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A novel polyaniline–fluoroboric acid–dodecylhydrogensulfate salt: versatile reusable polymer based solid acid catalyst for organic transformations

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Abstract

A novel polyaniline–fluoroboric acid–dodecylhydrogensulfate (PANI–HBF$_4$–DHS) salt was directly synthesized via emulsion polymerization pathway. Aniline was oxidized to polyaniline salt by benzoyl peroxide in presence of sodium lauryl sulfate and fluoroboric acid. This polymerization pathway leads to incorporation of both acid group as well as surfactant group into the polyaniline chain as dopants. The polyaniline salt was characterized by Fourier transform infrared spectroscopy, electronic absorption spectroscopy, X-ray diffraction studies, scanning electron microscopy, elemental analysis, viscosity and conductivity measurements. PANI–HBF$_4$–DHS salt is used as catalyst for the first time in various organic reactions such as Mannich-type reaction, Biginelli reaction, Pechmann reaction, esterification and carbonyl protection. The advantages of the PANI–HBF$_4$–DHS salt are ease of preparation, easy handling, recovery, simple work-up, reusability and versatility.

1. Introduction

Acid catalysts are often being used in organic syntheses and industrial processes. For example, sulfuric acid, fluorohydric acids are used in alkylation, esterification, and hydrolysis reactions, etc. [1–3]. However, these acid catalysts are toxic, corrosive and in addition, are hard to remove from the reaction medium. The environmental care is one of the worldwide increasing problems.

The replacement of environmental hazardous catalysts in existing processes, by the use of solid acid catalysts such as zeolites, alumina, resins, etc., is one of the innovative trends. Novel eco-friendly catalytic syntheses in the area of fine chemicals are having the largest potential for a fast application in the industry [4].

In our efforts to develop clean methods for organic transformations, we are especially interested in developing the potential use of simple, inexpensive polyaniline based solid acid catalyst. Among the conducting polymers, polyaniline is an important polymer because of its easy preparation, excellent electrical properties, number of intrinsic redox states, possible processability and good environmental stability [5,6]. Polyaniline has been extensively studied for many potential applications including lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and sensors [7].

The structure of polyaniline is known as para-linked phenylene amineimine. The salt form of polyaniline can, in principle, be described by the following general formula:
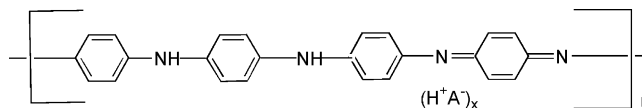
Generally polyaniline can be easily synthesized from monomeric aniline by either chemical oxidative

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polymerization or electrochemical polymerization [8–10]. The chemical polymerization of aniline is very important since it is the more feasible route for the production of polymers on a large scale.

The oxidant traditionally employed in the polymerization of aniline has been ammonium persulfate, which yields an insoluble and infusible polymer. Moreover ammonium persulfate being a strong oxidizing agent and aniline polymerization being exothermic, controlling reaction temperature is rather difficult and consequently polymers with a wide distribution of molecular weight results. The removal of inorganic byproducts (ammonium sulfate) from the polymer formed is also difficult. To overcome these difficulties, recently our group synthesized polyaniline–sulfosalicylic acid salt by inverted emulsion polymerization using benzoyl peroxide (BP) oxidant and sodium lauryl sulfate (SLS) surfactant [11].

This paper reports a direct synthesis of PANI–HBF$_4$–DHS salt by a simple but effective emulsion polymerization pathway. The polyaniline salt was characterized by physical, spectral and electrical methods. PANI–HBF$_4$–DHS salt is used as catalyst for various organic reactions such as Mannich-type reaction, Biginelli reaction, Pechmann reaction, esterification and carbonyl protection. The results of the all reactions have been compared with the results obtained from other reported polyaniline based solid acid catalysts [12–15].

2. Experimental

2.1. Materials

Aniline from E. Merck was distilled prior to use. Reagent-grade sodium lauryl sulfate (SLS), fluoroboric acid (HBF$_4$), benzaldehyde, cyclohexanone, ethyl acetoacetate, urea, capric acid and phloroglucinol (BDH, India) were used without further purification. Solvents were distilled by appropriate procedure prior to use. Benzoyl peroxide (BP) reagent-grade (BDH, India) was recrystallized from chloroform/methanol mixture.

