Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Yazdani-Pedram, M. , Lagos, A. , Retuert, J. , Guerrero, R. and Riquelme, P.(1995) 'On the Modification of Chitosan Through Grafting', Journal of Macromolecular Science, Part A, 32: 5, 1037 — 1047
To link to this Article: DOI: 10.1080/10601329508009346
URL: http://dx.doi.org/10.1080/10601329508009346

J.M.S.—PURE APPL. CHEM., A32(5), pp. 1037–1047 (1995)

ON THE MODIFICATION OF CHITOSAN THROUGH GRAFTING

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ABSTRACT

The feasibility of grafting poly(methyl acrylate) and poly[1-(methoxycarbonyl) ethylene] onto chitosan, poly-$\beta(1\rightarrow4)$-2-amino-2-deoxy-D-glucose, was investigated. The grafting reaction was carried out in aqueous solution by using ferrous ammonium sulfate (FAS) in combination with H_2O_2 as redox initiator. The effects of such reaction variables as chitosan, monomer and initiator concentrations, reaction time, and reaction temperature were determined. Through this study the grafting reaction could be optimized. The grafting yield reached its maximum

value of 332% when 0.3 g chitosan was copolymerized with 3 mL monomer at 70°C for 120 minutes with [FAS] = 6×10^{-5} M, [H_2O_2] = 6×10^{-3} M, and 8 mL water. The grafted chitosan was found to be insoluble in solvents for chitosan and solvents for poly(methyl acrylate), but did show swelling in dilute acetic acid, methanol, acetone, and in an ethanol/2% acetic acid 1:1 mixture. The thermal stability of chitosan and grafted chitosan were studied by dynamic thermogravimetric analysis. The results show that the graft copolymer is thermally more stable than pure chitosan. The overall activation energy for graft copolymerization was estimated to be 32.8 kcal/mol.

INTRODUCTION

Chitin, poly-β(1→4)-*N*-acetyl-D-glucosamine, is an abundant, naturally occurring polysaccharide that forms part of the shells of crustacea and insects. Chitin contains an acetamide group situated at C-2 of the anhydroglucose ring. Chitosan is the product obtained from the *N*-deacetylation of chitin with a strong alkali. The presence of free amine-groups in chitosan enhances the solubility of this polysaccharide in dilute acids as compared with chitin.

Some products obtained by chemical modification of chitin and chitosan have found multiple applications in medicine, food, polymer, and related industries. The modification of these biopolymers via grafting of synthetic polymers appears to be an attractive possibility, but to date only a few publications dealing with the grafting of chitosan have appeared [1–12]. The grafting of methyl acrylate, an industrially important monomer, onto chitosan has not been reported. Therefore, because of our interest in modifying natural polymers, we investigated the interrelated effects of the principal reaction variables on grafting methyl acrylate (MA) onto chitosan. This grafting reaction was carried out in the heterogeneous phase by using ferrous ammonium sulfate (FAS) in combination with hydrogen peroxide (Fenton's reagent) as the redox initiator.

EXPERIMENTAL

The chitosan sample was received from Bioquimica Austral Ltd., Punta Arenas, XII Region, Chile. Its degree of deacetylation and molecular weight were 86% and 1.14×10^6, respectively. It was purified by extraction with acetone in a Soxhlet apparatus for 24 hours, washed with methanol and then with diethyl ether, and finally dried under vacuum at room temperature. MA from Fluka was distilled under vacuum, and the middle fraction was used. Ferrous ammonium sulfate was an analytical grade reagent from Aldrich. Hydrogen peroxide from Merck was used as received. All solvents were from Aldrich.

