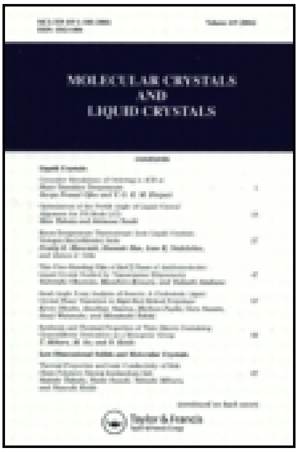

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Hybrid Chitosan-Mercaptopropyltrimethoxysilane Films with Ag and Au Nanoparticles: Synthesis and Properties

S. Fuentes [a] [d] , V. Vera [a] , F. Rivera [a] , M. Moreno [b] [d] , E. Benavente [c] [d] & G. Gonzalez [b] [d]

[a] Department of Chemistry and Pharmacy, Faculty of Sciences, Universidad Católica del Norte, Casilla, Antofagasta, Chile

[b] Department of Chemistry, Faculty of Sciences, Universidad de Chile, Casilla, Santiago, Chile

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

[d] Center for the Development of Nanoscience and Nanotechnology, CEDENNA, Santiago, Chile

Version of record first published: 30 Jul 2012.

To cite this article: S. Fuentes , V. Vera , F. Rivera , M. Moreno , E. Benavente & G. Gonzalez (2012): Hybrid Chitosan-Mercaptopropyltrimethoxysilane Films with Ag and Au Nanoparticles: Synthesis and Properties, Molecular Crystals and Liquid Crystals, 562:1, 229-241

To link to this article: http://dx.doi.org/10.1080/15421406.2012.664476

Mol. Cryst. Liq. Cryst., Vol. 562: pp. 229–241, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.664476

Hybrid Chitosan-Mercaptopropyltrimethoxysilane Films with Ag and Au Nanoparticles: Synthesis and Properties

S. FUENTES,[1,4*] V. VERA,[1] F. RIVERA,[1] M. MORENO,[2,4]
E. BENAVENTE,[3,4] AND G. GONZALEZ[2,4]

[1]Department of Chemistry and Pharmacy, Faculty of Sciences, Universidad Católica del Norte, Casilla, Antofagasta, Chile
[2]Department of Chemistry, Faculty of Sciences, Universidad de Chile, Casilla, Santiago, Chile
[3]Department of Chemistry, Universidad Tecnológica Metropolitana, Casilla, Santiago, Chile
[4]Center for the Development of Nanoscience and Nanotechnology, CEDENNA, Santiago, Chile

Flexible and transparent polymer complexes prepared by blending chitosan (CS) with about 1 M of oligo-mercaptopropilsiloxane were functionalized by incorporating silver or gold nanoparticles in a concentration range of 0.01 to 0.06 M. The heterosupramolecular polymeric materials obtained were characterized by chemical, spectroscopic, and morphological methods. Scanning electron microscope (SEM) and X-ray Spectroscopy (EDX) patterns of films indicate not only the homogeneous distribution of the components but also the morphological changes induced by the metal. Raman and UV-visible spectroscopic analysis as well as ionic conductivity after incorporation of ion–lithium point to a competition between metal–polymer end polymer–polymer interactions, which may be, to some extent, regulated by the nature and concentration of the metal. Due to the antiseptic effects of CS and noble metal nanoparticles, separately or synergistically coupled, the films produced would be potentially useful for designing tailor-made bioactive surfaces.

Keywords Chitosan; hybrid films; mercaptopropylsiloxane; metal nanoparticles

1. Introduction

Polymer complexes and composites in which the synergic combination of their components lead to particular properties that are tunable according to predetermined purposes have played an important role in the development of modern chemical, biological, and material sciences as well as applied science and technology [1,2]. Especially relevant nowadays are polymer multifunctional materials that have the ability of defining surfaces which may interact controllably with the environment, thus, providing key information for

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[*] Address correspondence to S. Fuentes, Department of Chemistry and Pharmacy, Faculty of Sciences, Universidad Católica del Norte. Casilla 1280, Antofagasta, Chile. Tel: +56-55-355383; Fax: +56-55–355495. E-mail: sfuentes@ucn.cl

innumerable types of applications. Among them, certainly, are those based on heterogeneous processes, such as catalysis, sensoring, or devices [3,4]. More recently, an interesting aspect of functional surfaces that has deserved much attention involves those fields related directly or indirectly with human health, biomedicine, and food preservation. Indeed, aspects concerning, for instance, drug delivery, septic protection, or active food packaging demand the development of new materials with active surfaces that are specially designed for predetermined purposes [5,6].

