**Full Paper:** A large number of carboxylic groups were introduced onto chitosan by grafting with poly(acrylic acid) as an efficient way of modification. The reactions were carried out in a homogeneous aqueous phase by using potassium persulfate and ferrous ammonium sulfate as the combined redox initiator system. The efficiency of grafting was found to depend on monomer, initiator, and ferrous ion concentrations as well as reaction time and -temperature. It was observed that the level of grafting could be controlled to some degree by varying the amount of ferrous ion used as a co-catalyst in the reaction. Evidence of grafting was obtained by comparison of FTIR spectra of chitosan and the graft copolymer as well as solubility characteristics of the products. The swelling behavior of chitosan samples, grafted with 115% and 524% poly(acrylic acid), was studied as function of pH, in distilled water and in aqueous NaCl solution. The sample that has 115% grafting swells considerably more both in distilled water (pH 5.8) as well as higher pH values than the sample with 524% grafting. In contrast, an inverse swelling behavior at pH 2 was observed. An unusual swelling behavior at pH 2 was found for the sample with 524% grafting, which swells to a greater extent than in distilled water. This was attributed to the amphiphilic nature of the modified chitosan from which complex inter- and/or intramolecular interactions could originate.
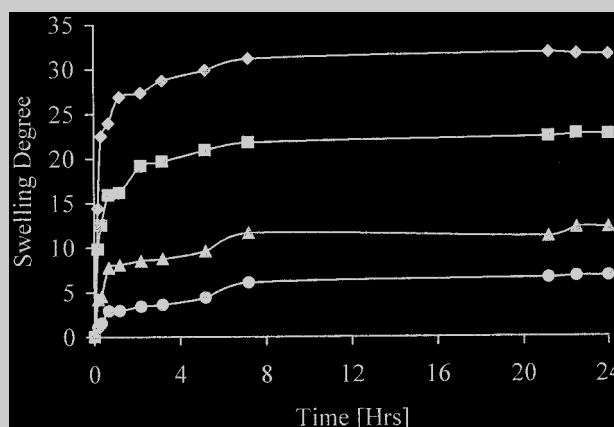
Swelling curves of chitosan grafted with poly(acrylic acid) in aqueous solutions at 37 °C: ● %G = 524 (0.86% NaCl); ▲ %G = 115 (0.86% NaCl); ■ %G = 524 (H₂O); ◆ %G = 115 (H₂O) (%G = percentage of grafting)

Hydrogels based on modified chitosan, 1

Synthesis and swelling behavior of poly(acrylic acid) grafted chitosan

*Mehrdad Yazdani-Pedram**[1], *Jaime Retuert*[2], *Raul Quijada*[3]

[1] Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile
[2] Departamento de Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 2777, Santiago, Chile
[3] Departamento de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 2777, Santiago, Chile

Introduction

The chemical modification of synthetic and natural polymers is a convenient route to obtain materials with different chemical and physical properties. Considerable interest has been focused on the modification by grafting synthetic polymers onto the most abundant naturally occurring polysaccharides such as cellulose, starch, and algi-

nates[1–5]. Many actual as well as potential applications for products obtained from natural and chemically modified polysaccharides exist as, for example, products with enhanced hydrophilic characteristics. For instance, modified polysaccharides containing carboxyl functions as anionic groups are adequate for the preparation of ionotropic gels. Ionotropic gels are products capable of inter-

acting with polyvalent metal cations. These are water insoluble but they swell considerably with the addition of water or aqueous metal salt solutions. Much recent research deals with this topic and its metal chelating capacity[6–13]. This type of material, with a large capacity for water retention, is known as a hydrogel.

Considerable efforts have been focused on the synthesis of hydrogels based on modification of some natural polymers[14, 15], in particular starch and cellulose. In spite of the fact that chitin is the second most abundant natural polysaccharide, its modification through grafting has not been widely explored, probably due to its insolubility in water and organic solvents. However the modification of chitosan, its principal derivative, has been carried out by grafting mainly in a heterogeneous medium and by using different catalysts[16–24].

Chitosan (poly-β(1→4)-2-amino-2-deoxy-D-glucose) is the product of deacetylation of chitin and shows enhanced solubility in dilute acids as compared with the parent chitin[9]. Chitin (poly-β(1→4)-N-acetyl-D-glucosamine) is distributed widely in nature forming the principal constituent of shells of crustaceans such as crabs, lobsters, prawns, Antarctic krill, etc. Recently chitosan has attracted great attention because the range of its applications has been extended, among other uses, to medical[25–29], wastewater treatment[30–32], membranes[33–36], flocculants[37, 38], etc. Chitin is structurally similar to cellulose, containing an acetamido group instead of the C-2 hydroxyl group.

In a previous paper we compared the reactivity of different redox initiator systems for grafting of methyl methacrylate onto chitin in the heterogeneous phase. Enhanced affinity of grafted chitin for some organic solvents was observed in this case[39]. Regarding the modification of chitosan, we studied the grafting of methylacrylate and methylmethacrylate in a heterogeneous medium by using potassium persulfate in combination with a number of organic and inorganic reducing agents such as cocatalysts. We found that the use of some co-catalysts increases the degree of grafting[16]. We have also used Fenton's reagent (H_2O_2/Fe^{2+}) for grafting poly(methyl acrylate) onto chitosan. In both cases the grafted chitosan showed enhanced thermal stability[40]. Recently, by grafting vinyl pyrrolidone, we were able to carry out the reactions in a homogeneous phase[21]. The chelating capacity of chitosan grafted with polyvinylpyrrolidone for Cu^{2+} ions were tested and it was found that, contrary to the case of chitosan, the complexation with Cu^{2+} ions resulted in completely soluble products in dilute hydrochloric acid. In general, it was observed that all the above mentioned modifications led to notorious changes in the properties of the grafted products in comparison to those of the ungrafted chitosan.

