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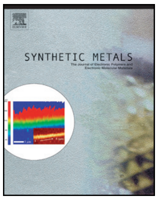

Synthesis of polyaniline by using $CuCl_2$ as oxidizing agent

Rizwan Ullah [a,b], Graham A. Bowmaker [a,*], Cosmin Laslau [a,c], Geoffrey I.N. Waterhouse [a,c], Zoran D. Zujovic [a,c], Khurshid Ali [b], Anwar-Ul-Haq Ali Shah [b], Jadranka Travas-Sejdic [a,c]

[a] Polymer Electronics Research Centre, School of Chemical Sciences, Department of Chemistry, University of Auckland, New Zealand
[b] Institute of Chemical Sciences, University of Peshawar, Pakistan
[c] MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand

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ABSTRACT

The reaction of aniline with copper(II) chloride in the presence of *p*-toluene sulfonic acid was investigated. The reactions were carried out in aqueous media for 24 h under a nitrogen atmosphere. The products obtained were characterized by FT-IR, UV–Vis XPS, SEM, N K-edge NEXAFS and CP MAS ^{13}C NMR. Elemental analysis was also carried out to determine the elemental composition of the product. The results showed the presence of partially oxidized, partially protonated polyaniline with $[CuCl_3]^-$ as the dopant counter ion. A decrease in the final pH and increase in the reaction yield was observed with an increase in the oxidant to monomer ratio. The increase in the yield is due to an increase in the oxidation potential of $CuCl_2$ with an increase in its molar concentration. The low product yields achieved are attributed to the co-formation of a copper(II) chloride aniline coordination complex.

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1. Introduction

Among the various conducting polymers synthesized to date [1,2], polyaniline (PANI) has received the most attention due to its unique structure, high chemical stability and high electrical conductivity when suitably doped. It is made from an inexpensive monomer, and typically a high yield of product is produced in a wide range of morphologies, depending on the synthesis conditions [3]. PANI has many industrial applications, such as corrosion prevention in the coatings industry, removal of mercury from water, and as a component of light emitting diodes, surgical instruments, light-weight batteries and solar cells [4–6].

The morphology and properties of chemically synthesized PANI and its derivatives depend strongly on the synthesis conditions, such as pH, temperature, reaction media, monomer concentration, monomer/oxidant ratio and also the nature of the oxidant. In recent years, the synthesis of PANI derivatives and PANI nanocomposites doped with metal ions has received attention, motivated by new practical applications, affording higher catalytic and sensing capabilities compared to pure PANI [7]. Zhang et al. [8] synthesized a PANI-*p*-toluenesulfonic acid-gold (PANI-*p*-TSA/Au) composite by using gold chloride trihydrate as the oxidizing agent in an oxidative polymerization of aniline. The composite particles were spherical in shape, and possessed high conductivity compared to PANI-*p*-TSA nanofibers. The spherical morphology was attributed to the low oxidation potential of gold chloride trihydrate and the high conductivity to the presence of gold particles decorated on the PANI spheres. Zhang et al. [9] prepared PANI fibers by replacing ammonium persulfate (APS) with $FeCl_3$ as an oxidizing agent in the presence of *p*-toluenesulfonic acid (*p*-TSA), β-naphthalensulfonic acid (β-NSA) and camphorsulfonic acid (CSA). The resulting particles of PANI doped with CSA, *p*-TSA and β-NSA have a smaller diameter (10–30 nm), a higher conductance and higher crystallinity compared to those prepared using APS as the oxidant. Polyaniline/gold composites were also chemically synthesized by Kinyanjui et al. [10] In that study, potassium tetrachloroaurate was used as oxidizing agent and produced a large reaction yield. The composites were reported to contain polycrystalline gold particles with a diameter of 0.8–1 μm. It was concluded that no significant change in the conductance results from encapsulation of Au in the composite.