The natural polymer, the chitosan (CS), poly-[(1-4)-2-amino-2-deoxy-D-glucose], deserves special attention, being indeed one of the most studied biopolymers during the last few years. Due to the presence of large free amino and hydroxyl groups in its chains, CS offers particularly promissory physicochemical properties, including an easy formation of polycationic species, film-forming ability, good adhesion, biocompatibility, nontoxicity, high mechanical strength, and metal-ion chelation capability [7]. Moreover, CS shows interesting antibacterial, antifungal, and antitumor activity [8]. Although the mechanism of the antimicrobial action of CS is still not well known, many efforts are inverted in improving its antiseptic performance, for instance, by introducing quaternary ammonium groups in order to modify the polymer surface [9]. The CS also appears to be effective for coating the surface of medical devices and implants in order to avoid the formation of bacterial films [10]. Its protective activity was demonstrated to be significantly improved by the concomitant action of silver particles on polymer films surface [11].

In spite of, in general, the excellent properties of CS for generating bioactive films, its coating ability in biological media is often somewhat limited, especially due to the relatively high water affinity produced by the strongly hydrophilic character of its functional groups and relatively poor flexibility of the films. The properties of CS may be to some extent modified, for instance, by a reaction with inorganic polymers such as poly(aminopropylsiloxane), which leads to single-phase polymer complexes with well-defined stoichiometries, typical morphologies, and characteristic decomposition temperatures [12]. Recently, we also found that blending CS with mercaptopropyltrimethoxysilane oligomers (MPS) leads to similar results but produces films functionalized by mercapto groups [13]. A schematic drawing of the interaction between CS and MPS is given in Fig. 1. There, the formations of molecular hybrids are stabilized by strong hydrogen bonding.

Currently, metal nanoparticles are intensively studied because of their relevant technological applications [14,15]. However, much attention has also been paid toward preparing gold and silver nanoparticles directed toward numerous bio-related applications, for instance, with antimicrobial agents [16], drug delivery [17], or medical diagnosis [18].

The development of antibiotic-resistant bacteria has resulted in a revival of the interest in the antibacterial properties of silver and gold ions. The use of nano-sized metal particles improves antibacterial properties due to the high surface area and large surface/bulk atom ratio, thus favoring the incorporation of metal species inside the bacteria and increasing their efficacy in a sustained manner [19,20].

Recently, CS–Ag+ complexes with high antibacterial activities and causing no harm to human cells were prepared [21]. On the other hand, the effect of gold nanoparticles on cell cytotoxicity has recently become a hot topic; so, many studies trying to correlate such effects with variables such as size, shape, and surface characteristics of the particles have been performed [22,23]. Recently, Long et al. [24] found that small gold nanoparticles can be endocytosed by cells, thus, forming aggregates inside the cell, thereby resulting in cytotoxicity. Meanwhile, when the aggregates become larger (25 nm), they cannot enter the cell; instead, they adhere onto its surface, and the growth rate of HeLa cells increases.

