Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Chitosan-Siloxane Nanocomposites. Formation, Structure, and Properties of Films

S. Fuentes [a] , J. Retuert [b] , E. Benavente [c] , H. Lozano [d] & G. González [d]

[a] Department of Physics, Faculty of Sciences, Universidad Católica del Norte, Angamos, Antofagasta, Chile

[b] Department of Material Sciences, Faculty of Mathematical and Physical Sciences, Universidad de Chile, Tupper, Santiago, Chile

[c] Department of Chemistry, Universidad Tecnológica Metropolitana, Santiago, Chile

[d] Department of Chemistry, Faculty of sciences, Universidad de Chile, Santiago, Chile

Version of record first published: 16 Jun 2008

To cite this article: S. Fuentes, J. Retuert, E. Benavente, H. Lozano & G. González (2008): Chitosan-Siloxane Nanocomposites. Formation, Structure, and Properties of Films, Molecular Crystals and Liquid Crystals, 483:1, 109-119

To link to this article: http://dx.doi.org/10.1080/15421400801900755

Mol. Cryst. Liq. Cryst., Vol. 483, pp. 109–119, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801900755

Chitosan-Siloxane Nanocomposites. Formation, Structure, and Properties of Films

S. Fuentes[1], J. Retuert[2], E. Benavente[3], H. Lozano[4], and G. González[4]

[1]Department of Physics, Faculty of Sciences, Universidad Católica del Norte, Angamos, Antofagasta, Chile
[2]Department of Material Sciences, Faculty of Mathematical and Physical Sciences, Universidad de Chile, Tupper, Santiago, Chile
[3]Department of Chemistry, Universidad Tecnológica Metropolitana, Santiago, Chile
[4]Department of Chemistry, Faculty of sciences, Universidad de Chile, Santiago, Chile

We have investigated the properties of films from polymer complexes obtained by the reaction of chitosan with poly(aminoproylethoxysiloxane) which are known to be constituted by molecularly compatibilized microdomains of the components. Specifically, we studied the influence that both, the acetylation degree the donor-acceptor activity of chitosan in the precursor solutions, have on the composition, thermal stability and morphology of the products. Comparison of the behaviour of two chitosans of similar molecular weight but different origin and acetylation degree, 12% and 17% respectively, shows that the latter is an important factor in stabilising the formation of chitosan aggregates in its solutions and films, thus making less efficient the formation of strong chitosan/polysiloxane interfaces. Dissolution of chitosan by microwave radiation improves polymer dissociation, thus increasing its donor-acceptor activity. That however also results, in this case, to disfavours strong hetero-polymer interfaces due to the large tendency of chitosan to self-aggregation.

Keywords: acetylation; chitosan-siloxane; degree; nanocomposites; polysaccharide; self-aggregationn

Research partially financed by FONDECYT (Grant 1050344), the Universidad de Chile, the Universidad Tecnológica Metropolitana and the Universidad Católica del Norte.

Address correspondence to Prof. Guillermo González, Department of Chemistry, Faculty of Sciences, Universidad de Chile, P.O. Box 653, Santiago, Chile. E-mail: ggonzale@uchile.cl

INTRODUCTION

The interest in natural polysaccharide like chitosan, chitin and cellulose has increased steadily during the last years especially because of its technological applications [1–2]. Chitosan, constituted principally by poly-(1-4)-2-amino-2-deoxy-D-glucopiranose units, (CHI), is a natural linear polymer produced by alkali metal treatment of the chitin contained in the skeletal structure of crustaceans, insects and mushrooms [1,3].

Chitosan based nanoporous films and membranes have many technical and biomedical applications mainly because of their biocompatibily. Its use for sequestering metal ions [4], for coating seeds [5] or as artificial skin [6] has been reported. The capacity of chitosan for interacting with drugs [7] or biomacromolecules like nucleic acid [8] and proteins [9] is also being widely explored. Interest is particularly focused on the formation of micro and nanoparticles in which the drug or the biocomponent is encapsulated within a chitosan envelop, which is seen as a promising method of carrying the encapsulated species into the cells.

