Polymer Bulletin 31, 559–562 (1993)

Polymer Bulletin

Cocatalyst effect in potassium persulfate initiated grafting onto chitosan

J. Retuert[1] and M. Yazdani-Pedram[2]

[1]Depto. de Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 2777, Santiago, Chile
[2]Depto. Química Orgánica, Facultad Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile

ABSTRACT

Methyl methacrylate and methyl acrylate were grafted onto chitosan by using potassium persulfate alone as redox initiator and in combination with $MnCl_2$ and $CuCl_2$, as inorganic, and both ammonium tartrate and oxalate as organic cocatalysts. The extent of grafting was found to depend mainly on the nature of the cocatalysts used.

INTRODUCTION

The modification of the most abundant naturally occuring polysaccharides such as cellulose, starch, pectins and alginates by means of grafting synthetic polymers has been reviewed[1-6]. However, only a limited number of publications on the modification of chitin and chitosan have appeared[7-19]

Chitin (poly-ß(1→4)-N-acetyl-D-glucosamine) is distributed widely in nature forming the principal constituent of the shell of a variety of crustacea. Chitin structurally is analogous to cellulose, containing an acetamido group instead of the C-2 hydroxyl group. On the other hand, chitosan (poly-ß(1→4)-2-amino-2-deoxy-D-glucose, is the deacetylated product of chitin showing enhanced solubility in dilute acids as compared with chitin [7].

To date the published works on grafting of synthetic polymers onto chitosan refer to methyl metacrylate, styrene, acrylamide, vinyl acetate, 2-hydroxyethyl methacrylate and the aminoacids D,L-alanine and L-glutamate [8-19]. In these works, the grafting reactions are carried out mainly by using a single redox initiator.

The aim of this work was to study the effect of the nature of the reducing agents used as catalysts in combination with potassium persulfate (KPS) to form a redox initiator system. This type of initiator allows one to modify polysaccharides such as chitosan through grafting reactions. Previously we found that the efficiency of KPS as initiator is dramatically enhanced by using ferrousammonium sulfate (FAS) as reducing agent in grafting of methyl methacrylate (MMA) onto chitin [19]. Here we report the results obtained in the grafting of MMA and methyl acrylate (MA) onto chitosan using a number of reducing agents in combination with KPS as initiator.

EXPERIMENTAL

The chitosan sample was supplied from Bioquimica Austral Ltd. Its degree of deacetylation and molecular weight were 86% and 1.14 x 10^6, respectively. It was purified by extraction with acetone in a Soxhlet apparatus for 24 h, washed with methanol and then with diethyl ether and finally dried under vacuum at room temperature. MMA and MA from Fluka were distilled under vacuum and middle fractions were used. Ferrous ammonium sulfate (FAS), cooper(II)chloride and manganese(II)chloride were analytical grade reagents from Aldrich and potassium persulfate (KPS) from BDH chemicals were used as received. All solvents were from Aldrich.

Graft copolymerization

Graft copolymerizations were carried out in.50cm^3 stoppered flasks by dispersing an exact amount of dry powdered (< 200 mesh) chitosan in the aqueous initiator solution. The monomer was then added and placed in a thermostated bath. The reaction mixture was shaken occasionally during the polymerization. At the end of the polymerization, an 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 for 24 h., and the remaining product after drying to constant weight was considered to be a graft copolymer.

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

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

$$\begin{array}{c}\% \text{ Grafting} \\ \text{efficiency}\end{array} = \frac{W_2 - W_1}{W_3} \times 100$$

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

where W_1, W_2, W_3, and W_4 denote, respectively, the weight of initial chitosan, grafted chitosan after acetone extraction, methacrylic acid, and grafted chitosan before acetone extraction. The grafting was also confirmed by comparing IR spectra of chitosan with that of grafted product. The main difference observed is the appearence of the carbonyl absorption band at 1739 cm^{-1} or at 1733cm^{-1} corresponding to the grafted poly(methyl methacrylate) (PMMA) or poly(methyl acrylate) (PMA) chains, respectively. Additionally other two absorption bands at 840 and 751cm^{-1} in the case of PMMA or at 826 and 757cm^{-1} for PMA are observed. These later bands are assigned to the rocking absorptions of methylene groups in PMMA or PMA. All these bands are absent in the IR spectrum of pure chitosan.

RESULTS AND DISCUSSION

Preliminary graft copolymerizations, using KPS alone as initiator, were carried out by examining the influence of reaction parameters such as relative amount of monomer (MMA or MA) to initiator, temperature and reaction time on grafting percentage. From the results of these studies, it was observed that a convenient set of reaction conditions for 0.3g of chitosan were 2ml of monomer, 10^{-2} mole of KPS, 90 minutes and a temperature of 60 °C for a total reaction volume of 10ml. Under these reaction conditions graftings of MMA and MA onto chitosan were carried out by using different cocatalysts in combination with KPS as initiator pair. The inorganic cocatalysts used in this work were $CuCl_2 \cdot 2H_2O$ and $MnCl_2$ whereas the organic co-catalysts were ammonium oxalate $(NH_4)_2C_4H_4O_6$ and tartrate $(NH_4)_2C_2O_4\ H_2O$.

