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Polydimethylsiloxane-modified chitosan. Complexes of divalent metals

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The paper describes the synthesis and properties of copper (II), nickel (II), cobalt (II) complexes with macromolecular ligands. Chitosan-polydimethylsiloxane graft and crosslinked copolymers were used as coordinating species. The chemical structure of metal complexes was investigated by FT-IR spectroscopy. As proved by X-ray diffraction, the metal complexes are materials of low crystallinity and their supermolecular structure depends on cation nature. The linking of metal cations to CS-PDMS copolymers slightly increases the materials conductivity.

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1. Introduction

Bio-based polymers present an increased attention worldwide due to their properties and potential biomedical applications [1-9] or as materials for micro/nanoelectronics [10,11]. Chitosan (deacetylated chitin) is one of the most investigated biopolymers. It is a linear polysaccharide containing statistically distributed β-(1-4)-linked 2-deoxy-2-amino-D-glucopyranose and β-(1-4)-linked 2-deoxy-2-acetamido-D-glucopyranose units. Chitosan is an attractive biocompatible, biodegradable, and nontoxic natural biopolymer that exhibits excellent film-forming ability [12]. Due to its interesting properties, chitosan has been widely used as an immobilization matrix for biosensors and biocatalysts [13-16]. Considering its relatively poor conductivity, chitosan was usually combined with redox mediators [17] and metal nanoparticles [18] for electrochemical biosensing platforms. To modify its solubility and some undesirable mechanical properties, this polymer was modified by grafting and/or crosslinking with vinyl monomers such as acrylonitrile, methyl methacrylate, methyl acrylate, N-vinyl pyrrolidone, and acrylic acid [19-27]. Our revious papers [28-31] reported the synthesis of graft and crosslinked chitosan-polydimethylsiloxane polymers, as well as the preparation of porous and mineralised hybrid membranes containing chitosan-polydimethylsiloxane graft copolymers and silica.

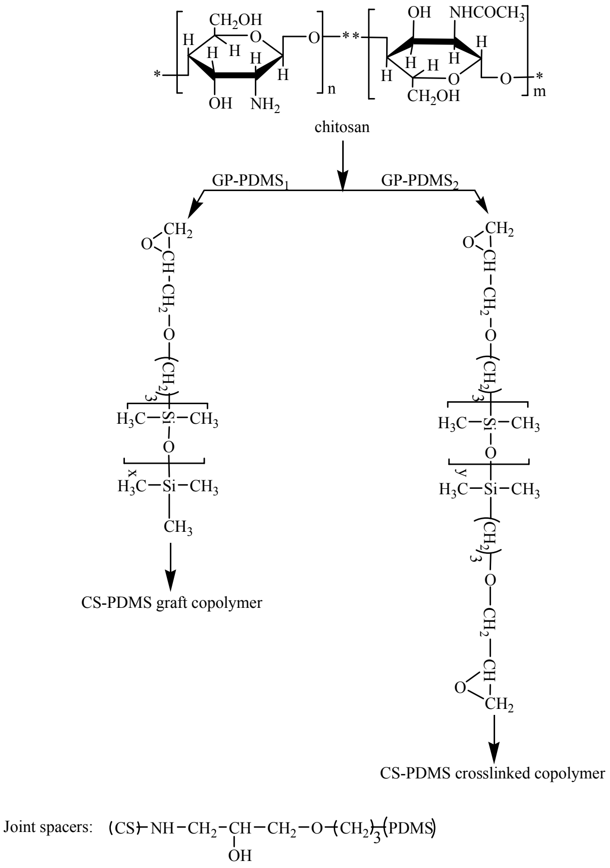
The objective of this study was to hydrophobically modify chitosan in order to induce an amphiphilic character and to investigate the ability of the new materials in the coordination of divalent metal cations. The molecular/supramolecular structures of the resulted metal/macromolecular ligand complexes as well as their electrical properties were also investigated.