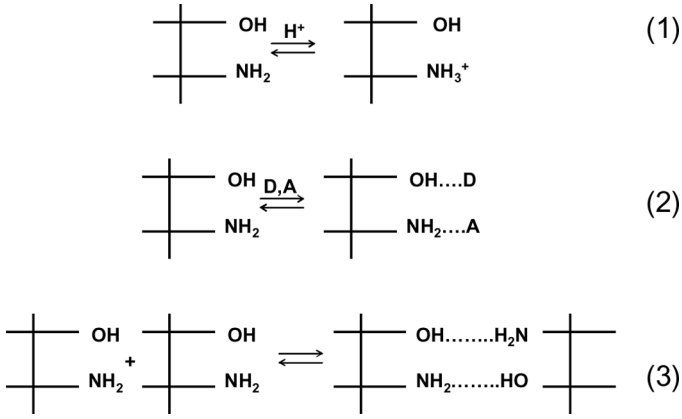
Most applications of chitosan are related to what is known of its molecular and supramolecular organization, particularly of the crystalline structure of its films and membranes, as well as of its behavior in solution. In general, the chemical activity of chitosan is mainly due to the presence of the amine group which, in addition to hydrophilic properties of the sugar moiety, leads to an interesting Lewis base activity. Thus, in addition to its ability for coordinating metal ions, chitosan is also able to form polymer aggregates and complexes stabilized by donor-acceptor interactions. Among the key features explaining the development of the chemistry and applications of chitosan, which contrasts with that of its parent polymer chitin, is its solubility in organic acid media. It is soluble in water at pH below 6.2 due to the protonation of the free amine groups [10]. Studies focused on the physical properties of these solutions have shown that, beyond the properties of the solvent and the pH of a given medium, there are intrinsic factors such as the degree of deacetylation (DD), the molecular weight and the distribution of acetyl groups which strongly affect the conformation of the chitosan molecule [11–12]. The presence of acetamide groups in the chains leads to strong intramolecular hydrogen bonds and provides hydrophobic moieties, which play an important role on the aggregation degree of chitosan in the solutions [13–15]. In spite of knowledge accumulated on chitosan chemistry, we are still far from understanding the relationship between its molecular structure and function. Appropriate knowledge on the equilibrium

between the tendency of chitosan to self-aggregation and its capacity for interacting with the guest species as well as on the influence of medium on these equilibria is still needed.

Considering the chemical functionality of chitosan, most of the reactions involved in the formation of chitosan-based aggregates and complexes, obtained from chitosan aqueous solutions under mild conditions, may be described by equilibria depicted in Scheme 1. Thus, the composition and properties of the products under given conditions are expected to be mainly determined by the relative activity of the species involved in these equilibria.

A system in which the problematic associated to the play of interactions concerning the obtaintion of chitosan homo- and heteropolymer aggregates is the preparation of new transparent ion conducting membranes by reaction of chitosan with poly(propylaminesiloxane) reported recently by us [16]. There, the formation of a single phase polymer complex with well defined stoichiometry, typical morphology and determined decomposition temperatures is described. This product is however constituted by domains of both the polysugar and the polysiloxane interacting each other through a molecularly compatibilized interface.

In the last years, microwave radiation assisted chemical reactions have deserved much attention [17], specially because of its effect in improving both the rates and selectivity of the reactions. Although in many cases, the effects of MW on reaction rates may be attributed



SCHEME 1 Equilibria involving chitosan in aqueous media under mild conditions. (1) Broensted Acid-Base interactions (2) Lewis Donor-Acceptor and Hydrogen Bonding interactions (3) Self-Association interactions.

to the alteration of hydrogen bonds, which are known to absorb efficiently this radiation [18–20], only few studies dealing the self-aggregation of chitosane have been reported.

