosan-g-PAM. The fine structures of chitosan-g-PAM, such as the distribution of grafting PAM on the chitosan backbone, would be studied in detail in the following work.

#### Determination of the grafting ratio of the graft copolymers by SRIIM

As was known, the grafting ratio has been one of the most important factors in describing the structure of the graft copolymer. Conventional methods for measuring the grafting ratio, such as weighing,<sup>20–22</sup> spectroscopy,<sup>23,24</sup> and the elemental analysis method,<sup>25</sup> all had their own limitations in practical application. The weighing method for measuring the grafting ratio was based on the mass increment of the final product compared with the weight of the backbone polymer. The basic requirement for measuring the grafting ratio accurately was fully reclaiming the product after it was purified. As for spectroscopy methods such as NMR and IR, the grafting ratio was determined by accurately calculating the relative intensity of the characteristic signals of backbone and branch chains in the spectrum. As for the method of elemental analysis, the grafting ratio could be measured based on the change in the content of certain characteristic elements of the samples before and after reaction, which required having enough of a difference in the content of the determined element between backbone and branch polymers. Moreover, to measure the content of the element correctly, the final product had to be extremely pure and homogenous. However, in this article, the SRIIM method was used to measure the grafting ratio in the solutions.

It was believed that the usual observed solution properties of polymers were those of the summation contributed from different components of the polymers.<sup>26,27</sup> The specific refractive index increment  $\left(\frac{dn}{dc}\right)$

was one of the basic parameters in polymer solutions. Based on the aforementioned rule, the observed  $\left(\frac{dn}{dc}\right)$  of the graft copolymer solution could be expressed as:

$$\left(\frac{dn}{dc}\right)_{obs} = W_1 \left(\frac{dn}{dc}\right)_1 + W_2 \left(\frac{dn}{dc}\right)_2 \quad (1)$$

where  $W_1$ ,  $W_2$  were the weight fraction of the backbone and the branch polymers, respectively.  $\left(\frac{dn}{dc}\right)_1$  and  $\left(\frac{dn}{dc}\right)_2$  were the specific refractive index increments of the backbone and the branch polymers, respectively. If there were only two components, the sum of  $W_1$  and  $W_2$  was equal to 1. Thus, eq. (1) could be deduced to:

$$W_2 = \frac{\left(\frac{dn}{dc}\right)_{obs} - \left(\frac{dn}{dc}\right)_1}{\left(\frac{dn}{dc}\right)_2 - \left(\frac{dn}{dc}\right)_1} \quad (2)$$

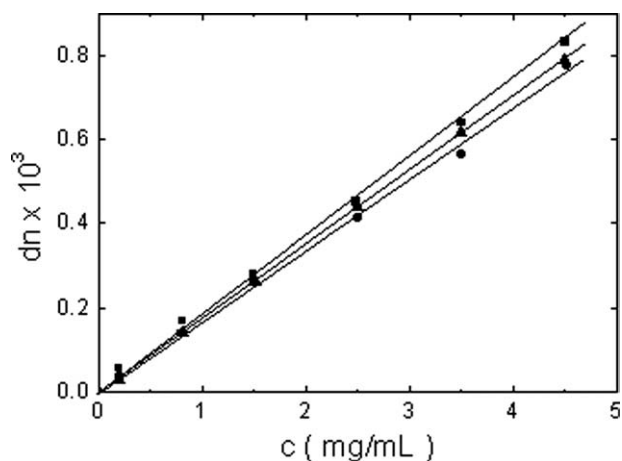
According to eq. (2), the grafting ratio could be calculated as:

$$G = \frac{W_2}{1 - W_2} \times 100\% \quad (3)$$

However, the SRIIM method for measuring the grafting ratio also had its own limitations in practical use. Based on eq. (2),  $\left(\frac{dn}{dc}\right)_1$  should not be equal to  $\left(\frac{dn}{dc}\right)_2$ , otherwise,  $W_2$  was not able to be calculated. On the other hand, the cosolvent should be found, which could dissolve the backbone polymer, branch polymer and the graft copolymer, respectively. The next step was to measure the  $\left(\frac{dn}{dc}\right)$  for calculating the grafting ratio further, based on eqs. (2) and (3).