Graft Copolymerization

Graft copolymerizations were carried out in 50 cm^3 stoppered flasks by dispersing an exact amount of dry, powdered (< 100 mesh) chitosan in the aqueous initiator solution. The monomer was then added and the flask was placed in a

thermostated bath. The reaction mixture was shaken occasionally during polymerization. At the end of polymerization, a small amount of hydroquinone was added to stop the reaction. The grafted chitosan was separated by filtration, washed with water to remove unreacted monomer, and dried under vacuum at 60°C to constant weight. In order to remove the homopolymer formed during the grafting reaction, the whole sample was extracted with acetone in a Soxhlet apparatus for 24 hours. The remaining product was then dialyzed against 2% acetic acid solution for 72 hours in order to remove any ungrafted chitosan. However, no measurable quantity of ungrafted chitosan was separated. The product, thoroughly washed with water and dried to constant weight, was considered to be a graft copolymer.

The methyl acrylate homopolymer separated by acetone extraction was precipitated in methanol and its structure confirmed by IR spectroscopy. No absorption bands from chitosan were observed. Selected homopolymer samples were characterized by gel permeation chromathography. The number-average molecular weight ($\overline{M}_n$) of the samples was in the 1.8×10^5 to 5.5×10^5 range.

Thermogravimetric Analysis

Dynamic thermogravimetric analysis was carried out by using a Mettler model TA 3000 thermal analysis system. Samples (8–10 mg) were placed in the sample holder, and the thermal degradation measurements were carried out in oxygen-free nitrogen atmosphere between 40 and 700°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Proof of Grafting

The increase in weight of the extracted copolymer sample compared with that of the original unreacted chitosan and the weight of initial monomer were used to calculate grafting parameters such as grafting percentage (%G) and homopolymer percentage (%H) as follows:

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

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

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

The grafting was also confirmed by comparing the IR spectra of chitosan with that of the grafted product (Fig. 1). The main difference observed is the appearance of a carbonyl absorption band at 1738 cm^{-1}, corresponding to the carbonyl group of poly(methyl acrylate) (PMA) chains. Two other absorption bands at 827 and 760 cm^{-1} are observed. These were assigned to the rocking absorptions of methylene groups in PMA. All these bands are absent in the IR spectrum of pure chitosan.

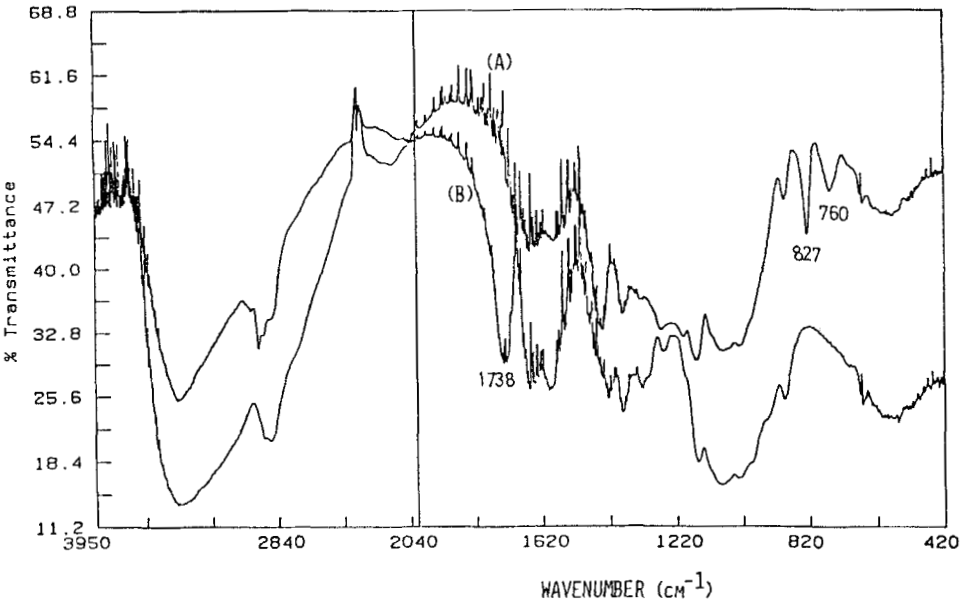

FIG. 1. IR spectra of chitosan (A) and chitosan-grafted PMA (B).

