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Highly Crosslinked Polysilane–Schiff Base

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Summary

N,N'-Bis(4-hydroxysalicylidene)ethylendiamine (salen) was attached to a poly[iodopropyl(methyl)-co-diphenylsilane)chain. Due to intermolecular crosslinking reactions, a high molecular weight polymer formation was observed. The resulted material was doped with metal cations through complexation reactions. The chemical structure of the polysilane-Schiff base metal complex was investigated by spectral analysis (IR, ^{1}H-NMR, ^{13}C-NMR, UV), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC).

Introduction

Polysilanes are a distinct class of conjugated polymers where the spatially delocalized band-like structure involves σ-electrons and is similar to the alternating single and double bonds in polyenes [1-6]. This peculiar structure allows the motion of the charge carriers within the conjugated backbone and gives them conductive properties [7-10]. The engineering of these electronic properties could be accomplished by narrowing of the polymer bandgap using various techniques like doping with electroactive organic or inorganic materials and by the creation of new types of polysilanes [11,12]. The narrowing of the polymer bandgap could be identified in the UV-VIS spectrum as a red shifting of the specific $\sigma-\sigma*$ electronic transitions [1,2].

This paper presents the synthesis of a new polysilane with redox active centers attached to the main conjugative chain. The novelty of the work is that the resulted hybrid redox-conjugative material is capable of crosslinking reactions but preserves reactive functionalities, which could be used further in complexing reactions with various metal cations.

The polymer was designed for electronic applications when thin layers with specific patterns of different electronic conduction could be prepared by wet-etching technique using solutions of various metal salts.

Several types of polysilanes bearing transition metals have been reported, which include the Co-containing silylene-diethynylene copolymers, silole-metal complex based polymers, the Pt-containing polymer, the bis(bipyridyl)Cu complex based cross-linking polymer, and tris(bipyridyl)Ru complex based polysilane[13-18]. All these present a $\sigma-\pi$ conjugation between oligosilylene units and π-conjugated moieties.

Here we report for the first time a polysilane-Schiff base complex based on electrons donor-acceptor systems where the conjugative effect between the two units is absent.
To obtain such a material is quite a challenging problem because the harsh reaction conditions of the Wurtz coupling procedure are incompatible with most of the known functional groups [19,20]. Therefore we took advantage of the previous experiments, which allow us to obtain Si-H reactive polysilanes with unimodal molecular weights distribution and a low content of cyclic byproducts using a homogeneous coupling reaction system [21]. This polymer has been used to prepare the polysilane derivative with reactive pendant groups.

Experimental

Materials

Allyl iodide (purum, >98%) was purchased from Sigma Aldrich and used without further purification. Hexachloroplatinic acid hexahydrate, $H_2PtCl_6.6H_2O$, (HCPA), was obtained from Fluka AG and used as 1% solution in tetrahydrofurane. N,N'-Bis(4-hydroxysalicylidene)ethylenediamine was prepared by reacting the 4-hydroxysalicylaldehyde with ethylenediamine (2:1 molar ratio) in ethanol [22]. The obtained yellow solid was then purified by recrystallization from ethanol (Mp= 125-126 ^{o}C, yield 80%). $C_{16}H_{16}N_2O_4$ (300.32) Calcd. C 63.99, H 5.37, N 9.33; Found C 64.5, H 5.00, N 9.50. ^{1}H-NMR ($CDCl_3$): δ = 10.13 (s, -O**H**), 8.09 (s, -H^7), 6.25-6.41 (m, H^3, H^5 and H^6), 3.91 (s, -C**H**$_2$-C**H**$_2$-). Poly[methyl(H)-co-diphenylsilane] with low molecular weight (Mn= 4450 g·mol^{-1}) and narrow molecular weight distribution (Mw/Mn= 1.20; Mp= 90-94 ^{o}C), was prepared through a homogeneous coupling process from methyl(H)dichlorosilane and diphenyldichlorosilane [21].
Teterahydrofurane (THF) was purchased from a commercial source and used after distillation over sodium wire.

