

New ferrocene-containing structures: Poly(silyl ester)s

Maria Cazacu^{a,*}, Grigore Munteanu^b, Carmen Racles^a, Angelica Vlad^a, Mihai Marcu^a

^a “Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487, Iasi, Romania

^b Chemistry Institute, Academy Street Nr. 3, Moldavian Academy, Chishineu, MD-2028, Republic of Moldova

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Abstract

Two new polymeric structures containing ferrocene units along the chains, namely poly(silyl ester)s, have been synthesized and characterized: a geminal poly(silyl ester) (g-PSE) and one having a disiloxane spacer between the silyl ester groups (s-PSE). The condensation polymerization of AA/BB monomer systems in solution was used in both cases as preparation method involving a silicon-containing diol, (diphenylsilane diol or 1,3-bis(hydroxy)-tetramethyldisiloxane), and 1,1'-di(chlorocarbonyl)ferrocene. The polymers were investigated by differential pulse voltammetry in order to evaluate the redox behavior. Due to the presence of the silyl ester groups in the chain, these polymers are hydrolytically degradable.

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1. Introduction

The ferrocene-containing macromolecules are of interest for their useful application in the chemical modification of electrodes, electrochemical sensors, charge dissipation materials, which provide protection with respect to ionizing radiation such as electrons, materials for the construction of liquid crystals and non-linear optical (NLO) systems, electronic devices or chiral ligands for asymmetric catalysis. The magnetic properties of oxidized poly(ferrocene)s have also attracted attention [1,2]. Poly(ferrocene) block copolymers allow access to nanostructured materials [1]. It has also been explored the utility of the ferrocene–ferricinium redox systems in the cancer treatments. Some polyamines and polyamides containing ferrocene have been synthesized as potential stimulants of antibody formation [3].

The utility of the siloxane-based redox polymers (i.e. siloxane polymers containing ferrocene derivatives) in

mediating electron transfer between an enzyme and electrode surface has already been demonstrated. The high flexibility of the polysiloxane backbone allows a sufficiently close contact to occur between the redox complex of the polymeric system and the enzyme's redox centers so that efficient charge transfer can be achieved. Sensors incorporating such redox polymeric systems may be of potential clinical value in implantable measuring devices [4].

There are many reports on macromolecular systems containing ferrocenyl moiety besides highly flexible dimethylsiloxane and more rigid organic [5] or silane sequences synthesized in general by transition metal-catalyzed ring-opening polymerization of the ferrocenophane [1,6–9] or by hydrosilylation of vinyl-functionalized ferrocene with methyl-H-siloxanes [2,10–12]. The literature on the synthesis of siloxane–ferrocene macromolecular systems by polycondensation is very scarce [13] although this procedure permits to use a large range of functionalized monomers having as a result polymers with internal polar functions (ester, amide, etc.), which could influence some of the properties [13,14]. More, these internal functions can confer degradability in certain conditions, when this is desired. The optimum loading of the ferrocene in the electroactive

* Corresponding author.

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

polymeric structures used as electron mediators can be easily controlled by spacer length between ferrocene units thus controlling the efficiency of mediated electron transfer [15].

There is a report on the synthesis by polycondensation of siloxane-based polymeric structures namely those in which the amide-linked ferrocenyl moieties are incorporated pendant or as a part of the polymer backbone [16]. In a previously paper [17], we also reported about synthesis and characterization of several polyamides and polyesters containing siloxane sequences and ferrocene units into the backbone. Starting from the same ferrocene derivative, 1,1'-ferrocenedicarboxylic acid, but using a silane or siloxane diol as condensation comonomer, in the present paper we synthesized new structures containing ferrocene: poly(silyl ester)s.