Modification of Physical Properties

It was observed that physical properties such as solubility, hydrophilic character, and thermal stability of the grafted products were significantly changed as compared with chitosan. This could be taken as an additional proof of grafting. The solubilities of the grafted products were tested in both solvents for chitosan and solvents for poly(methyl acrylate), dilute acetic acid, methanol, acetone, as well as in an ethanol/2% acetic acid 1:1 mixture. It was found that the grafted chitosan remained insoluble in all cases. However, it showed considerable swelling in the above-named solvents. This behavior can be attained to such factors as crosslinking by radical coupling of poly(methyl acrylate) chain ends, intermolecular hydrogen bonding, and the heterogeneous nature of the reaction leading mainly to surface grafting of chitosan.

The thermal decomposition behavior of chitosan and two representative samples of chitosan grafted with methyl acrylate are shown in Fig. 2. The first weight loss observed in pure chitosan could correspond to the loss of adsorbed water. This event is almost completely absent in the case of the graft copolymers since the heterogeneous nature of the grafting reaction allows essentially surface grafting of the chitosan molecules with strongly hydrophobic poly(methyl acrylate). Furthermore, it can be seen that the decomposition temperature (TD) at 50% weight loss (360°C) for pure chitosan is lower than the TDs for both grafted chitosan samples (402 and 412°C) with 139 and 332% graft-on, respectively. This indicates that the grafted chitosan is initially more stable than chitosan, but their main weight losses occur more rapidly at higher temperatures. This is most probably due to the lower thermal stability of poly(methyl acrylate) at temperatures higher than 400°C. How-

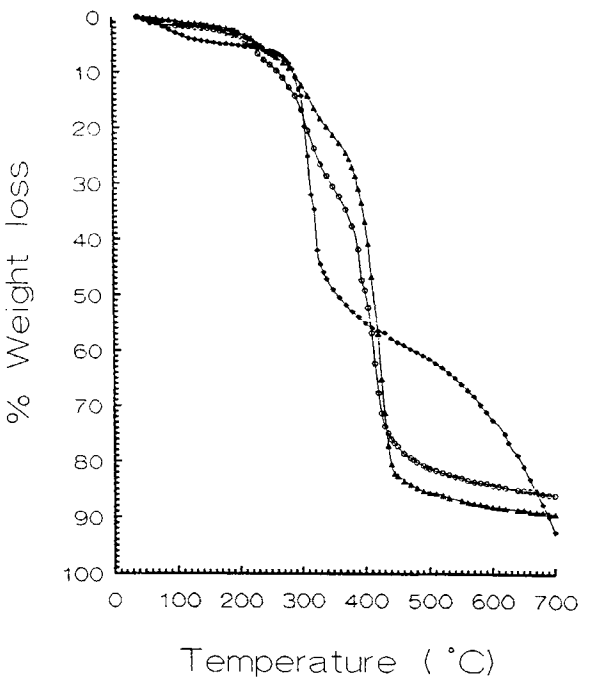

FIG. 2. TGA curves of chitosan (♦), chitosan with 139% grafted PMA (○), and chitosan with 332% grafted PMA (▲).

ever, the overall higher thermal stability of grafted chitosan could also be attributed to the possible crosslinking of the chitosan backbone by poly(methyl acrylate) chains.

Effect of the Reaction Variables on Grafting

It is well known [13] that redox initiators, such as Fenton's reagent, create active radical sites on cellulose chains, therefore producing macroradicals capable of initiating grafting of vinyl monomers. This can be extended to structurally similar polysaccharides such as chitosan. It has been shown [13] that the grafting of vinyl monomers on polysaccharides, mainly cellulose and its derivatives, depends strongly on the reaction conditions used. Therefore, the influence of different reaction variables on the extent of grafting of PMA onto chitosan was studied in detail.