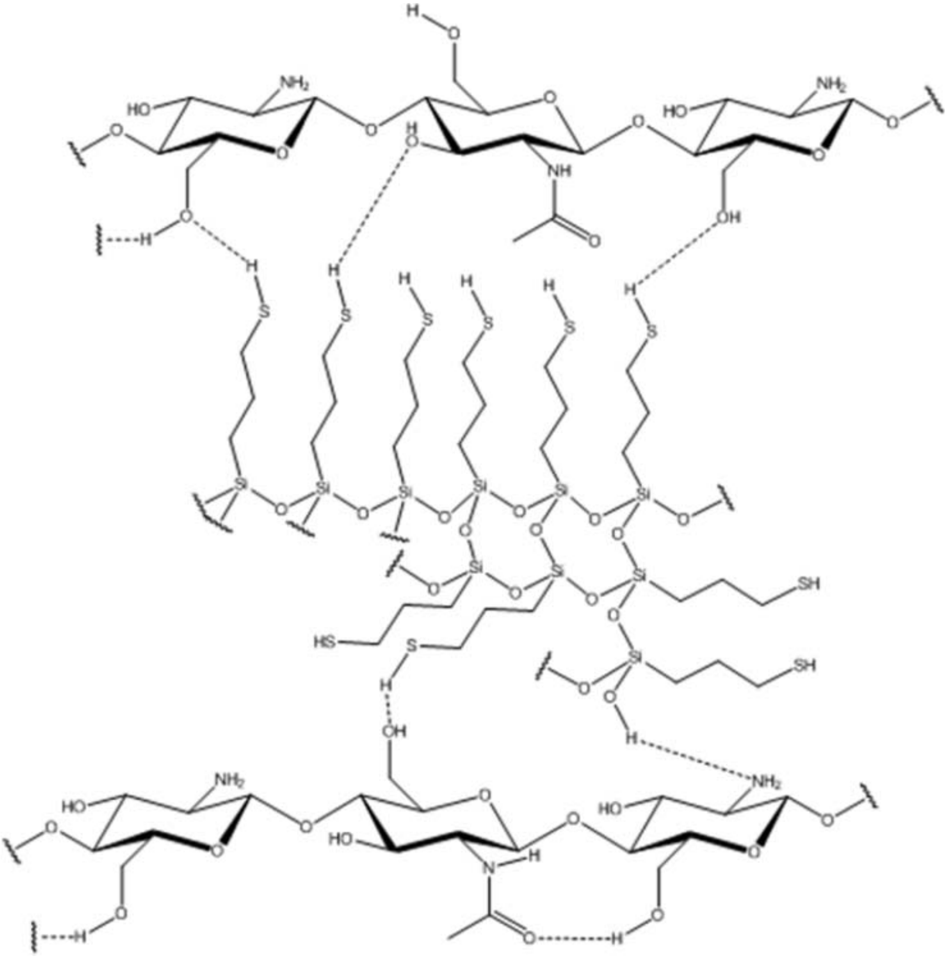

Figure 1. Schematic drawing of the interaction of Chitosan with mercaptopropilsiloxane.

As expected, the antiseptic properties of CS surfaces significantly improve by the concomitant action of silver ions on the surface [11]. In these experiments, the incorporation of the metal essentially occurs by the stabilization of metal ions by coordinating amine groups of CS.

The great potential of a synergic combination of two strong antiseptic agents such as CS and noble metal nanoparticles led us to formulate hetherosupramolecular polymers complexes, which are described in this work, that is, functional films containing CS, poly mercapto-propil siloxane, and silver or gold nanoparticles. The formation of these polymers complexes, together with increasing the flexibility and transparency of CS films, provides to the composite "soft" Lewis base sulfur sites that facilitate the incorporation of tunable amounts of metal nanoparticles, thus, bearing transparent, self-supported, and robust films which are potentially useful as active surfaces or coatings.

2. Experimental

2.1. Preparation of the Samples

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

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

2.2. Film Preparation

A suspension of colloidal gold nanoparticles of 50 nm mean diameter was purchased from Sigma. A suspension of colloidal silver nanoparticles of ca.100 nm was obtained by methods reported in the literature [25]. $AgNO_3$ (90 mg) from Merck was dissolved in 500 ml of H_2O triply distilled and brought to boiling. A solution of 1% sodium citrate (10 ml) from Merck was added. The solution was kept on boiling for ca. 1 h. The Ag solution prepared by this procedure was greenish yellow and had an absorption maximum at 420 nm.

The CS, MPS, and Au or Ag nanoparticle suspensions, in the appropriate concentration ratios, were mixed and then stirred for about 24 h at room temperature. Films were thereafter obtained by casting the resulting suspension onto a polypropylene film and letting the solvents to evaporate at room temperature. Thick films of 50 μm to 100 μm were obtained by regulating the concentration of the suspension.

The amounts of Au and Ag particles added to the hybrid films CS/MPS 1:0.09 molar ratio were in the range of 0.01 to 0.06 M.

2.3. Characterization of Films

The morphology of the samples was examined by using a Low Vacuum Scanning Electron Microscope (LV-SEM, JSM-5900LV) equipped with an Energy Dispersive X-ray Spectroscopy (EDX) detector. Raman spectra were recorded on a WITEC model CRC200, using a 5.5 mW laser with a wavelength of 514.5 nm. The optical properties were measured in the range of UV-vis from 250 nm upto 1100 nm using a Perkin Elmer lambda 20 model with a diffuse reflectance sphere.

2.4. Electrical Conductivity Measurements

The films were dipped in an $LiPF_6$–Acetonitrile (AN) 1 M solution for 24 h to promote the incorporation of the lithium salt, washed with acetonitrile, and dried under vacuum for 30 min. The electrical conductivities of the films, sandwiched between ion-blocking gold electrodes, were measured by the impedance electrochemical technique in an Autolab Potentiostat/Galvanostat-12 and an FRA 2 equipment at 25°C.

3. Results and Discussion

The rich intrinsic functionality of the monomer of CS, the aminoglucose, provides a variety of Lewis-base centers that are able to interact with metal species. Although it is known that CS has been also used for stabilizing metallic nanoparticles [26,27], the relatively "hard" nature of its Lewis-base centers makes its interactions with low-oxidation-state metal species, in general, be limited. Among a variety of methods available for changing the functional diversity of a polymer, from grafting new functional groups to simply blending polymers [28], the formation of supramolecular aggregates also appears as a relevant approach.

The latter is especially appropriate in the case of CS, which, as we have demonstrated [12,13], may indeed react with inorganic siliceous polymers that lead to supramolecular arrangements with regard to the improved properties of their components. In this regard, the functionalization of CS with Lewis-base "soft" sites was performed by forming a polymer complex with oligomers of mercapto propil siloxane (MPS). The reaction of CS with MPS, contrary to that with aminopropyl siloxane, leads to composed materials constituted by a single phase in a wide range of polymer mol ratios [13].

