ChemComm

Synthesis, characterization and thin film formation of end-functionalized organometallic polymers

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Received (in Bristol, UK) 9th November 1998, Accepted 12th January 1999

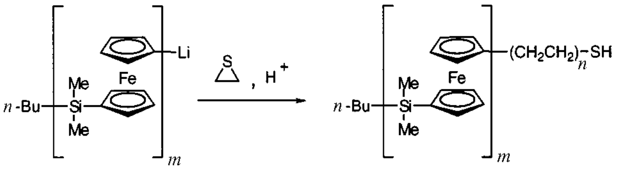
Poly(ferrocenyldimethylsilanes) (PFS) end-functionalized by ethylene sulfide form stable, electroactive layers on Au.

Interfacial electron transfer plays a fundamental role in a large number of biological and technical processes. Progress in the area of self-assembled monolayers resulted in a number of synthetic and physical developments which now allow one to perform systematic studies of surface electrochemistry of well defined molecular thin films of thiols terminated by (electroactive) ferrocene moieties, immobilized on Au.[1] Surface immobilization of redox active compounds, such as ferrocene derivatives, with a well defined structure and with a variable surface concentration of the electroactive centers offers the possibility of the control of charge transfer. We have undertaken a systematic study of thiol end-functionalized ferrocenylsilane polymers obtained by anionic polymerization.

In this contribution we describe the synthesis, molecular characterization and thin film properties of poly(ferrocenyldimethylsilane) (PFS), end-functionalized by ethylene sulfide (ES), denoted ES–PFS. This organometallic polymer has been chosen as it exhibits interesting electrochemical and other potentially useful properties owing to its unique structure which incorporates ferrocene units and Si atoms in the main chain.[2]

Poly(ferrocenyldimethylsilane) homopolymer and its thiol end-functionalized derivative were synthesized by anionic ring-opening polymerizations. The synthesis of the homopolymer has been described elsewhere.[3] ES–PFS was synthesized by treating an end-reactive living homopolymer with ethylene sulfide as shown in Scheme 1.

Molecular characterization of ES–PFS was carried out by ^{1}H NMR, GPC, FTIR and elemental analysis. GPC measurements were carried out in THF in order to determine the molar mass and its distribution. The molar mass of ES–PFS was referenced to a polystyrene calibration curve. The number average molar mass, M_n, was found to be 12.4×10^3. This value was expected from the molar ratio of monomer to initiator. The polydispersity ratio (M_w/M_n) was found to be equal to 1.11. The molar mass of the polymer was also estimated by end-group analysis using ^{1}H NMR[4] and a value of 12.3×10^3 was obtained. Thus, an excellent agreement between the molar masses according to the two techniques was found. The peak found in the ^{1}H NMR spectrum at δ 2.57 (spectrum not shown) was assigned to the methylene group next to sulfur in the end-group. The assignments of the ^{1}H NMR resonances at δ 4.00 3.80 correspond to the protons (4H) from the cyclopentadienyl rings, while the resonance at δ 0.28 corresponds to the 6H from the methyl groups attached to Si. Spectroscopic characterization of ES–PFS was undertaken by FTIR of ES–PFS in KBr pellets. The absorbances assigned to the C–H vibrations in the ferrocene rings and in the methyl, and methylene groups can be observed in the FTIR spectra. Results from elemental analysis are in a good agreement with the theoretically expected values [theoretical values (mass%): C, 59.14; H, 5.8; S, 0.97 and experimentally found values: C, 58.33; H, 5.92; S, 0.62].