2. Experimental

Materials. PDMSs with average number molecular weights of 1000 and 1400 Da were prepared according to previously described procedures [32,33]. Low molecular weight chitosan, (CS), with a degree of deacetylation (DD) of 75-85 %, was used as received (Aldrich). The precise value of the deacetylation degree was found to be about 80 % as determined from the nitrogen content of the sample (8.23 %). The intrinsic viscosity of CS sample was determined in 0.25 M acetic acid/0.25 M sodium acetate aqueous solution using an Ubbelohde viscometer kept in a constant temperature bath at 25 ^oC. The viscosity molecular weight was found to be approximately 380 KDa by using the Mark-Houwink-Sakurada equation (MHS), $[\eta] = k \times M^{\alpha}$, where $[\eta]$ is the intrinsic viscosity, M is the viscometric molecular weight, $k = 1.81 \times 10^{-3}$ (dl/g) and $\alpha = 0.93$ [34]. $CuCl_2*2H_2O$ 98%, $NiCl_2*2H_2O$ 98%, $CoCl_2*2H_2O$ 87% were purchased from Aldrich and used without further purification.

Synthesis. Chitosan-polydimethylsiloxane (CS-PDMS) graft and crosslinked copolymers have been prepared through the addition of amino groups of CS to the epoxy end groups of mono- and bifunctional PDMSs, respectively, as described elsewhere (Scheme 1) [28]. The fractions of the CS structural units having amino non reacted groups (f_1), amino groups linked to PDMS (f_2) and amido groups (f_3) were calculated according to silicon elemental analysis results (Table 1).

CS-PDMS/metal (II) (where metal is Cu, Ni, Co) complexes were prepared by mixing aqueous solutions of CS/PDMS copolymers and metal salts.



$$(CS)\!-\!NH-CH_2-\underset{\displaystyle OH}{CH}-CH_2-O-(CH_2)_3-(PDMS)$$

Scheme 1. Synthesis of CS-PDMS copolymers.

Table 1. Characteristics of CS-PDMS copolymers.

Characteristics	CS-PDMS$_1$	CS-PDMS$_2$
Structure	Graft copolymer	Crosslinked copolymer
Si content (%)	30.3	21.5
f_1	0.40	0.47
f_2	0.40	0.33
f_3	0.20	0.20

In a typical procedure, CS-PDMS/Cu(II) complexes were prepared by adding drop wise, under stirring, an aqueous solution of 1.12 % by weight of copper chloride over the crude solution of CS-PDMS$_2$ (amine/Cu = 2/1 molar ratio). After stirring at room temperature for 1 h, the colour of the solution changed slightly from blue to blue-green. The resulting mixture was neutralized by adding Na_2CO_3 aqueous solution up to a pH value of 7, and the complex was obtained as a blue-green precipitate. The precipitate was separated by filtration and washed with double-distilled water to eliminate free metal ions from the surface of the complex. The product was then dried at 40 ^{o}C for 24 h under reduced pressure (yield: 95 %).

Measurements. FT-IR spectra were obtained by using a Nicolet 60 SX FT-IR spectrometer, under dry air, at room temperature, on KBr pellets, in the range of 4000-400 cm^{-1}. X-ray diffraction patterns were recorded on a Rigaku Kmax-r AX diffractometer with scanning scope of 0-35^{o} (2θ), scanning speed of 4^{o}/min, using Cu Kα radiation. The electrical conductivity measurements of CS-PDMS copolymers and of their metal complexes were performed on a Teralin III electrometer, at room temperature.

3. Results and discussion

Two different structures of siloxane modified chitosan were prepared, i.e., graft and crosslinked copolymers. They show swelling in water and in organic solvents such as ethanol and chloroform (not shown). It was expected that the well known complexing ability of chitosan, due to the electron donor ability of nitrogen atoms of amine groups, will be preserved following its linking to polysiloxane chains. Moreover, as CS is hydrophobically modified, the resulted copolymers should be able to extract metal cations from both aqueous and organic media.

The interaction between divalent metal cations (Cu (II), Ni (II), and Co (II)) and CS-PDMS copolymers was followed by FT-IR. Fig. 1 shows FT-IR characteristic absorptions of CS-PDMS$_1$/metal complexes as compared to pure and modified CS. The same characteristic absorptions were obtained for CS-PDMS$_2$/metal complexes, except the characteristic bands are broader due to crosslinking. The large band at 3429 cm^{-1}, corresponding to the stretching vibration of NH_2 and OH groups in CS, shifted in complexes to higher frequencies, indicating the involvement of both amino and hydroxyl functional groups into complexation of the metal cations. The participation of OH groups in metal chelation is also proved by the moving of the band attributed to the OH bending vibration from 1421 cm^{-1} in CS to 1410 cm^{-1} in CS-PDMS/metal complexes. The absorption bands at 1650 and 1596 cm^{-1}, assigned to acetamide and to “free” amine groups, respectively, disappear in the complexes. Instead, new absorption bands, attributed to the association of CS to metal cations, appear at 1623, 1636, 1639, 1654 cm^{-1}, suggesting the interacting of the amine and acetamide groups with the cations.