The high molecular compatibility between the components of CS/MPS polymers complexes, leading to products that, independently of their composition, almost all have the ability to originate flexible films of high transparence, appears to be essentially caused by hydrogen bonding associated to the presence of the S–H bonds. Given the high affinity of sulfur for metals, the capacity of the products for absorbing low-valence metallic species should increase with the increasing sulfur content. However, for the experiments described here, polymers complex samples with only nearly 1 mol% of sulfur were selected. Although functionalized (passivated) metal nanoparticles are proved to be, in general, biocompatible, it is expected that they might have as biocide a role synergically complementary to that of CS.

SEM and EDS micrographs of hybrid films CS/MPS prepared with 0.06 M suspensions of gold (a) and silver (b) of colloidal particles, respectively, are shown in Fig. 2. The homogeneity analysis shown in the same figure reflects the distribution of atoms in the films. In these micrographs, it may be observed that in all the films, the matrix CS/MPS 1:0.09 M presents morphologies in which the micro-domains of MPS appear to be homogeneously distributed and intimately interacting with CS, similar to that observed for other CS/MPS stoichiometries [13]. The addition of nanoparticles (silver or gold), even in small quantities, affected the morphology of CS/MPS films. Indeed, the surfaces of both films are more uniform and smoother than the surface of hybrid films without metal doping. Independent of the metal, hybrid films efficiently incorporate the nanoparticles into their structure, so that the surface of the film presents a uniform appearance.

The chemical composition of the films was examined by EDX elemental analysis. EDX patterns in Fig. 3 were obtained with the electron beam focused on the material shown in the micrograph in Fig. 2. They clearly show that the samples only contain the elements C, N, S, O, and Au or Ag and that no indication of contamination is detected. The EDX atomic distribution maps of polymers atoms (Si, S, and O) in hybrid films agree well with the homogeneity of the film surface, which has already been commented on. Element distribution also indicates that metallic nanoparticles are homogeneously

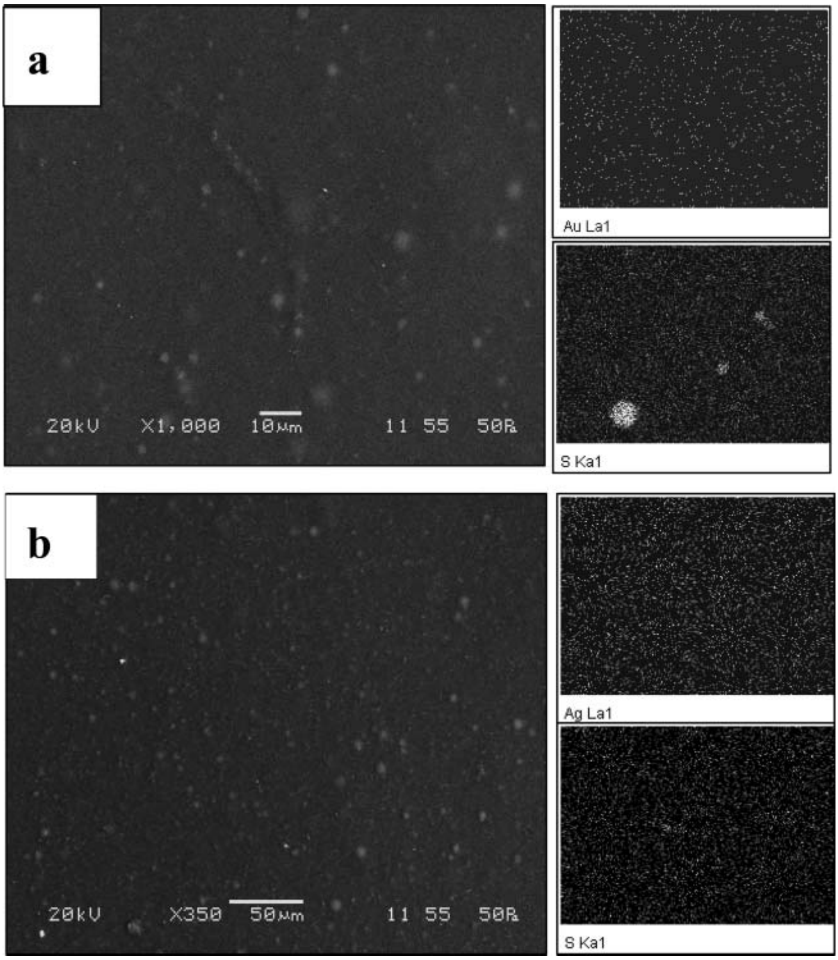

Figure 2. SEM and EDX micrographs of hybrid films: (a) CS/MPS/Au 1:0.09:0.06 M; and (b) CS/MPS/Ag 1:0.09:0.06 M.

immobilized onto the hybrid films without the formation of separated metal domains or as particles aggregates. Morphological properties of the hybrid films described here point toward a structural ordering created by the molecular affinity among their components. So, the formation of a new complex phase, possibly a heterosupramolecular arrangement of the components, is apparent. Molecular interactions engaged in such structures are expected to be reflected in changes of the properties of the films.