Sapurina et al. [11] compared the oxidative polymerization of aniline by the strong oxidizing agent APS with that of the weaker oxidizing agent $AgNO_3$. This was based on the idea that the use of oxidants with a lower oxidation potential than persulfates could favor polymerization to occur under milder conditions and formation of polymer structures with a lower number of defects and higher conductivity. They showed that polymerization in both alkaline and acid media can be accomplished almost quantitatively with $AgNO_3$, which has an oxidation potential less than +1 V.

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[*] Corresponding author. Tel.: +64 9 373 7599x8340; fax: +64 9 373 7422.
E-mail address: ga.bowmaker@auckland.ac.nz (G.A. Bowmaker).

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Several recent studies report interesting but diverse results regarding the synthesis of copper–polyaniline composites. Different synthetic techniques have resulted in different compounds. Mallick et al. [12] used copper(II) sulfate as an oxidizing agent for the polymerization of aniline and found microstructured flower-like PANI morphologies with the chemical structure of conventionally synthesized PANI. They proposed the reduction of copper sulfate to copper nanoparticles with a size range of 2–5 nm resulting in a PANI-metal composite having a conductivity comparable to that of emeraldine salt-PANI (ES-PANI) (0.5×10^{-1} S cm^{-1}). However, neither the proportion of copper present in the product nor its oxidation state were established in this study. A method involving UV irradiation of $Cu(NO_3)_2$/HCl/aniline solution for the synthesis PANI/CuCl nanocomposites was reported by Li et al. [13]. They found the presence of CuCl dispersed in the PANI matrix in the form of cubic crystals. The proportion of copper present in the product was not determined, but the presence of CuCl was established by XRD measurements. In contrast to this, a more recent study of the $Cu(NO_3)_2$/aniline system by Divya and Sangaranarayanan [14], proposed the formation of a PANI/copper metal composite with a remarkably high copper content (46.6 wt.%; considerably greater than the theoretical maximum amount of 39.4 wt.% for the proposed mechanism involving reduction of copper(II) to copper(0)). However, the only evidence for the presence of copper metal was a very weak XRD peak which was comparable in size to the surrounding noise peaks. Chen et al. [15] used Cu, CuCl or $CuCl_2$ as a catalyst for the oxidative polymerization of the aniline dimer *N*-(4-aminophenyl) aniline with O_2 or H_2O_2 as the oxidizing agent. The oxidative polymerization in aqueous solution under mild conditions leads to ES-PANI. The copper catalysts caused an increase in the reaction yield from 13–43 to 86–93% with the use of O_2 or H_2O_2, respectively. The corresponding reaction of aniline monomer with $CuCl_2$ is claimed to produce the emeraldine form of PANI, but with a small amount of branched structure present [16]. In neither of these studies was the presence of copper in the products investigated. Ding et al. [17] have used $FeCl_3$, $Fe_2(SO_4)_3$, $Ce(SO_4)_2$, APS and $CuCl_2$ as oxidizing agents to control specifically the diameter of PANI nanofibers. The products were claimed to be ES-PANI, but neither the nature of the dopant anions nor the presence of copper (in the $CuCl_2$ case) were investigated.

Thus, for proposed aniline polymerization reactions involving copper compounds, it is clear from the above that considerable uncertainty remains regarding the role of copper in the reaction (oxidant or catalyst) and the chemical form of copper in the products (copper metal, copper(I), etc.). In cases where the formation of ES-PANI is proposed, the nature of the dopant anion has not been established, but this raises the possibility that the dopant anion may contain copper, as has been observed in the product of reaction of ES-PANI chloride with $CuCl_2$ to form ES-PANI doped with the copper(II) anion tetrachlorocuprate(II), $CuCl_4{}^{2-}$ [18]. Thus, the full range of common oxidation states of copper (0, +1, +2) have been proposed, or are possibilities, for the copper incorporated in the proposed PANI products, although the evidence for the most interesting (and unexpected) case of copper(0) (i.e., copper metal, copper nanoparticles) is rather weak. Another weakness of previously published work in this area is that it is either assumed (without proof) that polyaniline is the reaction product, or measurements that establish the degree of oxidation and the degree of doping (and the nature of the dopant) in the product have not been made. Evidence for the formation of PANI in these reactions is based on physical (usually spectroscopic) measurements. However, it is known that the oxidation of aniline can yield products with spectroscopic properties similar to PANI, but which do not exhibit typical PANI chemical behavior [19], particularly under the conditions of low acidity that normally prevail in the previously reported copper(II)/aniline reactions. Therefore, characterization of the products should also include chemical tests to establish their true PANI nature.

