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Acid Blue dyes in polypyrrole synthesis: The control of polymer morphology at nanoscale in the promotion of high conductivity and the reduction of cytotoxicity

Patrycja Bober[a,*], Yu Li[a,b], Udit Acharya[a,c], Yaduram Panthi[a], Jiří Pfleger[a], Petr Humpolíček[d], Miroslava Trchová[a], Jaroslav Stejskal[a]

[a] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic
[b] Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an, 710049, People's Republic of China
[c] Faculty of Mathematics and Physics, Charles University, 121 16 Prague 2, Czech Republic
[d] Centre of Polymer Systems, Tomas Bata University in Zlin, 760 01 Zlin, Czech Republic

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ABSTRACT

Polypyrrole has been prepared by facile single-step chemical oxidative polymerization of the monomer in aqueous medium containing an anthraquinone dye, Acid Blue 25 or Acid Blue 129. The addition of the former structure-guiding agent results in the formation of polypyrrole nanowires with conductivity improved up from the units S cm^{-1} to 60 S cm^{-1}. The second closely related dye, Acid Blue 129, had no impact on polymer morphology but in its presence the conductivity of polypyrrole also increased. It has been shown that the pyrrole concentration and oxidant-to-pyrrole mole ratio significantly affect the conductivity of synthesized polypyrrole. Polypyrroles have been characterized by FTIR and Raman spectroscopies to assess their molecular structure and intermolecular interactions. Considering the applications in biomedicine, the cytotoxicity of the samples has also been tested. Polypyrrole prepared with Acid Blue 129 has significantly lower cytotoxicity compared to that prepared with Acid Blue 25. The cytotoxicity of both polypyrroles can be eliminated by purification step. Low cytotoxicity combined with high conductivity enables application of these conducting polymers in biomedicine.

1. Introduction

The preparation of conducting polymer materials has become an important branch of materials research. Nanostructured conducting polymers [1], such as polypyrrole (PPy) [2–4] or polyaniline [5,6], are fabricated by various chemical-oxidation methods. The preparation of one-dimensional polymer morphologies requires the presence of structure-guiding additives that produce hard templates [7,8], soft templates [9,10], reactive-templates [11], or self-degraded templates [12]. Template-free method has also been demonstrated in the preparation of polyaniline nanotubes [13]. The understanding of the processes underlying the formation of a specific morphology and its relation to the conductivity, however, is still a challenge.

Polypyrrole [14,15] in various nanostructures (e.g., nanoparticles, nanotubes, nanowires, thin films, etc.) has been prepared by oxidation of pyrrole in aqueous media and it has subsequently been used in supercapacitors [4,16–19], sensors [20–23], corrosion protection [24], as catalysts supports [25], and as anodes for high-performance lithium-ion batteries [26,27]. The promising applications are expected in biomedicine, where conducting polymers will be used in electrical monitoring or stimulation of biological objects. For example, polypyrrole and its composites can promote neurite outgrowth [28,29], be used as electrically controlled drug-delivery systems [30] or as artificial muscles [31,32].

A substantial effort has recently been exerted on the preparation of polypyrrole nanotubes, in order to increase the conductivity of resulting materials from units S cm^{-1}, which is typical for globular PPy, to 60 S cm^{-1} [2], and even above 100 S cm^{-1} [33]. The most common way how to convert the morphology in favour of nanotubes is represented by addition of methyl orange (MO) to the polymerization mixture [2,12,34,35]. The use of resulting materials in biological application, however, is difficult due to the toxicity of MO. Other dyes, such as Acid Blue 25 [36], Acid Blue 41 [37], Acid Red G [38], Acid Violet 19 [39], or methylene blue [40] have also been studied as structure-guiding agents for PPy preparation. The morphology of PPy prepared in the presence of Acid Blue 25 turned to clusters of nanowires with simultaneous increase in conductivity from units S cm^{-1} up to ≈20 S cm^{-1}. Such one-dimensional structures have successfully been

* Corresponding author.
E-mail address: bober@imc.cas.cz (P. Bober).

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tested as electrode material in supercapacitors [36]. Also the addition of Acid Violet 19 improved conductivity of PPy nanoparticles to ≈40 S cm^{-1} [39]. However, the presence of some other dyes, such as Acid Green 25, Reactive Black 5, Thymol blue or Indigo carmine, led to a significant decrease in conductivity of PPy [40].

The biocompatibility is a complex materials property for applications pertaining the field of biomedicine. The cytotoxicity is generally believed to be the test of the first choice when the biocompatibility of any material is considered. This is due to the fact that many biological tests can be predicted by the results of cytotoxicity. There are only few studies focused on the biocompatibility of PPy [41–43], especially in form of powders. It is generally accepted, that the biocompatibility of conducting polymers is influenced especially by protonating acids and the presence of residual precursors or oligomers rather than by the polymer itself [44]. The effort to find alternative dopants is therefore obvious in the literature. Also the study focusing on the purification of conducting polymers has been published [45]. The nanostructured conducting polymers possess physicochemical properties which enable their biomedical applications. Their cytotoxicity assessments, however, have been generally neglected in the literature and this motivated the present work.

