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Hybrid Chitosane-Mercaptopropylsiloxane Films – Synthesis and Properties

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A series of new Chitosan/poly(mercaptopropysiloxane) hybrid films were obtained by blending mercaptopropylsiloxane oligomers (pMPS) with chitosan (CHI). The MPS oligomers were prepared by sol-gel using as precursor 3-(mercaptopropyl)-trimethoxysilane. The products were characterized by chemical, spectroscopic and morphological methods. Comparison of the thermal stability and FT-IR spectra of the films with those of the pure components indicates the formation of macromolecular aggregates with peculiar properties, different from those of their components. Scanning electron micrographies of the films revealed an organized microscopic pattern suggesting the existence of systematic interactions among their components.

Keywords Chitosan; hybrid films; mercaptopropylsiloxane; sol-gel

Introduction

Nanocomposites are in general a combination of two or more phases where at least one dimension is in the range of the nanometers. These materials which often result from the combination of different inorganic and organic substrates behave as compounds displaying properties different from those of their components. For the production of such kind of materials sol-gel processes, combining organic and inorganic polymers [1,2], appear as useful and versatile methods. The syntheses of organic-inorganic composites containing a biopolymer are of special interest for preparing biomimetic materials [3,4].

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Chitosan, poly-β(1,4)-2-amino-2-deoxy-D-glucose, is the partial deacetylated product of the alkali treatment of chitin, an abundant biopolymer contained in the shell of crustaceans. This polymer possesses many advantages such as excellent membrane-forming ability, high permeability towards water, good adhesion, biocompatibility, nontoxicity, high mechanical strength and susceptibility to chemical modification due to the presence of abundant primary amino groups [5,6]. Because of its properties, chitosan has resulted to be very suitable for several and different applications [7,8]. For instance there is great interest in the biomedical applications of chitosan. It is hemocompatible and shows bioactivity being indeed successfully applied to problems related with blood vessel surface coating and artificial human skin.

The chemistry of chitosan is mainly determined by the presence of groups with Lewis acid-base activity in the polymer. This is reflected among others in its capability for absorbing metal ions, which is particularly strong because of chelating properties of this class of macromolecules [Casilla 9,11]. The use of chitosan for protection of metal nanoparticles has been also reported [12,13]. Depending of the type of application, this polymer often needs to be modified in order to improving its mechanical, physical and/or chemical properties. Regulating its cross linking for avoiding swelling [14], functionalizing with adequate groups for inducing specific chemical recognition [15,16], and polymer blending at molecular level for improving for instance flexibility or transparence are among the approximations usually used for preparing chitosan based membranes. Since the specificity and efficiency of this kind of composed materials is related to both the molecular and supramolecular structure as well as to the crystalline structure of the products [17,18], any approach to designing new chitosan based materials with predetermined mechanical, physicochemical, and selectivity properties requires to take in account the relationships between chemical composition, structural features and chemical recognition ability merging in the composites. In such a context we have been interested in the modification of chitosan membranes by building polymer complexes with inorganic hybrid networks like oligo aminosiloxanes which, together with modifiying the mechanical properties leading to more flexible and resistent films, are able to modulate the Lewis acid-base behavior of the biopolymer. By this way interesting transparent lithium-ion conductors were obtained [19]. However, because of the amino groups chitosan behaves prominently as a "hard" Lewis base, thus being a relatively poor ligand for coordinating "soft" Lewis acids like metal surfaces or heavy metal ions. For this reason we have investigated the functionalization of this biopolymer with "soft" centres like sulphur atoms.

(3-Mercaptopropyl)trimethoxysilane (MPT) has a thiol group able to bond covalently metal surfaces [20,21]. Moreover, MPT has a reactive trimethoxysilane terminal group which may condensate by hydrolysis leading to covalently linked siloxane networks [22], in which the functionality of the sulphur atoms is mantained As reported by Cai *et al.* [23]. the hydrolysis and condensation reactions of MPT self-assembled monolayers behave as molecular adhesion layers at Ag or Au surfaces.

In this work we are reporting the modification of chitosan by the formation of polymer complexes with poly(mercaptopropylsiloxane) in order to increase and diversify the Lewis base behaviour of the biopolymer, thus enhancing its potentiality for instance as material for sequestering heavy metal species or increasing its antebacterial properties by doping with metal particles. The products described here appear to be molecularly compatibilized polymer complexes which may be obtained as self supported flexible and transparent films.

