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A new precursor for conducting polymer-based brush interfaces with electroactivity in aqueous solution

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ABSTRACT

We present the synthesis of a novel conducting polymer (CP) incorporating both pyrrole and thiophene units in its monomer, which is also substituted with an initiator for grafting of sidechains by atom-transfer radical polymerisation (ATRP). The precursor monomer for the CP macroinitiator, 2-(2,5-di(pyrrol-2-yl) thiophen-3-yl)ethyl 2-bromopropanoate) (PyThon) is very readily electropolymerised at low monomer concentrations and low applied potentials. Density functional theory (DFT) predictions of ionisation potentials and spin-charge distribution for PyThon are in good agreement with these experimental results. We present also the grafting of sidechains from electropolymerised PolyPyThon (PPyThon) to yield surface-confined polymer brushes. Functionalisation with polystyrene (PS), poly(2,3,4,5,6-pentafluorostyrene) (PFS) and poly(ethylene glycol) methyl ether acrylate (PEGMEA) is demonstrated and confirmed by FT-IR and water contact angle measurements. These PPyThon-based molecular brushes are electroactive in both water and acetonitrile, and show evidence of changes in surface conformation related to the redox state of the CP. The growth of human fibroblasts on PPyThon films is also demonstrated, indicating good biocompatibility of the polymer. We conceive PPyThon-based molecular brushes as a substrate for electrical stimuli-responsive surfaces with application particularly in the biomedical field.

1. Introduction

In recent years, significant progress has been made in the design of functional and stimuli-responsive surfaces for applications including microfluidics, self-cleaning surfaces, and biomedical applications [1]. In this regard, conducting polymers (CPs) are a promising class of materials. CPs possess a conjugated structure and are readily switched between an oxidised (conductive) and neutral (insulating) state by electrical stimulus in an appropriate electrolyte solution. Oxidation and reduction is accompanied by the influx and efflux of dopant ions (along with solvent) to balance charge [2]. The stimuli-responsive characteristic of conducting polymers is derived from a combination of transitions of chemical, electrical and mechanical properties that accompany their oxidation and reduction [1a]. The reversible doping of CPs has been exploited for the design of stimuli-responsive surfaces with switchable wettability [1d,3].

Among the most commonly studied CPs are polypyrrole (PPy), polyaniline (PANi), and polythiophene and its derivatives [2a]. Molecular brushes based on these CPs have been described in the literature, primarily as a means to improve or alter properties of the backbone CP to enhance their utility. Research has focussed on improving solubility [4], processability/mechanical properties [4c,5], regioregularity [4a], and optical and electronic properties [4b,f,g,6] as well as optimising the morphology of CP-containing copolymers for photovoltaic applications [7]. CP-based molecular brushes have also been used to take advantage of properties of grafted chains for applications such as electrodes and sensing which make use of the electrochemical activity of the CP substrate [8]. With respect to biomedical applications, Kang et al. have described a range of CP-based molecular brushes with functional groups suitable for protein and enzyme immobilisation [4d,e]. CP-based molecular brushes that combine the electroactivity of PANi backbones and the

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anti-fouling nature of polyethylene oxide (PEO) sidechains have also been reported [9]. In terms of applications as stimuli-responsive surfaces, Wang et al. [10] have described a pH-responsive CP-based molecular brush comprising a polythiophene (PTh) backbone and grafted poly(N,N-dimethylacrylamide) (PDMA) sidechains. Recently, our group described Py-based molecular brushes, with grafted zwitterionic sidechains, that undergo electrochemically-mediated switching in conformation of grafted sidechains [11]. The above examples provide only a snapshot of the utility of CP-based molecular brushes, however in spite of these possibilities, the capacity of CP-based molecular brushes to be utilised as electrically-responsive switchable surfaces is only in its infancy.

