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

Synthesis and Characterization of Chitosan-graft-Poly(3-(trimethoxysilyl)propyl methacrylate) Initiated by Ceric (IV) Ion

M. Prabaharan[ab]; J. F. Mano[ab]
[a] Department of Polymer Engineering, University of Minho, Guimarães, Portugal [b] 3B's Research Group-Biomaterials, Biodegradables and Biomimetics, University of Minho, Braga, Portugal

Online publication date: 13 October 2010

To cite this Article Prabaharan, M. and Mano, J. F.(2007) 'Synthesis and Characterization of Chitosan-graft-Poly(3-(trimethoxysilyl)propyl methacrylate) Initiated by Ceric (IV) Ion', Journal of Macromolecular Science, Part A, 44: 5, 489 — 494
To link to this Article: DOI: 10.1080/10601320701235339
URL: http://dx.doi.org/10.1080/10601320701235339

Journal of Macromolecular Science ®, Part A: Pure and Applied Chemistry (2007) **44**, 489–494

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320701235339

Synthesis and Characterization of Chitosan-graft-Poly(3-(trimethoxysilyl)propyl methacrylate) Initiated by Ceric (IV) Ion

M. PRABAHARAN[1,2] and J. F. MANO[1,2]

[1]*Department of Polymer Engineering, University of Minho, Guimarães, Portugal*
[2]*3B's Research Group-Biomaterials, Biodegradables and Biomimetics, University of Minho, Braga, Portugal*

Received September, 2006, Accepted October, 2006

The grafting of 3-(trimethoxysilyl)propyl methacrylate (TMSPM) onto chitosan by ceric ion initiation was studied under homogeneous conditions in 2% acetic acid solution. The grafted polymer was characterized by FT-IR, ^{1}H-NMR, TGA and XRD and swelling studies. TGA results showed that the incorporation of TMSPM to the chitosan chains decreased the thermal stability of the grafted chitosan. Due to the grafting of TMSPM, the crystallinity of chitosan derivatives was found to be destroyed. The solubility of the grafted chitosan in water was improved. The effects of reaction conditions such as initiator concentration, monomer concentration, reaction temperature and reaction time were studied by determining the grafting parameters such as grafting and grafting efficiency. Under optimum conditions, the grafting parameters were achieved as 1440 and 97%, respectively.

Keywords: chitosan; 3-(trimethoxysilyl)propyl methacrylate; graft copolymerization; ceric ammonium nitrate; thermal studies

1 Introduction

Chitosan, poly[β-(1-4)-linked-2-amino-2-deoxy-*O*-glucose], is chemically prepared by *N*-deacetylation of naturally-occurring chitin, which is the second most abundant natural polysaccharide and exists largely in the marine crustacean. It displays interesting properties such as biocompatibility, biodegradability (1, 2) and its degradation products are non-toxic, non-immunogenic and non-carcinogenic (3, 4). It has been shown to be a reactive and functional polymer which has a wide range of applications in biomedicine, pharmacology, waste water treatment and agriculture. Recently, there has been growing interest in chemical modification of chitosan to improve its solubility and widen its applications (5–11). Among various methods, graft copolymerization is most attractive because it is a useful technique for modifying the chemical and physical properties of chitosan. Graft copolymerization of vinyl monomers onto chitosan and other natural polymers can introduce desired properties and enlarge the field of potential applications by choosing various types of side chains. Recently, researchers have shown that after primary deviation followed by graft modification; chitosan would achieve much improved water solubility and bioactivities such as antibacterial and antioxidant properties (12–14). Grafting chitosan is a common way to improve chitosan properties such as increasing chelating or complexation properties, bacteriostatic effect or enhancing adsorption properties (15–19). Although the grafting of chitosan modifies its properties, it is possible to maintain some interesting characteristics such as mucoadhesivity (20), biocompatibility (21, 22) and biodegradability (23, 24).