2.2. Emulsion polymerization pathway for synthesis of polyaniline salt

In a typical experiment, 3.0 g BP was dissolved in 30 ml chloroform while 1 g sodium lauryl sulfate is dissolved in 20 ml water. The reaction mixture was stirred at 40 °C. The aqueous solution of 5.5 ml fluoroboric acid and 1.0 ml aniline in 50 ml water was prepared and added drop wise in to the initiator–surfactant mixture for 15 min. After addition, the reaction was continued for 8 h. Chloroform layer containing polyaniline salt was separated from aqueous layer and washed thrice with distilled water. Polyaniline salt was precipitated from the chloroform containing polyaniline salt layer with 300 ml acetone. Precipitate of polyaniline salt was separated by filtration, washed with water followed by acetone and dried for 12 h at 100 °C.

2.3. PANI–HBF$_4$–DHS, solid acid catalyst for organic transformations

2.3.1. Experimental procedure for Mannich-type reaction

In a typical reaction procedure, aniline (0.5 g, 5.3 mmol), benzaldehyde (0.56 g, 5.3 mmol) and cyclohexanone (2.6 g, 26.0 mmol) were taken into a 10 ml round bottomed flask, 0.14 g of PANI–HBF$_4$–DHS (25% with respect to weight of benzaldehyde) was added into the reaction mass. The reaction mixture was maintained with constant stirring at 30 °C for 6 h. At the end of the reaction, 20 ml of acetone was added to the reaction mixture. Catalyst was filtered from the reaction mixture through G4 sintered crucible, filtrate was collected and the acetone solvent was distilled off completely. The obtained liquid was added to 25 ml of hexane and fine solid was separated. The solid product was separated by simple filtration.

2.3.2. Experimental procedure for Biginelli reaction

In a typical experiment, benzaldehyde (1.0 g, 9.43 mmol), ethyl acetoacetate (1.22 g, 9.43 mmol) and urea (0.56 g, 9.43 mmol) was taken in 25 ml round bottomed flask, 10 ml of ethanol was added followed by 50 mg of PANI–HBF$_4$–DHS (5 wt.% with respect to benzaldehyde). The reaction mixture was refluxed for 6 h. The reaction mixture was filtered at hot condition using whatmann 41 filter paper, ethanol solvent was evaporated under vacuum. The crude product obtained was washed with water, filtered and dried at 100 °C. The product was purified by recrystallization using methanol.

2.3.3. Experimental procedure for Pechmann reaction

In a typical experiment, 0.5 g of phloroglucinol (4 mmol) was taken in 10 ml round bottomed flask and 1.03 g of ethyl acetoacetate (8 mmol) was added followed by 0.1 g of PANI–HBF$_4$–DHS catalyst (20 wt.% with respect to phloroglucinol). The reaction mixture was heated at 150 °C for 6 h. At the end of the reaction, the product was separated out in the flask as a solid mass. The product was isolated by dissolving in acetone and filtered. The catalyst was removed by filtration and the filtrate was concentrated under vacuum. The resultant compound was washed with water, filtered and dried at 100 °C. The product was purified by dissolving in 1.0N NaOH solution and then regenerated with 1N H$_2$SO$_4$ solution. The precipitated product was filtered, washed with water and the sample was dried at 100 °C till a constant mass was reached.

2.3.4. Experimental procedure for esterification

In a typical experiment, esterification of capric acid (1 g) with methanol (5 ml) was carried out in 10 ml round bottom flask with 0.2 g of PANI–HBF$_4$–DHS salt (20 wt.% with respect to capric acid). The reaction mixture was refluxed at 70 °C for 24 h. At the end of the reaction, the mixture was filtered and washed with methanol to recover the catalyst. The solvent methanol was distilled off. Dichloromethane was

added to the crude product and washed with aqueous sodium bicarbonate solution, followed by distilled water. Anhydrous solid sodium sulfate was added to the dichloromethane solution, filtered and the dichloromethane was evaporated to obtain the product.

