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Transparent conducting polymer electrolyte by addition of lithium to the molecular complex chitosane–poly(aminopropyl siloxane)

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Abstract

Transparent lithium-ion conducting films were prepared by adding lithium perchlorate to a mixture of chitosane (CHI) and poly(aminopropylsiloxane) (pAPS) in a molar ratio 0.6:1 by sol–gel methods. The morphological and molecular properties, determined by scanning electron microscopy and FT-IR, respectively, depend on the lithium salt concentration. The same techniques were also used for performing a “titration” of the capacity of the film for incorporating lithium salt. Results show that about 0.8 mol lithium salt per mol chitosane can be added before the product loses the transparency and molecular compatibility characteristic of the pristine CHI/pAPS polymer complex. When lithium salt addition reaches the tolerance limit, anisotropically oriented patterns are observed in the hybrid films. Both transparency and ionic conductivity of the product appear to be related to the layered nature of formed nanocomposites. The properties of obtained films may be furthermore rationalized considering the chemical functionality and the Lewis donor–acceptor affinity of the components.

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Keywords: Chitosane; Organic–inorganic hybrid films; Lithium-ion; Ionic conductivity

1. Introduction

Interest in chitosane and other natural polysaccharide like chitin and cellulose has increased steadily during the last few years, especially because of their numerous technological applications [1,2]. In the case of chitosane, constituted principally by $\beta(1,4)$ -2-amino-2-deoxy-D-glucopyranose units, properties like its solubility and chemical functionality favor its utilization in the development of new materials [3,4]. Indeed, solutions of chitosane in organic acids lead to the formation of films useful for applications like coating and transport of drugs [5]. Products based on blends of chitosane with organic or inorganic phases appear to be promissory for the development of materials for sensors [6,7], ionic conductors for dry batteries [8] and, specially, for

biomimetic materials [9]. The chemical functionality of chitosane often induces different interactions permitting chemical recognition phenomena and molecular compatibilization of the blend components. Indeed we have recently reported [10,11] the formation of a highly transparent polymer complex of chitosane (CHI)/poly(aminopropylsiloxane) (pAPS) with a stoichiometric molar ratio 0.6:1 in which micro domains of the components are defining interfaces in the scale of the nanometers with a high degree of molecular compatibilization. The structure of this complex corresponds to a lamellar arrangement of the components domains.

In order to test hybrid organic–inorganic nanocomposites like that mentioned above in the development of chitosane-based ionic conductors, we performed the study of the capability of the complex CHI/pAPS 0.6:1 for incorporating lithium salt described in this work. Results lead to a product, which shows the layered structure and high transparency of the pristine complex displaying an ionic conductivity of the order of 10^{-6} S cm^{-1} at room temperature.

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2. Experimental

2.1. Reagents

Chitosane (CHI) (Bioquímica Austral Ltd., Chile) with an average molecular weight 3.5×10^5 , and a deacetylation degree 87.5% was washed with acetone and methanol and dried to constant weight. CHI was used as 1% solution in diluted formic acid (5%). 3-Aminopropyltriethoxysilane (APS) (Aldrich) was hydrolyzed in 0.5 M formic acid at 45 °C for 3 days leading to a solution containing 3-aminopropylsiloxane (pAPS) oligomers with $M_w \cong 800$ as determined by size-exclusion chromatography (Bruker LC 21B equipped with a Shodex OH pack 803-column). Anhydrous lithium perchlorate (Merck) was used as 1 M solution in absolute ethanol.

2.2. Film preparation

CHI and pAPS solutions in the appropriate ratios were stirred for about 24 h at room temperature. Anhydrous lithium perchlorate (Merck) was added as a 1 M solution in absolute ethanol. Films of 0.07–1.5 mm thick were prepared by solution casting on a polyethylene film and then dried by evaporation at room temperature.