The first reaction variable studied was the relative amount of chitosan for a set of reaction conditions based on preliminary experiments. As can be seen in Fig. 3, the maximum $\%G$ was obtained when 0.3 g chitosan was used. For greater initial amounts of chitosan, lower percentages of grafting were obtained. By considering that the grafting process in its initial stages requires prior generation of chitosan macroradicals, it is evident that, by maintaining the other reaction variables constant, the mass of chitosan used determines the amount of grafted product. On the other hand, the presence of a maximum implies the existence of an optimum relation among chitosan, monomer, and initiator quantities that could only produce a cer-

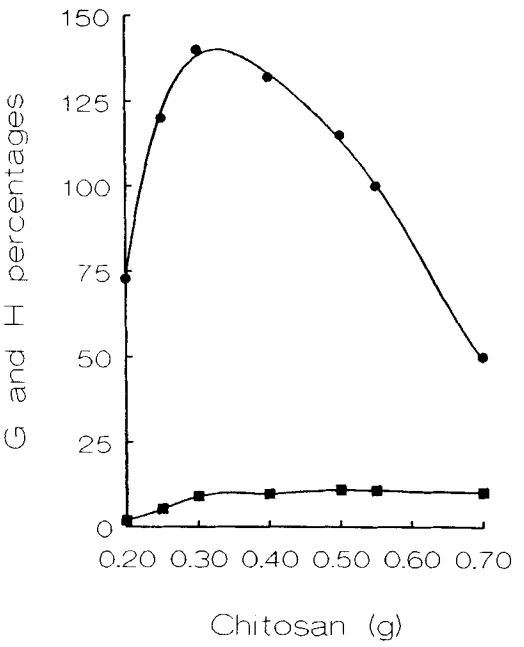

FIG. 3. Effect of the amount of chitosan on grafting. (●) %G; (■) %H. Reaction conditions: Fe^{2+} (10^{-3} M); H_2O_2 (10^{-2} M); MA, 2 mL; time, 120 minutes; 60°C; H_2O, 8 mL.

tain number of radical sites. This means that the number of free radicals on chitosan is not augmented further by increasing the amount of chitosan. Therefore, the mass of grafted chitosan should remain nearly constant. Obviously, %G decreases since its calculation is based on the amount of chitosan used in a particular experience.

It is interesting to note in Fig. 3 that the maximum amount of homopolymer formed coincides closely to the maximum grafting attained. This suggests that the homopolymerization process is not originated by direct attack of initiator on monomer but rather seems to result from a process related to the generation of chitosan macroradicals caused by the attack of the initiator on biopolymer chains. The fact that in this case the %H initially increases by increasing the amount of chitosan and then remains constant is in agreement with the above discussion. As already mentioned, the number of radical sites generated on chitosan remains constant after it reaches a maximum. This trend is also evidenced when the effects of other reaction variables were studied (see Figs. 4–8) where the close relation between %H and %G persists. This further supports the proposed explanation given above and that the thermal homopolymerization of MA does not take place under the reaction conditions used here.

Figure 4 shows the effect of Fe(II) concentration on the extent of grafting and homopolymerization. %G increases sharply with an increase in Fe(II) concentration due to an enhanced decomposition rate of H_2O_2 (Eq. 1). This means that the generation of hydroxyl radicals, which are able to originate chitosan macroradicals (Eq. 2) as well as homopolymer, requires the presence of Fe(II) ions adsorbed onto chitosan macromolecules. We observed in previous work [7, 14, 15] that the