In this paper we cover the synthesis and characterization of chitosan grafted with poly(acrylic acid) with the aim of obtaining modified chitosan with hydrogel characteristics. As we have previously observed, the extent of grafting vinyl monomers onto cellulose, chitin, chitosan, etc. is very sensitive towards reaction conditions[16, 21, 39, 40]. Therefore, a systematic study of the effect of different reaction variables on grafting of acrylic acid onto chitosan, is presented in this work. These reactions were carried out in a homogeneous medium and by using a combined redox initiator consisting of potassium persulfate (KPS) and ferrous ammonium sulfate (FAS). The hydrogel characteristics of selected grafted products were evaluated in different media in order to estimate their swelling capacity.

Experimental part

High molecular weight Chitosan is commercially available (Aldrich). The deacetylation degree was 82% as estimated by ¹H NMR and free amino group titration. It was purified by extraction with acetone in a Soxhlet apparatus for 24 h, and dried under vacuum at room temperature. Acrylic acid (AA, Merck) was distilled under vacuum and the middle fraction was used (34 °C, 1067 Pa). Ferrous ammonium sulfate (FAS, analytical grade, Merck) and potassium persulfate (KPS, BDH chemicals) were used as received. All used solvents were reagent grade from Aldrich.

Graft copolymerization

Graft copolymerizations were carried out in 50 cm³ stoppered flasks and under an atmospheric of oxygen by first dissolving an exact amount of dry chitosan in aqueous monomer solution, followed by the addition of the initiator. Then the flask was placed in a thermostated bath at the desired reaction temperature (50, 60, 70, and/or 80 °C). Polymerization was started and continued for a predetermined period, between 30 and 150 min. The reaction was stopped by rapidly cooling down the reactor, then the product was precipitated by pouring the polymerization mixture into a large amount of acetone. The precipitate was filtered, washed thoroughly with acetone, and dried under vacuum at 60 °C to constant weight. The dry sample was extracted with water in a Soxhlet for 24 h in order to remove unreacted monomer, initiator, and poly(acrylic acid) (PAA) homopolymer that eventually could form during the grafting reaction. The dried remaining product was the graft copolymer. The efficiency of grafting (%E) can be calculated as the weight ratio of the increase in weight of the extracted copolymer sample and the initial monomer. This can be calculated using the relation: $\%E = 100 (W_2 - W_1)/W_3$, where W_1, W_2, and W_3 denote the weight of initial dry chitosan, grafted chitosan after water extraction and drying, and the weight of monomer, respectively. As is already known, the composition of the grafted chitosan can be calculated in terms of the so-called percentage of grafting. This can be expressed on the basis of percent weight increase related to the initial weight of chitosan. Therefore, the extent of grafting can be calculated as percentage of grafting $\%G = 100 (W_2 - W_1)/W_1$.

Swelling determination

The swelling behavior of grafted chitosan samples was studied at 37 °C as a function of time in distilled water and in buffered solutions at different pH values. The well-known tea-bag method was used. An exact amount of pre-dried sample was placed into a tea bag made of 200 mesh nylon screen. This was then immersed in buffer solution at 37 °C. After certain time, the tea bag containing swollen sample was taken out and hung up for 5 min in order to eliminate excess unabsorbed liquid and then weighed. The degree of swelling at time, t, was calculated using the relation $(W_s - W_0)/W_0$, where W_s and W_0 are the weights of swollen and dry polymer, respectively.

Results and discussion

The extracted copolymer samples show insolubility in dilute acetic acid, a difference to chitosan. This solubility characteristic together with the increase in weight of the product, as compared with that of the initial chitosan, and their infrared spectra were taken as evidence of grafting. As expected, the FTIR spectra of higher grafted products are practically identical to those of pure poly(acrylic acid), and therefore the analysis requires the use of a sample with a rather low percentage of grafting. For that reason the IR spectra of chitosan and PAA-grafted chitosan with 104% grafting are shown in Fig. 1. In the spectrum of grafted chitosan, in addition to the chitosan characteristic bands, three new absorption bands appear at 1726, 799, and 616 cm^{-1}. The first one corresponds to the carbonyl absorption from grafted poly(acrylic acid) and the other two bands are also characteristic of PAA.
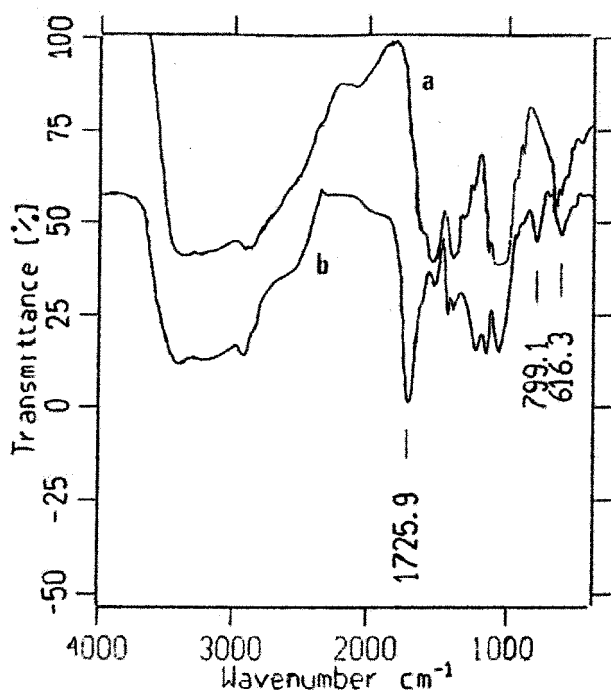