Experimental

Chitosan(CHI) purchased from Aldrich was washed with acetone and methanol and dried to constant weight. Its average molecular weight ($Mw = 3.5 * 10^5$) was determined by light scattering. CHI acetylation degree (A.D.) was estimated to be 17%. 1 g CHI was dissolved in 100 ml 5% formic acid and stirred during about 24 h at room temperature. Resulting solutions were successively filtered through coarse- and fine-fritted funnels and then, microfiltered in a Millipore system using, consecutively, membranes with pore size of 3.0, 0.45, and 0.2 μm.

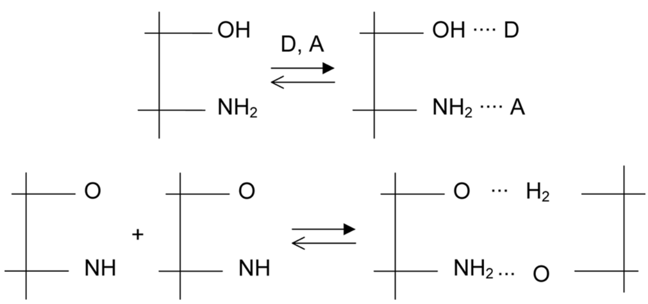
Poly(3-mercaptopropilsiloxane) (pMPS) was synthesized by a sol-gel procedure employing 3-(mercaptopropyl)-trimethoxysilane (MPTMS) from Aldrich as the precursor alkoxide, ethanol as solvent, formic acid as catalyst, and bidistilled water for the hydrolysis. 1.25 ml MPTMS dissolved in 2.5 ml of absolute ethanol were stirred with 0.1 ml 0.01 M formic acid at room temperature for three days; thereafter, the solvent was removed by evaporation until the solution stopped flowing. In this manner, a solution containing about 0.66 g of pMPS/ml was obtained.

Film Preparation. CHI and pMPS solutions were mixed in the appropriate ratios and the mixture stirred for about 24 h at room temperature. Films were then obtained by casting resulting solution onto a polypropylene film, after letting the solvents to evaporate at room temperature. Modulating the concentration of the solution, 50 to 100 μm-thick films were obtained.

Characterization of Films. The morphology of the samples was examined using a Low Vacuum Scanning Electron Microscopy (LV-SEM, JSM-5900LV) equipped with an Energy Dispersive X-ray Spectroscopy (EDX) detector. Films were characterized by simultaneous thermal analysis, DSC/TGA (STA625, Polymer Laboratories); FT-IR spectroscopy (Perkin Elmer 2000); and the optical properties were measured in the range UV-vis from 250 up to 1100 nm using a Perkin Elmer lambda 20 model with a diffuse reflectance sphere.

Results and Discussion

As previously reported by our laboratories, the reaction of chitosan with poly(aminopropylsiloxane) leads to the formation of single phase polymer complexes with well defined stoichiometries, typical morphologies and determined decomposition temperatures [25]. These products are however constituted by domains of both the polysugar and the polysiloxane interacting each other through a molecularly compatibilized interface. The composition of these phases corresponds therefore to the result of a competition between homo- and hetero-polymer complexes determined by specific donor acceptor interactions between the components, which may be roughly illustrated by equilibriums depicted in Scheme 1. Thus, any variable – such as pH, deacetilation degree and pre-treatment of chitosan solutions, or the presence of salts that could affect either the affinity of chitosan for the other polymer or its tendency to self-aggregation – will be reflected in the nature and composition of formed molecular complexes [26]. This work concerns molecular complexes of

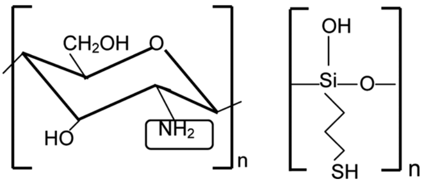


Scheme 1. Chitosan intermolecular interactions involved in the formation of polymer complexes.

chitosan with pMPS, a polymer that as observed in Scheme 2 is structurally similar to the pAPS studied before but that instead an amino group has a mercapto one. However, due to Broensted acidity of the mercapto group which is much higher than that of the amino one, the chemical reactivity of both siloxanes toward chitosan is expected to be different. In order to determine specifically the effect of such a change, both, chitosan (Aldrich, $Mw = 3.5 * 10^5$) and reaction conditions, used in the experiments described here are the same as one of those used before [25] for preparing composites with pAPS.