The results obtained by using a forementioned systems are shown in Table 1.

TABLE 1 Influence of initiator system on the percentages of grafting (%G), homopolymer(%H) and efficiency(%E) in the grafting of MMA and MA onto chitosan

Initiator system*	Monomer	%G	%H	%E
KPS	MMA	267.8	25.3	42.9
KPS	MA	280.8	55.8	32.8
KPS/A	MMA	197.1	12.8	31.6
KPS/A	MA	48.0	51.1	7.5
KPS/B	MMA	488.9	14.6	78.3
KPS/B	MA	335.4	15.1	52.7
KPS/C	MMA	396.9	26.4	63.6
KPS/C	MA	510.7	3.1	80.1
KPS/D	MMA	388.3	28.0	62.3
KPS/D	MA	338.5	35.2	53.1

* A= $CuCl_2 \cdot 2H_2O$; B=$MnCl_2$; C= $(NH_4)_2C_4H_4O_6$; D=$(NH_4)_2C_2O_4 \cdot H_2O$

It can be seen that a considerable variation in the %G is produced with the different co-catalysts used.

In our previous work [19] we found that the presence of Fe^{2+} ions as reducing agent enhances the grafting of MMA onto chitin. This fact was attributed to the possible adsorption of Fe^{2+} ions in the chitin molecules, thereby accelerating the decomposition of KPS in the vicinity of the polysaccharide chains and so the generation of active sites neccesary for grafting is promoted.

It is apparent that the different adsorption capacity of the cocatalysts on chitosan surface, their reducing power, the relative facility for decomposing KPS as well as the particular monomer used are the main factors affecting the grafting reactions.

From the results obtained it is evident that the use of $MnCl_2$ as cocatalysts increases substantially the grafting of both monomers on chitosan in comparison with KPS alone. This could be due to the tendency of Mn^{2+}ions to attain higher oxidation states which explains its marked reducing capacity. However, when $CuCl_2$ is used, the %G is even lower as compared with that obtained by using KPS alone. Clearly Cu^{2+} ions are not able to act as a reducing agent and therefore reduce the %G attained since the adsorbed Cu^{2+} ions on chitosan could diminish the inherent reducing character of this polysaccharide.

In contrast, ammonium tartrate and oxalate are organic reducing agents. These compounds could adsorb readily on the polysaccharide and therefore promote the formation of active sites for the graft polymerization. When these organic cocatalysts are used in grafting of MMA or MA onto chitosan the %G increases substantially as was expected.

Aknowledgements: The authors thank the Departamento Técnico de Investigación (DTI) Universidad de Chile for financial support.

REFERENCES

1. Hebeish A.,Guthrie J.T.; "The chemistry and technology of cellulosic copolymers". Springer, Berlin (1981)
2. Carraher C.E., Moore J.A., Ed.; "Modification of polymers"; Polym.Sci.and Technology, Vol21.Plenum Press, N.Y.(1982)
3. Philipp B.,Schleicher E.; Pure Appl.Chem., 51,2363 (1979)
4. Carraher C.E., Sperling J.H.,Ed.; "Polymer applications of renevable resource materials" Polym.Sci.and Technology, Vol.17,Plenum Press,N.Y.(1980)
5. Young R.A., Rowell R.M.,Ed.; "Cellulose, structure, modification and hydrolysis" Wiley N.Y.(1986)
6. Fanta G.F., Doane W.M. in "Modified starches, properties and uses" CRC Press, Boca Raton, Florida (1987)
7. Muzzarelli R.A.A., Chitin, Pergamon Press, Oxford, 1977
8. Kim K.H., Kim K.S., Shin J.S.; Polymer(Korea) 11(2),133(1987)
9. Inomoto M. ;Setchaku 26, 529 (1982).C.A. 99:54159v (1983)
10. Shijeno Y., Koichi K., Takemoto K.; J.Macromol.Chem.A17, 571 (1982)
11. Bercovich L.A., Tsyurupa M.P., Davankov V.A.; J.Polym.Sci.Polym.Chem. Ed. 21, 1281 (1983)
12. Aiba S., Minoura N., Fujiwara Y.; Int.J.Biol.Macromol.7, 120 (1985)
13. Lagos A., Reyes J.; J.Polym.Sci.Polym.Chem.Ed. 26, 985 (1988)
14. Takahashi A., Tanzawa J., Sugahara Y.; Kobunshi Ronbunshu,46, 329 (1989)
15. Cho S.H., Kim K.S., Kim K.H., Shin J.S.; Polymer (Korea)14(1), 9 (1990)
16. Kojima K.,Yoshikuni M., Suzuki T.; J.Appl.Polym.Sci.,24,1587 (1979)
17. Kurita K.,Kanari M.,Koyama Y.; Polym.Bull.(Berlin), 14, 511 (1985)
18. Kurita K., Yoshida A., Koyama Y.; Macromolecules, 21, 1579 (1988)
19. Yazdani-Pedram M., Lagos A.,Campos N.,Retuert J., Intern. J. Polymeric Mater.,18,25 (1992)

Accepted September 10, 1993 K