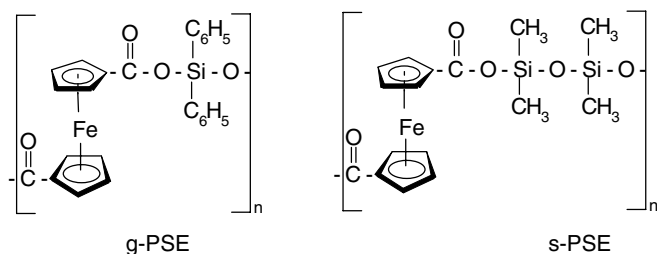
Poly(silyl ester)s have been reported as a novel class of degradable polymers based on the labile silyl ester linkage along the polymer backbone. The silyl ester bridge can be cleaved by either attack at the carbonyl or at the silicon atom. Due to this dual mechanism of cleavage, polymers with “tailor-made” degradation properties can be approached [18]. The site of nucleophilic attack can be controlled through modification of the substituents attached to the silicon atoms.

It has already been reported [14] the preparation of ferrocene-siloxane polymers containing the silyl ether group, Si-O-C, susceptible to nucleophilic attack by water. These resulted by condensation of bis(dimethylamino)-dimethyl or diphenylsilanes with 1,1'-bis(hydroxymethyl)ferrocene. Such polymers that possess the unique properties of being both electrochemically active and biodegradable are of interest as implantable biomaterials [19].

Our paper originality consists in obtaining the new polymers containing alternating ferrocene units and silicon-containing sequences along the chain with hydrolytically degradable silyl ester links between them. Depending on the silicone component, a poly(silyl ester), either geminal (g-PSE) or one having disiloxane spacer (s-PSE) has been obtained (Scheme 1).

The influence of the poly(silyl ester) type (geminal or spaced) on their main properties (thermal, redox) was evaluated.

Similarly polymers containing ferrocenyl moieties in the backbone have not yet been reported.



Scheme 1.

2. Experimental

2.1. Materials

1,1'-Di(chlorocarbonyl)ferrocene, ClCO-C₅H₄-Fe-C₅H₄-COCl, (CAFc) was prepared by a three-step procedure starting from the ferrocene, according to methods described in the literature [20,21].

Diphenylsilanediol, (C₆H₅)₂Si(OH)₂, DFSD, was prepared by hydrolysis of diphenyldichlorosilane in diethyl-ether/water or acetone/water mixture, in presence of an anion exchanger having weakly basic groups as hydrochloric acid acceptor. The product (recrystallized from benzene) with m.p. = 148–151 °C was obtained in 87% yield [22].

1,3-Bis(hydroxy)-tetramethyldisiloxane, [HO(CH₃)₂Si-]₂O, (D₂), was prepared according to a known procedure [22,23] by hydrolysis of dimethyldichlorosilane at 0–2 °C, maintaining a pH value between 6.5 and 8.5 in the reaction milieu by bubbling gaseous NH₃. The white crystalline product was obtained in 32% yield after recrystallization from hexane (m.p. = 67–68 °C).

Pyridine, Py, (Fluka) was used as received.

Methylene chloride, benzene and acetonitrile were used freshly dried before use.

2.2. Equipments

The IR spectra were recorded on a SPECORD M80 spectrophotometer.

The ¹H NMR spectra were recorded on a BRUKER Avance DRX 400 spectrometer, using DMSO-*d*₆ as a solvent.

Gel permeation chromatographic analysis (GPC) was carried out on a PL-EMD 950 evaporative mass detector instrument by using DMF or THF as eluants after calibration with standard polystyrene samples.

Thermogravimetric measurements were performed at a heating rate of 10 °C/min in air, using a Q-1500D System (F. Paulik, J. Paulik, Lerdey).

The reduced viscosities were determined based on the measurements of the polymer solution (about 0.5% w/v) in NMP done at 25 °C by using an Ubbelohde Suspended Level Viscometer.

Polarized light optical microscopy (POM) observations were made with an Olympus BH-2 microscope (Japan), equipped with a THMS 600/HSF9I hot stage.

The DSC analyses were done on a Mettler TA DSC 12E Instrument, with heating and cooling rate of 10 °C/min.

