



## Telechelic or side-functionalized diorganosiloxanes with ferrocenylimine groups

Angelica Vlad<sup>a</sup>, Maria Cazacu<sup>a,\*</sup>, Constantin Turta<sup>a,b</sup>, Radu Ionut Tigoianu<sup>a</sup>, Anton Airinei<sup>a</sup>, Adina Arvinte<sup>c</sup>

<sup>a</sup> Inorganic Polymers Department, "Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, Iasi, 700487, Romania

<sup>b</sup> Institute of Chemistry, Academy of Sciences of Moldova, Chisinau, Academy str. 3, MD-2028, Republic of Moldova

<sup>c</sup> Centre of Advanced Research in Nanobioconjugates and Biopolymers, "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica-Voda 41A, 700487 Iasi, Romania

### ARTICLE INFO

#### Article history:

Received 15 July 2011

Received in revised form

24 September 2011

Accepted 26 September 2011

Available online 21 October 2011

#### Keywords:

Siloxane

Ferrocene

Imine

Mossbauer spectrum

Cyclic voltammetry

Mixed valence

Electronic absorption spectra

### ABSTRACT

Formyl-ferrocene, FFc, was prepared and used as agent to attach ferrocenyl moiety to siloxanes through imine group. Thus, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, L1,  $\alpha,\omega$ -bis(3-aminopropyl)dimethylsiloxyloligodiphenylsiloxane, L2, and poly[dimethylmethyl(3-aminopropyl)siloxane], L3 (the last two prepared by us) were converted in the corresponding azomethine derivatives: 1,3-bis(3-ferrocenyliminepropyl)tetramethyldisiloxane, L1Fc,  $\alpha,\omega$ -bis(ferrocenyliminepropyl)dimethylsiloxyloligodiphenylsiloxane, L2Fc, and poly[dimethylmethyl(3-ferrocenyliminepropyl)siloxane], L3Fc. The iron spin state was determined by Mossbauer spectroscopy, emphasizing the presence of mixed-valence iron of interest for molecular electronics. Cyclic voltammograms of the compounds, both in solution and as films deposited on glassy carbon electrodes, showed quasi-reversible oxidation/reduction waves making them suitable for sensing applications. The solvent effect was studied by UV–Vis spectra.

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## 1. Introduction

It is believed that the discovery of ferrocene has contributed greatly to the rapid development of modern organo-transition metal chemistry. A variety of metals were used as central atoms in such sandwich compounds, including titanium, cobalt, zirconium, platinum, chromium, osmium, and uranium, resulting in the new compounds class, metallocenes. However, ferrocene has been most studied due to their interesting properties (thermal, redox, electrical, optical, magnetic, catalytical, etc.) [1] that have found application in various fields such as asymmetric catalysis, electrochemistry and development of new pharmaceuticals [1,2]. Ferrocene is relatively stable towards acids or bases but it is sensitive to oxidizing agents [1]. When is oxidized to the ferricinium species, the ferrocene moieties may act as oxidizing agents [3]. The most reversible Fc/Fc<sup>+</sup> system is useful in electron transfer and redox catalysis [2]. Due to the redox properties, ferrocene-containing materials can be used in sensing applications [4]. The redox potential of ferrocene derivatives may be tuned

in some extent by the proper functionalization [5]. Co-existence in the same compounds of Fe(II) and Fe(III) species results in mixed valence compounds. Such compounds are suitable for the study of intramolecular electron and energy transfer. The electronic properties of mixed valence compounds strongly depend on the extent of the electronic interaction between the redox centers [6]. Functionalized ferrocene is a useful tool for the incorporation of metal into polymeric or high organic structure [7]. In principle, one could prepare a whole series of functionalized redox-active polymers by combining the ferrocene-containing monomer with a variety of other monomers. Thus, this sandwich complex was incorporated into a variety of polymeric materials, including ferrocene-containing polyesters and amides, polyvinylferrocenes, ferrocene-containing polyurethanes, polysilanes and polysiloxanes [3], ferrocenyl-based polymers and copolymers being important due to their redox, electrical, optical, magnetic, catalytic, preceramic, and elastomeric properties. The ferrocene presence also induces high photochemical and thermal stability. The polymers containing ferrocene are useful for the manufacture of electronic devices such as microelectrochemical diodes, in the formation of redox gels, which show charge transfer properties, in the modification of electrodes, in the construction of amperometric biosensors, as precursors to ferromagnetic ceramics, in the area of non-linear optical (NLO) materials, etc. [2,5,8,9].