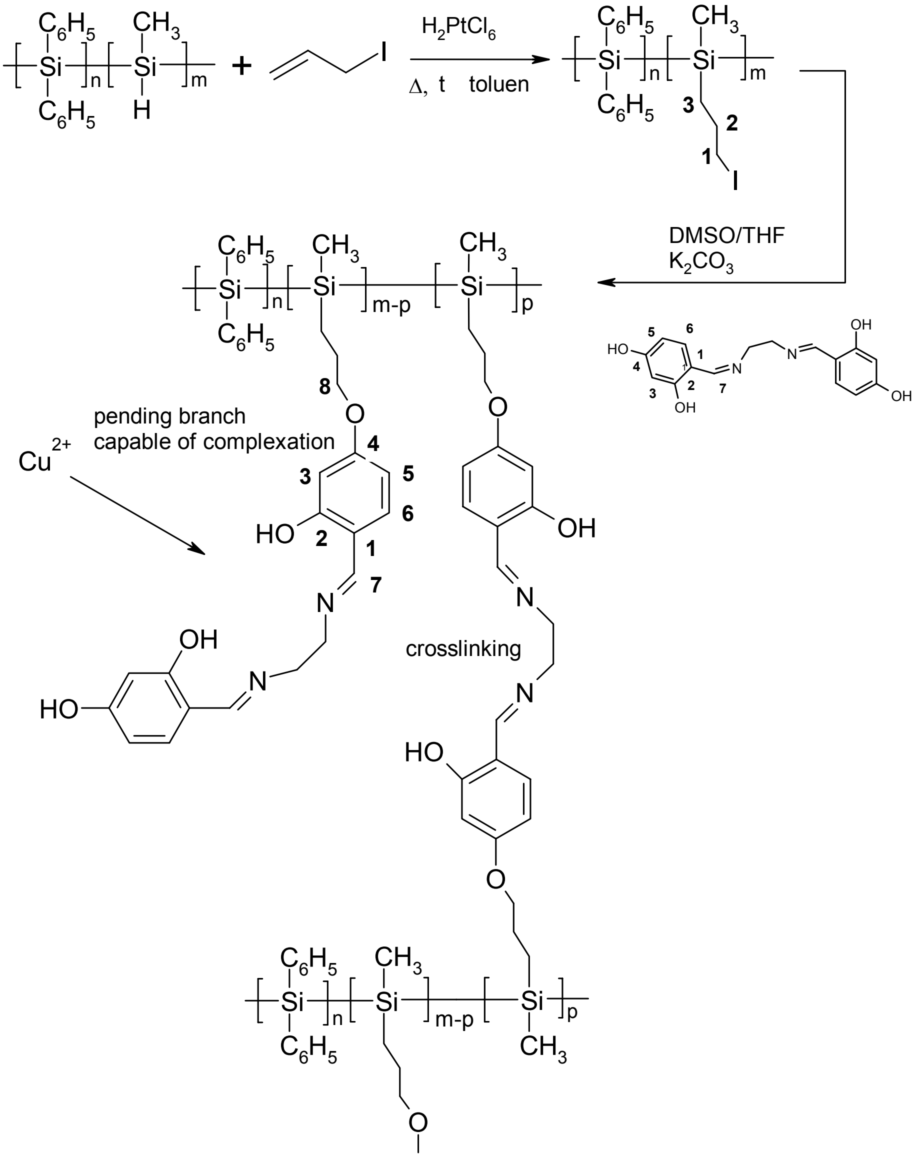
Instruments

Infrared spectrum was obtained on KBr pellets using a SPECORD M80 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker NMR instrument (Model DRX 400 MHz). Chemical shifts are given in parts per million (ppm) without TMS as internal standard.
UV-VIS absorption spectra were recorded at room temperature on a Carl Zeiss Jena SPECORD M42 spectrometer in 10 mm quartz cells and with DMSO as solvent. Gel permeation chromatography (GPC) experiments were carried out in dimethylsulfoxide (DMSO) solution at 30 ^{o}C, at a flow rate of 1cm^3/min. using a Spectra Physics 8800 gel permeation chromatograph with two PL-gel packed columns (10^{3}Å and 500 Å). A UV116 spectrometer and a R132 differential refractometer were used as detectors. The calibration was made following a method described in literature [23].
Thermogravimetric analysis was performed on a MOM Paulik-Paulik-Erdey derivatograph at a 10 ^{o}C/min heating rate, in air.