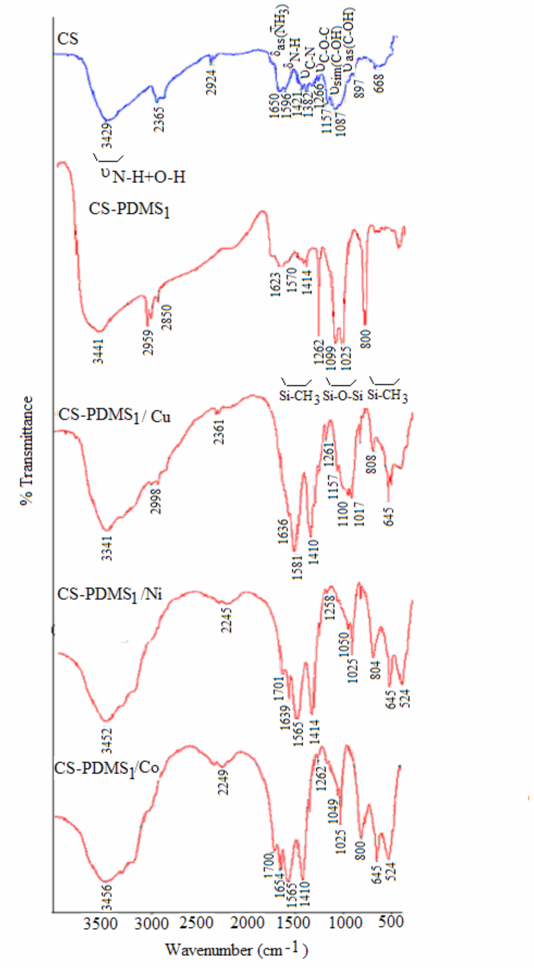


Fig. 1. FT-IR spectra of CS-PDMS$_1$/metal complexes.

The important intramolecular hydrogen bonding leads to chitosan's partially crystalline character [35]. As shown in Fig. 2, the XRD pattern of CS exhibits characteristic crystalline peaks at 2θ = 10.2° and 19°.

X-ray diffraction of CS-PDMS copolymers indicate that the bonding of PDMS to chitosan chains decreases the crystallinity. However, the copolymers still present a partially crystalline structure. It is interesting to notice that the graft and crosslinked copolymers present different X-ray patterns, not only as compared to CS, but also as compared to each other. The presence of amorphous siloxane chains linked to CS is disturbing the thermodynamic equilibrium conformation of CS and, as a consequence, the ordering of CS chains into crystalline domains is reduced and the planes giving rise to the diffraction peaks are modified.

The X-ray patterns of complexes derived from the crosslinked CS-PDMS copolymer are given in Fig. 3. As one can see, the peak at around 2θ = 20° is weakened and/or disappeared due to the destruction of the hydrogen bonds within chitosan by the metal ions that interact with NH_2 and OH groups. The modification of the X-ray patterns as compared to the non-complexed copolymer depends on the nature of the metal cation. The complexation of Co (II) and Cu (II) induces a diminishing of the peak around 2θ = 20°, while the Ni (II) complexes also show crystalline peaks in the range 2θ = 15-30°. Similar results were obtained for metal/CS-PDMS$_1$ samples.

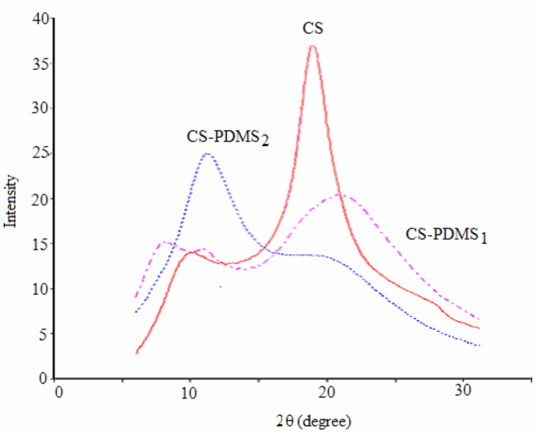


Fig. 2. XRD spectra of CS and of CS-PDMSs copolymers.