2.3. Film characterization

Products were characterized by simultaneous thermal analysis, DSC/TGA (STA 625, Polymer Laboratories), Scanning Electron Microscopy (Philips EM 300), UV–vis spectroscopy (UV-2450 Shimadzu), FT-IR spectroscopy (Perkin–Elmer 2000). Electrical conductivity measurements were performed by Electrochemical Impedance Spectroscopy (EIS, PAR Model 6310) in range from 100 mHz to 100 kHz using ion-blocking gold electrodes at 25 ± 0.2 °C. Since the conductivity slightly varies with the presence of moisture, the specimens were held under vacuum, at approximately 10^{-3} Torr, beyond the time (15–30 min) necessary for reaching constant conductivity values.

3. Results and discussion

Self-supporting hybrid films were obtained starting from mixed solutions containing CHI and pAPS in a molar ratio 0.6:1 and lithium salts. These films are transparent and present ion conducting properties. In Fig. 1 can be seen that the transmittance of the films reaches about 80% in the visible spectral range. The diagrams presented in the Fig. 2, obtained from complex impedance measurements, correspond to typical ionic conductors. The highest conductivity measured in the

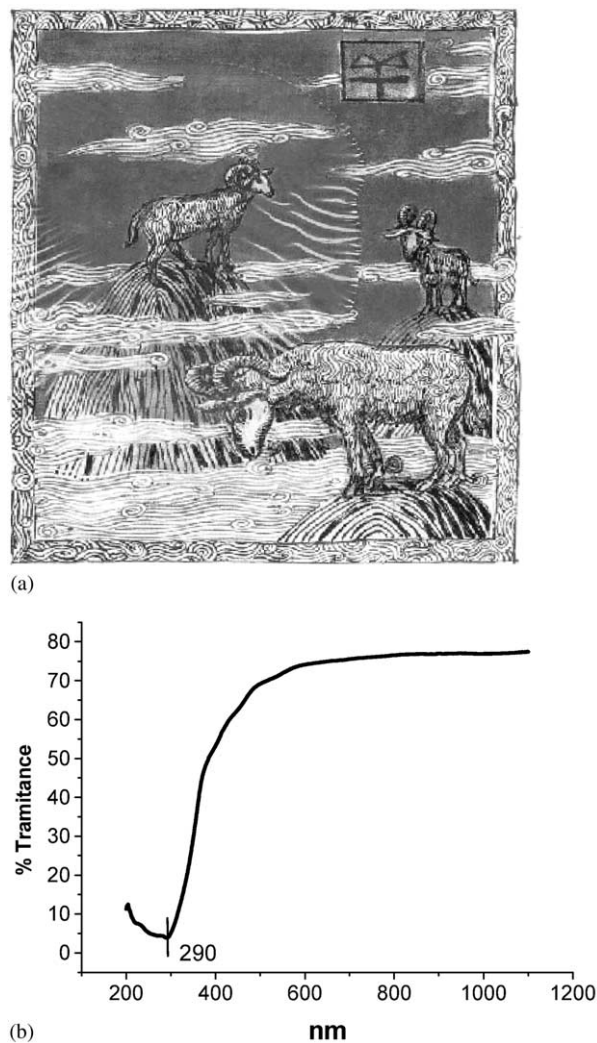


Fig. 1. (a) Transparence test and (b) transmission UV–vis spectrum of a film of the nanocomposite CHI/pAPS/LiClO₄ 0.6:1:0.8, 0.1 mm thick.

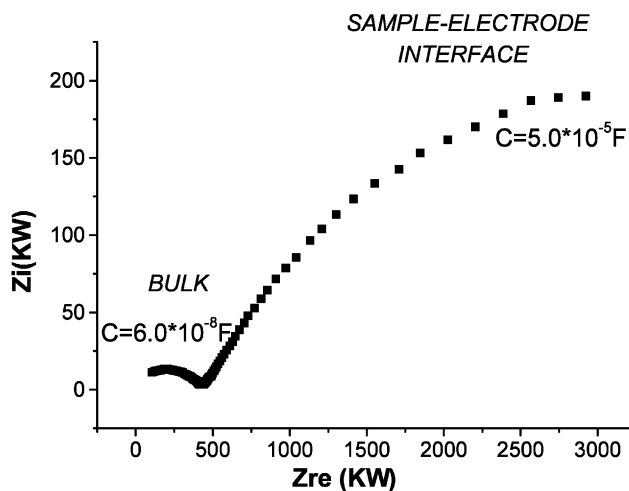


Fig. 2. Nyquist plot and corresponding equivalent circuit for the nanocomposite CHI/pAPS/LiClO₄ 0.6:1:0.8 film between ion-blocking gold electrodes.