The aims of the present study are therefore threefold: (a) to study the effect of the use of copper(II) as a milder oxidizing agent than those normally used (ammonium persulfate, benzoylperoxide, hydrogen peroxide, etc.) on the aniline polymerization reaction and its potential PANI product, (b) to unambiguously establish the presence of PANI in the product, not only by physical measurements, but also by chemical tests (dedoping, reduction, etc.) and (c) to determine the chemical nature of any copper incorporated in the reaction product. The latter is particularly important in relation to the proposed use of such reactions to produce polyaniline/metal composite materials, which are the subject of a recent review [20], but it is evident from the literature cited above that the chemical state of the copper that has been proposed to be incorporated in the product is quite variable [12,13,15,20]. Indeed, the formation of PANI by the oxidation of aniline by copper(II) compounds has been called into question in studies of reactions of aniline with $CuSO_4$, $CuCl_2$ and $CuBr_2$, where 2:1 coordination adducts of aniline with these copper(II) compounds precipitated rather than the expected PANI product [21]. In the present work, we extend the study of the $CuCl_2$/aniline system to explore the effect of using higher $CuCl_2$ concentrations; previous studies have shown that the oxidation potential of $CuCl_2$ increases with increasing concentration [22]. A previous study [15] has proposed a catalytic (rather than an oxidative) role for copper(II) in aniline oxidation reactions in the presence of copper(II). The possibility that PANI might be formed catalytically by aerial oxidation of aniline in the presence of $CuCl_2$ has been excluded in the present study by carrying out the reaction in the absence of air. It was found that polyaniline emeraldine base (EB-PANI) doped with $[CuCl_3]^-$ forms under these conditions. $CuCl_2$ is a weaker oxidant than, e.g., $AgNO_3$, and this study further supports the view that weak oxidizing agents can be used for aniline polymerization reaction. The reaction yield is low, but can be increased by increasing the $CuCl_2$ concentration.

2. Experimental

2.1. Materials

Aniline monomer (99.5%) was purchased from Sigma–Aldrich and distilled twice before use. *p*-Toluene sulfonic acid (synthesis grade) was purchased from Scharlau and used as received. Anhydrous copper chloride (97%) from Sigma–Aldrich was used as received.

2.2. Procedure

A solution of 0.2 M aniline and 0.2 M *p*-TSA was prepared in milli-Q water. The pH of the solution was 4.70. 10 mL of this solution was placed in a refrigerator for 10–15 min. 10 mL of 3 M pre-cooled copper(II) chloride solution was added dropwise to 10 mL of the aniline *p*-TSA solution under a nitrogen atmosphere. The reaction mixture was left undisturbed for 24 h at room temperature under a nitrogen atmosphere. The reaction mixture turned greenish black and had a final pH of 2. The precipitate was filtered and washed several times with milli-Q water followed by acetone. The product was dried for 24 h in a vacuum oven at room temperature and was labeled as B-PANI. Similar reactions with oxidant:monomer ratios *R* from 1 to 15 were investigated by varying the $CuCl_2$ concentration. The B-PANI was washed with 1 M HCl to remove basic impurities and the sample was labeled as H-PANI. The B-PANI when treated with 35% hydrazine was labeled as PANI (Scheme 1).

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