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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

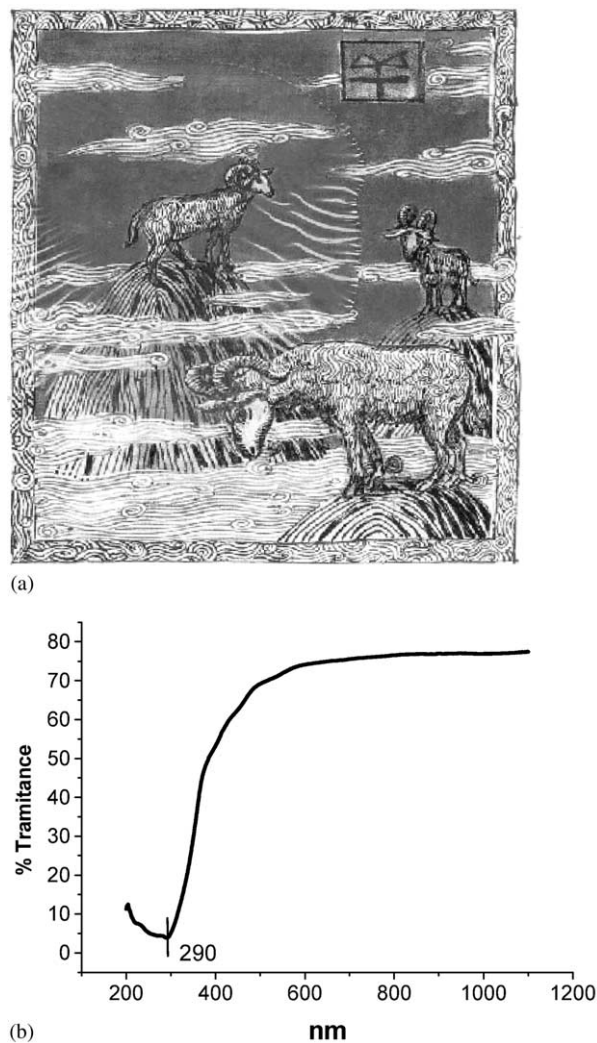


Fig. 1. (a) Transparence test and (b) transmission UV–vis spectrum of a film of the nanocomposite CHI/pAPS/LiClO₄ 0.6:1:0.8, 0.1 mm thick.

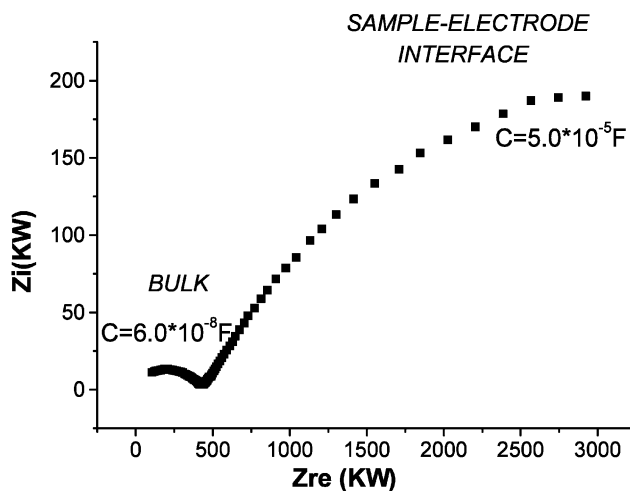


Fig. 2. Nyquist plot and corresponding equivalent circuit for the nanocomposite CHI/pAPS/LiClO₄ 0.6:1:0.8 film between ion-blocking gold electrodes.

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