Homogeneous Grafting Reaction of Vinyl Pyrrolidone onto Chitosan

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ABSTRACT: Modification of chitosan by grafting of vinyl pyrrolidone (VP) was carried out in homogeneous phase using potassium persulfate as redox initiator. The effect of the reaction variables on the extent of grafting was studied systematically. Values for grafting percentages up to 290% were reached. It was observed that the solubility of chitosan was markedly reduced after grafting with vinyl pyrrolidone. The grafted product is insoluble in common organic solvents as well in dilute organic and inorganic acids. However, the solubility of the grafted chitosan after adsorption of copper ions changed substantially, becoming completely soluble in dilute hydrochloric acid. This was attributed to the effect of complex formation produced by coordination of amino groups of chitosan with copper ions. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1321–1326, 1997

Key words: chitosan; graft copolymer; vinyl pyrrolidone

INTRODUCTION

The modification of natural polymers is a promising method for the preparation of new materials. This enables one to introduce special properties and enlarge the field of the potential applications of those biopolymers of abundance. Among the diverse modifications that are possible to achieve, grafting of synthetic polymers is a convenient method.[1–3]

Currently, we are working on the grafting of vinyl monomers on polysaccharides, such as chitin, pectin, and chitosan, where these polysaccharides carry functional groups, such as amido, carboxyl, and amino, respectively. These biopolymers show an enhanced solubility in aqueous solutions as compared with cellulose. Therefore, grafting reactions on these polysaccharides could be carried out easily in an homogeneous system.

Chitosan is the product obtained from *N*-deacetylation of chitin with strong alkali. The latter, poly-$\beta(1 \rightarrow 4)$-*N*-acetyl-*D*-glucosamine, is an intractable and abundant naturally occurring polysaccharide forming part of the shell of crustacea and insects. Whereas chitin contains an acetamide groups situated in the C-2 of the anhydroglucose ring, the presence of free amine groups in chitosan enhances the solubility of this polysaccharide in dilute acids as compared with chitin.

In spite of a rather wide range of applications of chitosan in medicine, food, and polymer, among other uses, only few publications on the grafting of chitosan macromolecular backbone have appeared.[1–14]

In this work, we studied the modification of chitosan by graft copolymerization with *N*-vinyl-

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2-pyrrolidone in order to investigate eventual changes produced in the properties of the products and to compare this with that of unmodified chitosan. Moreover, the combined effect of the principal reaction variables for the grafting process was studied systematically. This grafting reaction was carried out in homogeneous phase by using potassium persulfate ($K_2S_2O_8$) (KPS) as redox initiator in dilute acetic acid. Some tests on the capacity of the grafted chitosan for retaining copper ions was carried out to compare this feature with that of the unmodified chitosan.

EXPERIMENTAL

Samples

The chitosan sample was donated by Bioquimica Austral Ltd., Punta Arenas, XII Region, Chile. Its degree of deacetylation and molecular weight were determined as 86% and 1.11×10^6, respectively. Most of the impurities were removed by extraction with acetone and dried under vacuum at room temperature. *N*-vinyl-2-pyrrolidone from Aldrich was distilled under vacuum, and the middle fraction was used. Potassium persulfate was analytical grade reagent from BDH chemicals and was used as received. All solvents were from Aldrich.

Grafting Reactions

In a typical grafting reaction, an exact amount of dry chitosan was first dissolved in 2% acetic acid using a 50 cm^3 stoppered flask, followed by the addition of monomer and initiator in this order. Then, the flask was placed in a thermostated bath to initiate the polymerization. The reaction mixture was shaken occasionally, and, at the end, an small amount of hydroquinone was added in order to stop the reaction. The product was precipitated in acetone, separated by filtration, washed with water to remove unreacted monomer, and dried under vacuum at 60°C to constant weight. Exhaustive extraction of the product with methanol allowed us the separation of polyvinyl pyrrolidone (PVP) homopolymer formed during the grafting reaction. The remaining product was then dialyzed against 2% acetic acid solution for two days in order to remove eventual ungrafted chitosan. However, in all cases, no detectable amount of ungrafted chitosan was separated. The product, thoroughly washed with water, after drying to constant weight was taken as graft copolymer.

