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Short Communication

Efficient bromination of polyaniline base to poly(2-bromoaniline)-bromide salt and its application as a recyclable catalyst for the synthesis of 2-methyl-4-anilino-1,2,3,4-tetrahydroquinolines

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ABSTRACT

Efficient bromination of polyaniline base to poly(2-bromoaniline)-bromide is successfully carried out using bromodimethylsulfonium bromide. Poly(2-bromoaniline)-bromide salt was obtained in a dry amorphous nature, having high conductivity (2.5 S/cm) with agglomerated spherical morphology. Poly(2-bromoaniline)-bromide salt was proved to be a novel, efficient, reusable, cheaper and eco-friendly polymer-based solid acid catalyst in the reaction between aromatic amines and *N*-vinyl lactam under solvent-free conditions to provide 2-methyl-4-anilino-1,2,3,4-tetrahydroquinolines. These 2,4-disubstituted tetrahydroquinolines were synthesized with *trans* selectivity.

1. Introduction

Polyaniline (PANI) is one of the most interesting conducting polymers due to its good environmental stability, interesting redox properties, optoelectronic features and controllable electrical and electrochemical properties [1]. As a result, many technological applications have been demonstrated with polyaniline in the development of sensors, rechargeable batteries, super capacitors, electrochromic materials, electromagnetic shielding, light emitting devices, photovoltaic materials, ESD, and corrosion-protecting coatings [2–5]. Despite the vast bibliography devoted to PANI, new studies focusing on the polymerization process are reported each year [6–9]. Recently, PANI has been receiving considerable attention for catalytic reactions as a catalyst and support owing to its highly conducting and redox properties [10]. Furthermore, its easy preparative protocol from non-expensive starting material (aniline), controllable doping levels through an acid doping/base dedoping process, and non-solubility in most organic solvents and water make it useful in heterogeneous catalysts. By exploiting these properties, polyaniline-based solid acid catalysts have been reported earlier by our group for various organic transformations [11].

The tetrahydroquinoline scaffold is a core structure in many biologically-active natural products and synthetic pharmaceutical agents. 2,4-Disubstituted tetrahydroquinolines have been synthesized by Batey and other groups' research, via 1:2 coupling of substituted anilines with vinyl ethers [12–16]. Our group very recently reported the synthesis of *cis*-2-methyl-4-substituted tetrahydroquinoline derivatives from the reaction of substituted aniline and *N*-vinyl lactam [17] using polyaniline-based solid acid catalysts. In 2010, Jia et al. reported for the first time the synthesis of 2-methyl-4-anilino-1,2,3,4-tetrahydroquinoline derivatives [18] via a tandem cyclization of imine with its enamine isomer induced by the radical cation salt tris(4-bromophenyl)aminium hexachloroantimonate ($TBPA^+$). However, the drawbacks of this method include the non-reusable, toxic, and expensive nature of the catalyst. In order to improve the synthetic methodology, a polyaniline salt is used as a cheaper, reusable and environmentally-friendly catalyst in the stereoselective synthesis of *trans*-2-methyl-4-anilino tetrahydroquinoline derivatives.

2. Experimental

2.1. Preparation of poly(2-bromoaniline)-bromide salt (P2BrABr-I) using BDMS

Bromodimethylsulfonium bromide (BDMS) [19] and polyaniline base [20] were prepared by following a procedure reported earlier [19,20]. Polyaniline base (0.5 g) was added to 50 mL of dichloromethane solution containing 0.5 g BDMS and the mixture was stirred at ambient temperature for 4 h. The resultant mixture was filtered, washed with

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dichloromethane and then acetone until the filtrate is colorless and dried at 50 °C until the weight is constant.

2.2. Preparation of poly(2-bromo aniline)-bromide salt using Br_2 (P2BrABr-II)

Polyaniline base (0.5 g) was added to 50 mL of dichloromethane solution containing 2.57 mL of bromine and the mixture was stirred at ambient temperature for 4 h. The product was isolated by using the above procedure.

2.3. General procedure for P2BrABr salt-catalyzed domino tetrahydroquinoline synthesis

A mixture of aromatic amine (2 mmol), *N*-vinyl lactam (1 mmol) and P2BrABr catalyst (14 wt.% with respect to aromatic amine) under solvent-free conditions was stirred at 80 °C for a particular period of time. Ethyl acetate was added to the reaction mixture. The catalyst was separated by simple filtration. Ethyl acetate solution was washed with water, followed by brine, dried over anhydrous Na_2SO_4, and concentrated. The products were isolated by column chromatography using silica gel (60–120 mesh) and eluted with petroleum ether. All of the products were authenticated by ^{1}H NMR and mass spectroscopy data [18,21,22]. The recyclability experiment was carried out using the recovered catalyst, wherein, the recovered catalyst was washed with acetone and dried in an oven at 50 °C for 10 min.

3. Results and discussion

P2BrABr salt was prepared by oxidizing aniline using sodium persulfate oxidant in the presence of hydrochloric acid, followed by dedoping of polyaniline-hydrochloride salt (PANI-HCl) to polyaniline base (PANI) and subsequent doping with bromodimethylsulfonium bromide (BDMS) or bromine (Br_2) to 2-bromopolyaniline-bromide salts, P2BrABr-I and P2BrABr-II respectively.