The redox activity of the synthesized ferrocene-containing polymers was investigated by differential pulse voltammetry using a Polarograph PA-3 in pulse differential regime (5 impulse/s) and the impulse amplitude of 25 mV. The scan rates: $\nu = 10\text{--}50$ mV/s. DMF was used as a solvent and 0.1 M solution of NaClO₄ as the electrolyte. The working electrode has been prepared from carbon fiber UMV-1800 (5 mm length, 30 μm in diameter).

The silicon content was determined according to an adapted procedure [24]: disintegration with sulfuric acid and ignition at 900 °C to constant weight. Finally, the residue was treated with HF for silicon removal as SiF₄ and then calculation by difference. The iron content was determined from the residue remained after silicon analysis, considering that Fe₂O₃ is formed in such conditions.

2.3. Polycondensation

2.3.1. Synthesis of the poly(ferrocenyl-silylester-diphenylsilane), g-PSE

In a well-dried two-necked flask equipped with a reflux condenser having calcium chloride protection, nitrogen inlet and magnetic stirrer 0.9330 g (0.003 mole) DPSD was dissolved in 25 mL freshly dried benzene and refluxed to completely dissolving. An equimolecular amount, 0.6540 g (0.003 mole) CAFc of and Py in excess (0.5 mL) were added. The reaction mixture was stirred at reflux for about 2 h and until 24 h at room temperature. The chlorohydrate as a white precipitate appeared about in the first hour. Finally, the reaction mixture was filtered in order to separate the pyridine chlorohydrate. The solvent was

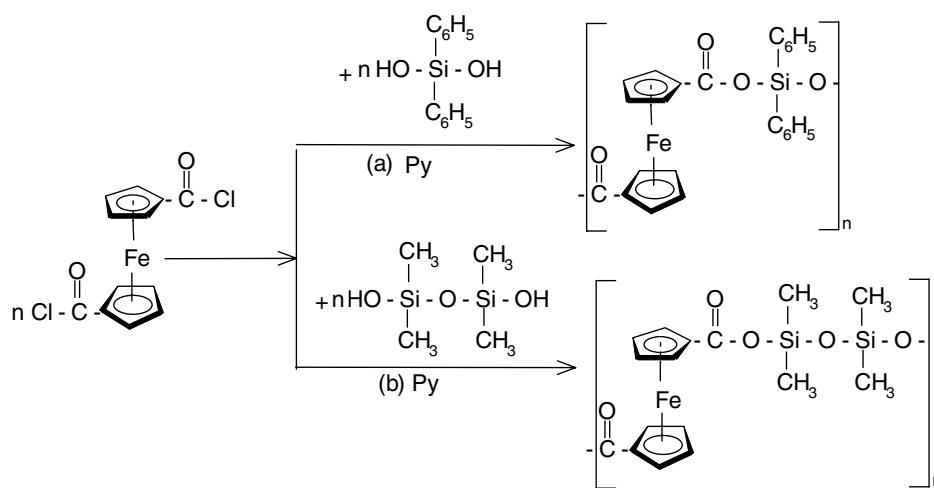
removed from the filtrate by rotavapor. The residue was repeatedly extracted with acetonitrile. The product was recovered from the cumulated extracted solutions by rotavapor. The reaction, separation and purification of the product have been led in dried environment. An orange grain solid was obtained and characterized (yield: 62%, 0.848 g).

2.3.2. Synthesis of the poly(ferrocenyl-silylester-tetramethyldisiloxane), s-PSE

In above described installation, the weighted amount D₂, 0.4980 g (0.003 mole) was dissolved in 10 mL freshly dried methylene chloride by refluxing. Then, the equimolecular amount CAFc, 0.933 (0.003 mole) and Py in excess (0.5 mL) were added. The reaction mixture was refluxed for about 3 h. Finally, the chlorohydrate appeared after 45 min, was removed by filtration. The reaction product was recovered by above described procedure (yield: 57%, 0.691 g).