In this article, the CHI/pAPS polymer complexes mentioned above have been used as a model for studying the relative importance of some of the variables involved in the equilibria described in Scheme 1 to the preparation and properties of chitosan polymer complexes. Specifically, we focus our attention on both, the role of chitosan acetylation degree and the effect of enhancing the chitosan donor-acceptor activity by microwave radiation on the structure and properties of the polymer complex films.

EXPERIMENTAL

Materials

Chitosan, purchased from Aldrich (CHI-2), was washed with acetone and methanol and dried to constant weight. Its average molecular weight ($Mv = 3.5 * 10^5$) was determined by light scattering. CHI-2 acetylation degree (AD) was estimated to be 17%.

Chitosan Solutions

1 g CHI-2 was dissolved in 100-ml 5% formic acid solutions by stirring about 24 h at room temperature. Resulting solutions were successively filtered through coarse- and fine-fritted funnels and then microfiltered in a Millipore system consecutively using a 3.0, 0.45 and 0.2-μm porosity membranes.

A solution containing about 0.7-g/ml polymerized poly(aminopropylsiloxane) (pAPS) was obtained by hydrolyzing 3-aminopropyltriethoxysilane (APS), Aldrich, in 0.5-M formic acid at 45°C for three days. The solvent was removed by evaporation until the solution stopped flowing. After size exclusion chromatography analysis (Bruker LC 21B with a Shodex OH pack 803-column), aminopropylsiloxane oligomers (pAPS) with an average molecular weight of about 800 was found in the remanent solution.

MW-Assisted CHI Dissolutions

Small CHI-2 (0.05 g) portions were added to 5-ml 5% formic acid solution and then put into a domestic microwave oven (SHARP R-450A, 1.55 kW at 2450-MHz frequency). A sequence of 5-s MW pulses was applied to CHI suspension until complete dissolution (660 s). In order

to avoid excess heating, temperature was controlled ($<40^{\circ}C$) after each pulse and, eventually, the sample was cooled. Thereafter the solutions were filtered as above.

Film Preparation

Two film series, using CHI both conventionally dissolved by mechanical stirring (MS) at room temperature and by microwave irradiation, were prepared; in both cases CHI-2 and pAPS solutions were mixed in proper amounts to get CHI-2/pAPS 1 : 1 molar ratios and then stirred at room temperature for 24 h. Films were then prepared by solution casting on a polypropylene film. The solvent was evaporated at room temperature. Depending on solution concentration, 50 to 100 μm-thick films were obtained.

Lithium Salt Addition

1-M lithium perchlorate ($LiClO_4$) ethanol solutions were added to mixed CHI-2/pAPS solutions in amounts calculated for preparing films with predetermined CHI/pAPS/Li^+ molar ratios. The upper limit for homogeneous salt addition may visually estimated by film transparency loss.

Characterization

Films were characterized by simultaneous thermal analysis, DTA/TGA (STA 409 NETZSCH), FT-IR spectra (Perkin Elmer 2000) and X-ray diffraction analysis (Siemens D-500). Morphological characterization was done by Scanning Electron Microscopy (Philips EM 300).

RESULTS AND DISCUSSION

In previous reports [16], the preparation of mechanically, transparent films of the polymer complex chitosan/poly(aminopropylsiloxane), CHI/pAPS, produced by the molecular compatibilization of microscopic domains of the components, was informed. The product obtained by treating Chilean chitosan (CHI-1), dissolved by mechanical stirring, with pAPS, is a pure phase, thermally more stable than the components and with a well defined stoichiometry (CHI/pAPS 0.6 : 1 molar ratio). When the films are prepared in the presence of lithium salts, their transparency is maintained after the incorporation of lithium up to a limit about 0.8 mol lithium per mol of the complex.