3.1. Physical properties of P2BrABr

Bromination of polyaniline base using BDMS and Br_2 yielded 0.7 g and 0.85 g (with respect to 0.5 g of PANI base used) respectively. Conductivity of the P2BrABr-I prepared using BDMS (2.5 S/cm) was found to be higher than that of the P2BrABr-II sample prepared using Br_2 (0.2 S/cm). This result indicates that the efficiency of bromination of polyaniline base is higher with the use of BDMS. Conductivity of P2BrABr is 12 orders of magnitude higher than that of PANI base (insulator level, $<10^{-12}$ S/cm). Increase in conductivity result confirms that insulating PANI base is converted to doped PANI salt. The densities of P2BrABr-I and P2BrABr-II were found to be 1.5 and 1.7 g/cm^3, respectively, which are higher than that of PANI base (1.2 to 1.3 g/cm^3). This result is due to the presence of higher density bromine on the polyaniline system. In order to determine the amount of moisture present in the brominated polyaniline salt, the sample was heated at 100 °C for 48 h and weighed. The weight of the brominated polyaniline salt before and after heating was found to be almost the same. This result indicates that the brominated polyaniline salt does not have moisture compared to conventional polyaniline salt, which contains 5 to 8% moisture [23,24].

3.2. Infrared spectra of P2BrABr

Infrared spectra of P2BrABr-I, P2BrABr-II and dedoped P2BrABr-I are shown in (Fig. 1). The major characteristic peaks obtained from 2000 to 750 cm^{-1} for the three polymer samples are reported in Table 1.

Infrared spectral peaks for P2BrABr-I are very similar to the infrared peaks reported in polyaniline salt [25]. Infrared spectral peaks of its corresponding base are nearly the same with that of the polyaniline base

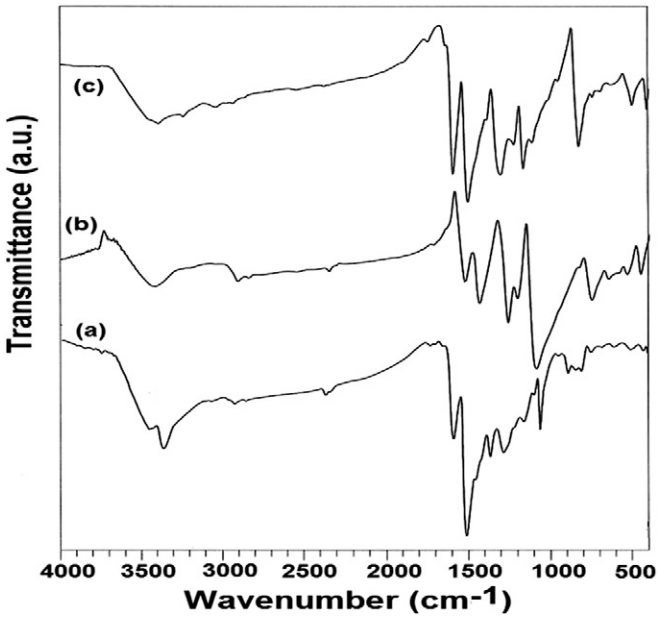

Fig. 1. Infrared spectra of (a) P2BrABr-II, (b) P2BrABr-I and (c) dedoped P2BrABr-I.

peaks reported in the literature [17] except the shifting of C – N str. of the quinoid ring peak from 1310 to 1295 cm^{-1}. This is due to the presence of bromine in the ortho-position of the polyaniline base. The IR spectral peaks of P2BrABr-II consisted of polyaniline base peaks in addition to salt peaks (Table 1). This result indicates the lower efficiency of doping of bromine on the polyaniline system by bromination of polyaniline base with bromine.

3.3. XRD pattern of P2BrABr

The X-ray diffraction pattern of conventionally synthesized semi-crystalline polyaniline salts showed four clear peaks around $2\theta = 9.3$, 15, 20–22, 25 and 27° [26–28]. In this work, the X-ray diffraction profile registered for P2BrABr-I (Fig. 2b) showed broad peaks around $2\theta = 7$, 14 and 24° with corresponding d-spacing 12.1, 6.3 and 4.3 respectively, indicating less crystallinity. The X-ray diffraction pattern of P2BrABr-II (Fig. 2a) showed a broad peak around $2\theta = 25°$, which indicates an amorphous nature for the polyaniline salt. The X-ray pattern of the dedoped P2BrABr-I sample showed a broad band around $2\theta = 25°$, similar to that of P2BrABr-II. Recycled P2BrABr-I showed a broad peak around $2\theta = 21°$ representing an amorphous nature.

3.4. FE-SEM and EDAX of P2BrABr

Morphologies of polyaniline samples are found out from field emission scanning electron microscopy. The SEM picture of brominated polyaniline base by BDMS (P2BrABr-I) showed aggregated nanofibers with spheres (Fig. 3a) and by bromination with bromine, morphology changed to agglomerated spheres (Fig. 3b). The SEM picture of dedoped P2BrABr-I showed nanospheres with a diameter of 55–105 nm (Fig. 3c). The SEM picture of recycled P2BrABr-I also showed nanospheres with a diameter of 55–110 nm (Fig. 3d). EDAX of polyaniline base brominated using BDMS, P2BrABr-I, showed 30 wt.% of bromine and its corresponding dedoped polyaniline base showed 14 wt.% of bromine. This result indicates that dedoped polyaniline base contains bromine due to the formation of poly(2-bromoaniline). Higher bromine weight percentage on polyaniline salt indicated that poly(2-bromoaniline) contains bromide dopant, i.e., formation of poly(2-bromoaniline)-bromide salt.