3. Results and discussion

The poly(silyl ester)s were synthesized by condensation polymerizations of the AA/BB monomer systems in stoi-



Scheme 2.

Table 1
Some analytical data for the synthesized ferrocene-containing poly(silyl ester)s

Sample	Reactants	Elemental analysis, %, found/calc. ^a		η_{red}^{25} (dl/g) ^d	GPC data	
		Si ^b	Fe ^c		Mn	Mw
g-PSE	CAFc, DFSD	5.7/6.2	13.1/12.3	1.07	6920 ^e	7120 ^e
s-PSE	CAFc, D ₂	12.8/13.9	14.4/13.9	0.85	10,660 ^f	15,460 ^f

^a Calculated for the idealized structural unit.

^b Determined according to Ref. [24].

^c Determined from the residue remained after silicon analysis, considering that Fe₂O₃ is formed.

^d Determined for a concentration of about 0.5 g/dl in NMP.

^e Eluant: DMF.

^f Eluant: THF.

Table 2
The solubility of the resulted poly(silyl ester)s

Sample	CH ₂ Cl ₂	CHCl ₃	Acetone	THF	NMP	DMF	CH ₃ OH	DMSO
g-PSE	+–	+–	–	+–	+	+	–	+
s-PSE	+–	+	+–	+	+	+	+–	+

–, insoluble; +–, partial soluble; +, soluble.

chiometric amounts, namely ferrocenyl diacid chloride and a silicon-containing diol: diphenylsilane diol or 1,3-bis(hydroxy)-tetramethyldisiloxane.

The polycondensation reactions occurred in solution at low concentration using either refluxing benzene or methylene chloride as a solvent, and a base, pyridine, as a hydrochloric acid acceptor. The maintaining of the reflux

temperature was necessary to assure the reaction homogeneity by dissolving of the diols.

A poly(silyl ester) geminal, g-PSE, (Scheme 2a) or one having a disiloxane spacer between the silyl ester groups, s-PSE, (Scheme 2b), respectively, resulted, depending on the diol structure, diphenylsilane diol or 1,3-bis(hydroxy)-tetramethyldisiloxane.