Fig. 1. FTIR spectra of (a) chitosan and (b) chitosan grafted with poly(acrylic acid)

Furthermore, it can be seen that the band at 1550 cm^{-1} of the pure chitosan (amido II band) is markedly greater than that in the spectrum of the grafted chitosan. This is most probably due to inter- and/or intramolecular hydrogen bonding or internal ammonium salt formation between carboxyl groups of grafted PAA chains and amino groups of chitosan. Naturally, the diminished solubility of the graft copolymer, in spite of containing large number of carboxyl groups, could be explained considering the already-mentioned possibilities.

In relation to the initiation system, it has been shown by Kolthoff et al.[41] that on heating KPS in aqueous solution, it decomposes to sulfate ion radicals (SO$_4^{\bullet-}$) These radicals may react with water to produce hydroxyl radicals ($^{\bullet}$OH). The formation and participation of $^{\bullet}$OH radicals in KPS and FAS (Fe^{2+})-KPS that initiated grafting of vinyl monomers onto cellulose has already been reported[1]. The possible mechanism for the formation of active sites on chitosan could hence be postulated, by analogy with cellulose, and by considering that chitosan can act as a weak reducing agent. Therefore, the reactions leading to grafting of a vinyl monomer onto chitosan and its subsequent propagation and termination are based on the primary formation of radicals:

$$SO_4^{\bullet-} + H_2O \rightarrow HSO_4^- + {}^{\bullet}OH \tag{1}$$

$$^{\bullet}OH + Chi\text{-}H \rightarrow H_2O + {}^{\bullet}Chi \tag{2}$$

When Fe^{2+} is present, the KPS decomposition is promoted according to:

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-} \tag{3}$$
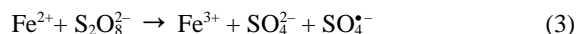
However, an excess of Fe^{2+} consumes both $^{\bullet}$OH and SO$_4^{\bullet-}$ radicals in the following manner:

$$^{\bullet}OH + Fe^{2+} \rightarrow {}^-OH + Fe^{3+} \tag{4}$$

$$SO_4^{\bullet-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \tag{5}$$
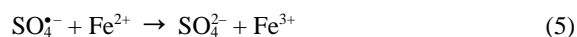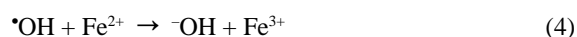
It should be noted that the convenience of using Fe^{2+} as co-catalyst depends on the relative extent of these reactions which, are affected by the particular system used. Therefore, the use of Fe^{2+} allows one to control, to some extent, the degree of grafting in order to obtain a product with desired properties.

The results obtained by studying the influence of reaction variables on grafting showed that the extent of grafting depends largely on rather small changes of some of the conditions used. These are as follows:

Amount of water

The influence of total amount of water used on %E obtained on grafting AA onto chitosan are shown in Fig. 2. The amounts of chitosan and monomer as well as molar concentration of initiator were kept constant in this
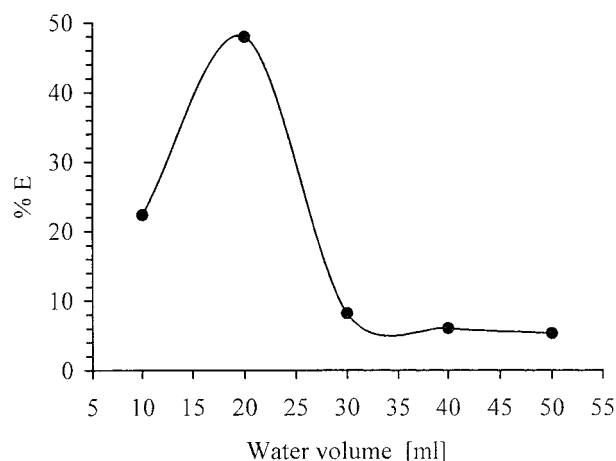
Fig. 2. Effect of the amount of water on percentage of grafting (%E). Reaction conditions: [KPS] (10^{-2} M); [FAS] (6×10^{-5} M); chitosan, 0.3 g; acrylic acid, 2 ml; temp. 70 °C; time, 120 min

Fig. 3. Effect of KPS concentration on percentage of grafting (%E). Reaction conditions: [FAS] (6×10^{-5} M); chitosan, 0.3 g; acrylic acid, 2 ml; time 120 min; temp. 70 °C; H_2O, 20 ml

Fig. 4. Effect of FAS concentration on percentage of grafting (%E). Reaction conditions: [KPS] (10^{-2} M); chitosan 0.3 g; acrylic acid, 2 ml; time, 120 min; temp. 70 °C; H_2O, 20 ml

case. It can be seen that after an initial increase, %E diminishes with further increase in water volume. A sharp maximum was obtained for a determined amount, in this case 20 ml. This fact can be explained by diffusion controlled phenomena. This means that whereas for less volume the diffusion becomes more difficult, for volumes greater than the optimum, the initiator could be partially deactivated due to the presence of a variety of radicals present in the reaction medium before it reaches the chitosan macromolecular chains. The minimum amount of water used in this work was 10 ml since for lower water volumes the viscosity of the medium was very high thus making the reactions difficult to handle.