In recent years, a number of initiator systems such as, ceric ammonium nitrate (CAN), ammonium persulfate (APS), potassium persulfate (KPS) and ferrous ammonium sulfate (FAS) have been developed to initiate grafting copolymerization (25, 26). By using these initiator systems, chitosan has been graft copolymerized onto butyl acrylate (27), 2- acrylamido-2-methylpropane-sulfonic acid (28), 4-vinylpyridine (29), acrylamide (30), acrylic acid (30), poly(*N*, *N*-dimethyl-*N*-methacryloxyethyl-*N*-(3-sulfopropyl)ammonium) (31), and methylmethacrylate (32). To our knowledge, no attempt has been made to graft chitosan onto 3-(trimethoxysilyl)propyl methacrylate (TMSPM). In this paper, the grafting of silicone containing monomer, TMSPM, onto chitosan using CAN as redox initiator in acetic acid solution was investigated. The effects of reaction conditions such as initiator concentration,

Address correspondence to: M. Prabaharan, Department of Product Development, Taiwan Textile Research Institute, Tucheng, Taipei County 23674, Taiwan. Tel: +886-2-2267-0321, ext 375; Fax: +886-2-2267-5109; E-mail: mprabaharan@yahoo.com

monomer concentration, reaction temperature and reaction time on graft copolymerization were studied. Some properties of the grafted chitosan were compared with that of the unmodified chitosan.

2 Experimental

2.1 Materials

Chitosan (Viscosity average molecular weight, 6.7×10^5 g/mol; degree of *N*-deacetylation, 75–85%) was purchased from Sigma Chemical Company. Before used, it was purified by the method of dissolving in acetic acid and separating with alkali. TMSPM and CAN were supplied by Sigma Chemical Company and used as supplied. Acetic acid and sodium hydroxide used were of analytical grade.

2.2 Graft Copolymerization

A definite amount of chitosan (0.125 g) was dissolved in 25 ml acetic acid solution (2% v/v) in a two-necked round bottom flask. To control the reaction temperature, the flask was placed in a thermostated water bath fitted with a magnetic stirrer. The mixture was heated to the desired temperature with constant stirring and was bubbled by a slow stream of nitrogen for 30 min to remove the dissolved oxygen. A predetermined amount of aqueous solution of CAN in 0.1 N nitric acid was added to the flask while purged with nitrogen. The solution was agitated for 15 min, followed by the addition of a predetermined amount of TMSPM monomer. The nitrogen atmosphere was maintained throughout the reaction period. After the specific reaction period, the pH of the final suspension was adjusted to about 12 by adding a 10% NaOH solution to precipitate the product. The product was then filtered, washed with cold and hot water until neutral. TMSPM homopolymer was removed by refluxing the raw products in methanol for 5 h and then the purified copolymers were dried in a vacuum oven at 60°C. The grafting parameters were calculated using the following equations:

$$\text{Grafting (G), \%} = (W_1 - W_2)/W_2 \times 100$$

$$\text{Grafting efficiency (GE), \%} = (W_1 - W_2)/W_3 \times 100$$

where W_1, W_2, and W_3 denote the weight of graft copolymer, chitosan, and monomer charged, respectively.

2.3 Characterization

The IR spectra of chitosan derivatives were recorded with a double-beam Perkin-Elmer 1600 FT-IR spectrometer in the range of 4000–400 cm^{-1}, using KBr pellets. The ^{1}H-NMR spectra were conducted on a 300 MHz ^{1}H-NMR instrument (Varian Unity Plus 300 MHz spectrometer) with deuterium oxide. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10°C/min from 25 to 600°C. XRD experiments were performed in a Philips PW 1710 diffractometer using a Cu K_α radiation source. Solubility tests were carried out as follows: 0.1 g graft copolymers were dissolved in 20 ml of solvent under stirring for 24 h.

3 Results and Discussion

Many researchers have studied the reaction mechanism and kinetics of the reaction of vinyl monomer with starch (33), cellulose (34) and chitosan (35). It has been shown that the starch or cellulose anhydroglucose units are predominantly oxidized through C_2-C_3 bond cleavage induced by Ce^{4+} ions. In the case of chitosan, the reactive vicinal OH and NH_2 groups may form a complex with ceric ion. The complex may dissociate, giving rise to free-radical sites to the polysaccharide backbone. The general reaction mechanism for grafting chitosan onto TMSPM is given in Figure 1.

