Journal of Electroanalytical Chemistry 786 (2017) 129–134

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electrochemical studies of ferrocene and maleimide containing alternating copolymers

Ahmed Alzharani, Charles Ault, Esam Allehyani, Chris S. Hance, Raymond B. Westby, Benjamin O. Tayo, Charles J. Neef *

Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762, USA

ARTICLE INFO

Article history:
Received 14 July 2016
Received in revised form 9 January 2017
Accepted 10 January 2017
Available online 12 January 2017

Keywords:
Ferrocenophane
Maleimide
Copolymer
Electrochemistry

ABSTRACT

Copolymers from vinylferrocene and 3-phenyl[5]ferrocenophane with *N*-ethyl and *N*-phenylmaleimide were electrochemically characterized. The deposition method of the polymer onto the electrode by oxidative deposition or cast film was studied and showed that films produced by cast film exhibited a greater electrochemical response. The oxidation potentials of these materials were dependent on supporting electrolyte when using $NaClO_4$, $NaNO_3$ or phosphate buffered saline, varying from 0.46 to 0.53 for oxidative deposited films and 0.35 to 0.43 V for cast films. Also, multiple redox waves were observed in the cyclic voltammograms of these materials at a pH of 1. Molecular modeling showed a low energy conformation with the ferrocenyl moiety in close proximity to the maleimide.

1. Introduction

Redox active polymers have received considerable attention within the past 25 years. The potential applications of redox polymers include electrochemical sensors [1], batteries [2], biosensors [3], photovoltaics [4], and biofuel cells [5]. To meet the requirements of these applications, redox polymers must be electrochemically stable and possess a high degree of redox material. Within redox polymers, a variety of polymer backbones and redox active materials have been utilized to meet these requirements. Poly(vinylpyridine) [3], poly(*N*-vinylimidazole) [6], poly(allylamine) [7], and poly(ethylenimine) [8] are included in the polymers reported for support of the redox mediator. Among the most popular redox mediators reported include ferrocene [9], osmium [10], and ruthenium [11].

Ferrocene polymers have received considerable attention due to their well-behaved reversible oxidation and redox stability. Due to these properties, a renewed interest in ferrocene has been observed in recent literature [12]. Strained ferrocenophanes have been extensively studied and polymerized by ring opening polymerization [13]. The versatility of ferrocene polymers can be seen in the tunability of their electronic, magnetic, and optical properties [14]. This tunability has also been observed pendant ferrocene polymers which change hydrophilicity upon oxidation [15]. With each approach, ferrocene has been shown to be an effective mediator for electron transfer and extremely versatile for a variety of applications.

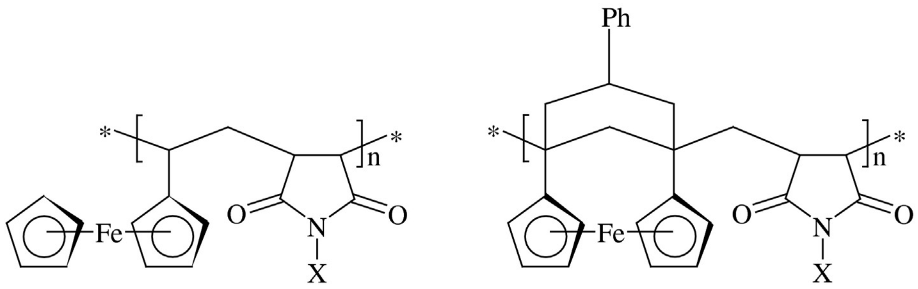
Although ferrocene polymers have been shown to be effective redox mediators, one of their limitations is low molecular weight, particularly in free radical polymerization. In addition to typical termination mechanisms, ferrocene monomers have an additional termination mechanism. Ferrocene can transfer an electron to the radical at the end of the growing chain, creating a zwitterion and stopping polymerization. To circumvent this problem, we recently reported the synthesis of copolymers from 3-phenyl[5]ferrocenophane-1,5-dimethylene or vinylferrocene with various *N*-substituted maleimides [16]. These copolymers were high molecular weight and amorphous films could be solution cast from typical solvents such as THF or $CHCl_3$. Initial electrochemical studies on these materials revealed one oxidation potential. Compared to the ferrocenophane homopolymer [16] which showed two redox waves due to electronic communication between neighboring ferrocenyl moieties, one oxidation potential for the copolymers indicated an alternating copolymer which isolates the ferrocenyl moieties. The cyclic voltammograms in CH_2Cl_2 showed a greater I_{pc} than I_{pa} and I_{pa} scaled linearly with the scan rate which is characteristic of adsorption of the oxidized polymer to the electrode surface. In addition, oxidative electrodeposition from CH_2Cl_2 gave films with good redox activity in an aqueous NaCl solution making these materials good candidates as chemically modified electrodes (CMEs).

In this paper, we report the electrochemical characterization of copolymers from vinylferrocene and 3-phenyl[5]ferrocenophane-1,5-dimethylene with *N*-ethyl and *N*-phenyl maleimide (Fig. 1). Previous results with these materials showed good electrochemical response in aqueous solutions, as well as, ease in preparation of the modified electrodes. In addition, the alternating distribution of the electron rich

---

* Corresponding author.
E-mail address: cneef@pittstate.edu (C.J. Neef).

http://dx.doi.org/10.1016/j.jelechem.2017.01.024



X = Et [PVFc-co-EMI]
X = Ph [PVFc-co-PMI]

X = Et [PPhFcP-co-EMI]
X = Ph [PPhFcP-co-PMI]

Fig. 1. Copolymers of vinylferrocene or 3-phenyl[5]ferrocenophane-1,5-dimethylene.

ferrocenyl moiety and the electron deficient maleimide creates an unusual motif along the polymer backbone. Due to these results, further characterization of these materials was warranted to determine their use in electrochemical applications. The electrolyte and pH effects on the materials, as well as, UV–Vis spectroscopy and molecular modeling were investigated.