In order to analyze the factors determining the ability of chitosan to form molecular complexes, the experiments above were repeated but using a chitosan of similar molecular weight (CHI-2) but from different origin and with a rather lower decetylation degree (83%). Working under similar conditions, the reaction of CHI-2 with pAPS also leads to the formation of films which are in general similar to those with CHI-1 discussed above.

The similarity between both products concerning features like the X-Ray diffraction patter of this molecular complex (Fig. 1) as well as the transparency of the films is similar to those of the CH-1 discussed above. As observed in the SEM image in Figure 2, the globular morphology, rather similar in both products and the formation of a molecular complex containing domains of the components is also apparent

However there also are some significant differences between both complexes. The stoichiometry of the product with CHI-2 results to be CHI-2/pAPS 1 : 1; i.e. a higher amount of chitosan units per mol pAPS is needed. Furthermore, the nature of the chitosan also appears to influence the thermal stability of the product. Thus, as observed in Table 1, the decomposition temperature of the CHI-2/pAPS molecular complex is lower than that of the complex with CHI-1. The incorporation of lithium salt to the CHI-2 product induces changes in the morphology of the films which are much more drastic than those observed

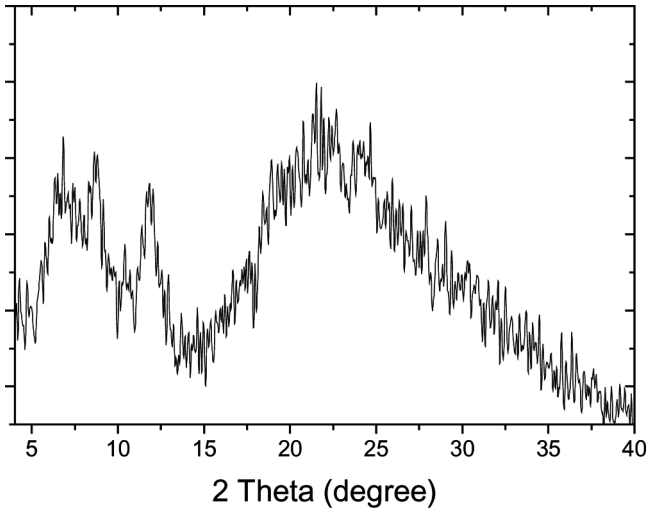


FIGURE 1 X-ray diffraction spectra CHI-2/pAPS 1 : 1 prepared from solutions generated by mechanical stirring of the film.

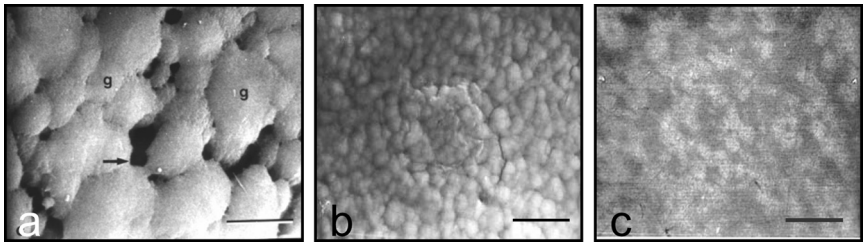


FIGURE 2 SEM micrographs of films. (a) CHI-1/pAPS 0.6 : 1 prepared from CHI-1 solutions generated by Mechanical Stirring (MS). (b) CHI-2/pAPS 1 : 1 prepared with CHI-2 dissolved by Mechanical Stirring (c) CHI-2/pAPS 1 : 1 with CHI-2 dissolved by Microwave (MW). Magnification bar: 4.4 μm.

for CHI-1. As observed in Figures 3a, b and c, even at low lithium content the globular surface is lost.