2.3.5. Experimental procedure for carbonyl protection

In a 50 ml round bottom flask was placed acetophenone (1 g, 8.3 mmol), 1,2-ethanediol (0.62 g, 10 mmol), 0.2 g PANI–HBF$_4$–DHS (20 wt.% with respect to acetophenone) and 25 ml of toluene. The mixture was refluxed for 6 h with Dean–Stark apparatus for azeotropic removal of water. The reaction mixture was cooled and filtered to remove the catalyst. The filtrate was washed with water and the organic phase was dried over anhydrous Na$_2$SO$_4$, filtered. The filtrate was concentrated in vacuum and the product was isolated.

2.4. Characterization

2.4.1. Resistance measurement

Polyaniline sample was pressed into disks of 16 mm-diameter and ca. 2 mm thickness under a pressure of 400 MPa. Resistance measurement of the pellet was carried out on a four probe connected to a digital multimeter (Keithley model-2010). Resistance was calculated based on the average of at least three pairs of consistent readings at different points on the pressed pellet (total error involved is <1%).

2.4.2. Pellet density

Polyaniline sample in the form of pellet was obtained by subjecting the sample to a pressure of 400 MPa. Pellet density was measured from mass per unit volume of the pressed pellet.

2.4.3. Elemental analysis

The content of elements in the polyaniline samples was determined using Elementor Vario EC Germany elemental analyzer.

2.4.4. Infrared spectra

The polyaniline sample was mixed with KBr powder and compressed into pellet, wherein, the polyaniline powder was evenly dispersed. Fourier transform infrared spectrum was recorded using GC-FT-IR spectrometer (MODEL 670 Nicolet Nexus, USA spectra).

2.4.5. Electronic absorption spectrum

Electronic absorption spectrum of the polyaniline sample was recorded at ambient temperature using GBC cintra 10e UV/V spectrophotometer.

2.4.6. X-ray diffraction spectrum

Wide angle X-ray diffraction spectrum for the polyaniline powder sample was obtained using a Siemens/D-5000 X-ray diffractometer using Cu Kα radiation of wavelength 1.54×10^{-10} m and continuous scan speed of 0.045°/min.

2.4.7. Scanning electron microscopy

A morphology study of polyaniline sample was carried out using Hitachi S520 scanning electron microscope instrument operating at 10 kV. The sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample charging problems.

3. Results and discussion

A novel PANI–HBF$_4$–DHS salt was synthesized via emulsion polymerization pathway. Aniline was oxidized to polyaniline salt by benzoyl peroxide in presence of sodium lauryl sulfate and fluoroboric acid. This polymerization pathway leads to incorporation of both acid group as well as surfactant group into the polyaniline chain as dopants.
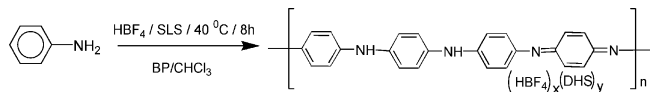
3.1. Effect of fluoroboric acid on polyaniline salt

The polymerization reaction of aniline was carried out in chloroform using different amounts of fluoroboric acid. The yield of PANI–HBF$_4$–DHS salt was found to be 1.0, 1.1 and 1.0 g (for 1.0 ml of aniline used in the reaction) with use of 2.7, 5.5 and 11.0 ml of fluoroboric acid, respectively. Conductivity (0.02–0.03 S/cm) and pellet density (1.19–1.21 g/cm^3) were found to be independent of acid used (2.7–11.0 ml). Use of less than 2.0 ml of HBF$_4$ did not give polyaniline. Use of 5.5 ml of fluoroboric acid afforded excellent yield (1.10 g) and reasonable conductivity (0.03 S/cm) of polyaniline salt.