Initiator system composition

The importance of this parameter was estimated starting from a set of preliminary tests with various KPS/FAS compositions and then by studying separately the effect of the KPS concentration and its combination with different FAS concentrations. In this way, by keeping all other reaction variables constant, the amount of KPS used was varied between 10^{-4} and 8×10^{-2} M. It can be observed from Fig. 3 that %E increases sharply reaching a maximum of nearly 50% at a KPS concentration of 10^{-2} M; thereafter grafting decreases to very low values at a higher KPS concentration (8×10^{-2} M). The lowering of %E from its optimum value is due to the possible combination of the chitosan macroradicals with the existing excess of free radicals that are present in the reaction medium and termination of propagating PAA grafted chains.

On the other hand, by maintaining the optimum quantity of KPS, the concentration of Fe^{2+} (FAS) was varied in the range shown in Fig. 4. It can be seen that the maximum grafting efficiency is attained when the concentra-
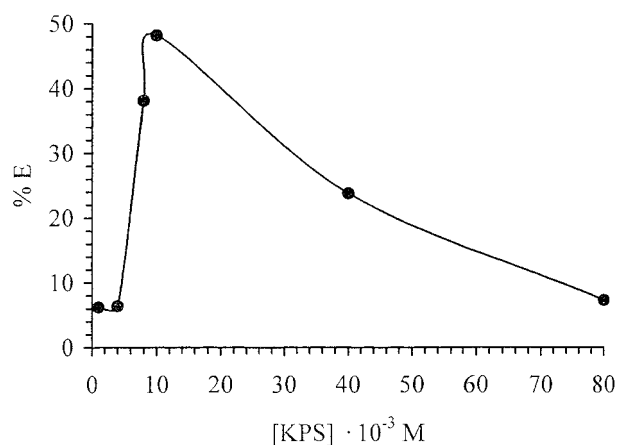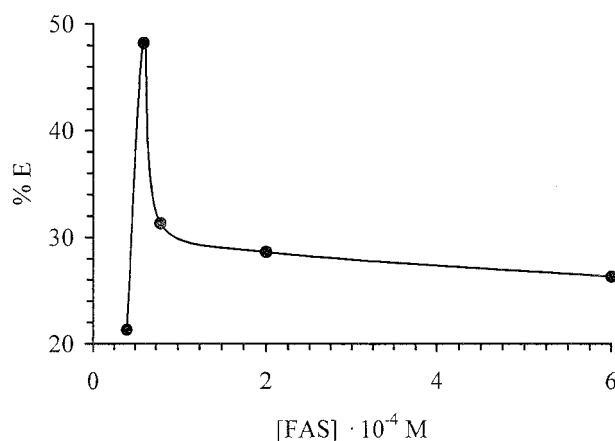
tion of Fe^{2+} reaches the value of 6×10^{-5} M. This finding can be attributed to the partial complexation of Fe^{2+} ions with amino groups of chitosan. These ions are capable of accelerating the KPS decomposition in the vicinity of the chitosan macromolecular chains, thus promoting the formation of the radical sites necessary for grafting. On the other hand, the grafting efficiency diminishes by further increasing the Fe^{2+} concentration due to the predominance of free radicals consumption by reactions 4 and 5.

Monomer concentration

It is apparent from Fig. 5 that by increasing the relative amount of monomer the %E increases markedly due to larger availability of monomer for grafting. However, when the amount of monomer is further increased, %E decreases. Once the maximum number of monomer units has been added, an excess of monomer only can change the optimum volume, affecting the diffusion controlled
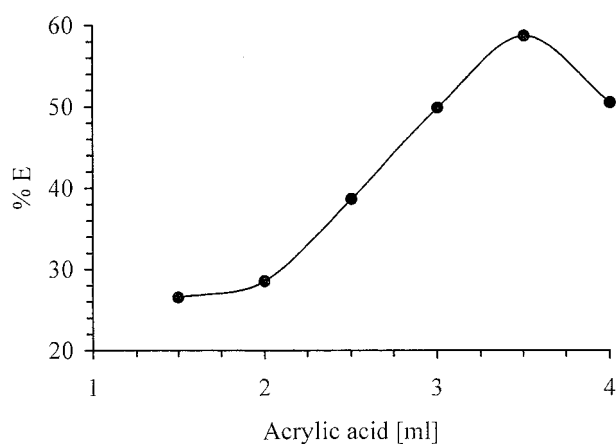
Fig. 5. Effect of monomer concentration on percentage of grafting (%E). Reaction conditions: [FAS] $(6 \times 10^{-5}$ M); [KPS] $(10^{-2}$ M); chitosan, 0.3 g; time, 120 min; temp. 70 °C; H_2O, 20 ml

Fig. 7. Effect of reaction temperature on percentage of grafting (%E). Reaction conditions: [FAS] $(6 \times 10^{-5}$ M); [KPS] $(10^{-2}$ M); chitosan, 0.3 g; acrylic acid, 3.5 ml; time, 120 min; H_2O, 20 ml

nature of the reaction which is governed by the dilution extent.

