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Pyrrolyl-silicon compounds with different alkyl spacer lengths: Synthesis, electrochemical behavior and binding properties

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ABSTRACT

This work reports a joint experimental-theoretical investigation of pyrrolyl-silicon compounds with different alkyl spacers, namely propyl, butyl and hexyl side chains carrying silicon-based end groups. For the electrochemical study, the monomers with methoxysilyl end groups spaced through butyl and hexyl chains were ad-hoc synthesized. Structurally different oligomeric domains are promoted during electropolymerization as a result of irreversible hydrolysis of methoxy end groups by acid intermediate σ-oligomers. The onset of OH-π stabilizing interactions and the charge pinning action of silanol promotes mixed n-p doping behavior of the hybrid films. The more important charge trapping in the case of propyl spacer is attributed to effective (through bond) inductive effects and conformational restrictions. MD simulations of chemisorption of hydrolyzed oligo-pyrroles onto γ-Al_2O_3 surface confirmed the propyl spacer as the optimum alkyl chain length for stratification and interpenetration of adsorbed hybrid layers.

1. Introduction

Since the discovery of intrinsically conducting polymers (ICPs) in 1976 by MacDiarmid, Shirakawa and Heeger [1,2], research efforts have provided the basis for the development of new applications and new processing technologies [3–12]. A key aspect in the up growth of semiconducting ICP films with specific physico-chemical properties is the adhesion of the polymeric material to a given substrate (metallic, inorganic, bioinorganic). Bifunctional grafting with organosilanes by virtue of silanol groups coordination onto hydroxylated surfaces through hydrogen bonds constitutes a promising approach [13–15]. Since the pioneering work of Simon et al. [16], the integration of silane chemistry in the development of composite ICPs films have attracted increasing scientific interest in the field of solid state electronic devices [17–20] and biomedical applications [21–23].

N-substituted pyrrole and aniline with methoxysilylpropyl groups as precursors for direct-to-metal treatment of aluminum alloys have been extensively investigated by some of the co-authors [24–27]. The surface treatment with the corresponding hydrolysed solutions allowed to overcome the limited barrier protection against corrosion and the poor adhesion of contiguous polymeric films [28–30]. However, differently from the aniline derivative, the parent pyrrolyl-silicon compound (Fig. 1a, ω = 3) presents peculiar properties such as the kinetic stabilization of silanol in solution and the n-type semiconducting behaviour of films deposited on FTO substrates. Theoretical studies indicated that intramolecular stabilization is determined by the donor-acceptor character of hydrolysed monomer and of oligomers linked α–α' *via* pyrrole rings, favouring non-covalent OH-π interactions between electron-deficient silanol group (Si—OH) and electron-rich pyrrole (Py) ring [31]. The charge-pinning action of Si—OH promoting Py ring saturation could explain the n-type semiconducting behaviour. Although these findings concur with the well-known importance of the electronic properties of the substituents on the building up of ICPs networks [32], pyrrolyl-silicon structures seems to be promising for tailoring hybrid macromolecular networks with specific functions. Of concern is the influence of the length of the alkyl spacer on the physico-chemical properties and molecular packing [33–37]. The special properties of Al and its alloys (low cost, light weight, high strength and surface reflectivity, among other) make them advantageous over other substrates [38], while damage due to environmental corrosion is prevented.

In this paper, the effect of the length of the alkyl chain spacer on the electrochemical behavior of *N*-[ω-(trimethoxysilyl)alkyl]-1H-pyrroles (Fig. 1a) and on the binding properties of hydrolyzed oligo-pyrrole structures (Fig. 1b) were investigated. For the electrochemical study, the monomers containing butyl and hexyl spacers (Fig. 1a, ω = 4,6) were ad-hoc synthesized and characterized by some of the co-authors with large experience in organic chemistry and structural elucidation [39–41]. The binding capabilities of hydrolyzed α–α' linked trimer

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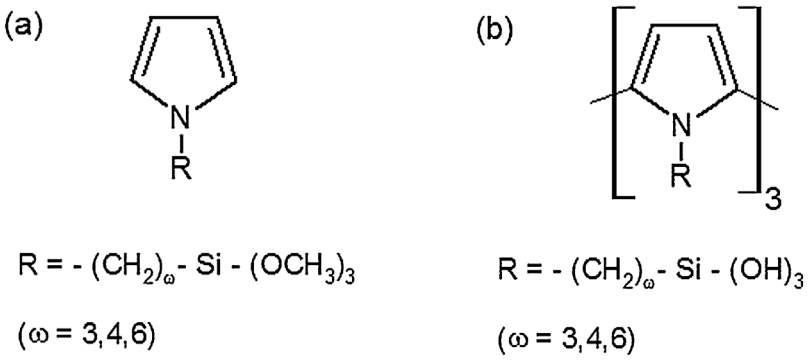

Fig. 1. Schematic structures of the investigated compounds: (a) *N*-[ω-(trimethoxysilyl)alkyl]-1H-pyrroles with different alkyl chain lengths (ω = 3, 4 and 6); (b) hydrolyzed α α' linked *N*-[ω-(trimethoxysilyl)alkyl]-1H-pyrroles.

structures (Fig. 1b) with hydroxylated ϒ-alumina (γ-Al_2O_3) surface were investigated by molecular dynamics (MD) by some of the co-authors with significant background on computational methods [42–44].

2. Experimental

2.1. Synthesis of N-[ω-(trimethoxysilyl)alkyl]-1H-pyrroles (ω = 4,6)

2.1.1. Materials and methods

All chemicals and anhydrous solvents were of reagent grade and used as supplied by Sigma-Aldrich, with the exception of dichloromethane CH_2Cl_2 which was distilled over CaH_2 under N_2 atmosphere before use. All the reactions were carried out under anhydrous inert conditions (N_2 atmosphere). All the glassware was dried in a heater over-night and cooled under vacuum.

