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Controlled release of dyes from chemically polymerised conducting polymers

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Abstract

The hydroxytriarylmethane family of dyes (sub-category sulfonphthaleins, e.g. phenol red) has shown sufficient chemical stability to remain unchanged when exposed to the oxidative environment required for chemical polymerisation of inherently conducting polymers (ICPs). This oxidative stability allows these dyes to be incorporated as counter-ions in polypyrrole or poly(3,4-ethylenedioxythiophene), and then later released when the ICP is reduced, either by change in potential or change in pH. The polypyrrole–dye composite can be applied to paper or plastic films by inkjet printing a dye–oxidant mixture which is then dried and used as a template for vapour phase polymerisation. For poly(3,4-ethylenedioxythiophene)–dye composites, polymerisation can be conveniently conducted in a single step in the liquid phase, using a volatile organic base as a retardant during application.

Keywords: Dye release; Phenol red; Conducting polymers; Polypyrrole; PEDOT; Inkjet printing

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1. Introduction

Controlled release from inherently conducting polymers (ICPs) has been reported by several groups [1–3]. The most common route has been to incorporate negatively charged molecules as counter-ions in the ICP during electrochemical polymerisation and to release these molecules when desired by reducing the ICP, i.e. by applying a negative potential to the ICP. Recently, it has been reported that phenol red in its anionic form (Fig. 1) can be released from electrochemically polymerised polypyrrole (PPy) on stainless steel by reducing the PPy using a simple galvanic cell with a Zn anode [4]. The release of dyes from ICPs on demand has advantages for the design and manufacture of devices in which a change in colour is used as a signalling mechanism. The colour contrast associated with the release of dye into a previously colourless electrolyte can be dramatic at only small dye concentrations. This means that the power required to stimulate a colour change is decreased compared with that required to stimulate a comparable electrochromic colour change. Further, the release of dye is essentially non-reversible, which can be a useful attribute for sensors that are required to

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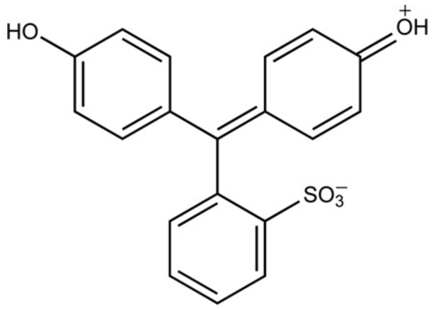

Fig. 1. Phenol red structure.

continue to signal a change in state without the need for a continuing power supply.

Unfortunately, from an industrial standpoint there are several disadvantages with the production of ICP–dye films by electrochemical polymerisation. First, application of ICP by electrochemical polymerisation can be slow, being limited by ionic diffusion. Second, the complexity of electrolytic equipment could mean higher capital costs. Third, electrochemical polymerisation requires a conducting substrate [5], which prevents direct application of the ICP to paper and plastic substrates.

The concept explored in the current investigation is to use chemical polymerisation to incorporate dye molecules in ICPs for later release. The key advantage of chemical polymerisation is that it potentially allows the use of high-volume, reel-to-reel printing processes that reduce unit costs in industrial-scale production [6,7]. The greater simplicity of printing methods compared with electrochemical polymerisation could widen the range of economically feasible applications of dye release technology, perhaps even to the extent of allowing use in packaging products, which are notoriously cost-sensitive.

Because of the highly acidic and oxidative chemical environment required, chemical polymerisation could limit the range of chemical entities that can remain intact during the polymerisation. Through earlier work [8–12] we and others have reported the chemical polymerisation of polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) using base-inhibited iron(III)salts as oxidants. It was reasoned that the higher pH of this procedure could provide some protection to the dye molecules during the polymerisation of the ICP.

Two variations of the chemical polymerisation method were investigated, whose differences may be expected to affect film morphology. In the first method, dye was dissolved in an oxidant solution (with the assistance of an organic base, pyridine) and applied to a substrate. After drying, the oxidant–dye film was used as a template for vapour phase polymerisation (VPP) by exposing the patterned oxidant surface to monomer vapour. This approach was suitable for the preparation of both PPy and PEDOT films on a variety of substrates. In the second method, the oxidant–dye solution was mixed directly with liquid monomer in the presence of pyridine, this time acting as a polymerisation retardant. The mixture was then applied to a substrate and polymerisation initiated by evaporating the pyridine by heating. This approach was only suitable for producing films of dye-doped PEDOT, as experiment showed that the polymerisation of PPy cannot be retarded by this means. However, since the relatively slow vapour phase polymerisation process is avoided, this second approach may have significant advantages for industrial production.

Dye anions can be released when the dye-doped ICP is reduced, for example by application of an electrical potential. Reduction leads to the non-conducting form of the ICP, so the extent of dye release by electrochemical reduction could be limited by the resultant increase in electrical resistance. To overcome this difficulty, the electrical potential must be applied evenly over the entire ICP area. This requirement in turn implies the need for an underlying conductive layer. For the half cell to be printable, this conductive layer itself must be an ICP. Specifically, the ICP used as the conductive layer must have a reduction potential lower than the dye-doped ICP.

Dye release can also be stimulated by high pH because ICPs can change oxidation state when the acidity of their environment changes [12,15]. For some applications, release at high pH may be advantageous [16,17] compared to a system driven by an electrochemical cell. In this case there would be no requirement for an underlying conducting layer, as the environment itself (atmosphere or liquid) might be assumed to uniformly reduce the area exposed. The resulting decrease in the complexity of the dye-release device could result in significant cost saving for industrial applications. In this paper we report device configurations that enable the release of dye from chemically polymerised ICPs, both by application of an electrical potential and by exposure to high pH.

2. Experimental

The first chemical polymerisation method, employing VPP, can be summarised as follows.