Reaction time and temperature

The influence of reaction time is shown in Fig. 6. As can be seen, the maximum %E attained after 2 h, reaches a value of 59% and then decreases slightly. Preliminary results obtained in our laboratories on this system[42] gave considerably higher value for grafting efficiency. However, a subsequent systematic study showed that this overestimation was due to the weight contribution from strongly bonded water by grafted chitosan that was not completely removed by the drying procedure used. Moreover, it should be noted that due to a very large capacity of grafted chitosan to retain water, our other previously reported values were also overestimated. This is due to the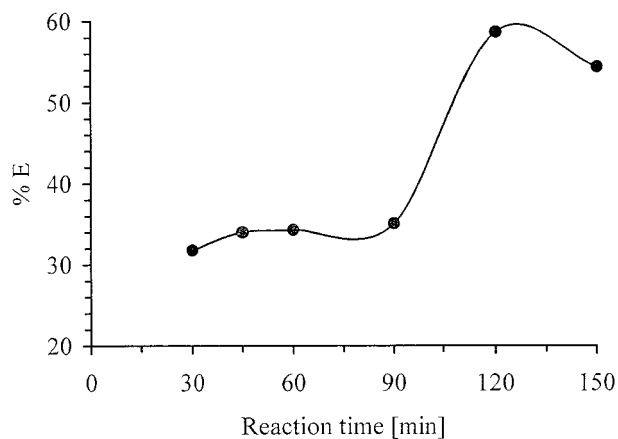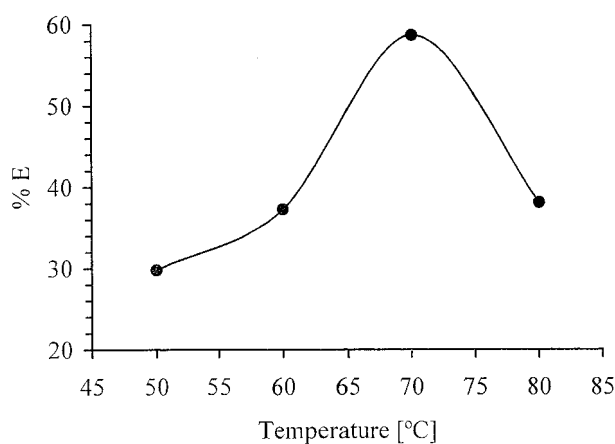 fact that the method used to calculate the %E is based on weight difference between the initial weight of dry chitosan and that of the grafted product and bonded water being difficult to remove. Although the %E of 59% is rather high, it is in the same range as values found by Kurita et al.[43] on grafting polystyrene onto mercaptochitin. The decrease in %E observed for longer reaction times cannot be explained at this stage. However, it could be due to gradual liberation of retained impurities or small molecules from grafted chitosan macromolecules.

A similar value for %E was also obtained later on by studying the effect of the variation of the reaction temperature between 50 and 80 °C and the results obtained is shown in Fig. 7. The maximum grafting efficiency is attained at a temperature of 70 °C. When the temperature was raised to 80 °C, %E diminishes sharply due to the chain transfer- and termination reactions, which are well known to be favored at higher temperatures in free radical polymerizations.

Swelling behavior

As already mentioned, all the grafted products were insoluble in water and in dilute acid solutions, a difference of chitosan and PAA which readily dissolve in these media. However, the grafted chitosan samples swell considerably in these media.

The swelling behavior of two samples grafted with 115% and 524% w/w of AA in buffer solutions at pH 2, 7.4, and 10 are shown in Fig. 8, 9, and 10 respectively. pH values of 2 and 10 were selected because of their physiological importance, while the pH value 7.4 was chosen in order to cover the intermediate pH range. Moreover, the swelling behavior of the samples was evaluated in distilled water (pH 5.8) and physiological salt solution (0.86% NaCl) in order to evaluate the potential application of these materials as superabsorbents (Fig. 11).
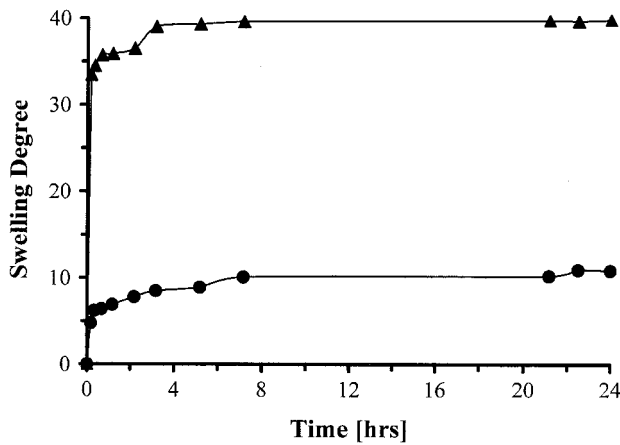

Fig. 6. Effect of reaction time on percentage of grafting (%E). Reaction conditions: [FAS] $(6 \times 10^{-5}$ M); [KPS] $(10^{-2}$ M); chitosan, 0.3 g; acrylic acid, 3.5 ml; temp. 70 °C; H_2O, 20 ml