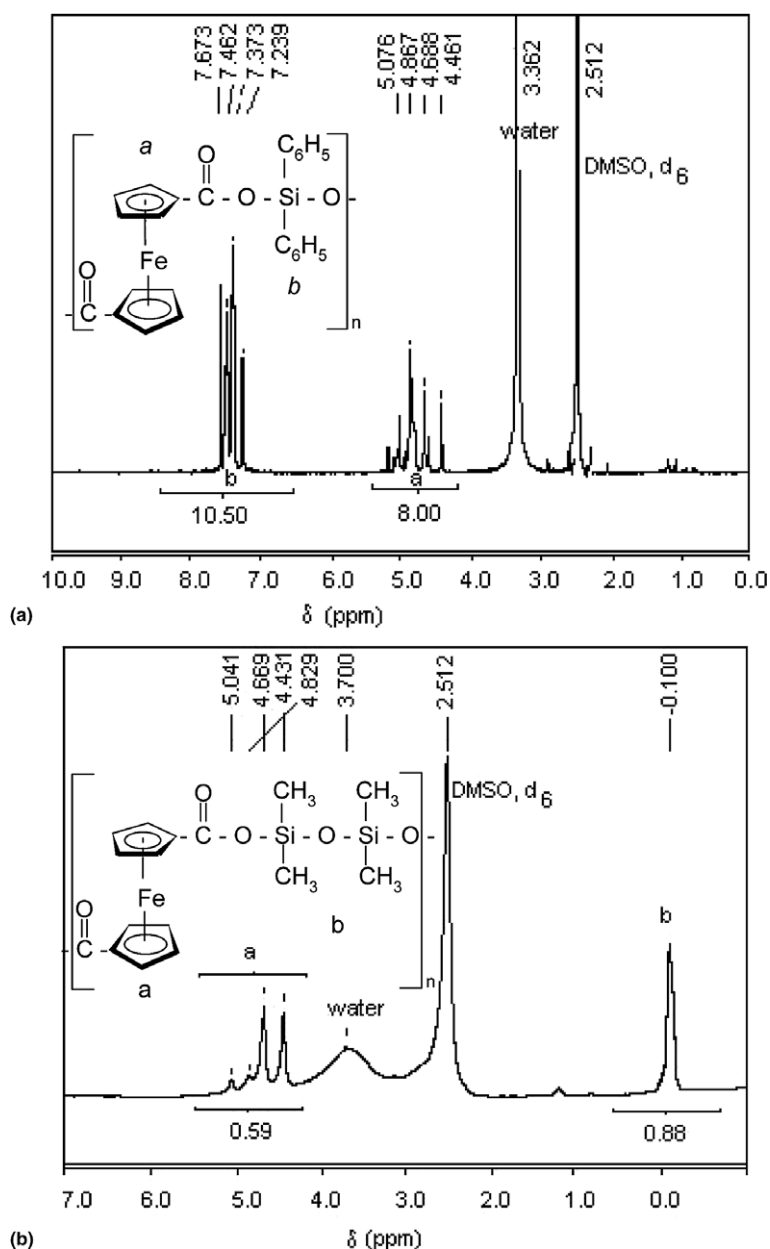


Fig. 1. ¹H NMR spectra for g-PSE (a) and s-PSE (b) in DMSO-*d*₆.

The obtained polymers were characterized by IR spectrometry, elemental analysis, viscometry, GPC (Table 1), DSC and POM.

Elemental analysis values for silicon and iron contents in polymers were found in relative good agreement with the presumed structures for a condensation polymeric structure (Table 1). However, as already has been reported in other papers on such type of polymers [5,16,25], the elemental analysis values for C were found to be lower as compared with those calculated. This is explained, in the case of polymers with interacting metal atoms in main chain, by the formation of a ceramic material in the analysis conditions for carbon. Therefore, such type of polymers are currently investigated as precursors to ceramics.

Taking into account the reduced viscosity values but in special the molecular weight values determined by GPC (Table 1), the resulted structures could be considered to be polymers.

The obtained polymers were soluble in common organic solvents as shown in Table 2.

IR (KBr):

g-PSE: 3100 (s, sp^2C-H), 2980 (sp^3C-H), 1775, 1715 (vs, $-CO-O-Si$), 1370, 1450 (s, Cp ring mode), 1130, 1000 (s, $Si-C_6H_5$), 1075 (vs, $Si-O-C$), 750, 720, 700 (s, C_6H_5) cm^{-1} , 530, 490 (s, Cp_2Fe) [14,26];

s-PSE: 3050, 2980 (s, sp^2C-H), 1775, 1710 (vs, $-CO-O-Si$) [23], 1450, 1370 (s, Cp ring mode), 1250 (vs, $Si-CH_3$), 1070 (vs, $Si-O-C$), 1050–1090 (vs, $Si-O-Si$), 800 (vs, $Si-CH_3$) cm^{-1} , 535, 495 (s, Cp_2Fe) [14,26].

As can be seen in the IR spectra of the polymers are evidenced all characteristic bands for presumed structures. It can be noticed that poly(silyl ester)s presents two bands for silyl ester groups. These can be justified by coexistence of the ferrocenyl and ferrocenium neighborhood. Thus, while the bands at 1715 cm^{-1} in g-PSE and 1710 cm^{-1} in s-PSE are assigned to silyl ester group neighbored to ferr-