3.1 Characterization of Chitosan Derivatives

3.1.1 FT-IR and ^{1}H-NMR Analysis

The FT-IR spectra of chitosan and chitosan-*g*-TMSPM are shown in Figure 2. From the chitosan spectrum, it can be found that the distinctive absorption bands at 1650 cm^{-1} (Amide I), 1593 cm^{-1} (-NH_2 bending) and 1380 cm^{-1} (Amide III). The absorption bands at 1151 cm^{-1} (anti-symmetric stretching of the C-O-C bridge), 1080 and 1033 cm^{-1} (skeletal vibration involving the C-O stretching) are characteristics of its saccharide structure. In the IR spectrum of chitosan-*g*-TMSPM, the strong peak at 920 cm^{-1} could be assigned to the stretching vibration of Si-OH groups. The relative intensity of the band at 1000-1150 cm^{-1} of chitosan-*g*-TMSPM is much higher and broader than the intensity of 1000–1150 cm^{-1} band of chitosan. This observation could be attributed to the presence of Si-O-C bonds in chitosan-*g*-TMSPM. The new absorption band at 1723 cm^{-1} (C═O of the ester group stretching vibration) can be detected from the spectrum of chitosan-*g*-TMSPM. In addition, the intensity of absorption bands at 2850 and 2950 cm^{-1} were increased which are associated with the stretching vibration of aliphatic groups (-CH_2) present in the grafted chitosan. These bands are taken as evidence of grafting of TMSPM onto the chitosan backbone. The proton NMR spectra of chitosan and chitosan-*g*-TMSPM are presented in Figure 3(a) and (b), respectively. As shown in the spectrum of chitosan-*g*-TMSPM, the signals at 3.5–4.2 ppm are multiplet and those are originated from chitosan. In comparison with the spectrum of chitosan, the spectra of chitosan-*g*-TMSPM showed three broad signals at 0.7, 1.8 and 1.94 ppm due to the methylene and methyl protons, respectively. Also, a new peak at 3.57 ppm was observed as the -OCH_3 groups were introduced into the chitosan-*g*-TMSPM. These results indicate that TMSPM has been successfully graft copolymerized onto chitosan.

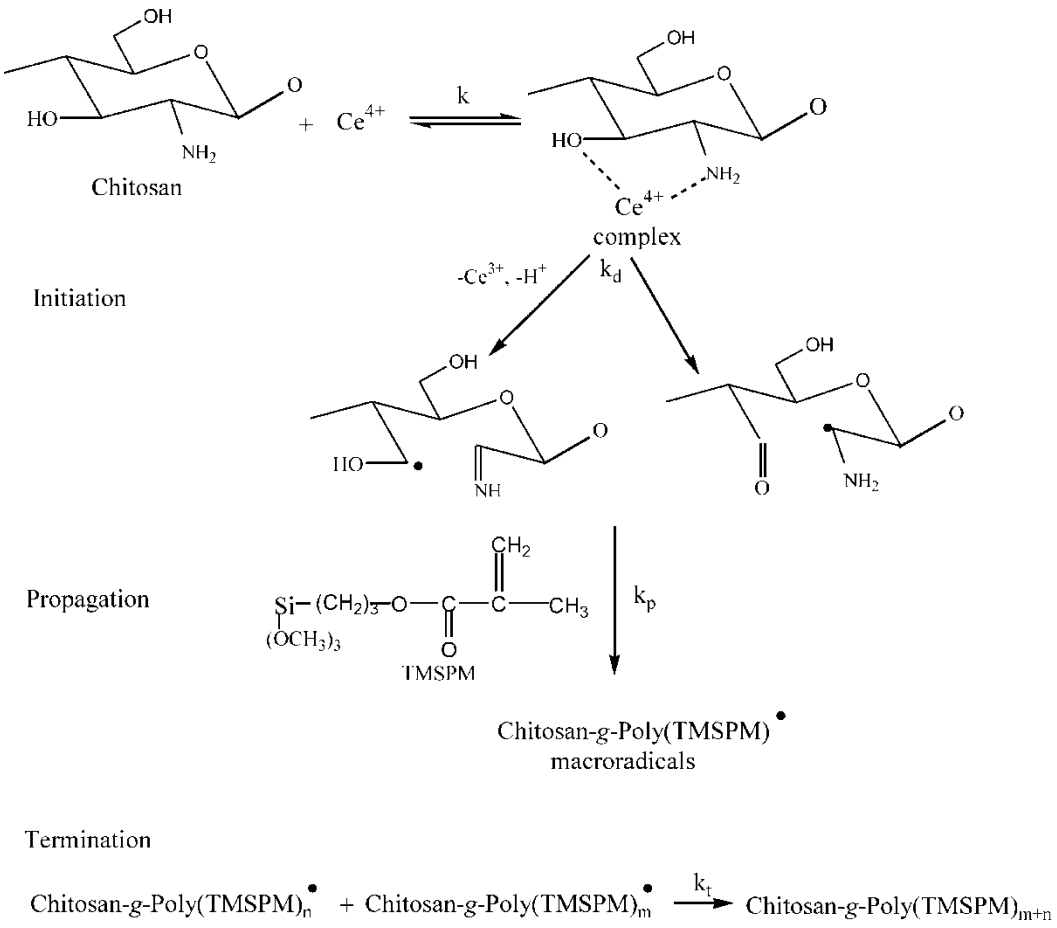

Fig. 1. General mechanism for ceric (IV) ion initiated graft copolymerization of TMSPM onto chitosan.