In this system, chitosan, PAM, and each chitosan-g-PAM sample was homogeneously dissolved in the acetic acid/sodium acetate buffer solution of pH = 4.4, respectively. Then, the  $\left(\frac{dn}{dc}\right)$  of each sample was measured. The detailed measurement process was described in the "Experimental" section. Figure 3 showed the concentration dependence of the refractive index increment for various samples. The value of the  $\left(\frac{dn}{dc}\right)$  could be calculated from the slope of the fitted line, which should pass through the (0, 0) point. From the calculated results, the  $\left(\frac{dn}{dc}\right)$  of PAM and chitosan were 0.1676 and 0.1842 mL/g, respectively. The  $\left(\frac{dn}{dc}\right)$  of each graft copolymer varied between that of PAM and chitosan. Furthermore, the difference in  $\left(\frac{dn}{dc}\right)$  between PAM and chitosan was  $1.66 \times 10^{-2}$  mL/g. In terms of the experimental error of  $\left(\frac{dn}{dc}\right)$  being  $\pm 5.0 \times 10^{-4}$  mL/g, the precision of this measurement was around  $\pm 3.0\%$ , indicating that the SRIIM method for measuring the grafting ratio in this system was applicable.

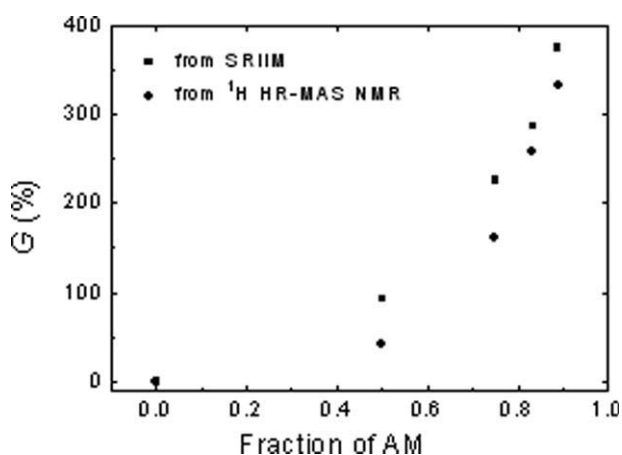




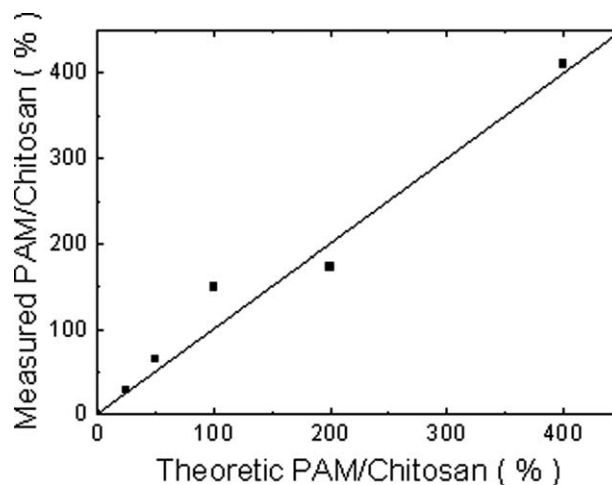
**Figure 3** The concentration dependence of the refractive index increment of ●: PAM; ■: Chitosan; ▲: Chitosan11.

Based on eqs. (1)–(3), the grafting ratio of various grafted chitosan samples have been deduced and summarized in Figure 4, where the grafting ratio increased with the amount of AM increase. Figure 4 also exhibited the grafting ratio calculated via  $^1\text{H-NMR}$ . It was found that there was the same trend of the grafting ratio by above two methods with the amount of AM increase. However, the grafting ratio of copolymers calculated from  $^1\text{H-NMR}$  were always lower than that from SRIIM, which might be related to incomplete dissolution of copolymers influencing the grafting ratio value obtained in the NMR measurement.