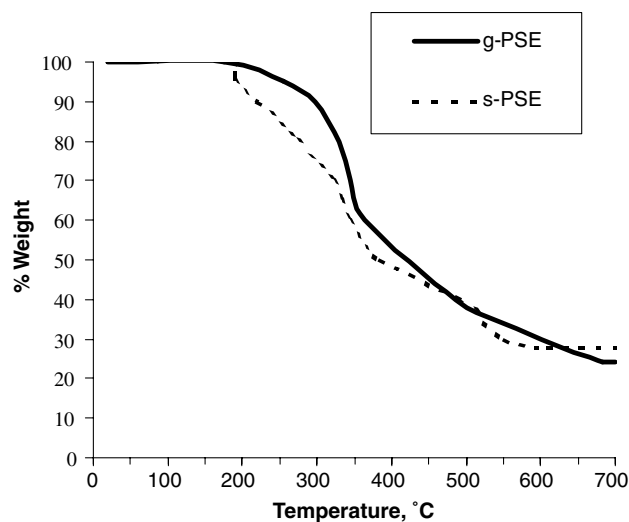


Fig. 3. Comparative TGA curves for the synthesized polymers.

ocenyl, the band at 1775 cm^{-1} in both polymers is assigned to silyl ester neighbored to ferrocenium group [14,16,26].

The 1H NMR spectra of the two polymers (Fig. 1), in DMSO, show the specific resonances for the two types of protons. In the spectrum of g-PSE, these are visible in 4.46–5.07 ppm and 7.24–7.57 ppm ranges for cyclopentadienyl and phenyl (C_6H_5-Si) protons, respectively, while in the spectrum of s-PSE, where the resonance at -0.1 ppm is assigned to the protons from $(CH_3)_2Si$ groups, the cyclopentadienyl protons resonances are slightly shifted to higher energy (4.43–5.04 ppm). The complexity of the resonances patterns for the cyclopentadienyl protons comes both from the co-existence of the reduced and oxidized forms and from the end groups that, at low values of the molecular mass (i.e., $M_n = 6920$ for g-PSE), show visible signals.

s-PSE is a brown waxy compound at room temperature. g-PSE is a solid one and two endotherms were observed by DSC (Fig. 2), one at 160 °C (melting temperature) and the

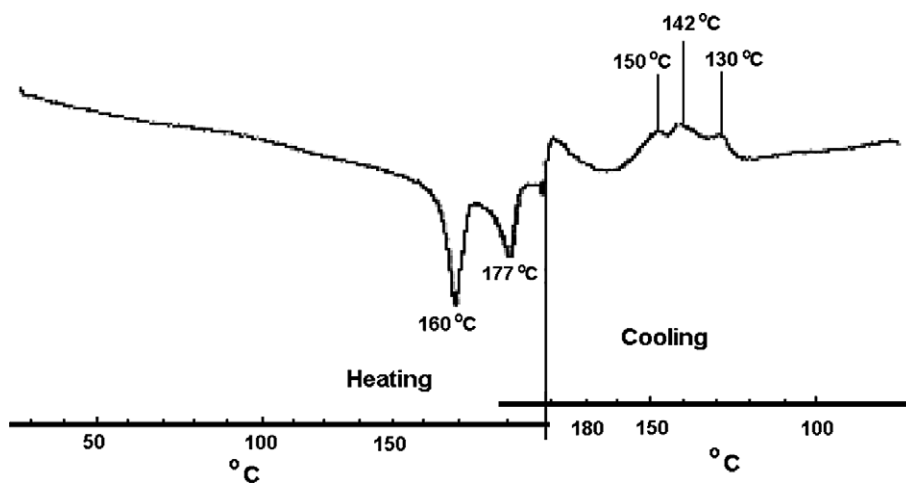
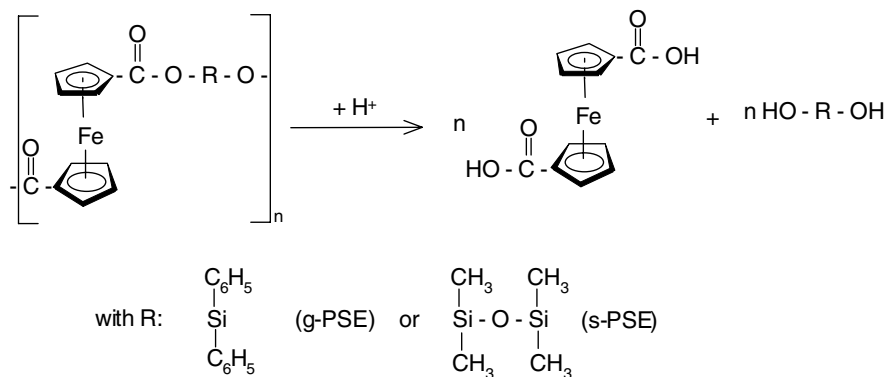