3.1.2 Thermal Analysis

The thermograms of chitosan and chitosan-*g*-TMSPM are shown in Figure 4. The thermogram of chitosan exhibits two distinct stages. One in the 22–120°C range with maximum decomposition rate at 70°C is associated with the evaporation of moisture, the other in the range of 220–415°C with maximum decomposition rate at 303°C is ascribed to a complex process including dehydration of the saccharide rings, depolymerization and decomposition of the acetylated and deacetylated units of the polymer (36).

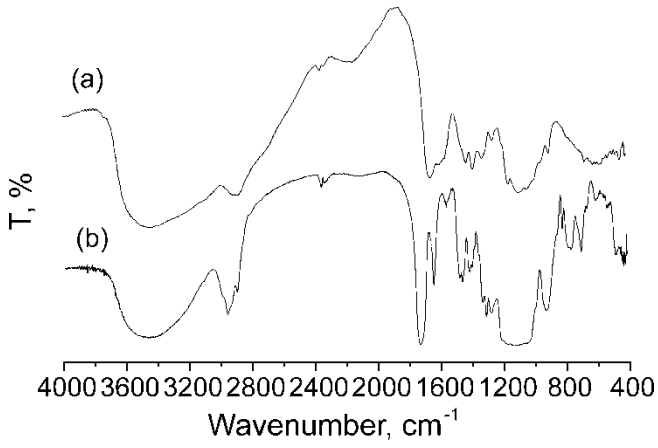

Fig. 2. FT-IR spectra of (a) chitosan and (b) chitosan-*g*-TMSPM.

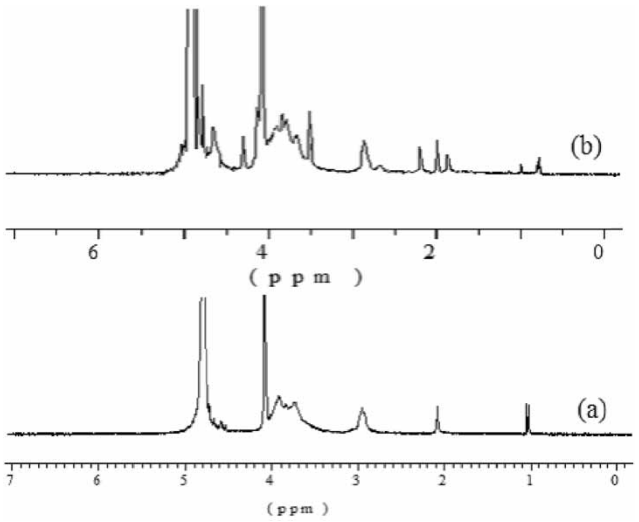

Fig. 3. ^{1}H-NMR spectra of (a) chitosan and (b) chitosan-*g*-TMSPM.

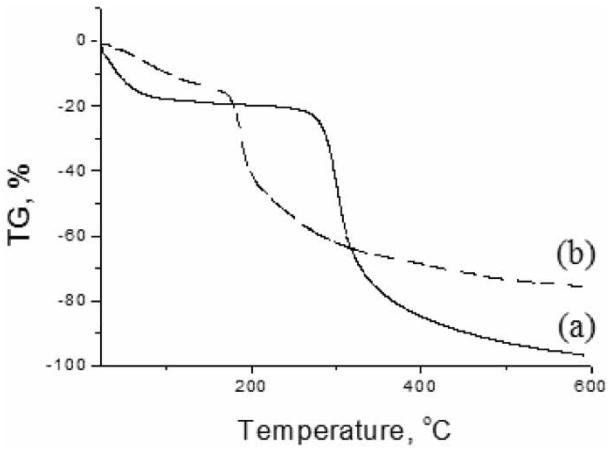

Fig. 4. Thermogravimetric curve of (a) chitosan and (b) chitosan-*g*-TMSPM.