The effect of including metal nanoparticles into the polymer complex films may be followed by observing vibration spectra of the products with different metal content. Multifunctionality along the polymer chains, hydroxy, and amine groups in CS and mercaptan groups in MPS, which is responsible for the interactions between the components in the polymer complex, is the same that permits the stabilization and immobilization of the metal particles in the polymer network. Therefore, the nature and extent of structural rearrangements in the polymers complex induced by the addition of silver or gold will depend on the relative affinity of the available functional groups toward these metals. So, in most

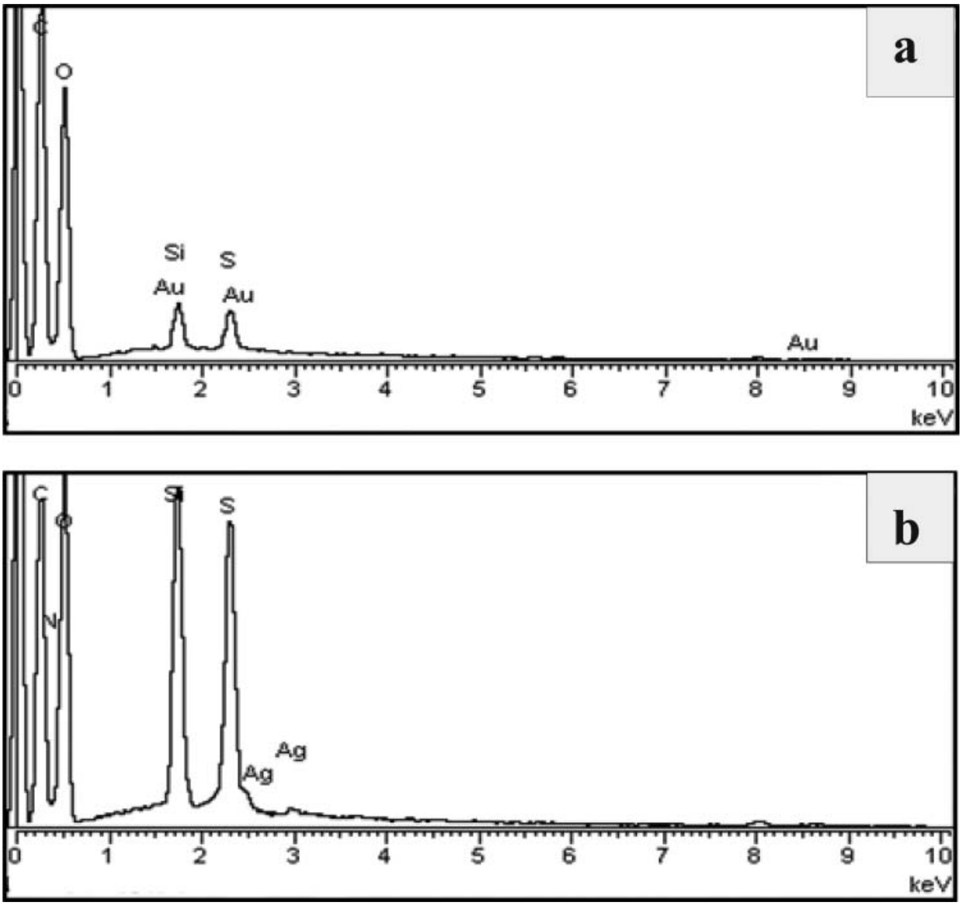

Figure 3. Distributions of atoms EDX of hybrid films: (a) CS/MPS/Au 1:0.09:0.06 M; and (b) CS/MPS/Ag 1:0.09:0.06 M.

changes of system properties associated to the capture of metal nanoparticles is expected to be involved amine and mercaptan functional groups mainly. MPS has been shown to form a strong covalent bond with different metals. Thus, this siloxane is able to anchor metal nanoparticles by the formation of a thiolate bond (M–S) between the mercaptan group and the metal. Due to the high affinity of sulfur toward gold or silver, the spontaneous formation of Au–S or Ag–S covalent bonds with the loss of hydrogen generally occurs [29].

On the other hand, CS has also been used for stabilizing gold nanoparticles, possibly involving NH_2 groups of the polymer [30]. In Figs 4(a) and (b), Raman spectra of the hybrid films CS/MPS with increasing amounts of metallic particles, Ag and Au, respectively, are reproduced. The frequencies observed for the CS/MPS/Ag or Au are listed in Table 1. Most interesting changes in the Raman spectra concerning MPS, particularly in the stretching S–H band, which is in the polymer complex with CS, appear with moderate intensity at about 2580 cm^{-1}. In the composite with silver (4a) at the lowest metal concentration (0.01 M), this band is observed at 2576 $cm^{-1,}$ with an intensity similar to that in the metal-free film. However, on increasing Ag concentration, the intensity of this band decreases, while being always observable even at maxima tested metal content (0.06 M). However,