Both chitosan complexes appear to be the result of specific interactions between aggregates of the individual components. However, the different behaviour of both products commented above make necessary to consider the influence of the acetylation degree, the main difference between both bioplymers, 17% in CHI-2 vs. 12% in CHI-1. The stabilising effect of the acetyl groups on chitosan aggregates is well known [13–15]. So a higher number of acetyl groups in the polymer implies a relatively lower solubility and a grater tendency to self-aggregation of chitosan in the solutions used for obtaining the films has to be expected. The availability of donor-acceptor sites on the surfaces of the aggregates per mol of the polymer, i.e. the activity of chitosan, results therefore to be lower for CHI-2 than for CHI-1. That explains the comparatively higher amount of chitosan needed for building the polymer complex observed in the stoichiometry of the product with CHI-2. Enhanced stability of chitosan aggregates, induced by the acetyl groups already commented, appears also to be the cause of the differences observed in the effect of lithium ion on the

TABLE 1 Decomposition Temperatures of Chitosan/pAPS Polymer Complex Films Determined Differential Scanning Calorimetry Under Nitrogen Atmosphere

Sample	Decomposition temperature (°C)
CHI-1/pAPS 0.6 : 1 (MS)	360
CHI-2/pAPS 1 : 1 (MS)	326
CHI-2/pAPS 1 : 1 (MW)	308

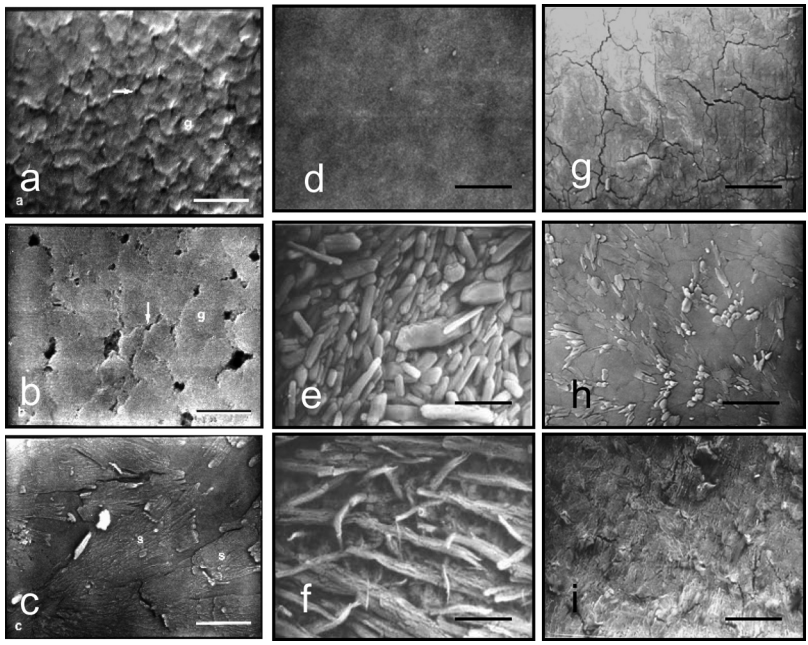


FIGURE 3 SEM micrographs of films CHI/pAPS/Li^+ prepared with increasing concentrations of $LiClO_4$ obtained from solutions of CHI-1 generated by MS (a) 1:1:0.1; (b) 1:1:0.5; (c) 1:1:0.8; of CHI-2 generated by MS (d) 1:1:0.1; (e) 1:1:0.5; (f) 1:1:0.8; and of CHI-2 generated by MW (g) 1:1:0.1; (h) 1:1:0.5; and (i) 1:1:0.8. Magnification bar: 4.4 μm.

morphology of the chitosan/pAPS polymer complexes commented here. The higher the stability of the chitosan domains in the complex, the higher the difficulty to incorporate lithium ions into chitosan domains will be. In the case of the CHI-2 polymer complex, the lithium ion appears to interact preferentially with CHI-pAPS interface, thus affecting more rapidly the morphology of the product than in case of CHI-1 (see Figs. 3d, e and f).