The differential thermogravimetric curve of the grafted chitosan shows three degradation steps. For the grafted chitosan, the second degradation stage starts at about 195°C and exhibits a maximum degradation rate at approximately 200°C, which is lower than that of chitosan. In the third stage of degradation in the range of 290–525°C, the grafted chitosan degrades less slowly than that of chitosan. The appearance of this stage indicates the structure of chitosan chains has been changed, which might be due to the grafting of TMSPM chains.

3.1.3 *X-Ray Diffraction*

X-ray diffraction profiles of chitosan and its graft copolymer are shown in Figure 5. Chitosan has two reflection falls at $2\theta = 10$ and 20°. The reflection fall at $2\theta = 10°$ was assigned to crystal forms I. The strongest reflection appears at $2\theta = 20°$, which corresponds to crystal forms II (37). Compared with chitosan, the grafting decreases the intensity at both peaks. The graft copolymer shows only one broad peak at around $2\theta = 27°$. It suggested that the ability of forming a hydrogen bond of chitosan was decreased after grafting. When TMSPM was grafted onto chitosan, the original crystallinity of chitosan was destroyed.

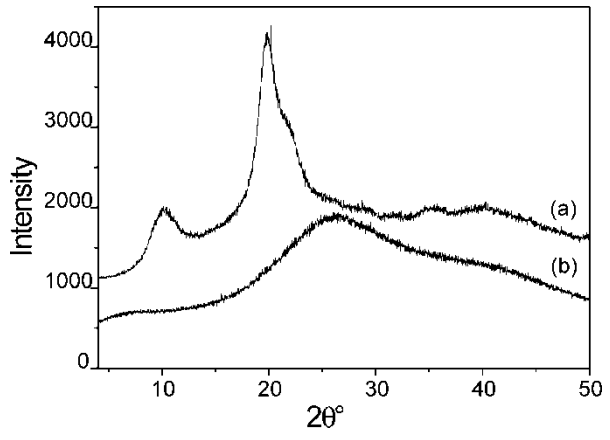

Fig. 5. X-ray diffraction pattern of (a) chitosan and (b) chitosan-*g*-TMSPM.

Table 1. Solubility of chitosan-*g*-TMSPM

Solvent	Observation
Water	Soluble (slowly)
1% Acetic acid	Soluble (slowly)
Ethanol	Insoluble
1% Acetic acid: ethanol (1:1)	Swelling
Glacial acetic acid: ethanol (1:1)	Swelling
DMF	Insoluble
DMSO	Insoluble
THF	Insoluble
Acetone	Insoluble

3.1.4 *Solubility Tests*

The results of the solubility tests are shown in Table 1. The grafted products are slowly soluble in both water and dilute acetic acid. However, they are insoluble in organic solvents and found to be swelling in 1:1 and 1:2 mixtures of glacial acetic acid and ethanol. TMSPM is soluble in ethanol, DMF and DMSO, and chitosan in glacial acetic acid. The solubility of the grafted samples in water indicates the structure of chitosan has been changed, which might be due to the grafting of TMSPM onto chitosan chains.

3.2 *Effect of the Reaction Conditions*

3.2.1 *Initiator Concentration*

To study the effect of the initiator concentration, graft copolymerization was studied at various CAN concentrations by keeping other reaction conditions constant. As shown in Figure 6, with the increase of the concentration of initiator,

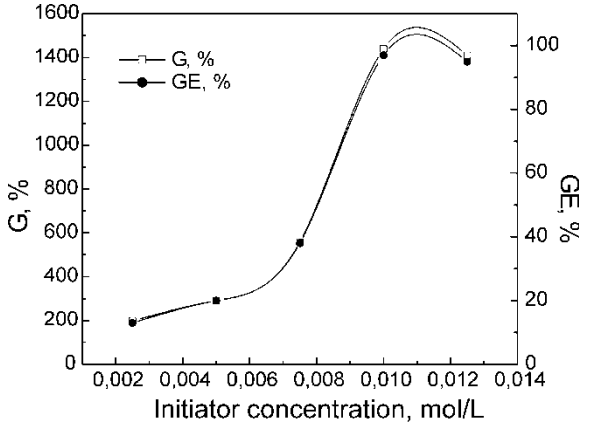

Fig. 6. Effect of initiator concentration on G and GE. (Reaction condition: Chitosan: 5 g/L; TMSPM: 0.3 mol/L; Time: 2 h; Temperature: 70°C).

