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Synthesis of polysilane–bis(salicyliden)ethylenediamine Ni(II) complex

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Abstract

This paper describes the synthesis of a new coordination polymer prepared through the polycondensation reaction of α,ω -bis(chloromethyl)-polymethylphenylsilane with the Ni(II) complex of bis(salicylidene)ethylenediamine (salen). For this purpose, a new preparation method of the chloromethylated polysilane was presented along with the synthesis and characterisation of the polymer–metal complex. IR, $^1\text{H-NMR}$ and UV–Vis spectral analyses as well as GPC and TGA were used to investigate the new chemical structures.

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1. Introduction

The widespread interest in the redox polymers has been demonstrated by their applicability in the area of chemically modified electrodes [1–3]. One goal of coating electrodes with electroactive polymers is the development of new materials with very active catalytic properties. The electrocatalytic reduction of O_2 is one example that has been of particular interest [3–7] for fuel cell applications. Embedding electrocatalytic transition metal species in a polymer modified electrode matrix is a means to endow the electrode with the chemical, electrochemical, optical, and other properties of the immobilised molecule [1]. The rate of electron exchange between the electrode and the catalyst sites is of obvious importance in the context of electrocatalysis. Facilitated electron transfer will translate to higher turnover rates.

It is commonly held that redox conduction in polymers occurs by the electron hopping process proposed by Kaufman and coworkers [8,9]. According to this, the electron transfer proceeds as a process of sequential self-exchange steps between adjacent redox groups, which

leads to a somewhat slow rate of electron transport. On the other side, the electronically conducting polymers exhibit rapid electron transport through a delocalised electronic structure.

Polymer–metal complexes could be obtained through complexation of polymeric ligand with metal [10–12] through complexation of difunctional ligand with metal ion [13–15], through polymerisation of metal complexes [16,17] or in the form of cluster complexes [18–20].

This paper presents the synthesis of a new polymer–metal complex with redox active centers enclosed in the polysilane-conjugated backbone. This kind of polymer is characterised by a highly localised electroactivity in the redox moiety combined with a specific σ -conjugative effect in the polysilane chain.

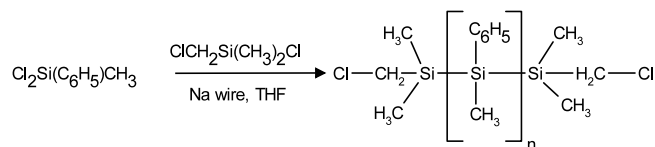
2. Results

A new polymer–metal complex was synthesised through the polycondensation reaction of α,ω -bis(chloromethyl)polysilane oligomer with salen complex of Ni(II).

The chloromethyl-polysilane was obtained through a modified Wurtz coupling technique in solvent THF according to reaction Scheme 1.

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Scheme 1. Synthesis of α,ω -bis(chloromethyl)polysilane.

For this purpose, methylphenyldichlorosilane was polymerised in the presence of chloromethyldimethylchlorosilane using sodium wire and anhydrous inert atmosphere. In these conditions, the difference of reactivities between the chloromethyl and chlorosilyl functional groups ensures protection of the chloromethyl functional groups avoiding excessive polycarbosilanes formation through secondary reactions.

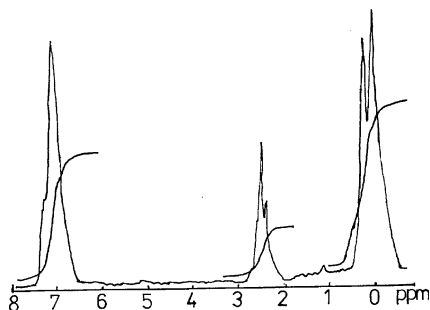
$^1\text{H-NMR}$ of chloromethyl-polysilane (Fig. 1) displays the characteristic chemical shift of the $-\text{CH}_2-\text{Cl}$ group protons at $\delta = 2.93$ ppm.

The molecular weight of the synthesised product was evaluated through $^1\text{H-NMR}$ analysis; $M_n = 580$.

The ligand synthesis and complex formation were made using a standard procedure involving first, salicylaldehyde reaction with diamine and then the Ni(II) complex formation using an aqueous solution of nickel acetate [21].

$^1\text{H-NMR}$ spectrum of the ligand (Fig. 2) shows the characteristic chemical shifts of the $-\text{N}-\text{CH}_2-$ and $-\text{CH}=\text{N}-$ groups protons at 3.80 and 8.30 ppm, respectively.