3.2. Dopant

Polyaniline base was prepared by dedoping the PANI–HBF$_4$–DHS salt using aqueous sodium hydroxide solution. PANI–HBF$_4$–DHS (1 g) was kept in 100 ml aqueous sodium hydroxide solution (1N) and stirred the solution for 12 h at ambient temperature. The mixture was filtered and washed with ample water. The polyaniline base was dried at 100 °C till constant mass (0.53 g). The filtrate was collected and neutralized with hydrochloric acid (1N) and then treated with aqueous potassium hydroxide (1N) to separate the potassium salt of fluoroboric acid and lauryl sulfate. The precipitated solid was separated by filtration and dried. Potassium salt of lauryl sulfate (KLS) is soluble in methanol and however, potassium salt of fluoroboric acid KBF$_4$ is insoluble in methanol and thus both the salts are separated using methanol. The authenticity of KBF$_4$ was confirmed from XRD technique and KLS was confirmed by NMR spectrum. These results indicate that in the course of polymerization,

the surfactant (SDS) get converted into dodecylhydrogensulfate (DHS) under the acidic condition and incorporated in polyaniline system along with fluoroboric acid. The amount of dopants (both fluoroboric acid and dodecylhydrogensulfate) present in polyaniline salt (47%) was calculated from the weight of polyaniline base obtained from polyaniline salt.

3.3. Elemental analysis

The value of percentage of carbon, hydrogen, nitrogen and sulfur observed for PANI–HBF$_4$–DHS salt was 61.6, 7.1, 7.4 and 5.2%. Polyaniline base showed that C = 79.5%, H = 5.2%, N = 14.9% which are close to the theoretical value of polyaniline base (C = 79.1%, H = 5.5%, N = 15.4%). This result indicates that all the dopant parts have come out from the polyaniline salt. The presence of sulfur content (5.2%) of the PANI–HBF$_4$–DHS salt indicates the presence of dodecylhydrogensulfate group.

3.4. Viscosity measurement

Viscosity measurement of polyaniline salt in dimethyl formamide was carried out by capillary viscometer and Schott gerate equipment system for automatic recording of flow time to the accuracy of 0.01 of a second. Viscosity was calculated using the formula

$$\log[\eta] = \log[\eta \, \mathrm{spc}/C] - K\eta\mathrm{spc}$$

The limiting viscosity number of the polyaniline salt was found to be 1.3 dL/g.

3.5. Infrared spectra

Infrared spectrum of PANI–HBF$_4$–DHS salt prepared by emulsion polymerization process is shown in Fig. 1. The
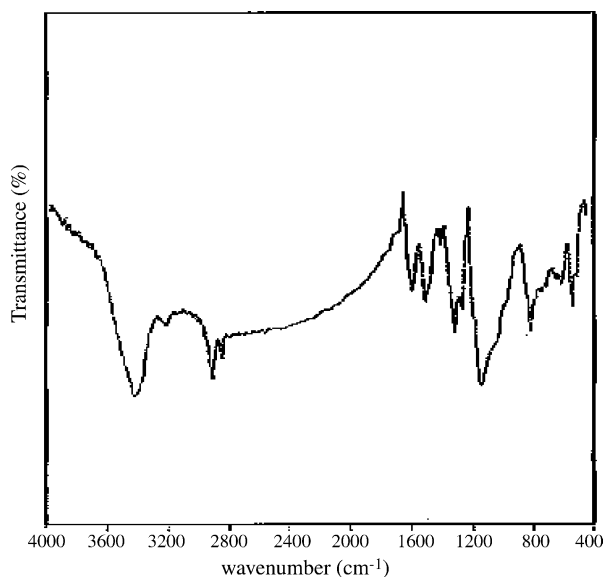
vibrational bands observed for the polyaniline salt are reasonably explained on the basis of the normal modes of aniline and benzene; a broad band at 3415–3460 cm^{-1} assigned to the N–H stretching vibration. The bands at 2920 and 2850 cm^{-1} are assigned to vibrations associated with the N–H part in C$_6$H$_4$NH$_2$C$_6$H$_4$ group or sum frequency. The 1565 and 1490 cm^{-1} bands due to quinonoid ring (Q) and/or benzenoid ring (B). The bands at 1370 and 1300 cm^{-1} are assigned to C–N stretching vibration in QBB, QBQ and BBQ, a 1240 cm^{-1} band to the C–N stretch vibration of aromatic amine. In the region of 1020–1170 cm^{-1} aromatic C–H in-plane-bending modes are usually observed. For polyaniline, a strong band characteristically appears at 1140 cm^{-1}, which has been explained as an electronic band or a vibrational band of nitrogen quinone. A band at 705 cm^{-1} is assigned to ring C–C bending vibration and the band at 580 cm^{-1} due to ring in plane deformation. The C–H out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. For the polyaniline salt, this mode was observed as a single band at 825 cm^{-1}, which fell in the range 800–860 cm^{-1} reported for 1,4-substituted benzene. The infrared spectrum of polyaniline salt prepared is very close to the infrared spectrum of the polyaniline salt system reported in the literature [16,17].