The preparation of pMPS was performed by controlled hydrolysis using low water content in order to optimize the formation of linear oligomers and thus favoring the interaction with chitosan and, by this way, enhancing film formation [24].

A series of experiments using different relative amounts of the polymers was performed. The compositions (molar ratios of monomer) of prepared films are consigned in Table 1. As indicated in the same table, in all the cases homogeneous, flexible and highly transparent films are obtained. Both polymers result to be fully compatible, so there being not any phase separation of the organic and inorganic phases in all the range of concentrations used in the experiments. Such a high degree of interaction between the components at molecular level is similar to that reported for well determined combinations of chitosan with silica networks obtained by sol-gel hydrolysis of tetraethoxysilane (TEOS) or aminopropyl-siloxanes (APS) [25]. In the latter however, phase separation was observed for many compositions. This, together with the fact that the preparation of transparent films of pure pMPS is not possible under similar conditions, the transparency of the composites of chitosan with pMPS appears to be a synergic effect due to the interaction between the components. This is expected to be reflected in the spectroscopic and thermal properties of the films described below.



Scheme 2. Chemical structure of chitosan and pMPS.

Table 1. Macroscopic properties of hybrid films with different compositions. T (transparent) F (flexible) and B (brittle)

Sample	CHI/MPS	Properties
CM1	1:5	T, F
CM2	1:3	T, F
CM3	1:1	T, F
CM4	1:0.5	T, F
CM5	1:0.3	T, F

FT-IR Spectra

In Figure 1 are compared the infrared spectra of the components, chitosan and pMPS, with those of the composites with molar ratios CHI/MPS 1:0.5 and 1:5. In the CHI film, the main absorption bands (Fig. 1a), namely the two bands characteristic of the amorphous form of CHI (1350 and 1380 cm^{-1}), are clearly identifiable. The bands at 1658 cm^{-1} (amide I) and 1595 cm^{-1} ($-NH_2$ bending) appears in the film as a broad band centered at 1582 cm^{-1} with a shoulder at 1635 cm^{-1}. The absorption bands at 1154 cm^{-1} (anti-symmetric stretching of C−O−C bridges), 1078 cm^{-1}, and 1032 cm^{-1} (skeletal vibrations involving the C−O stretching), characteristic of the saccharide structure, are also observed. This spectrum agrees with that of chitosan in its "amorphous" β form [27]. On the other hand, MPS exhibits the characteristic absorption band at 2566 cm^{-1} of pMPS, due to the S−H stretching vibrations (Fig. 1b).

The FT-IR spectra of all hybrid CHI/MPS composites studied here are similar to those illustrated in Figures 1c and 1d for films with molar ratios 1:0.5 and 1:5

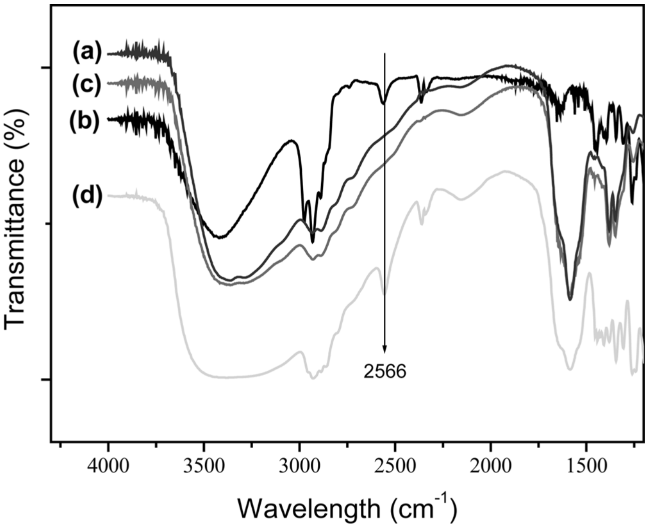


Figure 1. FT-IR spectra of films: (a) CHI; (b) pMPS; (c) MPS/CHI 0.5:1; and (d) MPS/CHI 5:1.