The homopolymer separated by methanol extraction was precipitated in acetone and its structure was confirmed by Fourier transform infrared (FTIR) spectroscopy, and, in some cases, its molecular weight was determined by viscosity measurements. In all cases, no absorption bands from chitosan were observed.

RESULTS AND DISCUSSION

Grafting parameters such as grafting percentage ($\%G$), efficiency percentage ($\%E$) and homopolymer percentage ($\%H$) were determined as follows.

$$\%G = \frac{W_2 - W_1}{W_1} \times 100$$

$$\%E = \frac{W_2 - W_1}{W_3} \times 100$$

$$\%H = \frac{W_4 - W_2}{W_3} \times 100$$

where W_1, W_2, W_3, and W_4 denote the weight of initial chitosan, grafted chitosan after acetone extraction and dialysis, vinylpyrrolidone, and grafted chitosan before acetone extraction and dialysis, respectively.

The existence of grafting is evidenced by observing the differences between the FTIR spectra of chitosan and that of graft copolymer. As shown in Figure 1, a notorious difference corresponds to the appearance of a carbonyl absorption band at around 1650 cm^{-1} attributed to carbonyl group of polyvinyl pyrrolidone chains. Moreover, a sharp absorption at 618 cm^{-1} present in the graft copolymer is not observed neither in chitosan nor in polyvinyl pyrrolidone spectra. In the same figure, it can be seen that the spectrum of a physical mixture of both components differs appreciably from that of the grafted chitosan. This confirms further that polyvinyl pyrrolidone chains are covalently bonded to the chitosan backbone.

Influence of Reaction Conditions on Grafting Extent

In preceding works,[12–14] we have established the existence of strong influence of the reaction variables employed on the extent of grafting as well as on the amount of homopolymer produced for a

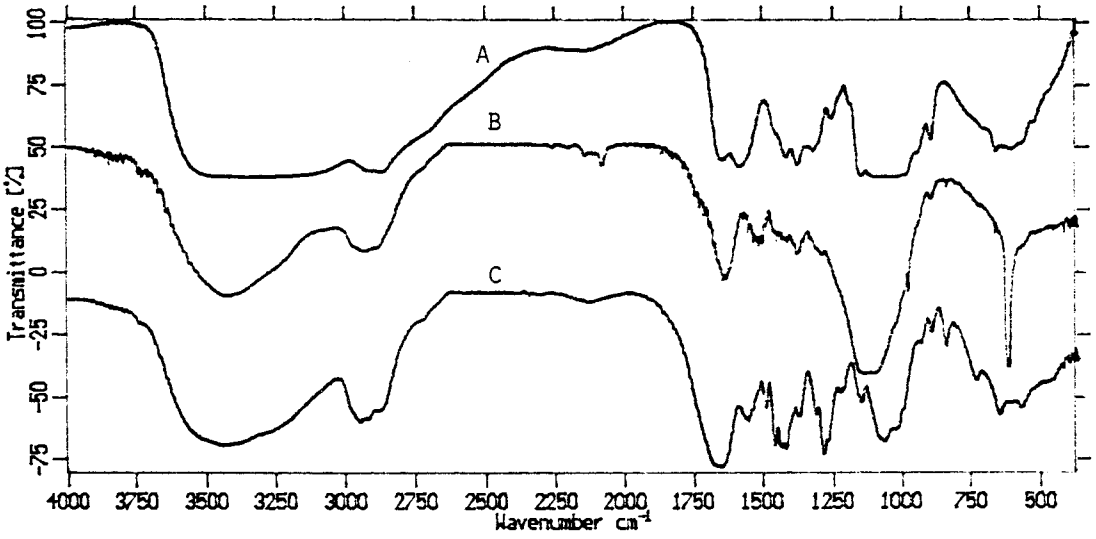

Figure 1 Infrared spectra of chitosan (A), chitosan grafted PVP (B), and physical mixture of PVP and chitosan (C).

specific experiment. For this reason, in a similar manner as previous works, we have studied the grafting reaction of vinylpyrrolidone onto chitosan by varying the initial concentration of monomer, initiator, and the relative amount of chitosan, as well as reaction times and temperatures. However, in contrast to previous works, these grafting reactions were carried out in an homogeneous medium. This was done by first dissolving the chitosan in dilute acetic acid, followed by the addition of monomer and potassium persulfate (KPS) as redox initiator.

