



Influence of biopolymer loading on the physicochemical and electrochemical properties of inherently conducting polymer biomaterials



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ABSTRACT

The physicochemical and electrochemical properties of polypyrrole (PPy) doped with the biological dopant dextran sulphate (DS) were shown to be significantly altered as a function of varying the salt concentration (0.2, 2 or 20 mg/ml) in the polymerisation electrolyte. Films grown in the presence of 0.2 mg/ml DS generated the highest potential during galvanostatic growth, with the potential decreasing with each subsequent increase in DS concentration. The electroactivity of the polymers was similar for all three DS concentrations, with the 20 mg/ml film drawing slightly more current upon reduction in PBS. Increasing the DS concentration reduced film interfacial roughness and increased polymer hydrophilicity. Polymer mass and thickness was larger for DS films grown from 0.2 mg/ml and 2 mg/ml DS electrolyte solutions, compared to the 20 mg/ml films. The latter also demonstrated a much higher shear modulus than the 2 mg/ml and 0.2 mg/ml films, respectively. The changes in the polymer physicochemical properties were associated with an increase in polymer densification with increasing DS loading, correlating with a likely higher conjugation generated during polymerisation at a potential closer to the ideal oxidation potential of pyrrole. Herein we describe a facile approach through which polymer properties may be varied significantly by varying the dopant concentration in the electrolyte, providing the ability to tune polymer properties for enhanced functionality while preserving fundamental polymer chemistry.

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1. Introduction

In the development of implantable bionic devices, a wide variety of polymeric systems directed at a suite of niche applications have been investigated in recent times. Polymer-based bionic systems' physical and chemical properties are readily tailored to specific needs, providing the potential to address diverse clinical criteria through regulation of cellular interactions and behaviour [1]. Of these, inherently conducting polymers (ICPs) have ignited particular interest due to their compatibility with a range of cell and tissue types, and their ability to perform multiple biologically related functions, including controlled delivery of drugs and biofactors [2], guided cell growth [3], and the electrical

stimulation of cells and tissues [4,5]. The ability to employ an array of polymer fabrication techniques provides the enormous flexibility to design and tailor ICP-based materials for particular applications, ranging from 2-dimensional films, nano- and micro-diameter fibres, hydrogels, and 3-dimensional scaffolds assembled using one or several of the above components to form the final material architecture.

ICP synthesis is facilitated by the oxidation of the monomer unit, producing a positively charged conjugated polymer backbone. The positive charge along the length of the polymer chain is counter balanced by the inclusion of an anionic species, a process termed doping [6]. The choice of dopant is known to influence the physical and chemical properties of the ICP, with the incorporation of biological dopants shown to influence cellular interactions and add specific functionality to the polymer materials. For example, incorporation of extracellular matrix components as the dopant species in polypyrrole ICPs has been shown to support increased neurite outgrowth in PC12 cells compared to films with a synthetic dopant [7], and the co-doping

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of polypyrrole with neurotrophin-3 protein has been shown to increase neurite outgrowth from explants via the enhanced release of the neurotrophin from the polymer during electrical stimulation [8].

Recently, attention has turned towards understanding the fundamental material properties that promote favourable polymer–biological interactions in an attempt to guide the development of the materials for targeted biofunctionality and biocompatibility. A number of studies have characterised ICP physicochemical properties as a function of the dopant species, and in turn attempted to correlate specific polymer characteristics with cellular behaviour on the polymer interface [9,10]. However there remains high variability within existing literature on specific polymerisation conditions employed during polymer synthesis, and often, evidence of a methodical approach to selecting or optimising polymerisation conditions is lacking. In particular, there has been no critical study of how modulating the concentration of large bioactive polyelectrolyte dopant species in the polymerisation electrolyte may influence biologically relevant polymer characteristics – a facile approach that may provide an avenue for further tailoring polymer properties for improved functionality. Herein we employ polypyrrole doped with a large biologically-relevant polyelectrolyte anion dopant with clinical application as an anticoagulant (dextran sulphate; DS) [11], as a model system by which to illustrate modulation of biologically relevant polymer physicochemical and electrochemical properties by varying the salt concentration in the polymerisation electrolyte. Previously we have demonstrated that varying the DS loading of PPy–DS films and polymerisation time influences key interfacial polymer properties, thereby influencing the nature of protein–polymer interactions [12]. We extend this previous work, focusing exclusively on the influence of DS loading on several polymer physicochemical and electrochemical properties, and thereby providing a means by which to fine-tune ICP biomaterials for specific therapeutic applications. Furthermore, we present the quartz crystal microbalance with dissipation monitoring as a powerful and highly efficient technique with which to characterise the physical properties of electrochemically polymerised organic conducting polymers, including the measurement of dynamic processes during electrochemical stimulation.