respectively. They in general correspond to the addition of the spectra of the components but with some slight changes. In all the molar ratios studied, the FT-IR spectra show the two absorption bands the amorphous chitosan (1350 and 1380 cm^{-1}), indicating that the CHI β-conformation remains in the composites. The characteristic bands of pMPS are also observed. Changes are mainly related to the bands involving the −OH and amino groups of chitosan and the S−H group in pMPS. The relative intensity of the band involving the $N{-}H_2$ bending in chitosan is somewhat lower in the composites. A broadening of high energy bands associated to the saccharide hydroxyls is observed. The at most notorious change is the shift of the absorption band of the −SH group from 2574 cm^{-1} in pMPS to 2555 cm^{-1} in the hybrid films. All these changes point to an interaction by intermolecular hydrogen-bonding between both polymers. Another change in the spectra (not shown in Fig. 1) was the disappearance of the band at 1154 cm^{-1}, corresponding to the anti-symmetric stretching of C−O−C, with the formation of the composites, indicating that in the latter, chitosan would acquire a more rigid structure due to the presence of pMPS.

Thermal Analysis

The thermal decomposition of studied CHI/pMPS hybrid composites was determined by Differential Thermal Analysis (DSC). The DSC patterns of the composites, illustrated in Figure 2 for samples with CHI/pAPS molar ratios of 1:0.5 and 1:5, always show a clear, single decomposition temperature in the range 150–400°C. These patterns differ from those observed for films of pure components and not any trace of charactersistic decomposition features of the latter is observed. Indeed, thermograms of chitosan films always show a single maximum corresponding to a characteristic decomposition temperature of about 300°C. In the case of pure pMPS, not any decomposition feature is observed up to 377°C. From these analyses it is possible to infer that hybrid films described here no longer correspond to a composite or blend, but to single new phases. These products can be regarded as inter-polymer complexes or as hybrid organic-inorganic nanocomposites of both organic and inorganic components. In these nanocomposites, chitosan does result thermally stabilized by the inorganic component.

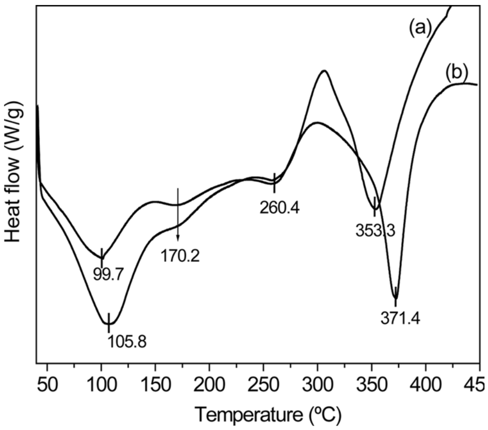


Figure 2. DSC of hybrid films with molar ratios (a) MPS/CHI 0.5:1 and (b) MPS/CHI 5:1.

UV-Vis Spectroscopy

The analysis of UV-Vis spectra illustrated in Figure 3 shows that the absorption bands characteristic of both CHI and pAPS observed at about 210 nm are notoriously red shifted in the nanocomposite. Thus, the absorption band of chitosan, assignable to transitions involving saccharide NH_2 and OH functional groups, is observed as a broad band centered at about 225 nm in the nanocomposite, while the band involving the $-$SH group in the siloxane is observed as an intense band at about 265 nm in the hybrid. The relative intensities of the two absorption bands in the hybrid films appear to correlate with molar fraction of the components. Moreover, maxima at wave lengths characteristic of the components are always absent in the spectra of the nanocomposites. Therefore the interaction between both polymers results in inducing changes in the electronic structure of both polymers. Observed red shifts are probably caused by synergic effects that stabilize the exited states of chromophores involved in the interaction between the components. These features again point to the formation of new phases with properties different from those of the components.

Scanning Electron Microscopy (SEM)

Homogeneity of prepared hybrid films was analyzed by scanning electron microscopy (SEM). Typical results are illustrated in the micrographies displayed in Figure 4, where it also is shown a homogeneity analysis performed for investigating the distribution of atoms of interest in the films.

Figure 4a and 4b concerning the nanocomposite CHI/MPS 1:0.5 show that when the amount of MPS is small, the morphology and the distribution of atoms (Fig. 4b) in the film is rather homogeneous. The film CHI/MPS 1:5 (Fig. 4c) that contains a greater amount of inorganic component leads to a morphology in which micro-domains of MPS appear to be interacting with chitosan. The image Figure 4d shows that the distributions of the elements Si, S, and O on the surface are more