The effect of the reaction variables on the extent of grafting (*%G*), as well as on grafting effi-

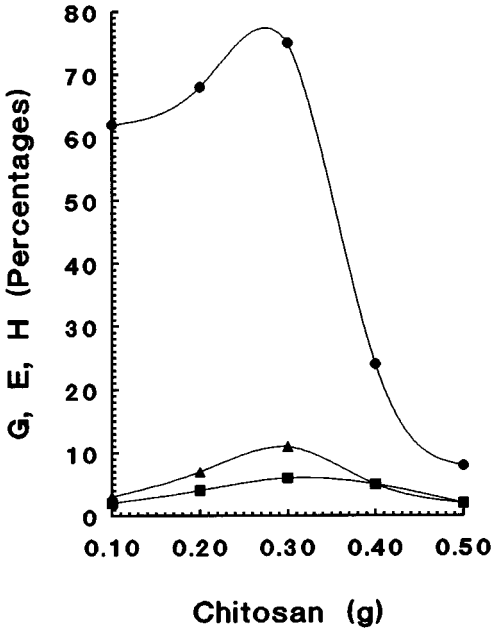

Figure 2 Effect of the amount of chitosan on grafting: ●, *%G*; ■, *%H*; ▲, *%E*. Reaction conditions: KPS ($4 \times 10^{-2} M$); VP, 2 mL; time, 120 min; temp., 60°C; solvent, 10 mL.

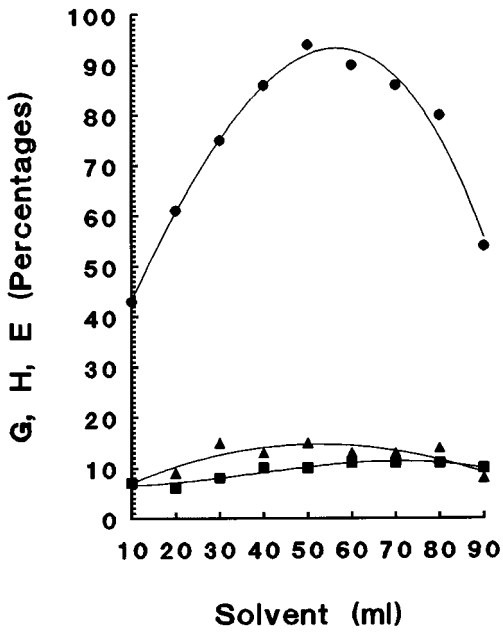

Figure 3 Effect of solvent volume on grafting: ●, *%G*; ■, *%H*; ▲, *%E*. Reaction conditions: chitosan, 0.3 g; KPS ($4 \times 10^{-2} M$); VP, 2 mL; time, 120 min; temp., 60°C.

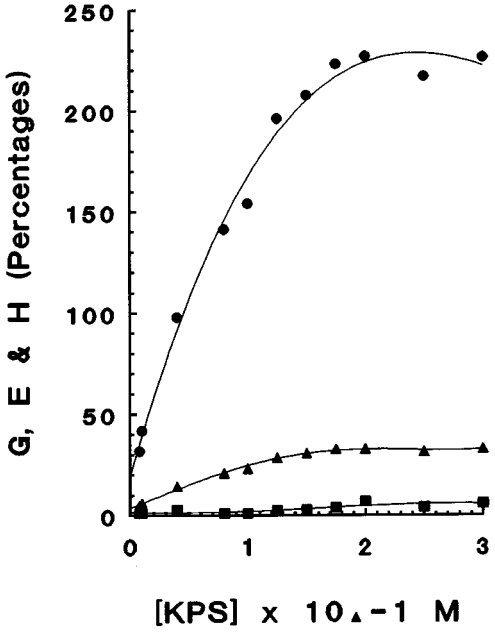

Figure 4 Effect of initiator concentration on grafting: ●, *%G*; ■, *%H*; ▲, *%E*. Reaction conditions: chitosan, 0.3 g; VP, 2 mL; time, 120 min; temp., 60°C; solvent, 30 mL.