G% and GE% had a slow increase at first, then a rapid increase to a maximum value, and finally a decrease. The increase of G, % and GE% may be ascribed to the increase of macroradicals. With the increase in initiator concentration, more CAN attacked the saccharide unit of chitosan, more chitosan macroradicals were generated, and thus more active sites of chitosan could react with TMSPM, and initiated the propagation reaction of TMSPM. With the further increase of CAN concentration (>0.010 mol/L), the GP% and GE% were decreased. The decrease in G% and GE% may be attributed to primary radical termination, i.e., the reaction of free radicals on the chitosan backbone with excess of ceric ion to yield oxidized products, which are incapable of initiating polymerization.

3.2.2 TMSPM Concentration

The influence of the amount of the monomer on graft copolymerization is presented in Figure 7. With the increase in concentration of TMSPM, G% increased continuously, reached the maximum value when the concentration of TMSPM was 0.4 mol/L, and then decreased. This behavior could be explained by the fact that an increase of monomer concentration led to the accumulation of monomer molecules in close proximity to the chitosan backbone. The decrease of G% after saturation could be associated with depletion in the available TMSPM concentration, as well as a reduction in the active sites on the chitosan backbone as the graft copolymerization proceeded. The decrease of GE% with the increase in TMSPM concentration may be due to the amount of TMSPM, which was more useful to copolymerization than grafting in the concentrations determined. On the other hand, TMSPM had a high affinity for its copolymer substrate, which meant that the copolymerization would occur in the polymer phase to a large extent. Thus, it was likely that homopolymerization had moreof a chance to occur, and as a result a decrease in GE% was observed.

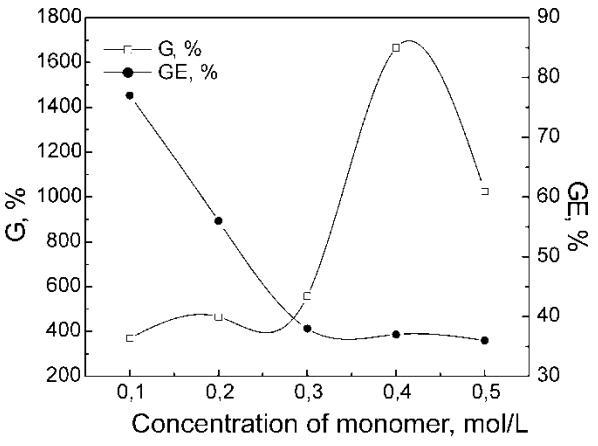

Fig. 7. Effect of monomer concentration on G and GE. (Reaction condition: Chitosan: 5 g/L; CAN: 0.0075 mol/L; Time: 2 h; Temperature: 70°C).

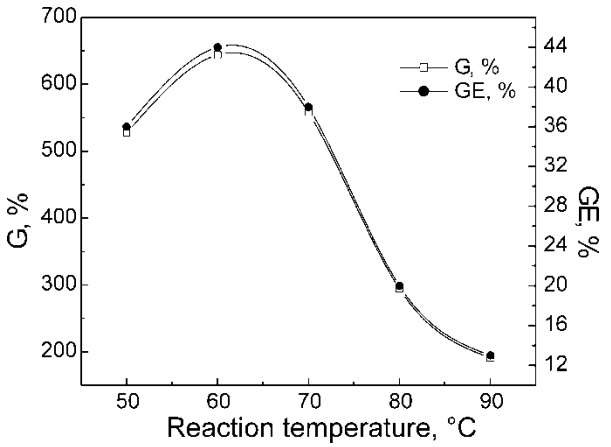

Fig. 8. Effect of reaction temperature on G and GE. (Reaction condition: Chitosan: 5 g/L; CAN: 0.0075 mol/L; TMSPM: 0.3 mol/L; Time: 2 h).

3.2.3 Reaction Temperature

To study the effect of reaction temperature on graft copolymerization, we chose the range of temperature from 50 to 90°C and the results are shown in Figure 8. As can be seen, G% and GE% increased with the increase in reaction temperature and reached a maximum at 60°C. This behavior could be attributed to the increased rate of polymerization at higher temperatures. A further increase in temperature could increase the rate of chain transfer reactions which would not result in grafting. It is also known that CAN is unstable at elevated temperatures (38). This would lead to less efficient initiation, causing a decrease in grafting. Consequently, the combined factors of less efficient initiation and increased rate of termination cause a decrease in grafting at elevated temperatures.