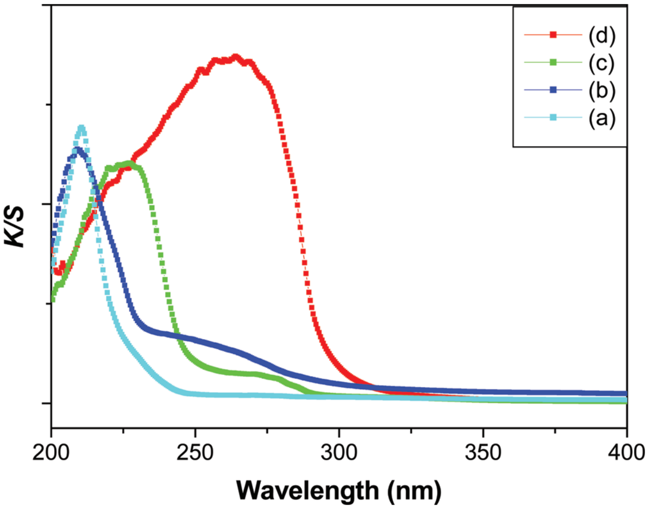


Figure 3. UV-vis absorption spectra of pure components: (a) CHI; (b) pMPS and nanocomposites with molar ratios; (c) MPS/CHI 0.5:1; and (d) MPS/CHI 5:1.

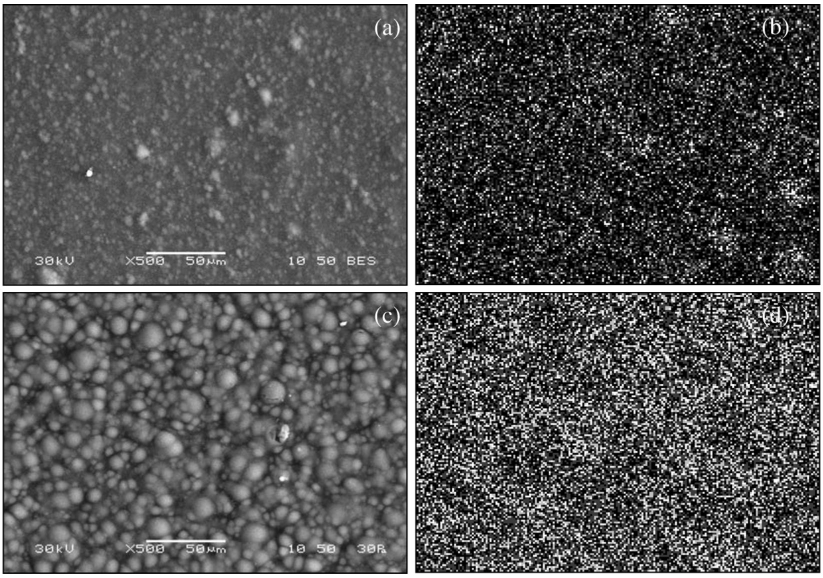


Figure 4. SEM micrographs of hybrid films: (a) MPS/CHI 0.5:1 M; and (c) MPS/CHI 5:1 M. Distributions of atoms of sin hybrid films: (b) MPS/CHI 0.5:1 M; and (d) MPS/CHI 5:1 M.

intense due to greater aggregation of one of the components (pMPS) used in the formation of the film. The degree of "roughness" and the composition of the film surface may be therefore modulated in some extent by regulating the polymers molar ratio.

Finally, it is interesting to remark that the hybrid films described in this work have high flexibility and transparency. The coincidence of these two features in the same film indicates a high degree of compatibility between the components of the film. The fact that the morphology and properties of the nanocomposites are maintained in a significant range of concentrations of the components indicates that in these products there is a balance between hetero- and homo polymer chains which is determined exclusively by the relative concentration of the components. Although the excess of some of the components implies an increase of a given homopolymer domain, the degree of molecular compatibility is maintained. This appears to be a result due to the influence of the minor component which would modulate the structure of whole product by producing intermacromolecular associations between the components that determine the uniqueness of the nanocomposite.

Conclusions

The reaction of chitosan with pMPS leads to composed materials with properties which differ from those of components. Products constitute a single phase with characteristic morphological, thermal and spectroscopic properties, independently of the mol ratio of the components.

The properties of described CHI/pMPS, together with their ability to originate flexible films of high transparence, thus implying high molecular compatibility between the components, permit to considerer the products as polymer complexes or nanocomposites. Although the nature of the products is similar to that of the polymer complexes formed by chitosan and aminopropilsiloxane (APS), the nanocomposite with pMPS are formed in a much wider range of polymer mol ratios. Like in the pMPS nanocomposites, the excess of one of the components beyond the stoichiometric hetero-polymer interaction appears to form homo-polymer domains, but maintaining the molecular compatibility in the whole film. In such materials the presence of other component, even in minor concentration, affects the structure as well as the morphological, mechanical and physicochemical properties of the whole solid. The properties of such materials may be thus tuned.