ciency (*%E*) and homopolymer percentage (*%H*), are shown in Figures 2 to 7. The effect of the relative quantity of chitosan (Fig. 2) was studied by using a set of predetermined reaction conditions based on preliminary tests. As can be seen from this figure, the maximum *%G* was obtained for approximately 0.3 g chitosan. This value was taken for the investigation of the effect of the second variable studied (quantity of solvent; Fig. 3). As can be noted from the subsequent study of the remaining variables (Figs. 4–7), the set of the reaction parameters were adjusted in each case in order to optimize the grafting process. Like in foregoing works, it can be noted here that there exists a maximum of grafting for the majority of the variables studied, even though, in this case, the reactions were carried out in homogeneous phase. Probable reasons for individual or combined effects leading to these tendencies could be originated from events such as velocities of diffusion, decomposition of initiator, generation of chitosan macroradicals, termination, and chain transfer reactions, etc., as was discussed elsewhere.[12–14]

From the results obtained in this work, it is apparent that one can control the extent of grafting in a rather wide range by setting the appropriate reaction variables.

Tests on Copper(II) Ions Retention

By considering the nature of the functional groups present in the products, a preliminary exploration

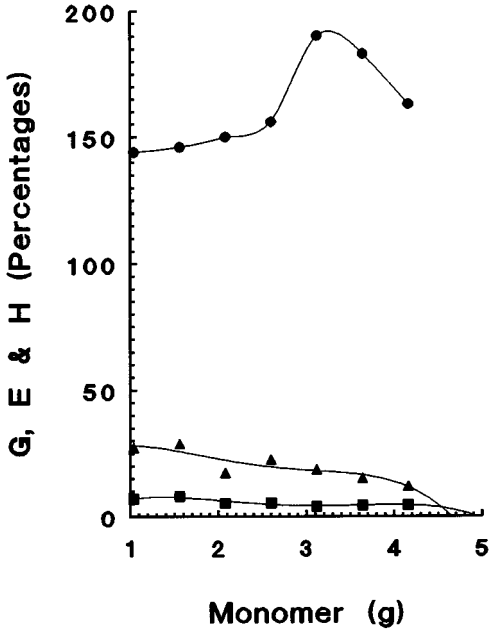

Figure 5 Effect of monomer concentration on grafting: ●, *%G*; ■, *%H*; ▲, *%E*. Reaction conditions: chitosan, 0.3 g; KPS ($1{,}5 \times 10^{-1} M$); time, 120 min; temp., 60°C; solvent, 30 mL.

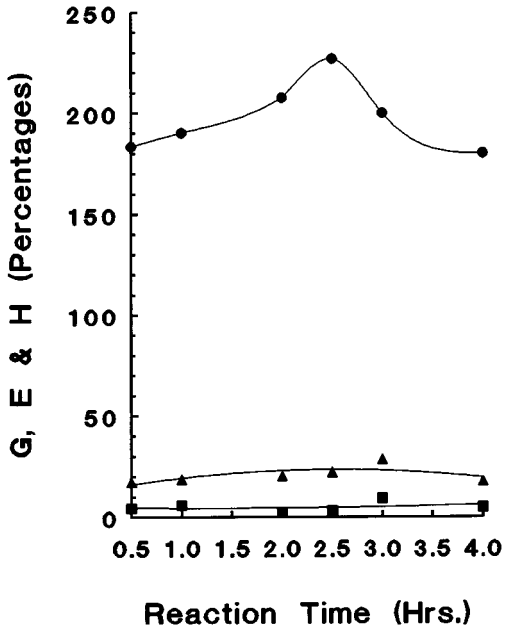

Figure 6 Effect of reaction time on grafting: ●, *%G*; ■, *%H*; ▲, *%E*. Reaction conditions: chitosan, 0.3 g; KPS ($1{,}5 \times 10^{-1} M$); VP, 3 mL; temp., 60°C; solvent, 30 mL.

on the capacity of the grafted chitosan for copper ions retention was done. To carry out the tests, an exact quantity of chitosan or chitosan modified with different percentages of grafting was placed in contact with dilute solutions (200 ppm) of copper(II) sulfate until the equilibrium was reached. After filtration, the quantity of copper captured by the grafted chitosan was estimated through the difference between the quantity of copper in the initial solution and the quantity of copper determined in the filtrate.