Synthesis of the poly[iodopropyl(methyl)-co-diphenylsilane

The polysilane with reactive iodopropyl pendant groups was obtained through the catalytic addition reaction of allyl iodide to poly[metyl(H)-co-diphenylsilane]

(Scheme 1). The general procedure was as follows: a 250 mL three-necked reaction flask was charged with 100 mL dry toluene, poly[methyl(H)-co-diphenylsilane] (12 g, 3 mmol) and allyl iodide (2.80 mL, 30 mmol). This reaction mixture was heated to gentle reflux and then a 0.01 N solution of hexachloroplatinic acid in tetrahydrofurane (5.10^{-6}g H_2PtCl_6/ mol compound with vinyl groups) was added. After 48 hours the reaction mixture was cooled to room temperature and the solvent was removed by vacuum distillation. The obtained solid product was washed several times with n-hexane then dried. Yield: 67% (5.9 g).



Scheme 1. Synthesis of polysilane-Schiff base

IR (KBr): 3080 (Car-H), 2980 (C- H), 2150 (Si-H), 1600 and 1513 and 1458 (Car-Car), 805 and 1265 (Si-CH$_3$), 470 and 1070 (Si-Si), 520 (C- I) cm^{-1}.
^{1}H-NMR (CDCl$_3$): δ= 0.15 (d, -C**H**$_3$), 0.9 (m, H^3), 1.75 (m, H^2), 3.01 (m, H^1), 4.21 (s, Si-**H**), 7.0 (m, -C$_6$**H**$_5$) (Figure 1).
The amount of iodopropyl moieties within the polymeric chain calculated from ^{1}H-NMR was 93%.

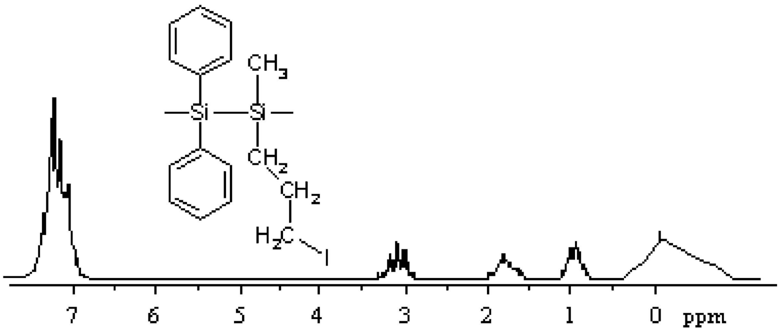


Figure 1. ^{1}H-NMR spectrum of iodopropyl-polysilane

Synthesis of polysilane-Schiff base (PSS)

N,N'-Bis(4-hydroxysalicylidene) ethylenediamine (0.685 g, 4.56 mmol) was solved in 5 mL of dried DMSO. A mixture of 1.575 g (11.4 mmol) K$_2$CO$_3$ and 2.2 g (3.8 mmol) iodopropyl-polysilane (dissolved in THF) was added (Scheme 1). After refluxing for two days under stirring the reaction was considered completed. The solvent was stripped out and the remained product was precipitated with water and dried.
The purified solid product was obtained by washing three times the polymer with chloroform, filtration and drying under vacuum (yield 50%).