Fig. 8. Swelling curves of chitosan grafted with poly(acrylic acid) at pH 2 (37 °C); ● %G = 115; ▲ %G = 524. (%G = percentage of grafting)
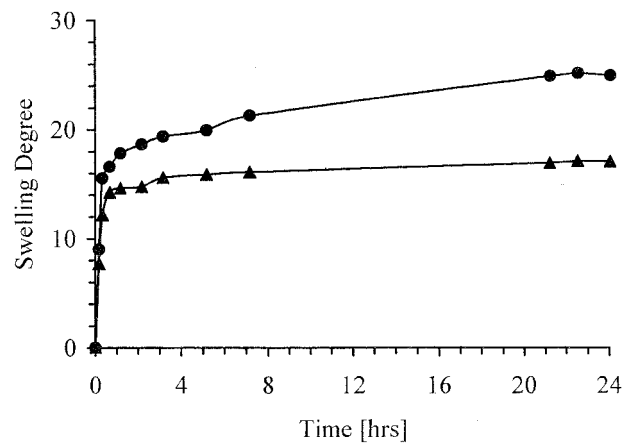

Fig. 10. Swelling curves of chitosan grafted with poly(acrylic acid) at pH 10 (37 °C): ● %G = 115; ▲ %G = 524. (%G = percentage of grafting)
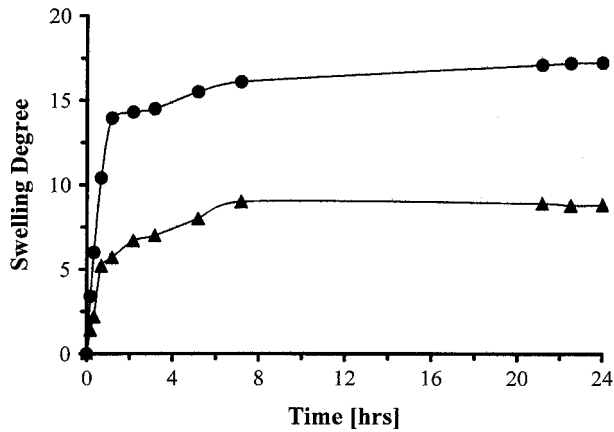

Fig. 9. Swelling curves of chitosan grafted with poly(acrylic acid) at pH 7.4 (37 °C): ● %G = 115; ▲ %G = 524. (%G = percentage of grafting)
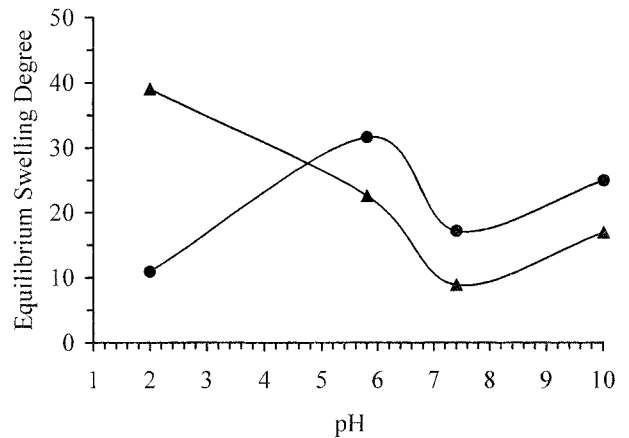

Fig. 11. Equilibrium swelling degree at 37 °C as function of pH for chitosan grafted with poly(acrylic acid): ● %G = 115; ▲ %G = 524 (%G = percentage of grafting)

Fig. 8 shows the swelling behavior of chitosan grafted with 115% and 524% PAA at pH 2. It can be seen that the sample with higher grafting shows enhanced swelling compared with the sample with lower percentage of grafting. Inverted results, as compared with the case of pH 2, were observed by determining the corresponding swelling at pH 7.4 (Fig. 9). This unusual behavior could be due to the amphiphilic nature of the modified chitosan. This characteristic is due to the fact that the hydrogels prepared in this work contain both, chitosan as cationic and PAA as anionic polyelectrolyte counterparts. Naturally, interchain salt bonds between amino groups of chitosan and carboxyl groups of PAA forms. Therefore, complex behavior resulting from inter- and/or intramolecular as well as possible electrostatic interactions should take place. The large swelling observed at pH 2 can be due to the dissociation of intermacromolecular ammonium salt. Moreover, the swelling degree increases with increasing number of carboxyl groups coming from the greater

degree of grafted PAA. In this case, an enhanced ammonium salt bond can be expected to form. Therefore, the higher swelling in this case is due to the dissociation of these interchain salt bonds at low pH. A similar behavior was observed by Yao et al.[44] when they studied the swelling behavior of Pectin/Chitosan complex films, in which both amino and carboxyl groups are also present.