Compositions, properties, and differences with known CHI/pMPS nanocomposites may be understood considering the Broensted acidity of mercaptan group, relatively much higher than that of amine group, which leads among others to the formation of strong hydrogen bonding between both polymers, thus competing much successfully with the tendency to self-aggregation of chitosan (Scheme 2) and favoring the insertion of the inorganic polymer between chitosan chains.

The films of chitosan/poly(mercapto propyl siloxane) nanocomposites appear therefore to be very versatile materials which, while maintaining their flexibility and transparence in the visible range, present properties which may be modulated, thus being interesting and promissory for the design of tailor-made new materials.

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References

[1] Lee, E. J., Shin, D. S., Kim, H. E., Kim, H. W., Koh, Y. H., & Jang, J. H. (2009). *Biomaterials*, *30*, 743.

[2] Reisfeld, R. & Saraidarov, T. (2006). *Opt. Mater.*, *28*, 64.

[3] Ma, P. X. (2008). *Adv. Drug. Deliv. Rev.*, *60*, 184.

[4] Zhang, L., Gao, Y., Kong, L., Gong, Y., Zhao, N., & Zhang, X. (2006). *Tsinghua Science & Technology*, *11*, 421.

[5] Guibal, E. (2005). *Prog. Polym. Sci.*, *30*, 71.

[6] Ravi Kumar, M. (2000). *React. Funct. Polym.*, *46*, 1.

[7] Knorr, D. (1984). *Food Technol.*, *38*, 85.

[8] Rinaudo, M. (2006). *Progress Polym. Sci.*, *31*, 603.

[9] Shih, C., Shieh, Y., & Twu, Y. (2009). *Carbohydrate Polymers*, *78*, 309.

[10] Huang, H., Yuan, Q., & Yang, X. (2004). *Colloid Surf. B: Biointerfaces*, *39*, 31.

[11] Huang, H., Yuan, Q., & Yang, X. (2005). *J. Colloid Interface Sci.*, *282*, 26.

[12] Xiulan, H., Ruo, Y., Yaqin, C., & Yintao, S. (2008). *J. Biochem. Biophys. Methods*, *70*, 823.

[13] Ma, Y., Zhou, T., & Zhao, C. (2008). *Carbohydrate Research*, *343*, 230.

[14] Huang, H., Hu, N., Zeng, Y., & Zhou, G. (2002). *Anal. Biochem.*, *308*, 141.

[15] Dong, Y., Sakurai, K., Wu, Y., & Kondo, Y. (2003). *J. Polym. Sci. Polym. Phys.*, *41*, 2033.

[16] Kang, H. M., Cai, Y. L., & Liu, P. S. (2006). *Carbohydrate Research*, *341*, 2851.

[17] Ogawa, K., Yui, T., & Okuyama, K. (2004). *Int. J. Biol. Macromol.*, *34*, 1.

[18] Ogawa, K. (1991). *Agric. Biol. Chem.*, *55*, 2375.

[19] Fuentes, S., Retuert, J., & Gonzalez, G. (2003). *Electrochim. Acta*, *48*, 2015.

[20] Robertson, J. W., Cai, M., & Pemberton, J. E. (2001). *Adv. Mater.*, *13*, 662.

[21] Thompson, W. R. & Pemberton, J. E. (1993). *Chem. Mater.*, *5*, 241.

[22] Brinker, C. J. & Scherer, G. W. (1990). *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press: San Diego, CA.

[23] Cai, M., Ho, M., Pemberton, J. E. (2000). *Langmuir*, *16*, 3446.

[24] Brochier, M., Abdelmouleh, M., Boufi, S., Naceur, M., & Gandini, A. (2005). *J. Colloid Interface Sci.*, *289*, 261.

[25] Fuentes, S., Retuert, J., Ubilla, A., Fernández, J., & González, G. (2000). *Biomacromol.*, *1*, 239.

[26] Rinaudo, M. (2006). *Prog. Polym. Sci.*, *31*, 603.

[27] Urbanczyk, G. W. & Lipp-Symonowicz, B. (1994). *J. Appl. Polym. Sci.*, *51*, 2191.