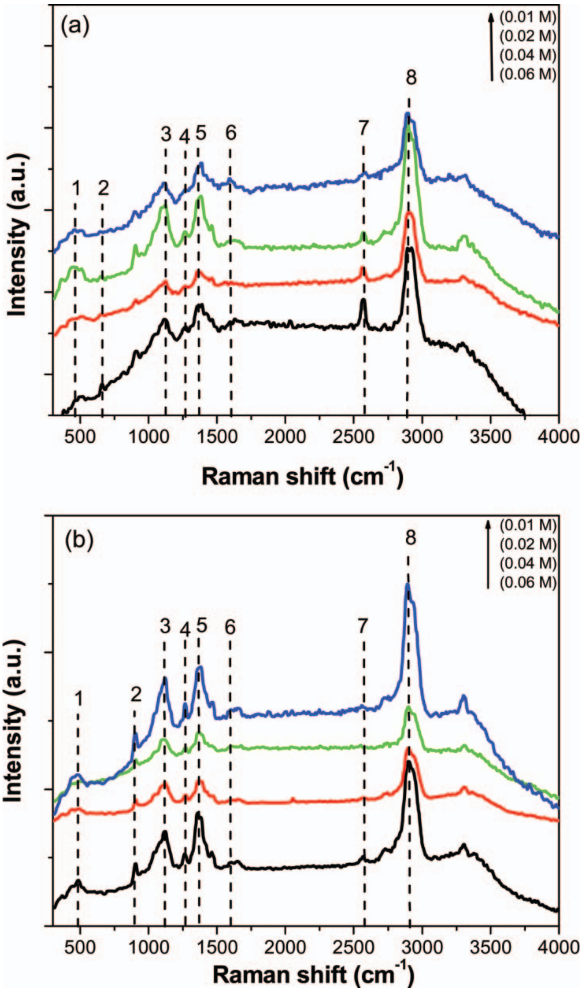

Figure 4. Raman spectra of the hybrid films CS/MPS 1:0.09 (molar ratio) with metal nanoparticles at different concentrations of: a) Ag and b) Au.

Table 1. Observed vibrational frequencies of CS/MPS/(Ag or Au) and corresponding assignments.

Number	Raman (cm^{-1})	Assignment
1	462	δ (OSiO)
2	650	ν (SiC)
3	1107	ν_a (SiOC)
4	1266	ω (CH_2)
5	1358	ω (CH_2)
6	1585	ν (NH)
7	2574	ν (SH)
8	2887	ν_s (CH_2)

with the addition of gold, the same band observed now at 2568 cm^{-1} is much more affected, practically disappearing at a metal concentration of 0.06 M [Fig. 4(b)]. This feature agrees with the well-known remarkably high affinity between gold and sulfur.

In general, when the molar ratio between gold or silver nanoparticles and MPS tends to be closer, there is a decrease in the band observed at about 2580 cm^{-1} with increasing metal content, probably due to bonds Ag–S or Au–S (see band 7). On the contrary, when the MPS to metal, Au or Ag ratio is high, then there is practically no significant decrease in this band. On the other hand, the intensity of the N–H bending vibration band [band 6, Fig. 4(a) and (b)] at about 1585 cm^{-1} gradually decreases with increasing concentrations of the metallic nanoparticles. However, this effect, due to a large concentration of $CS{-}NH_2$ groups relative to metal particles there are in all these experiments, results are much less notorious than those concerning the mercaptan groups already commented on. Due to the same reason, no preferential affinity of CS for any of the metals is detected, though this affinity should be certainly higher with silver than gold.

The results just commented on clearly show that the incorporation of metal particles into CS/MPS molecular complexes leads to new heterosuplamolecular arrangements, more than to a composite or blend, as well as that the products appear to be sensitive not only to the nature but also to the relative concentrations of the components. This is a feature that could be interesting as a tool relevant for regulating the properties of the products.

Electronic spectra may be useful for corroborating possible effects of the composition onto the properties of the films as well as also for detecting possible synergic features appearing in these new supramolecular arrangements. The effect of the formation of polymer complexes on the one hand, and the influence of the addition of metal particles on the former, are illustrated in Figs 5 and 6, respectively. Interestingly, the spectrum of the hybrid polymer complex CS/MPS (1:0.09) (Fig. 5) shows a characteristic spectrum, with a maximum at 224 nm, which differs from the features observed in those of the precursors, namely a broad