2. Materials and methods

All materials were commercially available and used as received unless otherwise stated. Vinylferrocene and 3-phenyl[5]ferrocenophane-1,5-dimethylene were synthesized by a Wittig reaction according to a literature procedure [17]. Copolymers (1:1 M ratio) were also synthesized by a known procedure [15]. Polyvinyl ferrocene (PVFc) was prepared by free radical polymerization of vinylferrocene using AIBN as the initiator.

Electrochemical measurements were carried out using a Gamry Interface 1000 potentiostat using a platinum working and counter electrodes with a Ag/AgCl reference electrode from Pine Research Instrumentation. Cyclic voltammetry experiments were carried out for three scans, unless otherwise stated, with the third scan shown in each figure to ensure reproducibility. Supporting electrolyte concentration were 100 mM, in all experiments. UV–Vis spectra were obtained with a Shimazu UV-1201 spectrophotometer with thin film UV spectra recorded on an ITO plate with a PET backing.

All calculations were performed using the GAUSSIAN 09 software package [18]. Computational resources were provided by the National Energy Research Supercomputing Center [19]. Molecular geometries of the polymers were created using the Build Polymer tool in the Maestro program [20]. Optimized geometries were analyzed in Maestro and AVOGADRO [21]. The geometry was optimized at the B3LYP level of theory using the 6-31G + LANL2DZ mixed basis set that utilizes effective core potential on the Fe atom and the 6-31G double zeta Pople type basis set on all other atoms. The combination of the B3LYP hybrid-GGA (generalized gradient approximation) functional with the 6-31G + LANL2DZ mixed basis set provides a reasonable basis set size for performing geometry optimizations especially for systems with large number of atoms like polymers. The optimized geometries of all different conformations were calculated and the lowest energy geometry was used. Vibrational frequencies were computed for the optimized geometry to ensure that the converged geometry was indeed a local minimum.

3. Results and discussion

3.1. Electrolyte effects

Deposition of copolymers onto a Pt electrode was carried out by two methods: oxidative deposition and cast film. Oxidative deposition was performed from CH_2Cl_2 solutions of the polymer (1.0 mmol) using tetrabutylammonium hexfluorophosphate (0.1 M) as the supporting electrolyte. The potential was stepped from 0.0 V to 1.0 V and maintained for 1 min. Since the polymers are not CH_2Cl_2 soluble in their oxidized state, they precipitated onto the surface of the electrode. The chemically modified electrodes (CMEs) were removed and allowed to air dry for 1–2 min. The CMEs were then placed into an aqueous solution of electrolyte ($NaClO_4$, $NaNO_3$, or PBS) followed by applying a potential of 0.0 V to reduce the polymer to its neutral form. For comparison, chemically modified electrodes were also prepared by solution cast films. A chloroform solution (2 μL) of the polymer (2 mg/mL) was directly cast onto the electrode followed by air drying for ca. 30 min.

Cyclic voltammograms (CVs) of a CME prepared by oxidative deposition of PVFc-co-EMI with $NaClO_4$, $NaNO_3$, or PBS as the supporting electrolyte are shown in Fig. 2. Similar results were observed for the remaining polymers. The oxidation potentials ($E_{1/2}$) of PVFc-co-EMI were 0.51, 0.53, and 0.46 V using $NaClO_4$, $NaNO_3$, or PBS, respectively, as the supporting electrolyte. The CVs using $NaClO_4$ or $NaNO_3$ showed a much greater I_{pc} than I_{pa}. In addition, the CV with PBS showed a greater separation between I_{pc} than I_{pa} than expected for an electrode bound species. These results indicate poor electrochemical response by copolymer deposited oxidatively. CVs of PVFc-co-EMI deposited by film casting are shown in Fig. 3. The oxidation potentials ($E_{1/2}$) of PVFc-co-EMI were 0.35, 0.43, and 0.42 V using $NaClO_4$, $NaNO_3$, or PBS, respectively, as the supporting electrolyte and were lower than the potentials observed for oxidatively deposited films. With each supporting electrolyte, the polymer showed a good current response. Compared to films oxidatively deposited, the CVs with cast films showed peak currents for oxidation and reduction that were closer in magnitude and the separation of the peaks were more consistent with an electrode bound

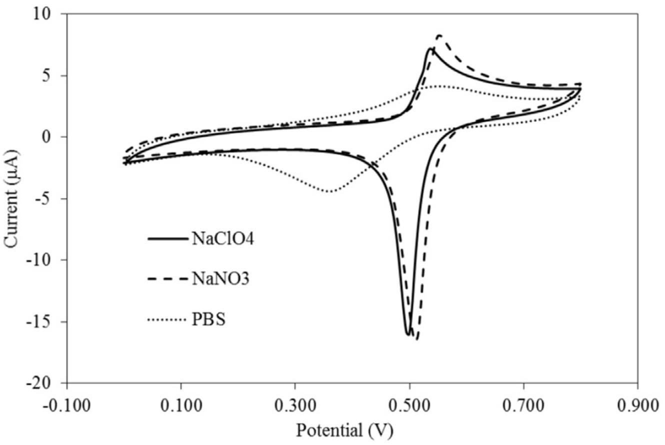


Fig. 2. Cyclic voltammograms of chemically modified electrode prepared by oxidative deposition of PVFc-co-EMI with aqueous solutions (0.1 M) of $NaNO_3$, $NaClO_4$, or phosphate buffered saline at a scan rate of 100 mV/s using a Pt counter electrode and a Ag/AgCl reference electrode.