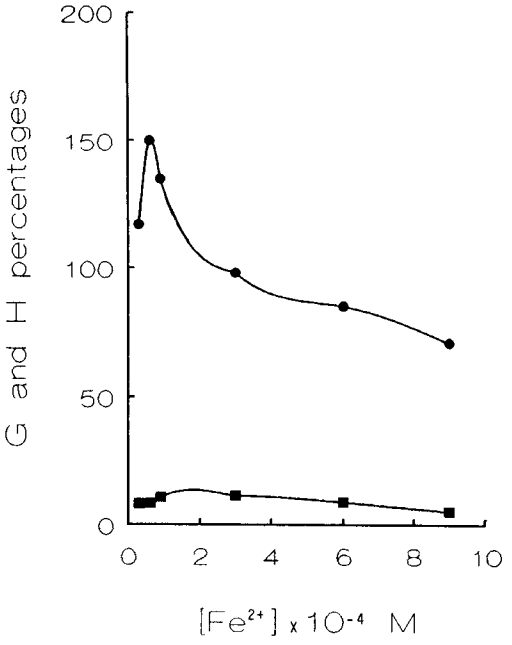

FIG. 4. Effect of Fe(II) concentration on grafting. (●) %*G*; (■) %*H*. Reaction conditions: Chitosan, 0.3 g; H_2O_2 (10^{-2} M); MA, 2 mL; time, 120 minutes; 60°C; H_2O, 8 mL.

decomposition of peroxides takes place in the vicinity of chitosan molecules due to these adsorbed Fe(II) ions. Homopolymer formation seems to follow the same tendency due to the already discussed relation between grafting and homopolymerization processes. At higher Fe(II) concentrations, and by considering Eq. (3), the decrease of %*G* could be attributed to the consumption of HO^0 in this case.

$$H_2O_2 + Fe^{2+} \rightarrow HO^0 + HO^- + Fe^{3+} \quad (1)$$

$$CHI{-}H + HO^0 \rightarrow CHI^0 + H_2O \quad (2)$$

$$HO^0 + Fe^{2+} \rightarrow HO^- + Fe^{3+} \quad (3)$$

By increasing the H_2O_2 concentration up to 6×10^{-3} M (Fig. 5), %*G* increases, reaching a maximum of nearly 175%, and then decreases sharply. The observed decrease of %*G* could be due to radical consumption through Reactions (4) and (5). It should be also mentioned that an excess of hydroxyl radicals could participate in termination of propagating poly(methyl acrylate) chains and consequently decrease %*G*.

$$HO^0 + H_2O_2 \rightarrow H_2O + HOO^0 \quad (4)$$

$$HOO^0 + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+} \quad (5)$$

The effect of reaction time is shown in Fig. 6. As can be seen, maximum %*G* is reached after 2 hours, and then it decreases slightly. The decrease in %*G* observed for longer reaction times cannot be explained at this stage. However, it could be

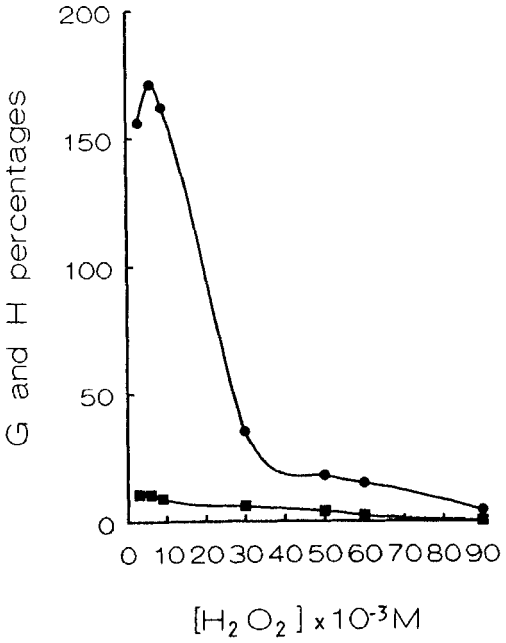

FIG. 5. Effect of H_2O_2 concentration on grafting. (●) %*G*; (■) %*H*. Reaction conditions: Fe(II) (6×10^{-5} M); chitosan, 0.3 g; MA, 2 mL; time, 120 minutes; 60°C; H_2O, 8 mL.