Analytical TLC were carried out on pre-coated plates (silica gel 60, 250 μm layer thickness), using an UV lamp (254 nm) for visualization. Column chromatographies were performed with silica gel 60 (230–400 mesh). The ^1H and ^{13}C NMR spectra were taken on a Varian Mercury Plus 200, operating at 200 MHz for ^1H and 50.3 MHz for ^{13}C. Chemical shifts were expressed as ppm (δ) using the central peak of chloroform as internal reference (δ_H = 7.23 ppm; δ_C = 77.3 ppm). The APT sequence was used to distinguish methine and methylcarbon signals from those of methylene and quaternary carbons. FT-IR spectra were collected using the Spectrum One Perkin Elmer (MA, USA) FT-IR Spectrometer in the spectral region between 4000 and 600 or 450 cm^{-1} for solid or liquid compounds, respectively, and analyzed by transmittance technique with 32 scans and 4 cm^{-1} resolution. Solid samples were mixed in a mortar with KBr (1:100) and pressed in a hydraulic press (10 T) into small tablets. One drop of a given liquid sample was placed between two plates of sodium chloride. Low resolution mass analyses were recorded with a Thermo-Finnigan LCQ advantage AP electro spray/ion trap equipped instrument by using a syringe pump device to directly inject sample solutions.

2.1.2. General synthetic procedures of pyrrolyl silicon compounds with butyl and hexyl spacers

N-[ω-(Trimethoxysilyl)butyl]-1H-pyrrole and *N*-[ω-(trimethoxysilyl)hexyl]-1H-pyrrole (Fig. 1a, ω = 4,6) were synthesized following three steps, according to the general synthetic route in Scheme 1.

The intermediate ω-alkenyl methanesulfonate (1a,b) and ω-alkenyl-1H-pyrrole (2a,b), and final *N*-[ω-(trimethoxysilyl)alkyl]-1H-pyrrole (3a,b) products were analyzed by ^1H and ^{13}C NMR, Mass spectrometry, and FTIR (Supporting information, Table S1). Details of each synthesis step are given here below.

2.1.2.1. ω-Alkenyl methanesulfonate (1a,b). To an ice-cold stirred solution of but-3-en-1-ol or hex-5-en-1-ol (5 g, 50 mmol) in dichloromethane (50 mL), triethylamine (10.52 mL, 75 mmol) and methanesulfonyl chloride (5.8 mL, 75 mmol) were added dropwise, and the mixture was stirred at 0 °C for 1 h. A saturated aqueous NH_4Cl solution (50 mL) was added to the reaction and the mixture was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with water and brine and then dried over Na_2SO_4. The solvent was removed under reduced pressure (750 mbar; 40 °C; nitrogen atmosphere) to give a yellow oil of the corresponding mesylate.

2.1.2.2. ω-Alkenyl-1H-pyrrole (2a,b). Under nitrogen atmosphere, pyrrole (2.66 mL, 483 mmol) was added to a stirred suspension of sodium hydroxide (3.86 g, 966 mmol) in dry DMSO (35.2 mL) at room temperature. After slow addition of a given methanesulfonate 1a-b (8.6 g, 483 mmol) at 0 °C, the mixture was stirred during 14 h at room temperature. The reaction mixture was poured into ice water (75 mL) and extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with water and brine, and then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using EtOAc/hexane 2:98, to give the corresponding 1-(hex-5-enyl)-1H-pyrrole as a yellow oil.

2.1.2.3. N-[ω-(Trimethoxysilyl)alkyl]-1H-pyrrole (3a,b). A mixture of ω-alkenyl-1H-pyrrole (6.39 g, 43 mmol) and a catalytic amount of hexachloroplatinic acid hexahydrate (0.72 mmol) was stirred during 30 min under nitrogen atmosphere. Trimethoxysilane (20.95 g, 172 mmol) was added dropwise, and the mixture was stirred during 6 h at room temperature. Distillation under reduced pressure gives *N*-[ω-(trimethoxysilyl)alkyl]-1H-pyrrole as a yellow oil.

2.2. Electrochemical experiments

Electrochemical experiments were performed with a computer driven Autolab PGSTAT 12 potentiostat/galvanostat (EcoChemie, The Netherlands), using GPES 4.9 software. The electrochemical system consisted in a one compartment three-electrode glass cell with a capacity of 5 mL. The working electrode was a Pt disk with geometrical surface area of 0.7 cm^2 (Ø = 3 mm, AMEL). Pt wire and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Unless otherwise stated, potentials are reported throughout vs. SCE. The experiments were performed at room temperature under N_2 atmosphere.

The electrolyte solutions were prepared at a concentration of 0.1 M of tetrabutylammonium perchlorate TBAP (≥99.0%, Sigma Aldrich) in acetonitrile MeCN (≥99.8%, Sigma Aldrich). The synthesis solutions were prepared at a concentration of 4 mM of a given pyrrolyl-silicon monomer (Fig. 1a) in 0.1 M TBAP/MeCN. The N-substituted monomer with propyl spacer (98%, Sigma Aldrich) was used as received. Pyrrole (Aldrich) was studied in parallel for reference purposes (R = H, Fig. 1a). This monomer was distilled under argon atmosphere before use. The films were grown potentiodynamically by single-cycle potential scan and by recurrent potential cycling, using different anodic potential limits (E_A of +2.0, +1.4, +1.2 V). Translucent and brownish thin films were observed on the Pt surface at the end of the experiments. The redox behavior was evaluated by cyclic voltammetry using