\* Corresponding author.

E-mail address: [mcazacu@icmpp.ro](mailto:mcazacu@icmpp.ro) (M. Cazacu).

The widespread utility of organosiloxane polymers has led to an increasing interest in modification of their properties by incorporation of various moieties in the polymer chain. The chemical insertion of the metals in siloxane-based polymeric structures constitutes a challenge for obtaining materials with new properties, taking into account the polysiloxanes uniqueness [10].

There are many attempts in literature to prepare ferrocenyl-siloxane structures [11–14]. Thus, a ferrocene-derivatized monomer was prepared in which ferrocene is appended to an oligosiloxane chain that is terminated in Si–H groups. Ferrocene grafted siloxanes were prepared in high yields via Rh-catalyzed dehydrogenative coupling of a series of monomeric, polymeric, and cyclic hydrosiloxanes with ferrocenemethanol [14]. It has been shown that the high conformational flexibility of the siloxane backbones allows close contact between ferrocene centers [10]. The fact that the ferrocenyl moieties are either an ending part of the main polymer chain or pendant groups attached to the flexible siloxane backbones is of significance in providing information about the influence of the polymer structure and ferrocene substituent mobility on the physical, chemical and electrochemical properties of these redox-active polymers [10].

In this paper we report the synthesis and characterization of some diorganosiloxanes possessing ferrocenyl units side or ending attached. The compounds were investigated by Mossbauer spectroscopy to identify the oxidation state of the iron ions. Due to the ideal redox properties of the ferrocenyl group, the compounds containing it have received considerable attention having high potential applications as electrochemical labels or redox mediators for the development of electrochemical biosensors. Electrochemical behavior was studied by cyclic voltammetry. The solvent effect was investigated by UV–Vis absorption spectroscopy in solution. The ferrocene derivatives containing atoms with donor abilities (imine nitrogen in our case) attracted great interest since the coordination of a metal to this heteroatom produces multicentre molecules [15]. The introduction of additional metal centers is a pathway to build a large range of coordination architectures of high potential for the development of functional materials [16].

## 2. Experimental

### 2.1. Materials

Formyl-ferrocene, FFC was prepared by formylation of ferrocene by using *N,N'*-dimethylformamide–phosphorus oxychloride system according to procedure described in literature [17]. Yield: 12.0 g (52%); Elemental composition: Calcd for  $C_{11}H_{10}OFe$  (M 214 g/mol), %: C, 61.7; H, 4.7; Fe, 26.2. Found, %: C, 61.5; H, 4.7; Fe, 26.0. FTIR (KBr pellet,  $cm^{-1}$ ): 3089w, 2832w, 2762w, 1681vs, 1663vs, 1619s, 1454s, 1410m, 1245s, 1106s, 1060w, 1035s, 1025m, 1003m, 840m, 823s, 759w, 744s, 619w, 525s, 499s, 481s, 457m.  $^1H$  NMR(400.13 MHz,  $CDCl_3$ ),  $\delta$ , ppm: 9.96 (s, 1H,  $CH=O$ ), 4.80, 4.61 (s, 4H,  $C_5H_4-$ ), 4.28 (s, 5H,  $C_5H_5$ ); intensity ratio: 1:2:2:5.

Octaphenylcyclotetrasiloxane [ $(C_6H_5)_2SiO$ ] $_4$ , Ph $_4$ , was supplied by ABCR (purity 98%).

Tetramethylammonium hydroxide pentahydrate  $(CH_3)_4NOH \cdot 5H_2O$ , TMAH, was obtained from Fluka (solution 25 wt% in water).

1,3-Bis(3-aminopropyl)tetramethyldisiloxane [ $H_2N(CH_2)_3(CH_3)_2Si$ ] $_2O$ , L1, supplied by Fluka with main characteristics: b.p. = 142 °C/11.5 mmHg,  $d_4^{20}$  = 0.901.

3-Aminopropyl(diethoxy)methylsilane  $CH_3Si(OC_2H_5)_2(CH_2)_3NH_2$ , APDEMS, was purchased from Aldrich (M = 191.34, bp = 85–88 °C/8 mmHg,  $d^{25}$  = 0.916 g/mL).

Diethoxydimethylsilane  $(CH_3)_2Si(OC_2H_5)_2$ , DEDMS, was purchased from Aldrich (b.p. 148.28,  $d$  = 0.865, 97%).

