# X-ray and Electrochemical Studies of Poly(vinylferrocene) under Redox Conditions

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**Abstract**

Poly(vinyl ferrocene), PVF, has been employed to study surface immobilized polymer modified electrodes that have potential applications in areas as diverse as electrocatalysis and sensors [1-2]. PVF contains localised sites that may be oxidised and reduced. The combination of *in situ* XAS and electrochemistry has proved to be an important tool for the characterisation of biological materials [3] and electrode materials used in fuel cells and batteries [4-5]. This combined approach can unambiguously establish the formal oxidation state of the samples and the structural distortions that might occur under redox conditions.

XAS (X-ray Absorption Spectroscopy), SAXS (Small Angle X-ray Scattering), WAXS (Wide Angle X-ray Scattering) and electrochemical studies of PVF films have been carried out in aqueous solution of 0.10M $LiClO_4$, $NaClO_4$, $NaBF_4$, NaCl and $NaSO_3C_6H_4CH_3$. The cyclic voltammograms obtained at gold and glassy carbon electrodes were typical of the ferrocene/ferrocenium redox behaviour. The peak potentials are very similar at both the gold and glassy carbon electrodes, indicating that the redox process is independent of these electrode materials.

We report the structural changes we have deduced for reduced and oxidized PVF from the XAS, SAXS and WAXS data as a function of the electrolyte media. Information on the oxidation state ($Fe^{2+}/Fe^{3+}$) of the PVF films was obtained from the near edge region of the XAS spectrum. The local structure around the Fe-centres of the oxidised/reduced films cycled in 0.25M $TBABF_4$ was investigated. There was an increase/decrease of ligand distances during the oxidation/reduction of the film, respectively [6]. In 0.10M $LiClO_4$, The scattering profiles at very low angles are consistent with an expansion/contraction of the overall size of polymer chains upon oxidation/reduction (figure 1).

**References**

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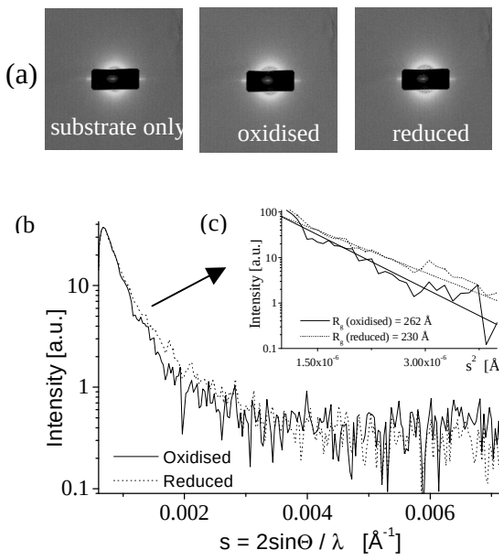


Figure 1 - Scattering from PVF films on glassy carbon substrate. 2D patterns (a) and radially averaged, substrate-reduced (i.e. background subtracted) 1D SAXS profiles (b) highlighting the structural expansion of the polymer chains