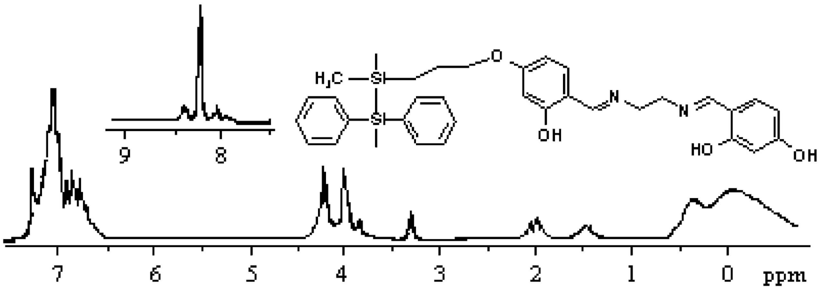


Figure 2. ^{1}H-NMR spectrum of polysilane- Schiff base

IR (KBr): 3050 (Car-H), 2830-2910 (C-H), 2150 (Si-H), 1645-1650 (C=N), 1530 1460 (C-C), 1250 (Si-CH$_3$), 1010-1100 overlapping (C-N, C-O-), 800 (C-H), 435-500 (Si-Si) cm^{-1}.
^{1}H-NMR (DMSO-d$_6$): δ= 0.15 (m, -Si-CH$_3$), 1.5 (s, H^{10}), 2.01 (s, H^9), 3.62 (s, -N-CH$_2$-), 4.15 (s, H^8), 4.21 (s, Si-H), 6.2-7.05 (m, H$_{ar}$), 8.27 (s, H^7) (Figure 2).

^{13}C-NMR (DMSO-d$_6$): δ= -2.5 (Si-CH$_3$), 64.81 (-CH$_2$-CH$_2$-), 69.52 (C^8), 113.40 (C^3 and C^5), 129.27- 133.02 (Car), 162.12 (C^7).
UV-VIS (DMSO): λ_{max}/nm (ε/(L· mol^{-1}·cm^{-1})) = 206 (2500); 280 (600); 330 (1480).
The GPC analysis of a 1% solution in DMSO shows a bimodal molecular weights distribution with maximums at Mw= 9630 g· mol^{-1} for the lower molecular weights and Mw= 14100 g· mol^{-1} for higher molecular weights.

PSS crosslinking study

To study the polysilane crosslinking process, a number of PSS samples has been prepared using the previously described reaction mixture as stock solution. These samples were maintained at 25 °C, 60 °C and 80 °C respectively for 2 to 13 days according to the experimental program presented in Table 1.

Table 1. Experimental data resulted from crosslinking of PSS

Sample	Time	Fraction soluble (wt. %)			Conversion[a)] (%)		
	(h)	80 °C	60 °C	25 °C	80 °C	60 °C	25 °C
1	20	90	88	90	30.5	36.0	35.5
2	30	88	89	89	35.2	41.2	40.1
3	40	83.5	87	88	43.3	51.8	56.8
4	50	41.1	54	62	55.3	56.7	64.5
5	60	22	32	41	65.4	65.0	72.0
6	70	12	29	39	87.1	82	79.6

[a)] Resulted from ^{1}H-NMR analysis

At the end of each experiment the sample was treated with DMSO in excess and separated into soluble and insoluble fractions. The DMSO soluble fractions were precipitated with water, washed three times with ethanol, dried, then weighed and analysed for conversion by ^{1}H-NMR. The process was considered completed when the insoluble fractions reached a constant weight. The results are summarised in Table 1.

Synthesis of the polysilane-Schiff base Cu complex (PSSC)

Polysilane-salen was doped with Cu^{2+} cations by mixing of a Cu (II) acetate solution in methanol with a warm alcoholic suspension of PSS (1:1 molar ratio). The solid product was collected by filtration, washed with methanol, and vacuum dried.
IR spectrum: 3080 (Car-H), 2880-2960 (C-H), 1600 (C=N), 1580 and 1460 (C-C), 805-870 (Cα-H), 435-500 (Si-Si) cm^{-1}.
UV-VIS (DMSO): λ_{max}/nm (ε/(L· mol^{-1}·cm^{-1})) = 233 (2000), 280 (450), 330 (650), 406 (400), 450 nm (200).
TGA analysis in air shows two regions of thermal decomposition: 90-150 °C for linear polysilane and organic segments; 280-380 °C for branched polysilane. 37 % ash. (SiO$_2$ + CuO).