Scheme 1

Thin films of ES–PFS were prepared by immersing gold substrates[5] into 0.1 and 1.0 mg ml^{-1} solutions of the polymers in toluene for 48 h to ensure maximum coverage. The samples were subsequently rinsed with toluene and dried in a nitrogen stream. The films were characterized by contact angle measurements, XPS and FTIR. Contact angles with water were measured to evaluate the wetting properties and the uniformity of the ES–PFS layers on gold. Advancing contact angles were found to be *ca.* 95° and receding contact angles *ca.* 76°, respectively, indicating a hydrophobic surface. Peaks associated with C 1s, Fe 2p (from the ferrocene ring), Si 2s (from the polymer backbone) and S 2p (from the end-function) can be distinguished in the XPS spectra of ES–PFS layers. This indicates that the polymer is immobilized on the gold surface. FTIR spectra of the monolayers taken in grazing incidence with perpendicularly polarized light confirm the presence of the end-functionalized polymer on the Au substrate. The observed vibration frequencies are in good agreement with literature data.[6]

Surface plasmon resonance spectroscopy (SPRS) experiments were carried out in order to study the adsorption kinetics of end-functionalized ES–PFS on gold in comparison with PFS, and to determine the optical thickness of the layers.[7] The formation of a thin film of ES–PFS on the gold surface results in an angular shift of the resonance angle [Fig. 1(a)] which is a function of the thickness and the refractive index. Curve 2 in Fig. 1(a) was recorded following 50 h of total sorption time. An average value of 39.8 Å was found for the limiting optical thickness of the polymer (refractive index $n = 1.687$) described in this study. The refractive index was determined previously by profilometry followed by ellipsometry. Measurements of the time dependence of optical reflectivity showed that a monolayer is formed with fast kinetics [Fig. 1(b)]. At between 800 and 3000 min the reflectivity remained constant. The adsorption of non-functionalized PFS on the gold surface did produce a small angular shift [Fig. 1(c)] from which an average thickness of 11.0 Å was determined. Curve 2 in Fig. 1(c) was measured following 800 min of total sorption time. The time dependence of the reflectivity showed [Fig. 1(d)] that in the case of non-functionalized polymer the adsorption rates are slower. In order to check whether the predominant process is physi- or chemisorption, the polymer films were washed after deposition using toluene. The layer formed of non-functionalized polymers

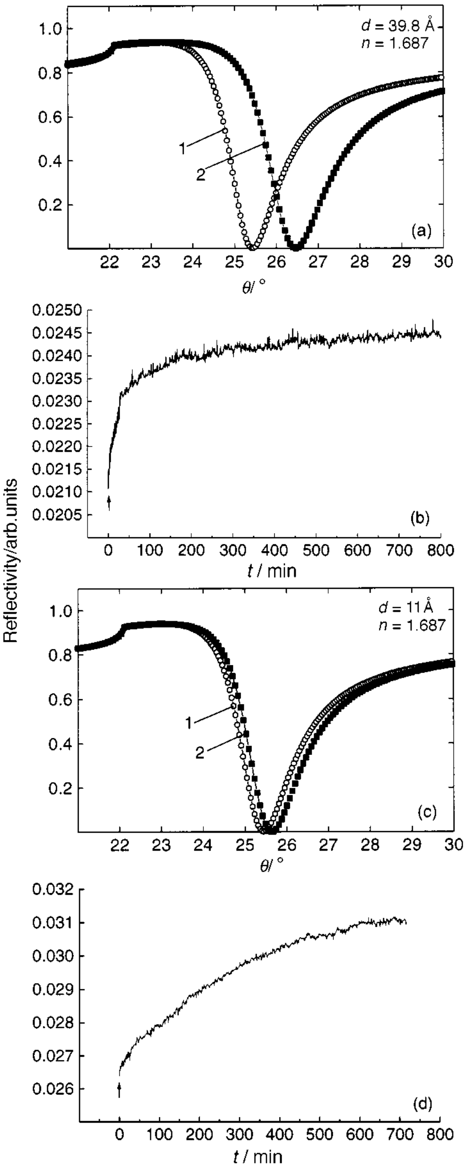


Fig. 1 (a) Angular reflectivity scans recorded in air (1) at bare Au/LaSFN9 (Berliner Glass) and (2) after immobilization of ES–PFS (c = 1.0 mg ml^{-1}) on Au/LaSFN9. (b) Time dependence of reflectivity for ES–PFS in toluene (c = 1.0 mg ml^{-1}) at an angle of incidence θ = 78° (the arrow indicates the injection of the polymer solution). (c) Angular reflectivity scans recorded in air (1) at bare Au/LaSFN9 (Berliner Glass) and (2) after adsorption of PFS (c = 1.0 mg ml^{-1}) on Au/LaSFN9. (d) Time dependence of reflectivity for PFS in toluene (c = 1.0 mg ml^{-1}) at an angle of incidence θ = 77° (the arrow indicates the injection of the polymer solution).

could be easily removed which indicated that only physisorption occurred for this polymer. The films of the end-functionalized ES–PFS were stable against washing with toluene indicating predominant chemisorption.