In the present paper, the influence of two closely related anthraquinone dyes, Acid Blue 25 and Acid Blue 129 (Fig. 1a), on the morphology and electrical conductivity of PPy has been studied. It is shown for the first time that, despite the similarity in molecular structure, their influence on PPy formation substantially differs. Acid Blue 25 acts as a template to produce PPy nanowires during the oxidation of pyrrole with iron(III) chloride as oxidant (Fig. 1b), with enhanced conductivity up to 60 S cm^{-1}, which is three times higher than that reported for this dye in the literature [30]. The presence of the second dye also improved the conductivity but it had no impact on morphology of PPy, which remained globular. The special attention was paid to investigate the cytotoxicity of new highly conducting polypyrroles.

2. Experimental

2.1. Preparation

Pyrrole (≥98%), iron(III) chloride hexahydrate, Acid Blue 25 (AB 25; sodium 1-amino-4-anilinoanthraquinone-2-sulfonate, dye content 45%) and Acid Blue 129 (AB 129; sodium 1-amino-4-(2,4,6-trimethylanilino)anthraquinone-2-sulfonate, dye content 25%), all from Sigma-Aldrich, have been used as supplied without any correction for true dye content.

Polypyrrole was prepared by the oxidation of pyrrole with iron(III) chloride in aqueous medium [40] (Fig. 1b). In a typical synthesis, 0.2 M pyrrole was oxidized with 0.2 M iron(III) chloride in the presence of 0.01 M dye. The AB 25 or AB 129 was dissolved in 50 mL of deionized water and treated in ultrasonic bath for 15 min until complete dissolution. Pyrrole monomer was added. Iron(III) chloride hexahydrate was separately dissolved in deionized water to 50 mL of solution. Then the monomer and oxidant solutions were mixed and left undisturbed at room temperature for 24 h. The reaction mixture was filtered and solid products were rinsed with 200 mL of 0.1 M hydrochloric acid, followed by 100 mL of ethanol. The products were left in air to dry at room temperature until their weights were constant.

Two series of experiments have been carried out. In the first series (*Series 1*), the concentration of pyrrole, [Py], was varied from 0.05 M to

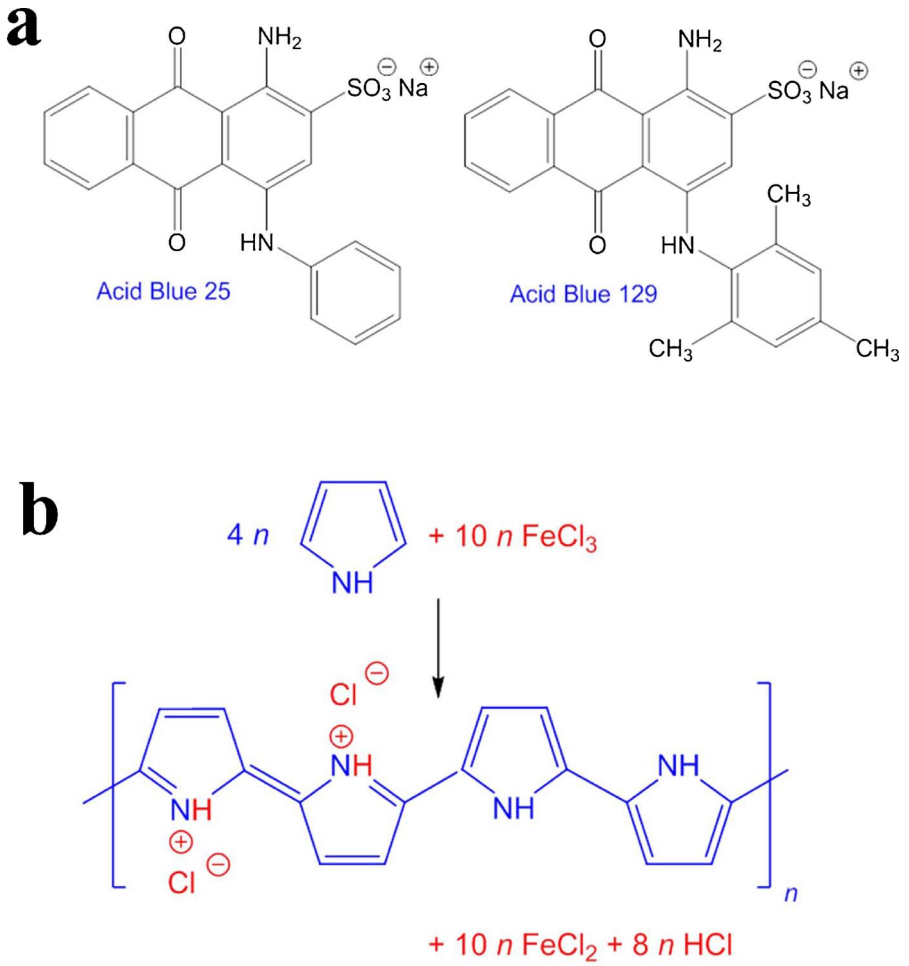

Fig. 1. (a) Formulae of Acid Blue 25 and Acid Blue 129. (b) Pyrrole was oxidized with iron(III) chloride to polypyrrole; stoichiometric oxidant-to-pyrrole mole ratio is 2.5.