Fig. 2. DSC scan of poly(silyl ester) g-PSE.



Scheme 3.

other at 177 °C (assigned to isotropization based on the POM observations). Three exotherms were registered on cooling, at 150, 142 and 130 °C, showing a supercooling effect.

The thermal stability of the two polymers was evaluated by thermogravimetric analysis (TGA) performed in air, at a heating rate 10 °C/min. Based on the curves showed in Fig. 3, it can be appreciate that both polymers have good thermal stabilities but a slight increase in thermooxidative stability can be observed in the case of the polymer having diphenyl-substituted silicon. It is also expected that, the diphenyl-substituted silicon alternating with ferrocenyl

units linked between them by silyl ester bridge to have also another interesting properties due to high conjugation possibilities.

The polycondensation of the chosen monomers leads to the formation of $-\text{Si}-\text{O}-\text{OC}-$ groups directly linked to the cyclopentadienyl ring. As it is well known, the $-\text{Si}-\text{O}-\text{OC}-$ group is very sensitive towards solvolysis, both hydrolysis and alcoholysis occurring readily even in the absence of acid or basic catalysts.

The IR spectra registered at various time range revealed in both cases a reduction of the bands assigned to the silyl ester group (1775, 1715 in g-PSE and 1775, 1710 in s-PSE)

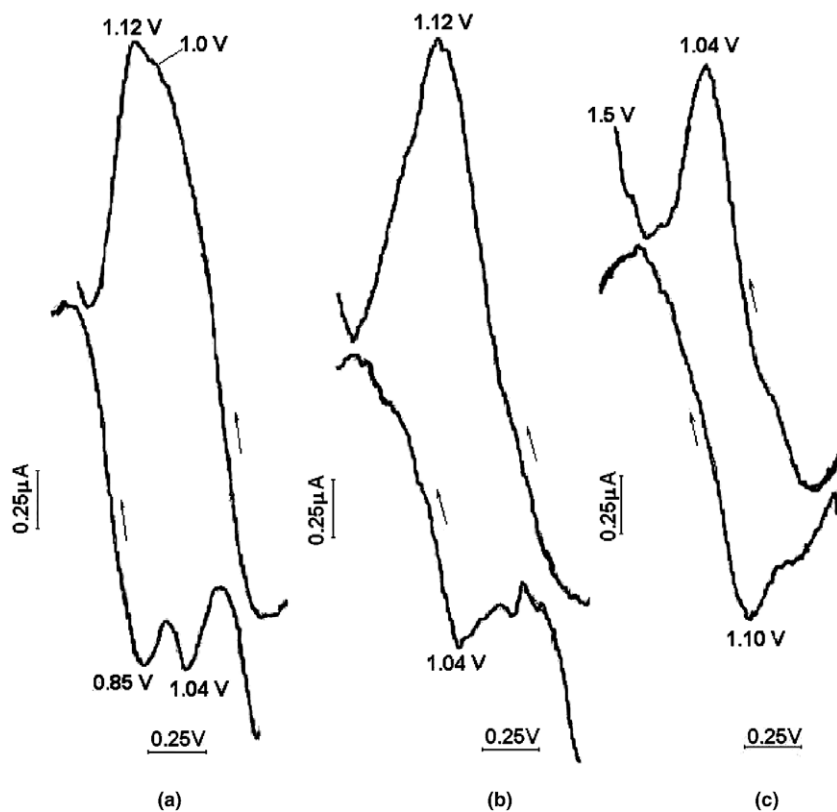


Fig. 4. Cyclic differential pulse voltammograms for: (a) s-PSE anodic-cathodic scan; (b) g-PSE anodic-cathodic scan; (c) g-PSE cathodic-anodic scan, at a carbon fiber electrode in DMF/0.1 M NaClO_4 solution. The cathodic curves (bottom curves) were reversed and rotated with 180°.