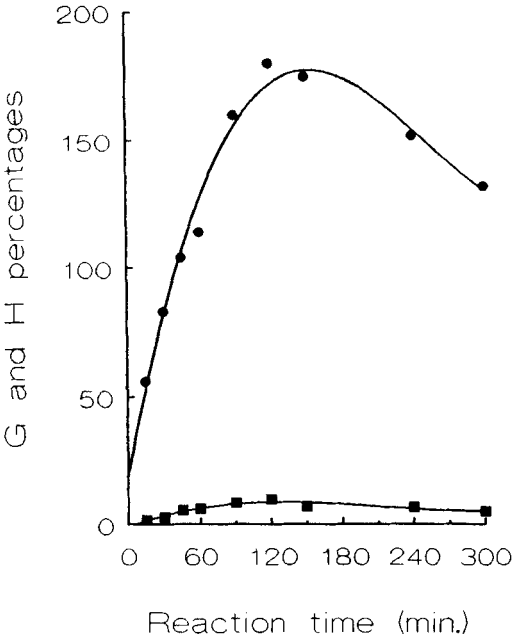

FIG. 6. Effect of reaction time on grafting. (●) %*G*; (■) %*H*. Reaction conditions: Fe^{2+} (6×10^{-5} M); H_2O_2 (6×10^{-3} M); chitosan, 0.3 g; MA, 2 mL; 60°C; H_2O, 8 mL.

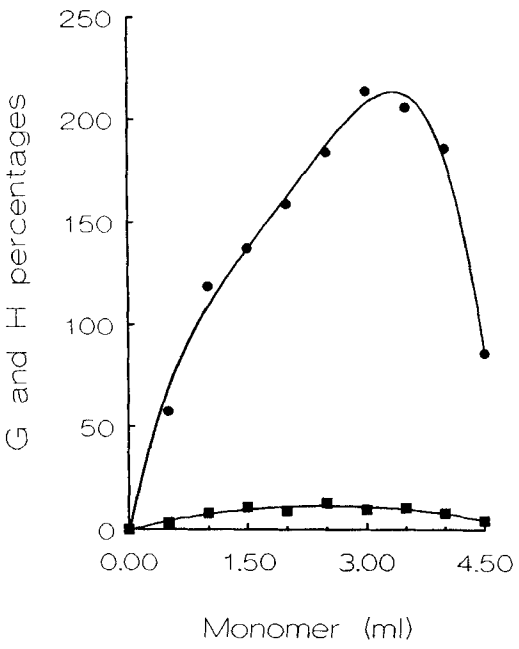

FIG. 7. Effect of monomer concentration on grafting. (●) %*G*; (■) %*H*. Reaction conditions: Fe^{2+} (6×10^{-5} M); H_2O_2 (6×10^{-3} M); chitosan, 0.3 g; time, 120 minutes; 60°C; H_2O, 8 mL.

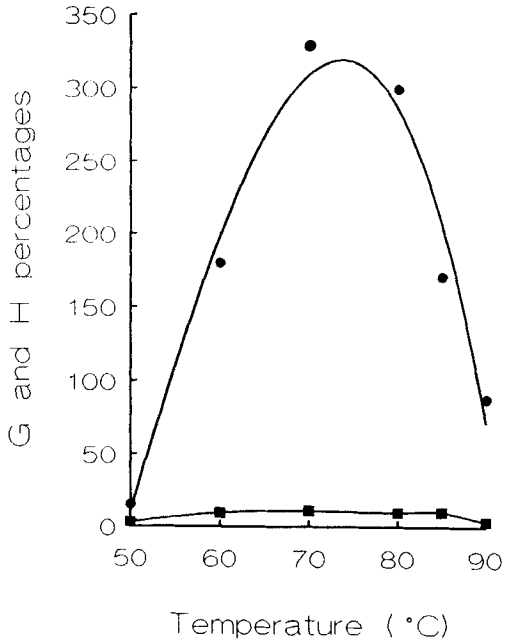

FIG. 8. Effect of reaction temperature on grafting. (●) %*G*; (■) %*H*. Reaction conditions: Fe^{2+} (6×10^{-5} M); H_2O_2 (6×10^{-3} M); chitosan, 0.3 g; MA, 3 mL; time, 120 minutes; H_2O, 8 mL.

caused by the gradual liberation of retained impurities or small molecules from grafted chitosan macromolecules.