Atomic force microscopy (AFM) was used to image the film topography. Well defined, triangular, monoatomic terraces of Au(111) were prepared by annealing sputtered Au substrates, on glass, in a H_2 flame. Tapping mode atomic force microscopy[8] (AFM) height and phase imaging were used to characterize the morphology of ES–PFS layers on Au(111). Owing to the adsorption of the end-functionalized polymer, corresponding AFM images exhibit a globular surface structure (Fig. 2), instead of the atomically smooth terraces of bare Au(111). The contours of the underlying triangular terraces of Au(111) can still be observed on the AFM images even for the specimen showing the chemisorbed polymer film.

The electrochemical behavior of ES–PFS layers in comparison with the physisorbed PFS layers was investigated by cyclic voltammetry. The experiments were performed on layers of physisorbed, non-functionalized PFS and end-functionalized, chemisorbed films of ES–PFS before and after immersion in pure toluene for 24 h. The current observed for the end-functionalized ES–PFS showed only a small change prior to, and following immersion into toluene. This can be considered as an indication for the fact that the end-functionalized PFS forms a stable layer on gold. For the non-functionalized physisorbed PFS the change in the intensity of the current in the cyclic voltammograms prior to, and following immersion into the solvent was significant (Fig. 3).

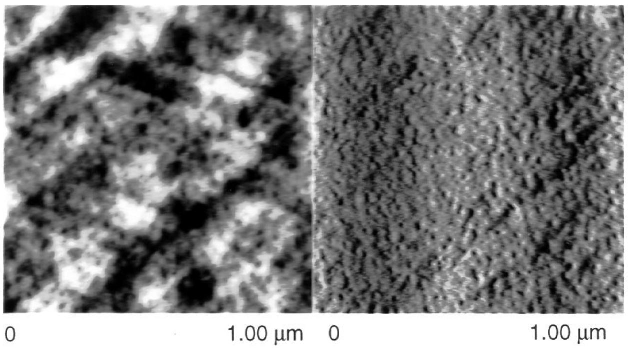


Fig. 2 Tapping mode height (left, z = 10 nm) and phase (right, z = 9°) images recorded for ES–PFS layers on Au(111).

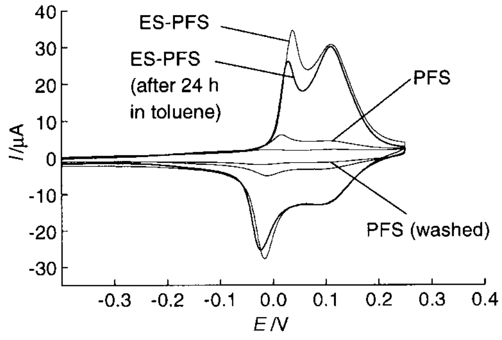


Fig. 3 Cyclic voltammograms of PFS, PFS (after 24 h in toluene), ES–PFS and ES–PFS (after 24 h in toluene) layers on gold at v = 50 mV s^{-1} scan rate (reference electrode Hg–$HgSO_4$, auxiliary electrode Pt, 0.1 M $NaClO_4$ electrolyte solution).

Further work is aimed at *in situ* studies of the electrochemical behavior of end-functionalized poly(ferrocenylsilane) layers on Au substrates by electrochemical AFM at different degrees of oxidation.

The authors would like to thank Mr H. Schönherr for his help with AFM experiments and for many helpful discussions. The contributions of Mr P. G. H. Kosters in the FTIR experiments, Mr A. H. J. van den Berg in the XPS measurements, and Mr C. J. Padberg with the GPC are acknowledged.

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Communication 8/09259A