Table 3
Differential pulse voltammetry data of the synthesized poly(silyl ester)s in anodic–cathodic scan

Code	E_{p1}^a (mV)	E_{p2}^a (mV)	E_{p1}^c (mV)	E_{p2}^c (mV)	ΔE_{p1} (mV)	ΔE_{p2} (mV)	I_{p1}^a (μ A)	I_{p2}^a (μ A)	I_{p1}^c (μ A)	I_{p2}^c (μ A)
g-PSE ^a	1110	–	1040	–	70	–	1.65	–	0.6	–
s-PSE ^b	1000	1120	1040	860	40	260	1.63	–	0.33	0.65

E_{p1}^a – first anodic peak potential.

E_{p2}^a – second anodic peak potential.

E_{p1}^c – first cathodic peak potential.

E_{p2}^c – second cathodic peak potential.

I_{p1}^a – first anodic peak current.

I_{p2}^a – second anodic peak current.

I_{p1}^c – first cathodic peak current.

I_{p2}^c – second cathodic peak current.

^a 6.35 mg in 2 ml DMFA.

^b 5.35 mg in 2 ml DMFA.

in the same time developing that assigned to carboxyl group (at 1680 cm^{-1}) as a result of the hydrolysis occurring under influence of the environmental humidity.

The corresponding ferrocene diacid and silicon-containing diol are formed as a result of the hydrolysis occurring under influence of the environmental humidity, according to Scheme 3.

There are many factors influencing the hydrolytically stability of the poly(silyl ester)s, which would be evaluated as such, type of the silyl ester (a geminal poly(silyl ester) being less stable to nucleophilic reagents than the spaced one), the steric bulk around the silicon or electronegativity of substituents attached to the silicon atoms [27]. An advanced study on the kinetic of the hydrolytically degradability will be described in a future articles.

Electrochemical behavior of the synthesized ferrocene-containing poly(silyl ester)s was investigated by differential pulse voltammetry (DPV). This technique has an increased sensitivity and permits to better identify if the electrochemical process gradually occurs. The peaks are better shaped as compared with cyclic voltametry (CV). The cyclic differential pulse voltammograms for the two polymers have been processed by reversing and rotating the cathodic curves with 180° (Fig. 4).

Although both poly(silyl ester)s proved to be redox active, their voltammograms differ in shape as can be seen in Fig. 4. Thus, for s-PSE containing a disiloxane bridge between the ferrocene units, two reversible oxidation waves are registered (Fig. 4a). In the case of g-PSE only a single reversible oxidation wave appears, the splitting of the anodic peak being almost imperceptible (Fig. 4b, c). This could be explained by the differences in chemical structures suggesting that by varying the condensation partners can to design polymers with desired redox behaviors. The main electrochemical data for the synthesized polymers are presented in Table 3.

4. Conclusions

Diphenylsilane diol and 1,3-bis(hydroxy)-tetramethyl disiloxane were polycondensed with 1,1'-di(chlorocarbonyl)ferrocene resulting in polymeric structures having silyl ester as internal groups. Depending on the used diol,

a geminal or spaced poly(silyl ester) resulted. The structures of the products were verified by spectral and elemental analysis and characterized by solubility tests, GPC, viscometric measurements, thermal and electrochemical analyses. It has been emphasized that the two obtained polymers differ in the thermal stability and particularly in electrochemical behavior due to the differences in their structure. Both polymers are hydrolytically degradable.

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