3.2.4 Reaction Time

The effect of reaction time on graft copolymerization is shown in Figure 9. Both G% and GE% increased gradually with the increase in the reaction time and then leveled off after 3 h. This observation could be attributed to the depletion of initiator and monomer concentration with the progress of the reaction. It is also likely that during the course of grafting, chitosan undergoes modification, as some of the amino group sites are now occupied by the graft chains, and the modified chitosan derived is not amenable for grafting as the unmodified chitosan.

4 Conclusions

Grafting of TMSPM onto a chitosan backbone was successfully achieved by CAN as a redox initiator, in 2% acetic acid solution, under homogeneous conditions. The graft copolymerization was confirmed by FT-IR and ^{1}H-NMR spectral analysis. The TMSPM grafted chitosan was characterized by TGA, XRD, and solubility studies. TGA results showed that the thermal

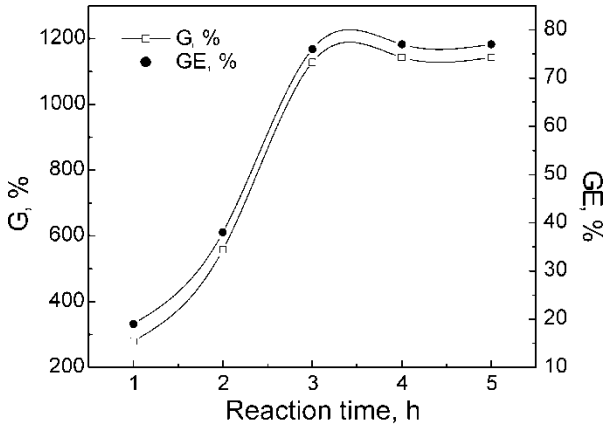

Fig. 9. Effect of reaction time on G and GE. (Reaction condition: Chitosan: 5 g/L; CAN: 0.0075 mol/L; TMSPM: 0.3 mol/L; Temperature: 70°C).

properties of chitosan are changed after grafting with TMSPM. XRD studies showed that due to the grafting of TMSPM onto the chitosan backbone, the original crystallinity of chitosan was destroyed. The incorporation of TMSPM to the chitosan chains increased its solubility in water. The reaction conditions such as initiator concentration, monomer concentration, reaction temperature and time had a great influence on grafting copolymerization. The optimum conditions for graft copolymerization were determined to be the following: chitosan amount 5 g/L; acetic acid 2% v/v; reaction temperature 70°C; TMSPM 0.3 mol/L; CAN concentration 0.01 mol/L; time 2 h. The maximum grafting and grafting efficiency obtained under these conditions were 1440 and 97%, respectively. Chitosan-*g*-TMSPM is a novel kind of silicone containing biomaterial that can be useful for several biomedical applications. Since chitosan-*g*-TMSPM is amphiphilic in nature, it may be formed by polymeric micelles in aqueous solution. These micelles can be used as a promising delivery carrier for the entrapment and controlled release of hydrophobic drugs.

5 Acknowledgements

M. Prabaharan thanks the Portuguese Foundation for Science and Technology (FCT), for awarding a post-doctoral research grant (SFRH/BPD/14671/2003). Financial support for this work was provided by FCT, through the POCTI and FEDER programs and by the European Union funded STREP Project HIPPOCRATES (NMP3-CT-2003-505758).