By studying the influence of the relative amount of methyl acrylate (Fig. 7), it was found that $\%G$ reaches a maximum and then falls sharply. This could be due to the limited solubility of the monomer in the reaction medium, and so its adsorption onto chitosan macromolecules is enhanced. This would interfere considerably with the approach of both Fe(II) ions and the initiator molecules, which is necessary for grafting, as already explained.

As expected, the extent of grafting increases with an increase in the reaction temperature (Fig. 8) since the generation of active sites is promoted. The $\%G$ falls sharply for temperatures higher than 70°C, probably due to the dominance of termination and chain transfer reactions.

CONCLUSIONS

The feasibility of grafting MA onto chitosan by using Fenton's reagent as the redox initiator has been demonstrated through this work. A systematic study of reaction conditions allowed us to reach a grafting percentage as high as 332%, which is considerably larger than the values reported for other vinyl monomers. The results obtained allowed us to propose that interrelated effects among the reaction variables take place. This is supported by the existence of similar tendencies for grafting and homopolymerization processes. The grafted copolymer samples present an enhanced hydrophobic character and their solubilities differ substantially from that of ungrafted chitosan. Modified chitosan also shows enhanced thermal stability.

ACKNOWLEDGMENT

The authors are grateful to the Departamento Tecnico de Investigacion (DTI), Universidad de Chile, for financial support (Project Q3570-9313).

REFERENCES

[1] M. Inomoto, *Setchaku, 26*(12), 529 (1982); *Chem. Abstr., 99*, 54159w (1983).

[2] L. A. Bercovich, M. P. Tsyurupa, and V. A. Davankov, *J. Polym. Sci., Polym. Chem. Ed., 21*, 1281 (1983).

[3] S. Aiba, N. Minoura, and Y. Fujiwara, *Int. J. Biol. Macromol., 7*(2), 120 (1985).

[4] K. Kurita, M. Kanari, and Y. Koyama, *Polym. Bull. (Berlin), 14*(6), 511 (1985).

[5] K. H. Kim, K. S. Kim, and J. S. Shin, *Polymer (Korea), 11*(2), 133 (1987).

[6] A. Takahashi, Y. Sugahara, and Y. Horikawa, *Sen'i Gakkaishi, 43*(7), 362 (1987); *Chem. Abstr., 107*, 97249b.

[7] H. S. Blair, J. Guthrie, T. Law, and P. Turkington, *J. Appl. Polym. Sci., 33*, 641 (1987).
[8] A. Lagos and J. Reyes, *J. Polym. Sci., Polym. Chem. Ed., 26*, 985 (1988).
[9] K. Kurita, A. Yoshida, and Y. Koyama, *Macromolecules, 21*(6), 1579 (1988).
[10] M. Yazdani-Pedram, A. Lagos, and J. Retuert, *Proc. XVIII Jorn. Chil. Quim.*, p. 402 (1989).
[11] A. Takahashi, J. Tanzawa, and Y. Sugahara, *Kobunshi Ronbunshu, 46*(5), 329 (1989).
[12] S. H. Cho, K. S. Kim, K. H. Kim, and J. S. Shin, *Polymer (Korea), 14*(1), 9 (1990).
[13] A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer, Berlin, 1981.
[14] M. Yazdani-Pedram, A. Lagos, N. Campos, and J. Retuert, *Int. J. Polym. Mater., 18*, 25 (1992).
[15] J. Retuert and M. Yazdani-Pedram, *Polym. Bull. (Berlin), 31*, 559 (1993).

Received April 28, 1994
Revision received August 5, 1994