The polysilane-metal complex was obtained through the polycondensation reaction of the chloromethyl functional polysilane with the Ni-salen diphenol complex in the presence of triethylamine as proton acceptor. This procedure requires an attentive selection of the appropriate reaction solvent system knowing that polysilanes have good solubilities in inert or low polar solvents and the Ni(II) complex is soluble in polar solvents. To obtain reasonable reaction ratios at low temperatures a dimethylformamide-chloroform mixture should be used. This ensures a good homogeneity of the reaction medium and an easiest separation of the final products.

Fig. 1. $^1\text{H-NMR}$ of chloromethyl-polysilane.

Spectral analyses were performed in order to determine the chemical structure of the product.

IR spectra presented in Fig. 3 show the specific absorption bands starting from ligand to the polymer-metal complex. It is possible to observe that the polysilane-metal complex displays the characteristic absorption band of the $-\text{C}=\text{N}-$ bond in almost the same position as in the salen-Ni complex (1650 cm^{-1}). Due to overlapping of specific absorption bands, the assignment for the $-\text{Si}-\text{C}-$ and $-\text{C}-\text{O}-$ bonds could not be made very clearly using IR spectral analyse.

$^1\text{H-NMR}$ Spectrum of polysilane-metal complex is presented in Fig. 4.

The specific chemical shifts of the $-\text{CH}_2-\text{O}-$ group protons could be clearly observed at $\delta = 4.15$ ppm confirming the polysilane-metal complex formation. The peaks at $\delta = 3.80$ and 8.27 ppm were assigned to the methylene bridge protons and $-\text{CH}=\text{N}-$ group protons, respectively, both present in the ligand structure. The broad signal at $\delta = 0.15$ ppm of $-\text{Si}(\text{CH}_3)$ group protons and the $\delta = 6.2-7.05$ ppm multiplet of the phenyl group protons could be also observed.

The spectral analyses sustained the chemical structure of the metal complex modified polysilane as presented in Fig. 5.

TGA analysis of the polysilane (Fig. 6) shows a continuous weight loss with a singular differential peak resulting in 51.72% ash (SiO_2). The polysilane-metal complex thermal decomposition presents two differential peaks: the first one (within $100-200\text{ }^\circ\text{C}$) corresponding to the loss of the crystallisation water and the second one at higher temperature, representing the thermal decomposition of the polymer chain.

Observing that TGA analysis of the polysilane-metal complex yields 41.63% ash (SiO_2 and NiO) it was possible to estimate the concentration of metal in the polymer backbone: 8.3% Ni.

The UV-Vis spectrum of the polymer is shown in Fig. 7. An absorption band at 320 nm is attributed to both the conjugative interactions between phenyl substituent and the silicon backbone which acts as a $\sigma-\sigma^*$ or $\sigma-\pi$ chromophore and the conformational strain from steric interference of the phenyl substituent.

The presence of the Ni-complex results in metal to ligand carrier transitions (MLCT) visible at 390 nm. The $\pi-\pi^*$ -specific transitions of the phenyl rings were also present at 270 nm.

GPC analysis of the polysilane-Ni complex shows a narrow unimodal molecular weight polydispersity with a maximum at $M_w = 5600$.

3. Experimental

IR spectra were recorded on a Specord M80 spectrophotometer using KBr pellets.

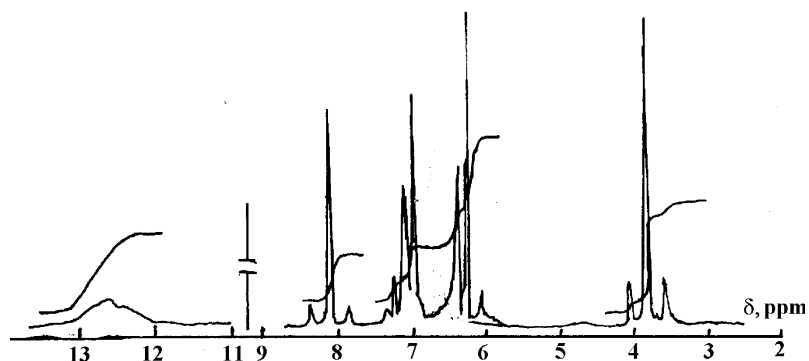
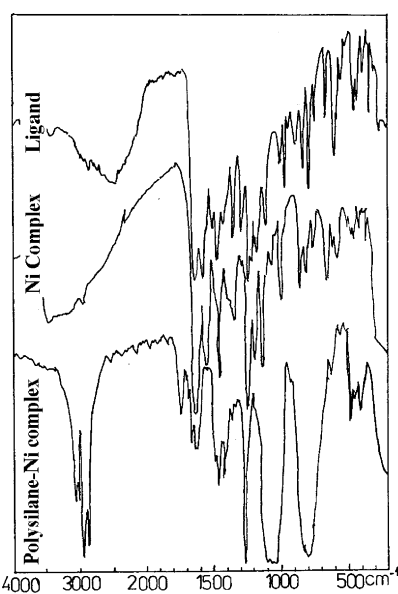
Fig. 2. $^1\text{H-NMR}$ spectrum of bis(salicylidene)ethylenediamine.