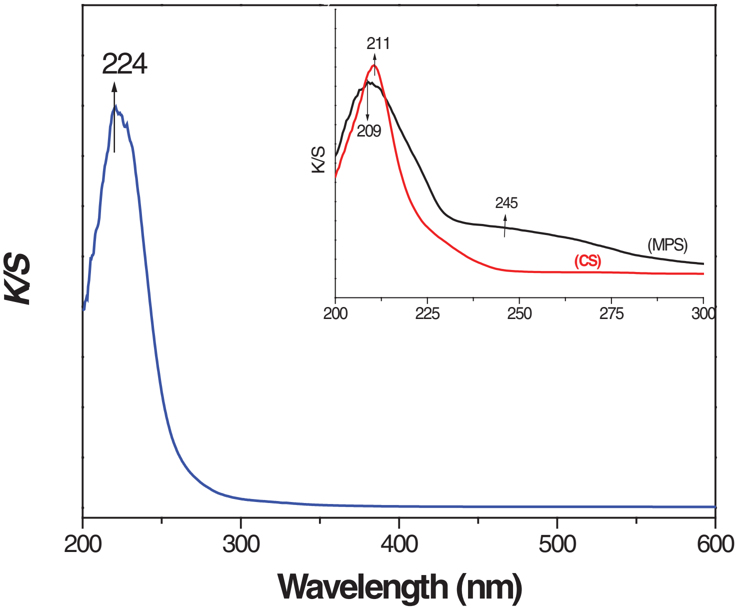

Figure 5. UV-vis spectra of the hybrid films CS/MPS 1:0.0.9 (molar ratio).

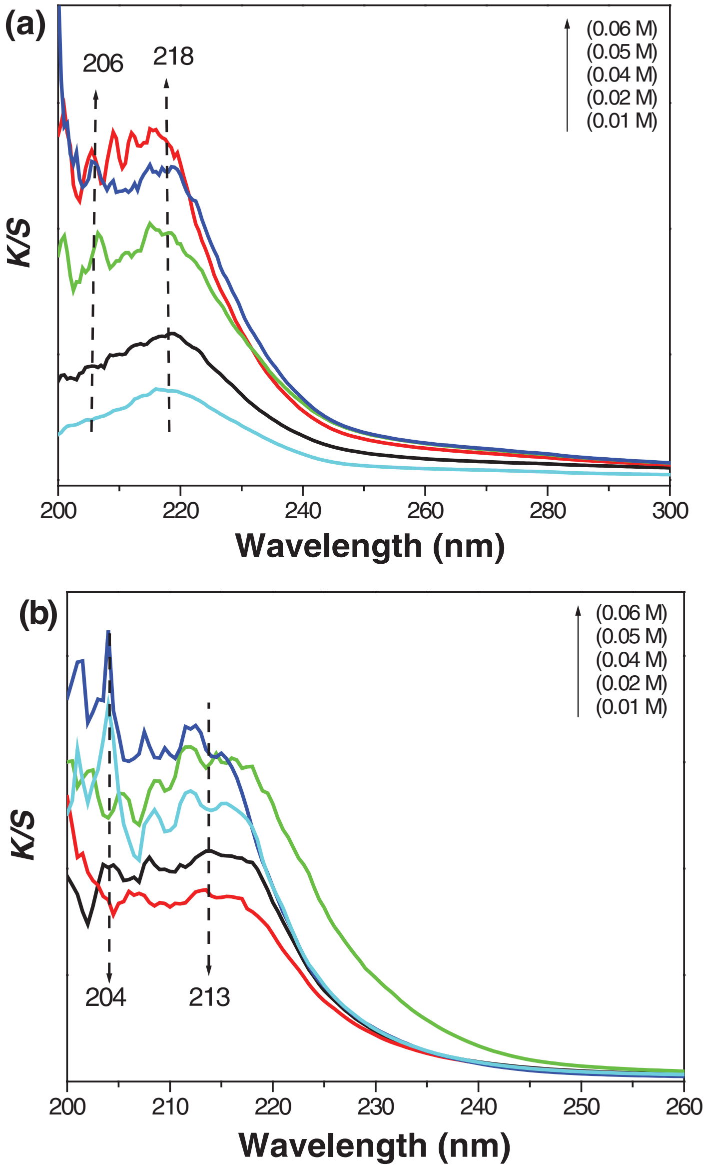

Figure 6. UV-vis spectra of the hybrid films CS/MPS 1:0.0.9 (molar ratio) with metal nanoparticles at different concentrations of: a) Ag and b) Au.

band centered at about 211 nm assignable to transitions involving NH_2 and OH functional groups in CS, and two bands centered at 209 nm and 245 nm corresponding to the mercapto siloxane group in the MPS. The resulting complex clearly appears to be electronically a new entity.

Interestingly, as observed in Figs 6(a) and (b), the addition of metal produces an effect in the opposite direction, that is, spectra shift to higher energies, showing a shape roughly more similar to the superposition of spectra from the components, pristine CS and MPS, than to that of the polymers complex. That notwithstanding, new characteristic and strong bands, centered at about 206 nm and 218 nm for the CS/MPS complex with silver and at about 204 nm and 213 nm for the CS/MPS complex with gold, which neither appear in the spectra of the hybrid films CS/MPS 1:0.09 nor correspond to pristine polymers, are clearly apparent, especially in the samples with a higher metal content.