Results and discussion

A polysilane derivative with pendant iodopropyl groups was synthesized through the addition reaction of allyl iodide to poly[methyl(H)-co-diphenylsilane] in the presence of the hexachloroplatinic acid catalyst.

The IR spectrum showed little changes in the 800-1400 cm^{-1} region comparative with the starting polyhydrosilane. The newly formed I-CH_2- bond could be observed at 520 cm^{-1}.

The ^{1}H-NMR spectrum (Figure 1) shows the presence of the propyl group protons at 0.9, 1.75 and 3.01 ppm. The methyl protons of the Si-CH_3 group give a broad peak at 0.15 ppm.

The polysilane-Schiff base was obtained by the condensation reaction of the poly[iodopropyl(methyl)-co-diphenylsilane]silane with N,N'-bis(4-hydroxy salicylidene)ethylenediamine in the presence of K_2CO_3 as proton acceptor. A DMSO-THF mixture has been used to obtain reasonable reaction ratios at low temperatures. This ensured a good homogeneity of the reaction medium and an easier separation of the final products.

Spectral analyses were performed to study the chemical structure of the product.

The IR spectrum shows the absorption band of the –C=N- bond at 1650 cm^{-1}. The absorption bands of the Si-CH_3 group appear at 805 cm^{-1} and 1265 cm^{-1}. The absorption bands of the aromatic ring carbon atoms are also present at 1458, 1513 and 1600 cm^{-1}. The C-H bond absorption bands could be observed at 2910- 2970 cm^{-1}.

The polysilane structure is also studied through ^{1}H-NMR spectral analysis (Figure 2). The phenyl group substituents at the silicon atoms give a multiplet signal within 6.88-7.65 ppm. The –CH=N- protons appear at 8.15 ppm and the protons of the –N-CH_2- group show a chemical shift around 3.62 ppm. The propylene's bridge protons could be noticed at 2.01 ppm and 1.5 ppm. The methyl protons of the Si-CH_3 group give a broad peak at 0.15 ppm.

GPC analyse of the polysilane-salen shows that the system switched from the unimodal molecular weights distribution of the starting polysilane (Mw= 5280 g·mol^{-1}) to a bimodal molecular weights distribution. The maximum around 9630 g·mol^{-1} represents the domain of the lower molecular weights, where linear and partially crosslinked polysilane chains could be found. The presence of the second molecular weights maximum, at 14100 g.mol^{-1}, suggests that unexpected new crosslinked polymeric structures with higher molecular weights were formed. These are the result of intermolecular polycondensation reactions due to the participation of two HO-functionalities of bis(salicylideneimine).

In order to investigate the ability of the salen segments to participate to crosslinking intermolecular reactions, a specially designed experiment has been performed. The results of this experiment provided the necessary conditions for both HO- groups to react and to form the crosslinked polysilane structure. A strong influence of the temperature on the crosslinking time could be noticed mainly below 60 ^{o}C, as shown in Table 1 and Figure 3. A constant crosslinking time was reached at higher temperatures (80 ^{o}C).

At specific values of the conversion, the sol content decreases sharply (Figure 3) with formation of a gel point. Taking into account this observation, the relative position of the gel point versus conversion and temperature was determined at 48.5 % (80 ^{o}C), 51.8 % (60 ^{o}C) and 56.8 % (25 ^{o}C). Furthermore, the presence of a threshold suggests a different behaviour of the reaction system near the gelation point (Figure 3). In the first stage of the process the crosslinking reaction occurs mostly in the liquid state and allows the functional groups to react until gelation is reached. This means that the salen reactive molecules have a greater mobility and a moderate diffusion constraint. Both hydroxyl reactive groups could react with the iodopropyl functionalities of the polymer. In the second stage of the process, after the gelation point, the reaction system becomes a solid polymeric lattice with partially reacted salen molecules trapped within. Because of the high diffusion constraints, this rigid system hinders the access of the second hydroxyl group of salen to the iodopropyl reaction centers. These partially reacted salen molecules are responsible for the complexation reaction in the next stage. The temperature has a relaxing effect switching the gelation point to lower conversions.