Considering the self-aggregation of chitosan is an important factor in determining properties of the polymer complex, experiments directed to investigate the dissolution process of this polymer were performed. Specifically, the use of microwave radiation was studied. This technique commonly associated to migration and rotation processes which inducing friction among the particles generate heat, has been also related to an efficient energy absorption by hydrogen bonded systems [18–20]. We expect therefore microwave-assisted

dissolution of chitosan to enhance the dissociation degree of the polymer in the solution. The experiments, curried out by using short radiation pulses to avoid temperature effects, lead as expected to dissolution rates about 10^2 times higher than those by the conventional magnetic stirring. Moreover, a notorious effect on the viscosity of solutions is observed, namely 170 cP for the solutions prepared by microwave radiation against 340 cP in those using mechanical stirring. In order to corroborate that the MW assisted process is mainly affecting the interchain associations and that does not produce chain degradation, chitosan from both kind of solutions was precipitated by rapid addition of alkali and, then, re-dissolved by mechanic stirring. Viscosity measurements of these solutions, reported in Table 2, show practically the same value in both cases. Since viscosity values are related to the structure and conformation of the polymer in the solution [21], specially to the inter- and intramolecular aggregation [22], results in Table 2 indicate that in our case any significant microwave-induced polymer degradation may be discarded.

Similarly to the molecular complex CHI-2/pAPS 1:1 described above, the chitosan dissolved using MW radiation, CHI-2(MW), leads to a transparent product constituted by a single phase. However the thermal stability of this polymer complex results to be rather lower than that prepared using chitosan dissolved by mechanical stirring (Table 1). Although the morphology of the product also appears to present a globular structure, Figure 2c, the shape of the lobules is much more diffuse than in the films with CHI-1(MS) and CHI-2(MS). The effects on the properties of the films produced by the incorporation of lithium ions are in this case also different. As observed in the SEM micrographics in Figures 3g, h and i, the changes in the morphology of the film surface produced by the addition of lithium are much more drastic than in the precedent cases; even at a slightly lithium content, the lobular morphology is totally destroyed. Similarly to the other chitosan coplexes, further addition of lithium leads to a

TABLE 2 Falling-Ball Viscosity at 25°C of Chitosan Solutions Prepared Under Different Experimental Conditions

Experimental conditions	Viscosity (cp)
Chitosan dissolved with MW(660 s)	203
Chitosan dissolved by mechanical stirring, precipitated and redissolved with MW (660 s)	200
Chitosan dissolved by mechanical stirring, precipitated and redissolved with MW (660 s)	136

homogenous incorporation of salt with formation of oriented flakes up to a limit where the excess of salt is clearly segregated.

The effect of using chitosan solutions obtained by MW radiation on the properties of the CHI/pAPS polymer complex films appears to go in the same direction than that produced by increasing the acetylation degree; i.e. a relative destabilization of the CHI/pAPS interface. However the way by which that is occurring is not only different but just the opposite one. Thus, the main effect of MW radiation is expected to be an enhanced dissociation degree of chitosan in the solution, increasing the activity of the donor acceptor sites available in the polymer, while the degree of acetylation works in the opposite direction, i.e. enhancing the polymer aggregation in the solution.

The enhanced activity of chitosan donor and acceptor sites achieved by MW-assisted dissolution will increase its affinity toward the formation of both homo- and hetro-suprapolymer structures. Then the formation of the molecular complex with pAPS has to compete with the self-aggregation of chitosan, thus being both, its formation and properties, determined by the relative affinity of chitosan towards the siliceous component. In the particular case discussed here, the incremental activity of chitosan induced by the MW treatment appears to favour more the homo-biopolymer interactions than those with pAPS, thus leading to polymer complexes in which the interface appears to be less stable than in the complex obtained by the same chitosan but using solutions prepared by mechanical stirring. Moreover, the greater dissociation degree in the precursor solutions is expected to produce a better packing of the polyglycoside chains in the film thus leading to an additional stabilisation of the chitosan domains in the complex.