To confirm these results further, the PAM/chitosan weight percents of the PAM and chitosan mixtures, with a known weight mixed ratio, were measured using the SRIIM method. Figure 5 compared the measured and theoretic values of the chitosan and PAM mixtures with various mixed ratios. It was found from Figure 5 that the measured values were



**Figure 4** The grafting ratio of various chitosan samples measured by ■: SRIIM and ●:  $^1\text{H}$  HR-MAS NMR, respectively.



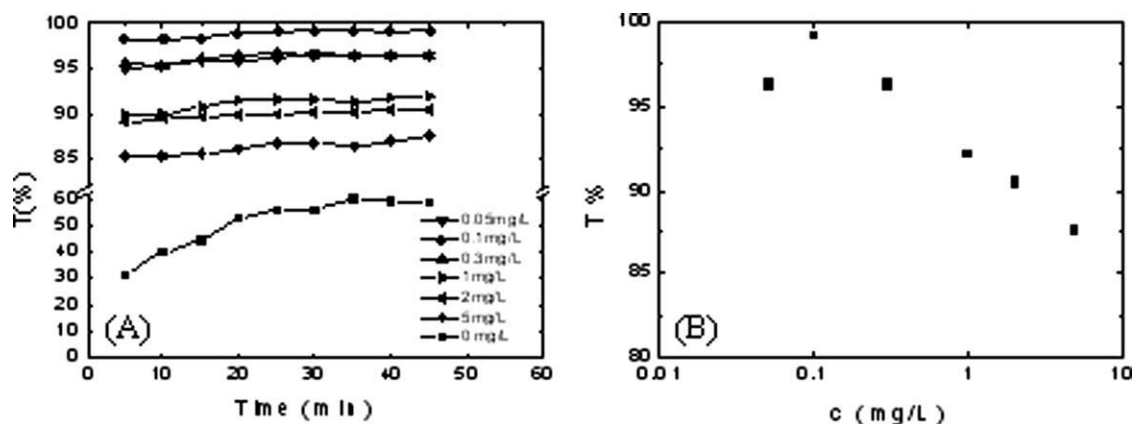
**Figure 5** The measured PAM/chitosan weight percents measured by SRIIM vs. the theoretic values in various mixtures of chitosan and PAM; the solid line in this figure obeyed the function of  $y = x$ .

quite similar to the theoretic ones, illustrating that the grafting ratio measured using the SRIIM method was also believable. However, the measured values between 100% and 200%, as shown in Figure 5, were a little bit far from the theoretic ones. This could be ascribed to the simplification of the basic theory for SRIIM method as described in eq. (1), which was deduced based on only the contributions from components of graft copolymers. In fact, the solvation effect and others in solutions would also influence the observed  $(\frac{dn}{dc})$ . Furthermore, the acetic acid and sodium acetate in solutions might interact with polymers, which could also affect the solution properties of polymers. Thus, to measure the grafting ratio accurately using this method, some improvements should be made to eq. (1), and further study would be necessary.

### The flocculating properties of the graft copolymers

Effect of the concentration of flocculants on the flocculating properties

As was known, the concentration of flocculants was a very important factor for the flocculating properties. Figure 6 showed the effect of the concentration of chitosan15 on the flocculating properties using the 700 mg/L kaolin suspension (with particles 74  $\mu\text{m}$  in diameter) as simulated waste water. As Figure 6(A) showed, the concentration of the flocculants, which was neither too high nor too low, could result in better flocculating effects. As seen in Figure 6(B), 0.1 mg/L of the flocculants showed the best flocculating properties in the measured concentration range. In terms of the charge neutralization mechanism for flocculation, chitosan presented abundant free amino groups along the chain