Dimethylformamide and tetrahydrofuran (Fluka AG) were dried and freshly distilled before use. Other solvents (acetonitrile, dichloromethane, dioxane, chloroform, etc.) were used as such.

### 2.2. Techniques

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer. Analyses were performed in the transmission mode in the range 400–4000  $cm^{-1}$  at room temperature with a resolution of 2  $cm^{-1}$  and accumulation of 32 scans. The samples were incorporated in dry KBr and processed as pellets in order to be analyzed.

The proton magnetic resonance ( $^1H$ NMR) spectra were acquired in  $CDCl_3$  at 25 °C with a Bruker Avance DRX 400 MHz spectrometer operating at 400.13 MHz for  $^1H$ . The spectrometer was equipped with a 5 mm four nuclei, direct detection z-gradient probehead. Chemical shifts are reported in ppm and are referenced to chloroform  $\delta^1H$  = 7.26 ppm.

The Mössbauer spectra were carried out using a conventional spectrometer in the constant-acceleration mode (MS4, Edina, USA) equipped with a  $^{57}Co$  source (3.7 GBq) in a rhodium matrix. Isomer shifts are given relative to  $\alpha$ -Fe at room temperature. The samples were measured at room temperature and the spectra were fitted using the NORMOS Mössbauer Fitting Program.

The voltammetry measurements were carried out using an Autolab PGSTAT-302N potentiostat from Echo Chemie (Utrecht, Netherlands) connected to a PC with GPES software. An electrochemical cell containing 5.0 ml of 0.1 M  $NaClO_4$  electrolyte solution with an Ag/AgCl electrode as reference, a Pt wire as auxiliary and the modified glassy carbon electrode (GC) with 3 mm diameter as working electrode were used for all measurements. Prior to experiments, the GC electrodes were polished with alumina slurries, followed by washing with distilled water.

Ultraviolet–visible absorption spectra were recorded on an Analytik Jena SPECORD 200 spectrophotometer.

### 2.3. Procedure

#### 2.3.1. Synthesis of

##### $\alpha,\omega$ -bis(3-aminopropyl)dimethylsiloxy)oligodiphenylsiloxane, L2

Three drops of TMAH solution 25% in water were introduced in a three-necked flask and the water was removed in vacuum at 80 °C, when a white-yellowish solid remained. Then, 3 ml dimethylformamide, DMF, 1 ml (0.95 g, 3.8 mmol) 1,3-bis(3-aminopropyl)tetramethyldisiloxane, L1, and 3.09 g (3.9 mmol) octaphenylcyclotetrasiloxane, Ph $_4$ , were added. Reflux condenser with  $CaCl_2$  protection, inert gas inlet and mechanical stirrer were attached to the flask. The reaction mixture was mechanically stirred under a steady stream of nitrogen at 80 °C for 5 h. Then, the temperature was increased to 150 °C for 1 h to decompose the catalyst. Finally, the reaction product was dried under vacuum at room temperature for degasation and then at 150 °C to remove the solvent and eventually other volatile fractions.

FTIR (KBr pellet,  $cm^{-1}$ ): 3137m, 3091m, 3071s, 3049s, 2955s, 2925s, 2868m, 1680s, 1592s, 1488m, 1429s, 1253s, 1186m, 1125s, 1053s, 1028s, 998s, 921m, 840s, 741s, 717s, 698s, 575m, 520s, 489s.

$^1H$  NMR (400.13 MHz,  $CDCl_3$ ),  $\delta$ , ppm: (7.62, 7.30, 5H,  $-C_6H_5$ ), 2.67 ( $-CH_2-NH_2$ ), 1.47 ( $-CH_2-CH_2-CH_2-$ ); 0.54 ( $-Si-CH_2-$ ), 0.09 ( $CH_3-Si-$ ); intensity ratio: 15:2:2:2:6. Molecular formula estimated based on  $^1H$  NMR:  $C_{46}H_{58}O_4N_2Si_5$  (M 842 g/mol).

#### 2.3.2. Synthesis of

##### poly(dimethyl-methyl(3-aminopropyl)siloxane), L3

20 ml (18.32 g, 95.7 mmol) 3-Aminopropyl(diethoxy)methylsilane (APDEMS), was mixed with 16.4 ml (14.19 g, 95.7 mmol) Diethoxydimethylsilane (DEDMS) in a round bottom flask. 3 ml

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