Fig. 3. IR spectra of ligand, Ni complex and polysilane–Ni complex.

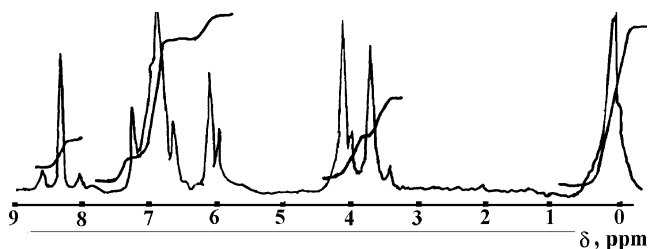


Fig. 4. NMR of polysilane–metal complex.

$^1\text{H-NMR}$ spectra were registered using a Bruker AC-80HL spectrophotometer without TMS as an internal standard.

UV–Vis spectral analysis was performed on a Spe-cord M42 spectrophotometer.

GPC experiments were carried out in DMF solution at $30\text{ }^\circ\text{C}$, at a flow rate $1\text{ cm}^3\text{ min}^{-1}$, using a Spectra Physics 8800 gel permeation chromatograph with two PL-gel packed columns (10^3 and 500 \AA).

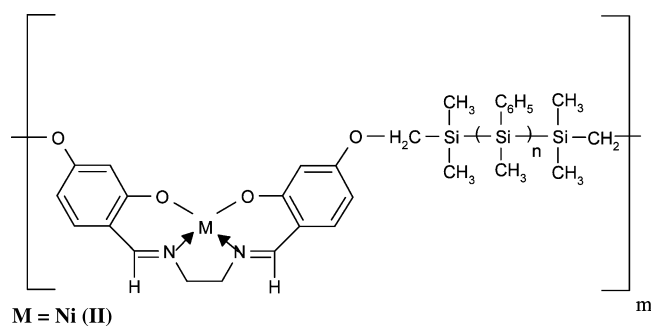


Fig. 5. The chemical structure of the polysilane–metal complex.

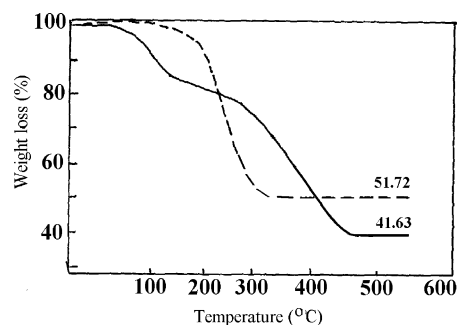


Fig. 6. TGA trace: polysilane (---) polysilane–metal complex (—).

TGA analysis was performed using a derivatograf MOM Paulik-Paulik-Erdey, within $20\text{--}900\text{ }^\circ\text{C}$ temperature range at a 10° min^{-1} heating rate in air.

3.1. Synthesis of difunctional polymethylphenylsilane oligomer

In order to obtain the chloromethyl-functional polysilane, a heterogeneous Wurtz coupling technique, was used [22]. The general procedure was as follows: a 500 ml three-necked reaction flask was charged with dry THF and sodium wire (10 g, 0.4 mol). A mixture of methylphenyldichlorosilane (25.3 g, 0.1 mol) and chloromethyldimethylchlorosilane (11.5 g, 0.1 mol) in 30 ml dry THF was added dropwise maintaining a gentle

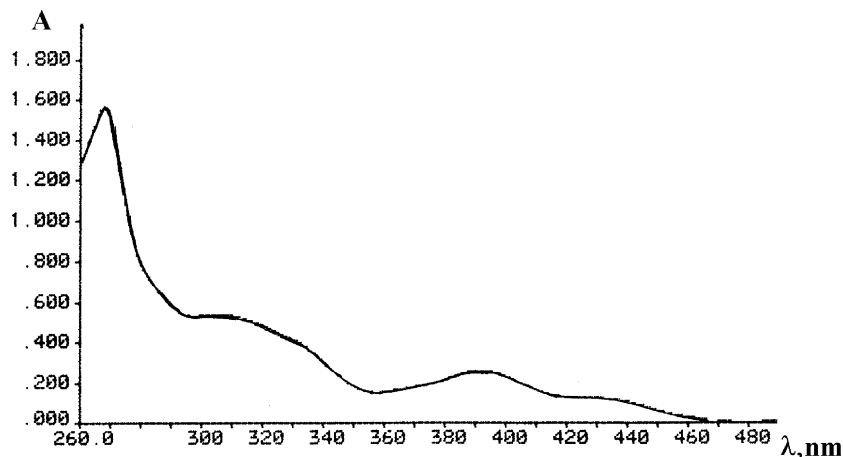


Fig. 7. UV spectrum of polysilane–Ni complex.