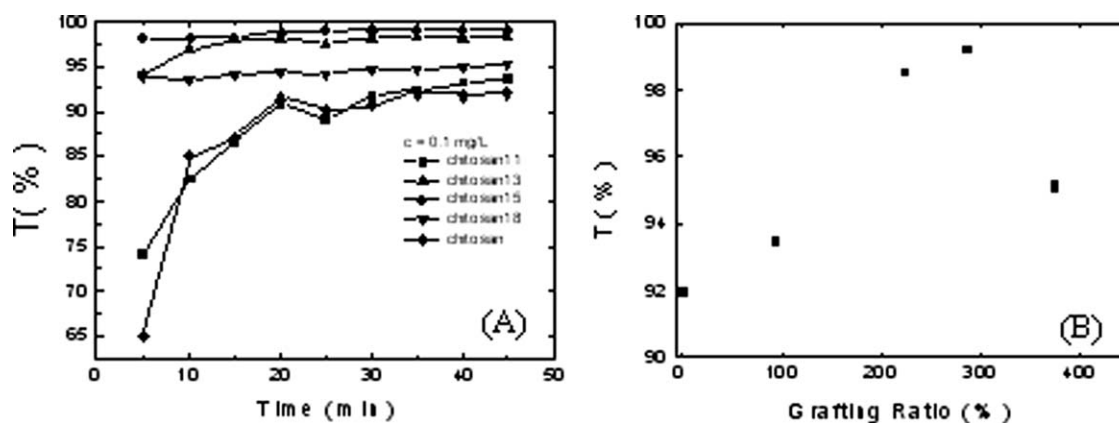
**Figure 6** The effect of chitosan 15 on the flocculating properties. (A) The time dependence of the transparency of the treated water with different concentrations; (B) the concentration dependence of the equilibrium transparency of the treated water.

backbone that could be cationically charged in acidic media. With the proper amount of flocculants, the anionic kaolin particles could be efficiently neutralized and coagulated. However, if the amount of flocculants was too great, the excessive cationic flocculants would partially restabilize the kaolin particles in the water again, and the flocculating effects would decrease.

#### Effect of the grafting ratio of flocculants on the flocculating properties

Based on the aforementioned findings, the effect of the grafting ratio of PAM grafted chitosan flocculants on the flocculating properties has been further investigated. Figure 7(A) showed the time dependence of the flocculating properties for various chitosan samples. It was found that the flocculating performances of the chitosan-g-PAM flocculants were, as a whole, better than nonmodified chitosan. Furthermore, chitosan15 showed both a faster floccula-

tion rate and a higher flocculation effect than other flocculants. Based on the aforementioned calculated grafting ratio results and Figure 7(A), the grafting ratio dependence of the flocculating properties for various chitosan samples was summarized, and shown in Figure 7(B). Interestingly, there was no direct proportional relationship between the grafting ratio and flocculating properties. The flocculating effect increased with the increase in grafting ratio until a maximum was reached, at which point the flocculating effect decreased. In terms of the bridging flocculating mechanism, the higher grafting ratio was beneficial for increasing the molecular weight of flocculants and improving actual flocculating properties. On the other hand, longer and more PAM branch chains would also efficiently shield the cationic groups of  $\text{NH}_3^+$  on the chitosan backbone, as shown in Figure 8. According to the viewpoint of the charge neutralization mechanism, this effect would reduce the flocculating performances. However, the experimental facts related to the effect



**Figure 7** The effect of various chitosan samples on the flocculating properties. (A) The time dependence of the transparency of the treated water; (B) the transparency of the treated water after reaching flocculating equilibrium based on Figure 7(A) vs. the grafting ratio. The concentrations of flocculants are all 0.1 mg/L.



**Figure 8** The available structures of chitosan-g-PAM samples dissolved in acidic media.

of the grafting ratio on the flocculating properties could be ascribed to the cooperative effects of the charge neutralization and bridging flocculating mechanisms. Thus, as the grafting ratio increased further, the flocculating properties decreased.

### CONCLUSION

In this article, graft copolymerization has been accomplished to prepare chitosan-based flocculants: chitosan-g-PAM copolymers. The results showed that the grafting ratio was one of the key factors affecting the flocculating properties. However, to determine the grafting ratio accurately, the SRIIM method was used, based on the usual observed solution properties of graft copolymers equal to those of the summation contributed from their components. The grafting ratio dependence of the flocculating properties indicated that the branched PAM chain could efficiently improve the bridging flocculating effect, but also shield the cationic groups on the chitosan backbone, and reduce the abilities of charge neutralization. However, the final flocculating effects were due to the cooperative effects of the two flocculating mechanisms. Therefore, chitosan-g-PAM flocculants should be prepared with a proper grafting ratio in order to achieve improved flocculating properties.

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