6 References

1. Ravikumar, M.N.V. (2000) *React. Funct. Polym.*, **46**, 1.
2. Prabaharan, M., Borges, J.P., Godinho, M.H. and Mano, J.F. (2006) *Mater. Sci. Forum*, **514–516**, 1010.
3. Chuang, W.Y., Young, T.H., Yao, C.H. and Chiu, W.Y. (1999) *Biomaterials*, **20**, 1479.
4. Prabaharan, M. and Mano, J.F. (2005) *Drug Delivery*, **12**, 41.
5. Sugimoto, M., Morimoto, M. and Sashiwa, H. (1998) *Carbohydr. Polym.*, **36**, 49.
6. Kurita, K., Kojima, T., Munakata, T., Akao, H., Mori, T., Nishiyama, Y. and Shimojoh, M. (1998) *Chem. Lett.*, **27**, 317.
7. Sashiwa, H. and Shigemasa, Y. (1999) *Carbohydr. Polym.*, **39**, 127.
8. Prabaharan, M. and Mano, J.F. (2006) *Carbohyd. Polym.*, **63**, 153.
9. Sridhari, T.R. and Dutta, P.K. (2000) *Indian J. Chem. Technol.*, **7**, 198.
10. Heras, A., Rodriguez, N.M. and Ramos, V. (2001) *Carbohydr. Polym.*, **44**, 1.
11. Lu, S., Song, X., Cao, D., Chen, Y. and Yao, K. (2004) *J. Appl. Polym. Sci.*, **91**, 3497.
12. Xie, W.M., Xu, P.X., Wang, W. and Liu, Q. (2001) *Bioorg. Med. Chem. Lett.*, **11**, 1699.
13. Jayakumar, R., Prabaharan, M., Reis, R.L. and Mano, J.F. (2005) *Carbohyd. Polym.*, **62**, 142.
14. Prabaharan, M. and Mano, J.F. (2005) *Macromol. Biosci.*, **5**, 965.
15. Yang, Z.K. and Yuan, Y. (2001) *J. Appl. Polym. Sci.*, **82**, 1838.
16. Chen, S. and Wang, Y. (2001) *J. Appl. Polym. Sci.*, **82**, 2414.
17. Jung, B.O., Kim, C.H., Choi, K.S., Lee, Y.M. and Kim, J.J. (1999) *J. Appl. Polym. Sci.*, **72**, 1713.
18. Kotze, A.F., Luessen, H.L., Leeuw, B.J.D., Boer, A.G.J.D., Verhoef, J.C. and Junginger, H.E. (1997) *Pharm. Res.*, **14**, 1197.
19. Thanou, M., Verhoef, J.C. and Junginger, H.E. (2001) *Adv. Drug Deliv. Rev.*, **52**, 117.
20. Hoffman, A.S., Chen, G., Wu, X., Ding, Z., Kabra, B., Randeri, K., Schiller, M., Ron, E., Peppas, N.A. and Brazil, C. (1997) *Polym. Prepr.*, **38**, 524.
21. Ono, K., Saito, Y., Yura, H. and Ishikawa, K. (2000) *J. Biomed. Mater. Res.*, **49**, 289.
22. Prabaharan, M., Rodriguez-Perez, M.A., de Saja, J.A. and Mano, J.F. (2006) *J. Biomed. Mater. Res. Part B: Appl. Biomater.* DOI 10.1002/jbm.b.30680.
23. Singh, D.K. and Ray, A.R. (1998) *Carbohydr. Polym.*, **36**, 251.
24. Prabaharan, M. and Mano, J.F. (2006) *Macromol. Biosci.*, **6**, 991.
25. Escamilla, G.C., Trujillo, G.R., Franco, P.J.H., Mendizabal, E. and Puig, J.E. (1997) *J. Appl. Polym. Sci.*, **66**, 339.
26. Athawala, V.D. and Lele, V. (1998) *Carbohydr. Polym.*, **35**, 21.
27. Retuert, J. and Pedram, M.Y. (1993) *Polym. Bull.*, **31**, 559.
28. Najjar, A.M.K., Yunus, W.M.Z.W., Ahmad, M.B. and Rahman, M.Z.A. (2000) *J. Appl. Polym. Sci.*, **77**, 2314.
29. Caner, H., Hasipoglu, H., Yilmaz, O. and Yilmaz, E. (1998) *Eur. Polym. J.*, **34**, 493.
30. Kurita, K., Kawata, M., Koyama, Y. and Nishimura, S.I. (1991) *J. Appl. Polym. Sci.*, **42**, 2885.
31. Zhang, J., Yuan, Y., Shen, J. and Lin, S. (2003) *Eur. Polym. J.*, **39**, 847.
32. Sun, T., Xu, P., Liu, Q., Xue, J. and Xie, W. (2003) *Eur. Polym. J.*, **39**, 189.
33. Lutfor, M., Silong, S., Yunus, W.M.Z.W., Rahman, M.Z.A. and Haron, M.A.M.J. (2000) *J. Appl. Polym. Sci.*, **77**, 784.
34. Zhang, J., Yuan, J., Yuan, Y., Shen, J. and Lin, S. (2003) *Colloids Surf.* B, **30**, 249.
35. Don, T.M., King, C.F. and Chiu, W.Y. (2002) *J. Appl. Polym. Sci.*, **86**, 3057.
36. Peniche, C., Arguelles-Monal, W. and San Roman, J. (1993) *Polym. Degrad. Stab.*, **39**, 21.
37. Dung, P.M., Rinaudo, M. and Desbriers, J. (1994) *Carbohyd. Polym.*, **24**, 209.
38. McDowall, D.J., Gupta, B.S. and Stannett, V.T. (1984) *Prog. Polym. Sci.*, **10**, 1.