The results are presented in Table I. As can be seen, the amount of copper retained ($mgCu^{++}$/g product) remains nearly constant for different grafting degrees under the conditions employed. It should be taken into account that when the percentage of grafted PVP increases, the amount of chitosan contained per mass unit of the grafted product decreases. This could indicate that either PVP and chitosan have similar capacity for copper ion capture or the global process of copper adsorption is controlled by diffusion towards the inner of the entangled macromolecules.

Table I Retention Capacity for Copper (II) Ions of Chitosan Grafted with Different Amounts of PCP[a]

%G	Cu^{2+} Retention (mg/g)[b]
0	18
25	14
43	14
61	15
80	16
98	15
146	15
154	16
163	15
183	17
190	15
208	17
226	18
247	17
269	18

[a] Conditions: Sample = 1 g; cu (II) concentration = 200 ppm; solution volume = 100 mL; contact time = 20 h.
[b] mg Cu^{2+} retained by 1 g of sample.

Solubility Characteristics

It was observed that the solubility of chitosan was markedly reduced after grafting with vinylpyrrolidone. This appreciation was based on solubility tests carried out on the grafted products in typical solvents for chitosan such as dilute organic acids and hydrochloric acid. It was found that the grafted chitosan remained insoluble in all cases independently from the specific grafting degree. This is probably due to partial cross-linking by radical coupling of polyvinylpyrrolidone chain ends and/or intermolecular hydrogen bonding. On the other hand, when the grafted chitosan contains adsorbed copper ions, its solubility characteristics change dramatically, becoming completely soluble in dilute acid media. This behavior could be due probably to the disruption of the existing strong inter- and/or intramolecular hydrogen bonding through complex formation with copper ions in the grafted product. To our best knowledge, such behavior has not been reported hitherto.

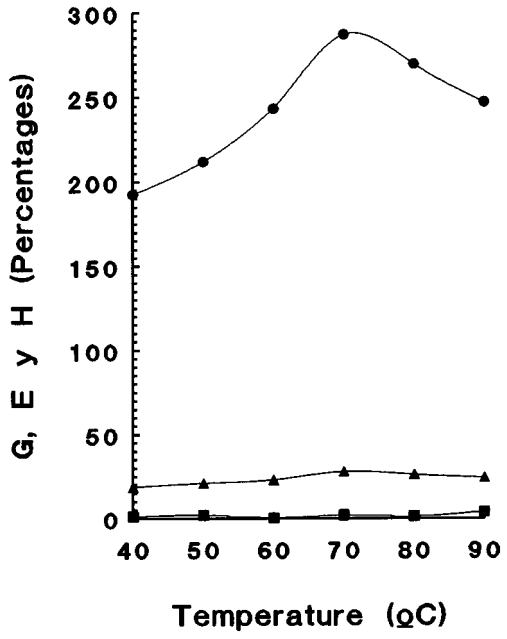

Figure 7 Effect of reaction temperature on grafting: ●, $\%G$; ■, $\%H$; ▲, $\%E$. Reaction conditions: chitosan, 0.3 g; KPS ($1{,}5 \times 10^{-1}M$); VP, 3 mL; time, 150 min; solvent, 30 mL.

CONCLUSIONS

Polyvinylpyrrolidone could be grafted onto chitosan up to 290% in an homogeneous phase by using potassium persulfate as redox initiator. It was possible to control the extent of grafting by varying the reaction conditions. The grafted copolymer samples are insoluble in common solvents includ-

ing diluted acid solutions, evidencing an enhanced hydrophobic character as compared with ungrafted chitosan. However, after capture of copper (II) ions, the polyvinylpyrrolidone grafted chitosan becomes fully soluble in dilute hydrochloric acid.

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