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Metal chelation and spatial profiling of components in crown ether functionalised conducting copolymer films

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ABSTRACT

Crown ether functionalised conducting polymer films were used to complex barium ions from acetonitrile solution. It was found that fully-functionalised N-derivatized polypyrrole films do not possess adequate mechanical stability, but dilution with unfunctionalised bithiophene co-monomer leads to a series of copolymer films with excellent stability. Film reactivity, composition and structure were investigated using electrochemical, nanogravimetric, FTIR, XPS and neutron reflectivity techniques. The first three of these provided spatially *integrated* barium populations and neutron reflectivity provided spatially *resolved* compositional profiles. Measurements at various stages of film fabrication yielded spatial distributions of co-monomer, crown ether, solvent and barium (as perchlorate) components. Critically, the amount of free volume to accommodate crown motifs and barium within the film was limited by the film's internal microstructure and solvent content; the low solvent volume fraction creates a different local environment to solution.

1. Introduction

The modification of electrode surfaces with electroactive films commonly involves the juxtaposition of several functional elements, typically including a reactive centre to mediate electron transfer, a recognition site to bind the target species (ideally with some molecular specificity) and an efficient means of transporting electrons across extended distances within the film. In addition, the film must contain adequate solvent to allow facile, liquid-like reactant transport and to generate an appropriate environment for reactant partition and electron transfer (although not so much solvent that film dissolution is significant). Assembling all these molecular components on the electrode surface generally involves a number of (electro)chemical steps and, as is true of any synthetic procedure, the extent to which the reality is a faithful realization of the concept must be investigated. The majority of techniques employed for this purpose yield spatially integrated populations of the film components. However, practical application in any device requires *spatial disposition* of the components such that the reactive sites are fully accessible electronically to the underlying electrode (at the metal/polymer interface) *and* chemically to reactant species from solution (at the polymer/solution interface). In this report we describe the use of *in situ* neutron reflectivity to determine the *spatial distributions* of individual film components and account for the viability of a sensor fabrication strategy as a conducting (co-)polymer film is deposited, functionalised, and applied to the task of metal ion complexation.

Over the last two decades, a substantial literature has accumulated on the electrodeposition and characterization of electronically conducting polymer films based on pyrrole, thiophene and aniline monomers [1,2]. In a number of cases, the conducting polymer spine, whose electronic or optical properties can be manipulated by substitution chemistry [3–5], has been used as a "molecular wire" to facilitate electron transport between the underlying electrode and chemical functionalities with useful mediation [6], complexing [7] or redox [2,7,8] properties. Such electrochemically addressable films may have applications in electrocatalysis [9,10], chemical [11] and biological [12] sensing, light emitting [13] and electrochromic [14] devices, corrosion inhibition [15], and protection against surface fouling [16].

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In the design of what may be rather complex interfacial architectures, it is commonly presumed that the desirable characteristics – chemical, electrochemical, optical, recognition – of each component can be considered in an additive manner and that they can be assembled in a relatively homogeneous, albeit amorphous, film. However, despite its inherent simplicity and attraction, the above view is too simplistic in that it ignores the different environments of the interior of a polymer film and a bulk solution. The idea that the polymer segment density within the film is independent of distance from the electrode is also at variance with much of the literature on polymer adsorption at the solid/liquid interface [17]. The issue that determines which of these visions of the interface is the better description is the spatial distribution of solvent within the film. This is widely recognized to influence both ion transfer dynamics (doping/undoping in the context of conducting polymers) and polymer dynamics. One manifestation of solvent distribution is film viscoelasticity, characterized in terms of film shear moduli using high frequency acoustic wave devices [18].