prepared films reaches $5.5 \times 10^{-6} \text{ S cm}^{-1}$. Furthermore, it was found that the inclusion of lithium salts changes significantly the morphology of the film respect to that of the polymer complex CHI/pAPS 0.6:1 [10,11]. This can be observed in the micrographs presented in the Fig. 3 where the surface characteristics of the pristine film without lithium can be compared with those containing three different amounts of lithium perchlorate. Lithium ions transform the globular pattern of the pristine film into another much smoother one.

Changes in the microscopic organization of the films induced by lithium ions were also detected by FT-IR

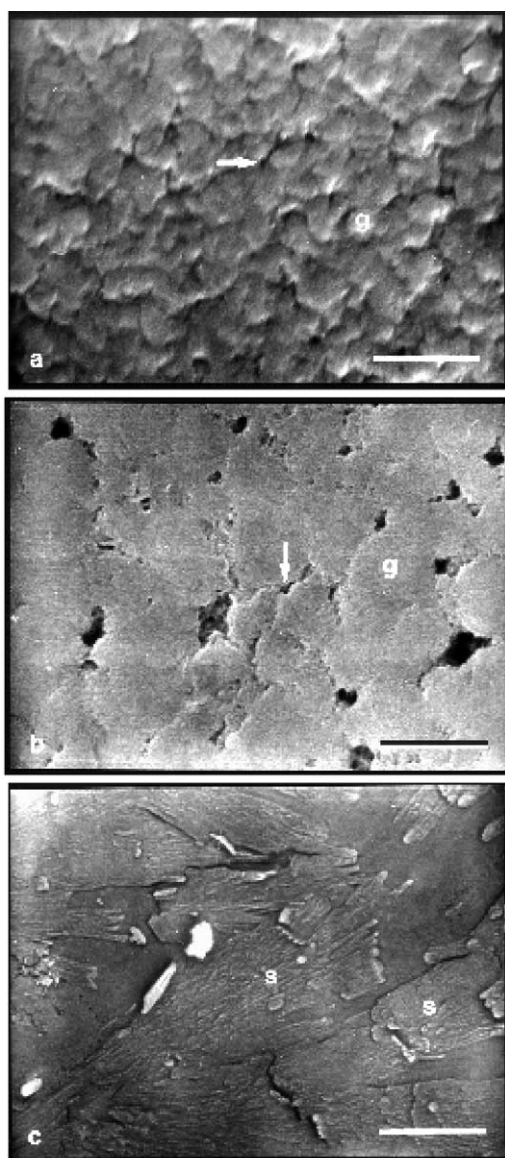


Fig. 3. Effect of the addition of LiClO_4 on the morphology of the film surface of the polymer complex CHI/pAPS/ LiClO_4 (a) 0.6:1:0.1 (b) 0.6:1:0.5 and (c) 0.6:1:0.8 mol ion Li^+ per mol CHI, respectively.

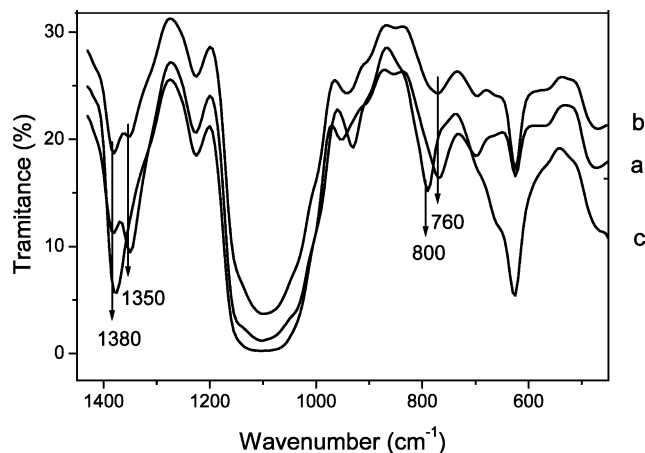


Fig. 4. Effect of the addition of LiClO_4 on the selected IR bands of films of the polymer complex CHI/pAPS/ LiClO_4 (a) 0.6:1:0.1 (b) 0.6:1:0.5 and (c) 0.6:1:0.8 mol ion Li^+ per mol CHI, respectively.