reflux. When the addition was complete, the mixture was stirred for 2 h then quenched with a solution of 50 ml ethanol in 100 ml water and washed with 500 ml of distilled water. After filtration of residuals, the remained organic solution was vacuum distilled in order to eliminate the solvent. The chloromethyl-functional polysilane (10 g, 27.5% yield) was obtained through precipitation in 800 ml of isopropanol.

$^1\text{H-NMR}$ of chloromethyl-polysilane (Fig. 1) (δ ppm, CDCl_3): 0.15, d, 21H ($-\text{SiCH}_3$); 2.93, s, 4H ($-\text{CH}_2-\text{Cl}$); 7.0, s 15H ($-\text{SiC}_6\text{H}_5$).

The molecular weight ($^1\text{H-NMR}$) $M_n = 580$.

3.2. Synthesis of salen–Ni complex

This Schiff base was prepared using a standard procedure involving reaction of the appropriate salicylaldehyde with the corresponding diamine (2:1 molar ratio) in ethanol. The yellow imines were purified by recrystallisation from ethanol (yield: 80%).

The Ni(II) complex was prepared by reaction of an aqueous solution of nickel(II) acetate with a boiling alcoholic solution of the corresponding Schiff base ligand (1:1 molar ratio). The precipitated product was collected by filtration, washed with H_2O –ethanol mixture, and then recrystallised from absolute ethanol and or chloroform (yield: 60%, m.p.: 128–129 °C).

IR spectrum (λ , cm^{-1}): 3560, OH; 3080, C–H (ar); 2880–2960, C–H (alif.); 1645–1650, C=N; 1580, 1460 C–C; 1190, 1095 C–N; 805–870, $\text{C}\alpha$ –H.

$^1\text{H-NMR}$ spectrum (δ ppm, DMSO): 3.80, s, 4H, $-\text{N}-\text{CH}_2-$; 6.2–7.5, m, 6H (arom.); 8.30, s, 2H, $-\text{CH}=\text{N}-$; 13.2, s, 4H, OH.

Elemental analysis (%): Calculated: C, 48.89; H, 4.58; N, 7.12; O, 24.47; Ni, 14.94; Found: C, 49.10; H, 4.23; N, 6.25; O, 27.15; Ni, 13.27%.

Molecular formula: $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4\text{Ni}\cdot 2\text{H}_2\text{O}$.

3.3. Synthesis of polysilane–metal complex

The salen–Ni complex (1.008 g) was solved in 15 ml of dried DMF. Over this mixture 0.721 ml of anhydrous triethylamine and 1.49 g difunctional polysilane (dissolved in chloroform) were added. After stirring for 2 days at room temperature, the reaction mixture was heated at reflux for another 10 h. Finally, the solvent was striped out and the remained solid product was precipitated with water and dried. Washing three times the polymer with chloroform and filtration made further purification of the product (yield: 50%).

$^1\text{H-NMR}$ spectrum of polysilane–metal complex (δ ppm, DMSO): 0.15 (m, 21H, $-\text{Si}(\text{CH}_3)$), 3.80 (s, 4H, $-\text{N}-\text{CH}_2-$), 4.15 (s, 4H, $-\text{O}-\text{CH}_2-$), 6.2–7.05 (m, 21H (arom.)); 8.27 (s, 2H, $-\text{CH}=\text{N}-$).

IR spectrum of polysilane–metal complex (λ , cm^{-1}): 3050, $\nu_{\text{Car-H}}$; 2830–2910, $\nu_{\text{Calif-H}}$; 1645–1650, $\nu_{\text{C=N}}$; 1530, 1460 $\nu_{\text{C-C}}$; 1250, $\nu_{\text{Si-CH}_3}$; 1010–1100 overlapping (C–N, C–O–); 800, $\nu_{\text{C-H}}$; 435–500, Si–Si.

UV–Vis spectrum (λ , nm): 390 (π –d MLCT); 320 (σ – σ^* or π – π^* polysilane); 270 (π – π^* phenyl).

TGA analysis: 100–200 °C water loss; 200–470 °C polymer decomposition; 41.63% ash ($\text{SiO}_2 + \text{NiO}$).

4. Conclusion

A new polysilane–metal complex was synthesised and characterised. Further investigations will analyse the redox activity of this material in order to determine the utility of the product for electrochemical devices.

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