CONCLUSIONS

The reaction of chitosan with poly(amine propylsiloxane) leads to transparent mechanically stable films formed by the molecular compatibilisation of microscopic domains of the components. The products may be considered as single phase polymer complexes with well defined stoichiometries. The composition, the thermal stability and the morphology of the films as well as the effects of the incorporation of lithium salts in the products are essentially determined by the degree of acetylation of the chitosan used for the preparation of these suprapolymer arrangements. With increasing acetylation degree increases the stability of the chitosan domains and decreases the relative stability of the chitosan-pAPS domain interface in the polymer complex.

The use of microwave radiation for assisting chitosan dissolution appears as a relevant method for regulating the properties of the polymer complexes. Since chitosan molecule dissociation in the solution increases with the radiation–thus increasing the activity of the donor and acceptor sites of chitosan and with that its reactivity, including its tendency to self-aggregation–the properties of the polymer complex will be mainly determined by the relative affinity of chitosan towards the other polymer. Higher chitosan dissociation rates permit moreover a better packing of the polymer molecules in the films, thus contributing additionally to the stability of chitosan microdomains in the polymer superstructures.

REFERENCES

[1] Knorr, D. (1984). *Food Technol.*, *38*, 85.
[2] Ravi kumar, M. (2000). *React. Funct. Polym.*, *46*, 1.
[3] Robert, G. A. (1992). *Chitin Chemistry*, Macmillan Press: London.
[4] Qin, Y., Zhu, C., & Chen, J. (2007). *Journal of Applied Polymer Science*, *105*, 527.
[5] Bautista-Baños, S., Hernández-López, M., Bosquez-Molina, E., & Wilson., C. L. (2003). *Crop Protection*, *22*, 1087.
[6] Rao, S. & Sharma, C. (1997). *Biomed. J. Mater. Res.*, *34*, 21.
[7] Nadai, M., Tajiri, C., Yoshizumi, H. (2006). *Biological & Pharmaceutical Bulletin*, *29*, 1941.
[8] Schwente, P., Ball, V., Zzalantai, B., Haiker, Y., & Vogel, J. (2002). *Biomacromolecules*, *3*, 1135.
[9] Constantine, C., Mello, S., Dupon, A., Cao, X., Santos, D., & Oliveira, O. (2003). *J. Am. Chem. Soc.*, *125*, 1805.
[10] Rinaudo, M., Pavlov, G., & Desbrieres, J. (1999). *International Journal of Polymer Analysis and Characterization*, *5*, 267.
[11] Ottoy, M., Varum, K., & Smidsrod, O. (1996). *Carbohydrate Polymer*, *29*, 17.
[12] Tsaih, M. & Chen, R. (1997). *Int. J. Biol. Macromol.*, *20*, 233.
[13] Amiji, M. (1995). *Carbohydrate Polymers*, *26*, 211.
[14] Schatz, C., Viton, C., Delair, T., Pichot, C., & Domard, A. (2003). *Biomacromolecules*, *4*, 641.
[15] Desbrieres, J. (1999). *International Journal of Polymer Analysis and Characterization*, *5*, 267.
[16] Fuentes, S., Retuert, J., Ubilla, A., Fernández, J., & González, G. (2000). *Biomacromolecules*, *1*, 239.
[17] Alimenla, B., Kumar, A., & Jamir, L. (2006). *Radiation Effects and Defects in Solids*, *161*, 687.
[18] Tagaya, H., Asiecki, J., & Casi, M. (1995). *Mater. Res. Bull.*, *30*, 1161.
[19] Wiu, T., Chan, L., Kho, S., & Wan, P. (2002). *Journal of Controlled Release*, *84*, 99.
[20] Xing, R., Liu, S., Yu, H., & Wang, P. (2005). *Carbohydrate Research*, *340*, 2150.
[21] Feng, Y., Billon, L., Grassl, B., Bastiat, G., Borisov, O., & Francois, J. (2005). *Polymer*, *46*, 9283.
[22] Esquenet, C., Terech, P., Boue, F., & Buhler, E. (2004). *Langmuir*, *20*, 3583.