spectroscopy. As shown in Fig. 4, growing addition of lithium induces a gradual transformation of the absorption bands characteristic of chitosane, a feature that has been associated with the changes of the crystalline forms of chitosane. Samuels [12] and Urbanczyck [13] have shown that some prominent features observed in the FT-IR spectra of chitosane may be related to the crystalline structure of a particular sample. Indeed, they have identified two principal forms of chitosane: an “amorphous” (β) form and a crystalline (α) form. The β -form shows two absorption bands at 1350 and 1380 cm^{-1} and a third characteristic band at 760 cm^{-1} , while the α -form has only one peak at 1380 cm^{-1} , and the low frequency absorption is observed at 800 cm^{-1} . Thus FT-IR spectra permit to monitoring the transformation of the β into the α form. The bands at 1350 and 1380 cm^{-1} seem to arise from stretching vibrations of the methyl group in approximately 12% residual acetamido groups, which are present in the chitosane samples due to incomplete deacetylation of the parent chitin. It is well known [14] that from these two bands that at 1350 cm^{-1} is strongly affected by vicinal functional groups. Specifically, the degrees of freedom of these amide CH_3 -group vibrations are definitely influenced by intermolecular hydrogen bonding interactions undergoing the amide group with its neighborhood. Consequently, in chitosane samples with high crystallinity (α -form) where interaction capacity of the polymer is fully exploited, this band practically disappears. In the case of the nanocomposite CHI/pAPS the FT-IR spectra show two absorption bands at 1350 and 1380 cm^{-1} . However, in this case, the band at 1350 cm^{-1} is much stronger than the other one, indicating that neither the $-\text{OH}$ or the $-\text{NH}_2$ groups of chitosane or the NH_2 groups of pAPS are involved in the

intermolecular interactions affecting the residual CH_3 -amide groups.

Furthermore, residual amide groups would not participate in the intermolecular CHI/pAPS connectivity responsible of the compatibility of the components observed in our products. When lithium is added, a redistribution of the supramolecular bonding system occurs. The observed film morphology changes discussed above indicate that the pAPS domains steadily disappear along lithium addition. Meanwhile, as detected in the FT-IR spectra, the neighborhood of the amide groups in chitosane results increasingly perturbed. Such behavior may be explained on the basis of the trend of the NH_2 -groups to coordinate preferentially the Li^+ ions. Added lithium ions would be inserted into the chitosane domains saturating available amino groups and simultaneously extracting further amine ligands from the pAPS domains. Thus, along lithium addition, the globular surface became smoothly planar until reaching the saturation point where no more pAPS is available. Morphological and molecular changes as well as the visual observation of the film transparency permit to determine the upper limit for salt incorporation without producing phase separation. The maximal amount of Li^+ able to be incorporated is lower than 0.8 mol lithium per mol of the complex, i.e. the film CHI/pAPS/ Li^+ 0.6:1:0.8. In this film, the formation of new phases may be univocally detected by optical microscopy. Furthermore when a small excess of Li^+ is added, beyond the upper limit accepted by the films, opaque, fragile materials are obtained. There the excess lithium salt crystallizes in separated domains as a pAPS/ LiClO_4 complex as verified by X-ray diffraction [10]. Considering that each chitosane unit may act as a trivalent Lewis base through its hydroxyl groups and the amine nitrogen atom and that APS does it as a monovalent Lewis base, the maximal capacity of the system for coordinating tetrahedrally lithium ions would be about 0.7 mol Li^+ per mol complex ($0.6 \times 3/4 + 1.0 \times 1/4$). This value is not far from observed features.