2. Experimental

2.1. General

Pyrrole was purchased from Merck, purified by distillation and stored at -18°C . Dextran sulfate sodium salt (D-6001) was purchased from Sigma–Aldrich. All other reagents were purchased from commercial houses and used as received.

2.2. Electrochemical polymerisation of polymer films

Electrochemical polymerisation of conducting polymer films was performed using a Q-Sense Electrochemistry Module (QEM 401) axial flow cell with a Q-Sense E4 Quartz Crystal Microbalance system (Q-Sense AB, Västra, Frölunda, Sweden), allowing simultaneous QCM–D parameter recording of film properties during polymerisation. The QCM sensor was an A-T cut quartz crystal with a 10 mm diameter gold electrode (QSX301) with a fundamental resonance frequency of 5 MHz (Q-Sense AB, Västra, Frölunda, Sweden). Prior to each experiment, the gold sensor surface upon the quartz crystal was cleaned with piranha solution (70% sulphuric acid and 30% hydrogen peroxide) for 3 min, and then rinsed thoroughly with deionised water and dried with nitrogen gas. Aqueous solutions for polymer synthesis consisted of 0.2 M pyrrole in deionised water with 0.2 mg/ml, 2 mg/ml or 20 mg/ml

dextran sulfate. Each solution was deoxygenated for 10 min via bubbling with nitrogen gas before use. The Q-Sense electrochemistry cell consisted of a platinum counter and a gold working electrode with a World Precision Instruments® Dri-Ref™ reference electrode. PPy–DS films were grown galvanostatically onto gold coated Q-Sense quartz sensors using an eDAQ e-corder 410 recorder and EA163 potentiostat connected to the Q-Sense electrochemistry module. Aqueous polymer growing solution was flowed through the electrochemistry module at $60\ \mu\text{l}/\text{min}$, and films grown at a current density of $0.25\ \text{mA}/\text{cm}^2$ for either 1 or 10 min. The temperature within the E-module chamber during polymer polymerisation was kept constant at 22°C using the instrument software. Thereafter, the quartz sensors were removed from the E-cell and rinsed in distilled water and dried under a flow of nitrogen gas.

2.3. Film characterisation

2.3.1. Electroactivity

PPy–DS films were polymerised for 10 min using the Q-Sense electrochemistry module as described in Section 2.2. Polymer films grown on the QCM sensors were then placed in an electrochemical cell containing a platinum mesh counter electrode, Ag–AgCl reference electrode, and the PPy–DS film on the QCM sensor as the working electrode. PBS was employed as the electrolyte and 30 cyclic voltammograms (CVs) were undertaken using an eDAQ e-corder 410 recorder and EA163 potentiostat at a potential range of $\pm 500\ \text{mV}$ and scan rate of $20\ \text{mV}/\text{s}$.

2.3.2. Chemical characterisation

2.3.2.1. Raman spectroscopy. Raman spectra were acquired using a JY HR-800 Raman spectrometer at 632 nm using a 300 line/mm grating and a $\times 50$ optical magnification.

2.3.3. Physical characterisation

2.3.3.1. Atomic force microscopy topography. The surface morphology of the polymer films were examined using a Mikromash NSC15 cantilever (spring constant $\sim 37\ \text{N}/\text{m}$) in alternating current (AC) mode with an MFP-3D AFM (Asylum Research, CA). Image scans of $5\ \mu\text{m}$ were obtained at a scan rate of 0.5 Hz in air. R_{RMS} roughness were calculated using Asylum Research Analysis software with the Igor Pro Software Package (WaveMetrics, OR).

2.3.3.2. Quartz crystal microbalance with dissipation monitoring (QCM-D) modelling of polymer thickness and shear modulus. Polymerisation of polymer films in-situ enabled the detailed analyses of the physical and mechanical properties of the polymer films using the QCM–D measurement parameters. QCM is an extremely sensitive mass sensing technique that in its simplest application can measure the mass of an adsorbed layer to the QCM sensor electrode surface through the application of the Sauerbrey equation [13]. As a material adsorbs to the sensor electrode surface, a decrease in the oscillating frequency of the sensor is recorded. The Sauerbrey relationship provides a linear correlation between the change in the resonance frequency of the oscillating crystal and the mass deposited on the sensor, with modern instruments reporting a sensitivity of $0.5\ \text{ng}/\text{cm}^2$. However this relationship is dependent on the assumption that the coupled mass to the sensor is rigid (i.e. elastic), the mass is deposited evenly across the sensor surface and the mass load does not exceed $\sim 2\%$ of the total quartz sensor mass. In the event that a mass deposited on the sensor exhibits inelastic or viscoelastic behaviour, the Sauerbrey relationship is inapplicable and more complicated models are

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