Under more basic conditions, at pH 10 (Fig. 10), the maintenance of a similar difference between the swelling profiles is seen by comparing with that observed at pH 7.4. However, the degree of swelling at equilibrium is higher for both samples with different degrees of grafting, probably due to the predominance of the anionic character of the hydrogel. The sample with a higher degree of grafting carries a major proportion of carboxyl groups and is therefore expected to swell more at high pH values than the less grafted sample. However, a different behavior was observed, as shown in Fig. 10. This can be attributed to the more compact structure of the polymeric
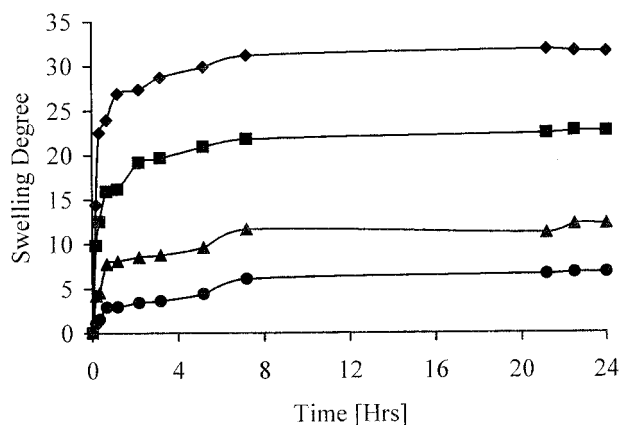
Fig. 12. Swelling curves of chitosan grafted with poly(acrylic acid) in aqueous solutions at 37 °C: ● %G = 524 (0.86% NaCl); ▲ %G = 115 (0.86% NaCl); ■ %G = 524 (H₂O); ◆ %G = 115 (H₂O) (%G = percentage of grafting)

gel with a high level of grafting. In this case the diffusion of water towards the interior of the macromolecular network is rather difficult. This effect has been also observed by Miyata et al.[45] when they studied the swelling behavior of hydroxyethylcellulose grafted with either poly-(acrylic acid) sodium salt or partially hydrolyzed polyacrylamide. They observed that the water absorbancy increases by increasing the grafting percentages up to about 150–300%, then water absorbency decreases markedly for higher grafting levels.

It is known that the properties of superabsorbents with carboxyl groups have a weakpoint in relation to its strong pH dependence of water absorbency, showing a sharp maximum at neutral pH[45, 46]. It should be noted that in contrast to this behavior, the copolymers prepared in this work were considerably less sensitive to pH, as can be seen in Fig. 11. As it was already mentioned, the sample with 524% grafted PAA shows a very high equilibrium swelling degree at pH 2. This is notably higher than the corresponding values at pH 7.4 and also in distilled water. This unusual swelling behavior at pH 2 should be due to the expansion of the macromolecular network due to an extended dissociation of the inter- and intra-chain salt bonds. Moreover, there is also an increase in positive charges inside the gel structure, caused by the protonation of the chitosan amino groups, which contributes to the network expansion. Swelling behavior in water (pH 5.8) and aqueous saline solution (NaCl 0.86% W/V; pH 6.0) are shown in Fig. 12. It can be seen from this figure that again the sample with a lower degree of grafting swells more in these media. This could be due to the more compact structure of the sample with higher grafting, as was discussed above. The water absorbencies of both samples in water without added salt is higher than the corresponding swelling in NaCl solution. This behavior is well known and can be explained as follows: in the presence of NaCl, the osmotic pressure inducing the penetration of

water inside the gel structure decreases leading to reduced swelling.

Conclusions

Chitosan was modified with poly(acrylic acid), a well-known hydrogel forming monomer, using a grafting reaction in a homogeneous phase. A large variation in the extent of grafting was observed by studying the effect of reaction parameters used for each specific reaction. In particular, the use of FAS as reducing agent in combination with KPS as a redox initiator pair has shown to be a convenient method of controlling the extent of grafting. The maximum efficiency of grafting attained in this work (52%) is rather high but it is comparable with values reported recently in the literature for the grafting of vinyl monomers onto polysaccharides. This indicates that in homogeneous systems the grafting reactions take place not only on the surface but also in the molecules of the whole substrate.

The hydrogel property of the samples with two levels of grafting was tested. The sample with 115% grafting swell considerably more in distilled water (pH 5.8) and also at higher pH values than the sample with 524% grafting. In contrast, inverse swelling behavior at pH 2 was observed. An unusual swelling behavior at pH 2 was found for the sample with 524% grafting, which swells to a greater extent than in distilled water. This was attributed to inter- and/or intramolecular interactions caused by inter-chain salt bond formation as well as the presence of both cationic and anionic charges in the macromolecular network.

[1] A. Hebeish, J. T. Guthrie, "*The Chemistry and Technology of Cellulosic Copolymers*", Springer, Berlin 1981
[2] C. E. Carraher, J. A. Moore, Ed., "*Modification of Polymers*", *Polymer Science and Technology*, Vol. 21, Plenum, New York 1982
[3] C. E. Carraher, J. H. Sperling, Ed., "*Polymer Applications of Renewable Resource Materials*" *Polymer Science and Technology*, Vol. 17, Plenum, New York 1980
[4] R. A. Young, R. M. Rowell, Ed., "*Cellulose, Structure, Modification and Hydrolysis*", Wiley, New York 1986
[5] G. F. Fanta, W. M. Doane, in: "*Modified Starches, Properties and Uses*", CRC Press, Boca Raton, FL 1987
[6] E. Piron, M. Accominotti, A. Domard, *Langmuir* **13** (6), 1653 (1997)
[7] Y. Inukai, T. Chinen, T. Masuda, Y. Kaida, S. J. Yasuda, *Analytica Chimica Acta* **371** (2–3), 187 (1998)
[8] C. H. Peng, Y. T. Wang, Y. R. Tang, *J. Appl. Polym. Sci.* **70** (3), 501 (1998)

9) Y. Baba, N. Matsumura, K. Shiomori, Y. Kawano, *Anal. Sci.* **14** (4), 687 (1998)