The features just discussed indicate that in the formation of polymer complexes with oligo-mercaptosiloxanes, CS always involves its Lewis acid–base functionality to an extent that certainly depends on the stoichiometry of the complex. Any further function of this polymer, inside the film or as an active surface toward the environment, should imply a restructuration of its functionality, as occurs, for instance, by the formation of heterosupramolecular structures with metal nanoparticles already discussed. In that particular case, equilibriums appear to be mainly determined by the soft base character of mercaptan groups. In order to corroborate whether these equilibriums may be to some extent somewhat further modulated, we also performed some preliminary experiments by modifying the system by inclusion of a “hard” Lewis acid, the cation Li^+, analyzing the effect by taking as criterion the ionic conductivity of the film. Similar to polymer electrolytes, ionic conductivity, in this system the mobility of lithium, is expected to be determined by equilibriums involving interactions of Li^+ with available Lewis base sites in the polymers; that is, amino and mercapto groups, as well as by segmental movements of the polymer chains. Given the similitude of materials obtained in the presence of metal particles, inferred from UV-vis spectra just commented on, the effect of the polymer chain movements may be neglected at least in a first approximation.

Conductivity values measured at room temperature to a selected series of films containing different metal concentration are reported in Table 2. In general, conductivities are rather poor compared with those observed for similar systems, namely CS/APS based polymer electrolytes [31]. Differences probably arise from both the type of interaction occurring in these heterosupramolecular species and the procedure used for the incorporation of lithium. In our case, incorporation of lithium was performed by spontaneous absorption from the solution into preformed film, instead of incorporating the lithium salt during preparation of the films, as frequently done.

That notwithstanding, we expect that the differences in the mobility of lithium between samples with different concentrations in metal nanoparticles, at least roughly, be determined by the occupancy of available Lewis base sites by the nanoparticles and, possibly in a minor extent, by segmental movements of the polymer chains. As observed in Table 2, the effect

Table 2. Conductivity values measured at room temperature of CS/MPS/Ag or Au 1:0.09:0.06 M.

Sample	Composition CS/MPS/Ag or Au (molar ratio)	σ at 25°C (S/cm^{-1})
1	1:0.09	2.44×10^{-8}
2	1:0.09:0.001 (Ag)	7.96×10^{-8}
3	1:0.09:0.002 (Ag)	2.02×10^{-9}
4	1:0.09:0.003 (Ag)	3.01×10^{-9}
5	1:0.09:0.001 (Au)	$2,66 \times 10^{-11}$
6	1:0.09:0.002 (Au)	$2,98 \times 10^{-8}$
7	1:0.09:0.003 (Au)	$1,31 \times 10^{-7}$

of the concentration of metal on the conductivity is very different in both cases, Ag and Au, namely an opposite tendency in both cases. In the cases of silver, clearly the conductivity remains rather low, while, with gold, a significant increase is observed with a higher metal concentration.

The effect of the incorporation of metal particles on networks CS/MPS have to be understood as changes of intra and intermolecular interactions that are stabilizing the polymers complex, particularly by forming strong H_2N–HS hydrogen bonding. The effect of this on ion-lithium conductivity will be, in turn, determined mainly by the availability of free "hard" NH_2 centers. In the case of silver, given its higher relative affinity to amine groups, it would compete with lithium for these sites. Meanwhile, gold, due to its high affinity to sulfur, would not only saturate sulfur sites but also partially break the polymer network, thus, increasing both the concentration of available NH_2 groups available for coordinating lithium ions and the enhanced polymer chain segmental mobility. These experiments are, thus, in line with the structural features just commented on. Thus, the heterosupramolecular materials described here appear to be a system whose physicochemical properties, and, thus, potential applications, are mainly determined by being generalized Lewis acid–base interactions, thus, offer much room for easy tailoring of their properties by simply selecting the nature and concentration of the components.

4. Conclusions

New CS-based films constituted by heterosupromolecular arrangements of CS, oligomercaptopropilsiloxanes, and silver or gold nanoparticles are described. These two polymers are highly compatible with each other, thus, leading to single-phased polymers complexes with properties distinct from those of the components. The natural ability of CS to interact with metal species through its amine groups becomes enhanced in the polymers complexes by the presence of mercaptan, a soft Lewis base site. So, polymer films functionalized with silver or gold nanoparticles may be easily obtained.

As depicted, the effects of the composition of the products on Raman and electronic spectra as well as on the morphology and the lithium-ion conductivity of the films, the activity of free CS in the products is rather sensitive to both the concentration of MPS and the nature and concentration of the metal nanoparticles. Therefore, properties such as, for instance, the antiseptic effect of CS and noble metal nanoparticles, separately or synergically coupled, could be easily tuned by adequate selection of the component ratios. Experiments directed to test the potentiality of films of these materials for designing tailor-made antiseptic surfaces are in progress.

Acknowledgments

Research partially funded by FONDECYT (Contracts 1090282, 1070195), Basal Financing Program CONICYT, FB0807 (CEDENNA), Millennium Science Nucleus, Basic and Applied Magnetism Grant No. P10-061-F.

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