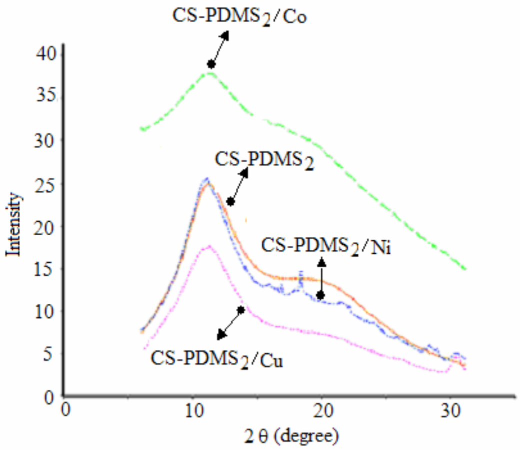
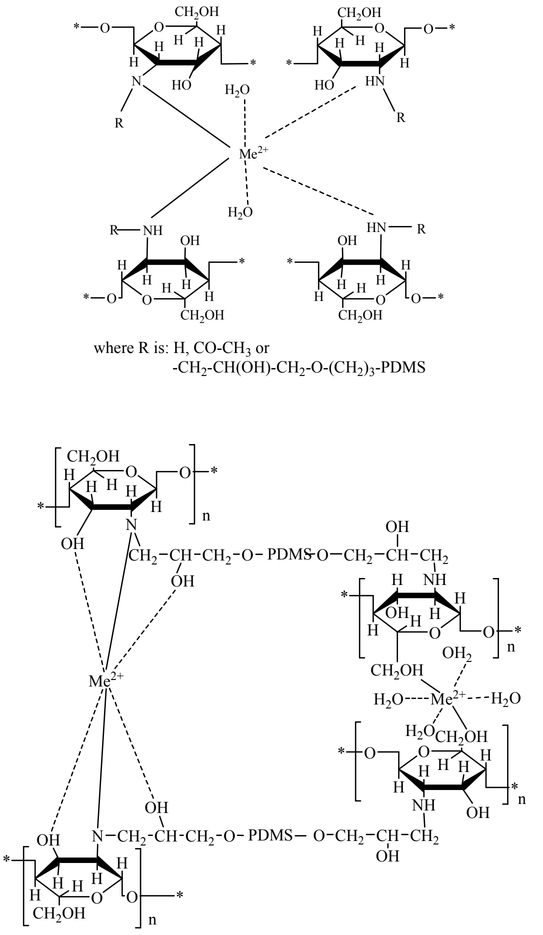


Fig. 3. XRD patterns of CS-PDMS$_2$ and of its metal complexes.

Based on FT-IR and X-ray results, the molecular structure shown in Scheme 2 can be considered for CS-PDMS/metal complexes. The metal ions are located like a bridge, connecting one or more chains of chitosan through OH and NH_2 groups.

The electrical properties of metal/ macromolecular ligand complexes were determined on disk samples of a thickness and a diameter of 0.7 and 12 mm, respectively. The electrical conduc-tivities of metal complexes are slightly higher as compared to the corresponding CS-PDMS precursors and do not depend significantly on cation nature (Table 2).



where R is: H, CO-CH$_3$ or
-CH$_2$-CH(OH)-CH$_2$-O-(CH$_2$)$_3$-PDMS

Scheme 2. Possible structures of CS-PDMS/metal complexes.

Table 2. Electrical conductivity of CS-PDMS/metal complexes.

Sample	σ (Ω.cm)$^{-1}$
CS-PDMS$_1$	9.1×10^{-13}
CS-PDMS$_1$/Cu	2.6×10^{-12}
CS-PDMS$_2$/Ni	3.7×10^{-12}

4. Conclusions

The hydrophobic modification of CS with PDMS does not affect its metal complexing ability. As revealed by FT-IR spectroscopy, different functional groups linked to CS sequence, i.e., amino, amido and hydroxyl groups participate in the coordination of bivalent metal cations. As shown by their X-ray diffraction patterns, the crystalline structure of metal complexes depends on cation nature. The electrical conductivity of CS-PDMS copolymers was slightly increased following the complexation.

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