10) G. R. Maurelia, C. R. Zamora, M. M. Gonzalez, B.M. Guevara, C. G. Diaz, *Afinidad* **55** (473), 57 (1998)

11) O. A. C. Monteiro, C. Airoldi, *J. Colloid Interface Sci.* **212** (2), 212 (1999)

12) S. Y. Tan, Y. T. Wang, C. H. Peng, Y. R. Tang, *J. Appl. Polym. Sci.* **71** (12), 2069 (1999)

13) H. Minamisawa, H. Iwanami, N. Arai, T. Okutani, *Anal. Chim. Acta* **378** (1−3), 279 (1999)

14) N. A. Peppas, A. R. Khare, *Modern Hydrogel Delivery Systems, Advanced Drug Delivery Reviews* **11**, 1 (1993)

15) R. Pó, *"Water Absorbent Polymers: A Patent Survey", J.M.S.-Rev. Macromol. Chem. Phys.* **C34** (4), 607 (1994)

16) J. Retuert, M. Yazdani-Pedram, *Polym. Bull. (Berlin)* **31**, 559(1993)

17) D. K. Kweon, *Polym. Bull. (Berlin)* **41** (6), 645 (1998)

18) D. K. Singh, A. R. Ray, *Carbohydr. Polym.* **36** (2−3), 251 (1998)

19) L. A. Nudga, V. A. Petrova, M. F. Lebedeva, G. A. Petropavlovskii, *Russ. J. Appl. Chem, Eng. Tr.* **69** (7), 1058 (1996)

20) H. Saito, X. Wu, J. M. Harris, A. S. Hoffman, *Macromol. Rapid Commun.* **18**, 547 (1997)

21) M. Yazdani-Pedram, J. Retuert, *J. Appl. Polym. Sci.* **63**, 1321 (1997)

22) H. Caner, H. Hasipoglu, O. Yilmaz, E. Yilmaz, *Eur. Polym. J.* **34** (3−4), 493 (1998)

23) T. Ouchi, H. Nishizawa, Y. Ohya, *Polymer* **39** (21), 5171 (1998)

24) G. E. Yu, F. G. Morin, G. A. R. Nobes, R. H. Marchessault, *Macromolecules* **32** (2), 518 (1999)

25) K. D. Yao, M. X. Xu, Y. J. Yin, J. Y. Zhao, X. L. Chen, *Polym. Int.* **39**, 333 (1996)

26) R. A. A. Muzzarelli, V. Ramos, V. Stanic, B. Dubini, M. Mattioli Belmonte, G. Tosi, R. Giardino, *Carbohydr. Polym.* **36** (4), 267 (1998)

27) J. P. Chen, J. Y. Chen, *J. Mol. Catal. B-Enzyme* **5** (5−6), 483 (1998)

28) Y. E. Fang, Q. Cheng, X. B. Lu, *J. Appl. Polym. Sci.* **68** (11), 1751 (1998)

29) D. K. Singh, A. R. Ray, *J. Membr. Sci.* **155** (1), 107 (1999)

30) F. L. Mi, T. B. Wong, S. S. Shyu, S. F. Chang, *J. Appl. Polym. Sci.* **71** (5), 747 (1999)

31) M. Gandhirajan, C. S. Swaminathan, *J. Indian Chem. Soc.* **74** (3), 257 (1997)

32) C. Milot, J. McBrien, S. Allen, E. Guibal, *J. Appl. Polym. Sci.* **68** (4), 571 (1998)

33) X. P. Wang, Z. Q. Shen, F. Y. Zhang, *J. Appl. Polym. Sci.* **69** (10), 2035 (1998)

34) K. Yoshizuka, K. Fujikawa, K. Inoue, *J. Membr. Sci.* **137** (1−2), 201 (1997)

35) K. Inui, K. Tsukamoto, T. Miyata, T. Uragami, *J. Membr. Sci.* **138** (1), 67 (1998)

36) S. Y. Nam, Y. M. Lee, *J. Membr. Sci.* **153** (2), 155 (1999)

37) H. Serita, *Kobunshi Ronbunshu* **52** (7), 410 (1995)

38) J. R. S. Pan, C. P. Huang, S. C. Chen, Y. C. Chung, *Colloids Surf. A* **147** (3), 359 (1999)

39) M. Yazdani-Pedram, A. Lagos, N. Campos, J. Retuert, *Int. J. Polymeric Mat.* **18**, 25 (1992)

40) M. Yazdani-Pedram, A. Lagos, J. Retuert, R. Guerrero, P. Riquelme, *J. Macromol. Sci. Chem.* **A32**, 1037 (1995)

41) I. M. Kolthoff, A. I. Medalia, H. P. Raaen, *J. Am. Chem. Soc.* **73**, 733 (1951)

42) M. Yazdani-Pedram, J. Retuert, *Proc. MRS Fall Meeting*, Boston Massachusetts, USA, Nov. 30 1998, p. 592

43) K. Kurita, S. Hashimoto, S. Ishii, T. Mori, *Polym. Bull. (Berlin)* **36** (6), 681 (1996)

44) K. Yao, J. Liu, G. X. Cheng, X. D. Lu, H. L. Tu, J. A. Lopes da Silva, *J. Appl. Polym. Sci.* **60**, 279 (1996)

45) N. Miyata, I. Sakata, *Sen'i Gakkaishi* **47** (2), 95 (1991)

46) T. Motohashi, *Kobunshi Kagaku* **33**, 452 (1984)