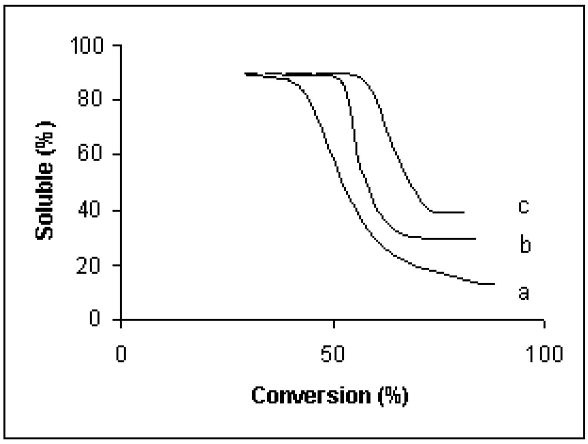


Figure 3. Gelation plot: soluble fraction versus conversion. Experiments made at: a-80 °C; b-60 °C; c-25 °C

Experiments of doping polysilane with Cu^{2+} cations have been performed by the complexation reaction of the pendant salen segments. The formation of the polymer-metal complex could be observed by both spectral and analytic techniques.

The IR spectrum of the doped polysilane shows a characteristic switch of the –C=N- absorption band from 1650 cm^{-1} (salen) to 1600 cm^{-1} (polymer-metal complex).

Generally, the first longest wavelength UV-VIS absorption band of polysilanes is formed mainly from delocalized (σ–σ*) transitions [24,25,21]. The energy of these transitions is conformational-dependent and varies strongly with the length of the molecule [25]. The polyhydrosilane copolymer used in this work encloses methyl(H)silyl- segments statistically distributed within the polydiphenylsilane backbone. This specific structure shifts the position of the longest wave band to 330 nm [21].

The UV-VIS absorption spectrum of the polymer-metal complex shows that in addition to the specific absorption bands of the polysilane, the characteristic transitions of the metal-complex appear at 402 nm (d-π* transitions) and shoulder at 450 nm (MLCT transitions). The position of these absorption bands is almost the same as in the free salen-metal complex, which suggests that attaching of the metal-complex groups to the backbone through propylene bridges preserved unaltered the electrons distributions of both the polysilane and metal-complex. This specific structure should allow for both kinds of conduction, conjugative and redox, to be possible in the system.

Unlike the TGA analysis of a linear polyhydrosilane, which shows a singular differential peak, the thermal decomposition of the synthesised polysilane presents two differential peaks and suggests the existence of two different structures [21]. The first one (90-150 ^{o}C) corresponds to the thermal decomposition of the linear low molecular weights polysilane chains and organic segments (15 % weight loss). The second one (280-380 ^{o}C) represents the thermal decomposition of the crosslinked polysilane structure.

The TGA analysis could be used to obtain quantitative information about the amount of metal enclosed within the polymeric network. Therefore the thermal decomposition process, in air yields 37% ash as a mixture of SiO_2 and CuO. Knowing the Si content (determined through elemental analysis) as 15.6 %, the content of Cu^{2+} within the polymeric network was estimated to 4.6% [26].

Conclusion

A new polysilane with pendant metal complex segments was synthesized and characterized. For this purpose a macroligand has been prepared starting from a iodopropyl-functionalized polysilane and a bis(salicylideneimine) derivative. Under mild reaction temperature this polymeric ligand has been able to form higher molecular weights structures, which could be doped with metal cations. The UV-VIS spectrum of this new material indicates that the electronic structures of the conjugate polysilane chain and metal complex remained unaffected by the condensation reaction process. Further investigations will study the hybrid redox-conjugative conduction of the material.

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