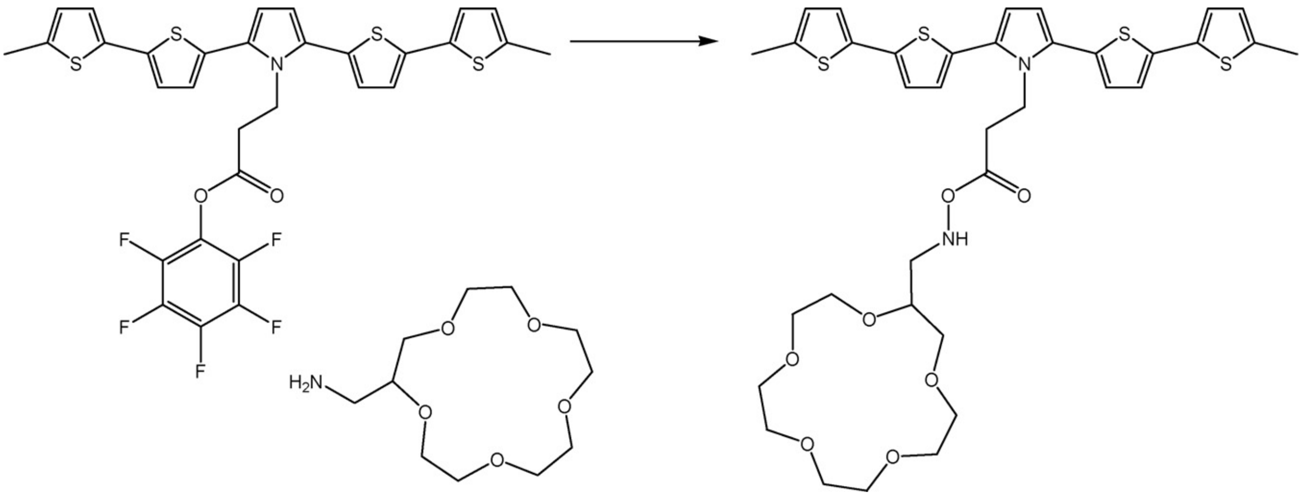
Practically, assembly of functionalised polymer films can be approached either by electropolymerization of a pre-functionalised monomer or by electropolymerization of a generic reactive monomer with a labile group that can (post-deposition) be replaced by any one of a range of suitable species containing the desired functionality [19,20]. The former strategy offers apparent simplicity and unambiguous knowledge of the degree of functionalization. Unfortunately, as discussed below, a range of chemical factors may frustrate this approach. The latter strategy has the advantages that electrodeposition conditions for the parent polymer need only be established once and the resulting film can subsequently be used to make patterned substrates suitable for use in multi-function or multi-analyte sensing devices [21]. The limitation of this strategy is that it does not necessarily lead to complete or homogeneously distributed film functionalization, with deleterious effects on device performance.

Here we report on the characterization of a family of conducting polymer films prepared using the post-deposition functionalization approach to immobilise crown ether receptors for metal ions within an electrochemically addressable matrix. The objectives are to establish the relationship between film composition, structure and functionality, and the factors that control film dynamics. With observations of the polymer functionalization reaction and electrochemical response suggesting that film solvation is crucial, the primary non-electrochemical technique we employ is neutron reflectivity (NR) [22]. The penetrating power of neutrons allows one to study “buried” interfaces, in the present instance solid/liquid interfaces under electrochemical control [23–25]. NR is similar in a number of respects to optical reflectivity (ellipsometry) [26] but, since the neutrons interact with the nuclei in the sample, it is isotopically sensitive. This “contrast variation” method is most commonly exploited via selective deuteration of a chosen species (here, the solvent). When a sample is sequentially exposed to hydrogenous and deuterated solvent, the neutrons interact differently with the isotopically distinct species, although the chemistry is essentially constant. As a consequence, one can obtain spatial distribution information on the isotopically substituted species (here, solvent) within the film. In the present study, we detect the specularly reflected neutrons, with the result that the measured composition is averaged laterally (parallel to the electrode) and the spatial resolution is in the vertical direction (perpendicular to the interface) [22].

The objective was to construct an electrochemically addressable film containing ligand sites capable of complexing metal ions from solution. For the purpose of developing the concept, we initially chose to complex electro*in*active metal ions (barium and potassium) so that coulometric assay of the polymer could be undertaken without ambiguity in the attribution of charge to different species. The receptor ligand selected was a crown ether; we chose a 15-crown-5 moiety, but the generic characteristics and versatility of a range of crown ethers are well known [27]. As will be described below, neither the simplistic one-step approach of electropolymerizing a crown ether-functionalised pyrrole monomer nor the post-deposition functionalization of a labile N-substituted pyrrole were successful. Evidence presented below suggests that the common problem for these two homopolymer systems is steric in origin. Put simply, there is insufficient space around every pyrrole ring to accommodate the 15-atom crown and its (amide) tether.

We therefore adopt a co-polymerization approach, in which N-functionalised pyrrole units are “diluted” with 2,2′-bithiophene (BT) units; this maintains the required high electronic conductivity but relieves the mechanical strain associated with accommodating bulky substituents on the pyrrole rings. We have previously studied the electrochemistry and structure of homopolymer films based on pentafluorophenyl 3-(pyrrol-1-yl)propionate (PFP) [28,29], whose ester-bound pentafluorophenyl group can readily be replaced by amines to generate amide-bound functional groups. Here we extend this approach by the post-deposition functionalization of poly(BT-co-PFP), illustrated in Scheme 1.

The work is novel in that it employs a co-polymerization strategy to vary the upper limit of crown ether functionalization and uses a range of techniques to determine the extent to which this



Scheme 1. Poly(BT-co-PFP) crown ether functionalization reaction.