Therefore, the interaction between chitosane molecules to form homo-molecular aggregates, the formation of interfaces of chitosane with pAPS as well as the spectroscopical and morphological changes induced by the presence of lithium ions may be described as Lewis acid–base interactions in a way that lithium is preferentially stabilized by the stronger Lewis bases available in the system, i.e. the amine groups in pAPS and chitosane. Since microstructure of chitosane due to remaining acetylamido leakage is stronger than that of the pAPS, lithium will result finally anchored to the former. The way in which these interactions lead to observed arrangement in both the pristine polymer complex and the products of the lithium addition are illustrated schematically in Fig. 5. Thus, along lithium

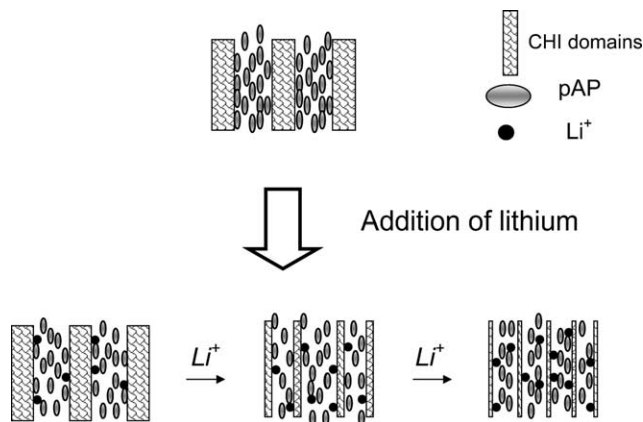


Fig. 5. Scheme illustrating the composition and arrangement of the components of the nanocomposite CHI/pAPS 0.6:1 pure, and containing LiClO_4 .

addition, the globular surface became smoothly planar until the saturation point where no more pAPS sites are available. Furthermore, microscopy studies indicate that the CHI/pAPS/ Li^+ nanocomposites show near layered structures. Such a feature can be rationalized considering the formation of layers constituted by a chitosane network, stabilized by residual acetyl amide interchain linkages, flanked by pAPS chains, sharing both the coordination sphere of Li ions. According to our experience with MoS_2 -based intercalation compounds [15,16] a layered structure like that proposed here would be propitious for obtaining fast ionic conductors.

Results discussed above indicate that in the system CHI/pAPS/ Li^+ there is a Lewis acid–base supramolecular organization whose knowledge should be useful for understanding the structure–property relationships analyzed here but also for the design of new materials.

Acknowledgements

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References

- [1] J. Mark, P. Calvert, *Mater. Sci. Eng. C1* (1994) 159.
- [2] G.A. Ozin, *Adv. Mater.* 4 (1992) 612.
- [3] P. Calvert, P. Rieke, *Chem. Mater.* 8 (1996) 1715.
- [4] H.J. Watzke, C. Dieschbourg, *Adv. Colloid Interf. Sci.* 50 (1994) 1.
- [5] A. Makishima, T. Tani, *J. Am. Ceram. Soc.* 69 (1986) 72.
- [6] D. Levy, L. Esquivias, *Adv. Mater.* 7 (1995) 120.
- [7] S. Bandyopadhyay, P.P. De, P.K. Tripathy, *J. Appl. Polym. Sci.* 61 (1996) 1813.
- [8] K. Ito, H. Ohno, *Electrochim. Acta* 43 (1998) 1247.

- [9] P. Calvert, P. Rieke, *Chem. Mater.* 8 (1996) 1715.
- [10] S. Fuentes, P.J. Retuert, G. González, E. Ruiz-Hitzky, *Int. J. Polym. Mater.* 35 (1997) 61.
- [11] S. Fuentes, P. Retuert, A. Ubilla, J. Fernández, G. González, *Biomacromolecules* 1 (2000) 239.
- [12] S. Fuentes, Ph.D. thesis, Faculty of Sciences, University of Chile, 2001.
- [13] R.J. Samuels, *J. Polym. Sci. Polym. Phys.* 19 (1981) 1081.
- [14] G.W. Urbanczyk, B. Lipp-Symonowicz, *J. Appl. Polym. Sci.* 51 (1994) 2191.
- [15] E. Benavente, M.A. Santa Ana, F. Mendizábal, G. González, *Coord. Chem. Rev.* 224 (2002) 87.
- [16] G. González, M.A. Santa Ana, V. Sanchez, M.A. Santa Ana, *Mol. Cryst. Liq. Cryst.* 353 (2002) 301.