In the majority of the examples given, the CP backbone is polymerised in solution via chemical oxidative polymerisation prior to grafting of sidechains [4b–g,6a,7,9,10,12]. Only limited examples exist in the literature of CP-based molecular brushes where the CP-backbone is surface-confined; that is, deposited on a substrate *prior* to grafting of sidechains (or with sidechains incorporated in a copolymer with the CP *during* its deposition), as opposed to solution-grafting of sidechains followed by deposition of the already-formed brush on an appropriate substrate for further use [5,8,13]. A surface-confined backbone is expected to limit self-assembly effects driven by solvent-polymer and polymer–substrate interactions that may occur during deposition of a block or graft copolymer on a substrate by spin-coating, drop-casting etc. Thus surface-initiated grafting would favour a preferential exposure of sidechains at the polymer/air (or solution) interface. Approaches for synthesising CP-based molecular brushes with surface-confined backbones include electrocopolymerisation of CP monomers with macromonomers which incorporate insulating sidechains in their structure [5,8b], or electropolymerisation of macromonomers with dendritic moieties followed by ‘grafting through’ of sidechains [13b]. A more flexible approach is to prepare a CP ‘macroinitiator’ for controlled radical polymerisation (CRP) by electropolymerisation of a monomer incorporating a reversible addition-fragmentation chain transfer (RAFT) agent [13a] or atom transfer radical polymerisation (ATRP)-initiating site [8a,11b,13c]. The use of surface-initiated ATRP or RAFT allows for deposition of polymer brushes with low polydispersity, provides good control over molecular weight of grafted sidechains, and gives access to grafting of a wide range of monomers with desirable chemical functionalities [14]. We recently described the synthesis and characterisation of a polyterthiophene (PTTh) – based molecular brush with grafted polystyrene-*block*-polyacrylic acid (PS-*b*-PAA) amphiphilic block copolymer sidearms where changes in morphology and surface wettability were observed between oxidised and reduced states [13c]. However a drawback of these surfaces is their lack of electroactivity in water, driven by the well-characterised hydrophobicity of polythiophenes, resulting in microstructure collapse in aqueous solution [15]. This renders such polymer brushes unsuitable for biomedical applications, which would primarily require good electroactivity in an aqueous buffer solution. The research described in this paper seeks to develop more hydrophilic CP macroinitiators, which would give access to a range of CP-based brushes with electroactivity in aqueous, and therefore buffer, solution.

We report here the electrochemical synthesis of a CP backbone from a novel termonomer, 2-(2,5-di(pyrrol-2-yl)thiophen-3-yl) ethyl 2-bromopropanoate) (PyThon) which incorporates an ATRP-initiating site. PyThon comprises both thiophene and pyrrole units, thus combining two key properties; the facile functionalisation of polythiophene [15b] and the electroactivity in aqueous solution of the relatively hydrophilic CP, polypyrrole [16]. We found that PyThon is readily electropolymerised at a low oxidation potential to yield electroactive films that are suitable precursors for grafting of various monomers by surface-initiated ATRP (Fig. 1). The resultant polymer films are electroactive in both water and acetonitrile. Furthermore, as a lead-in to future work on using this novel polymer as a precursor for CP-based brushes for biomedical applications, we demonstrate the growth of human fibroblasts on PPyThon films, thus indicating good biocompatibility of the polymer. These results highlight the promise of PPyThon as a macroinitiator for the synthesis of CP-based molecular brushes for stimuli-responsive surface applications, in particular within the biomedical field.

2. Experimental

2.1. Materials

N-Boc-pyrrole, 2,2,6,6-tetramethylpiperidine, *n*-butyllithium, trimethyl borate, potassium hydrogen difluoride, palladium(II) acetate, sodium carbonate, 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (RuPhos), *N*-bromosuccinimide, 3-(2-hydroxyethyl)thiophene, trifluoroacetic acid, 2-bromopropionyl bromide, *N*′-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC.HCl), 4-

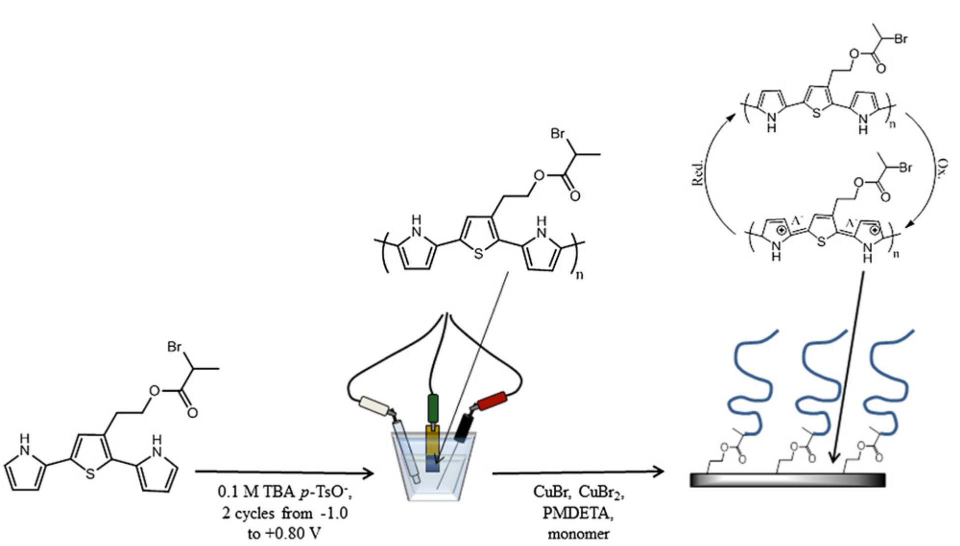

Fig. 1. Preparation of PPyThon electroactive polymer brushes.