3.6. Electronic absorption spectra

UV–vis absorption spectrum of PANI–HBF$_4$–DHS salt prepared by emulsion polymerization pathway was shown in Fig. 2. UV–vis absorption spectrum of PANI–HBF$_4$–DHS salt in chloroform–dimethyl formamide showed three peaks in the range, $\lambda_{\max}$ at 750, 430 and 330 nm. This UV–vis spectrum was similar to Tzou and Gregory [18] results in which bands around 430 and 750 nm have been assigned for polaran transitions and band at 330 nm is for amine segments. This
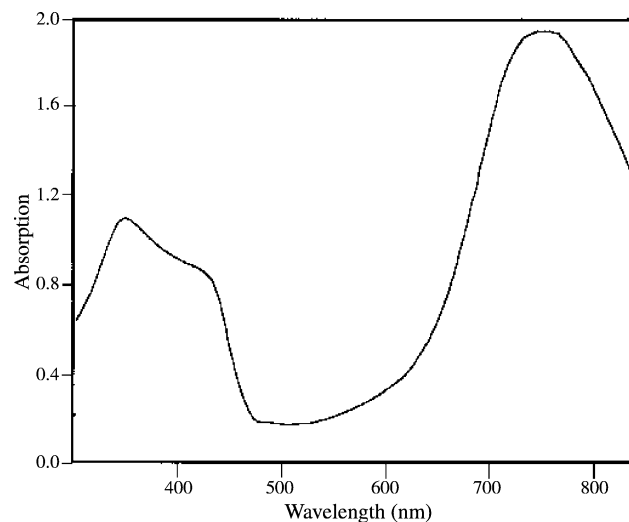

Fig. 1. Infrared spectrum of PANI–HBF$_4$–DHS salt.

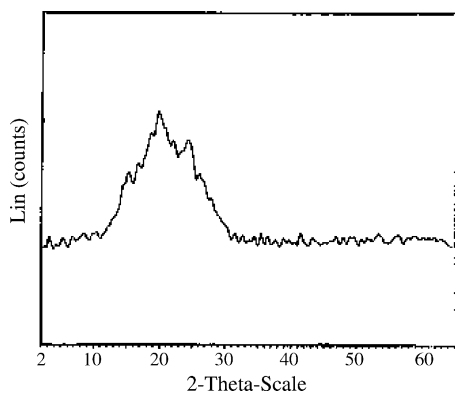Fig. 2. Electronic absorption spectrum of PANI–HBF$_4$–DHS salt.

Fig. 3. X-ray diffraction pattern of PANI–HBF₄–DHS salt.

result supports the presence of PANI–HBF$_4$–DHS salt in salt form.

3.7. X-ray diffraction spectra

X-ray diffraction pattern of PANI–HBF$_4$–DHS salt is shown in Fig. 3. X-ray diffraction studies revealed the polyaniline salt was partially crystalline and shows peaks at $2\theta = 14.5$, 20.7, 25.0 and 27.0 corresponding to the interface distances (d) 6.093, 4.290, 3.549 and 3.284 Å, respectively. These positions are in accordance with the earlier report for polyaniline salt [19].

3.8. Scanning electron microscope

Morphology of PANI–HBF$_4$–DHS salt is shown in Fig. 4. The scanning electron micrograph of PANI–HBF$_4$–DHS shows aggregated granular morphology. The scanning electron micrograph picture obtained for the polyaniline salt is similar to our earlier report for PANI–SSA salt [11].
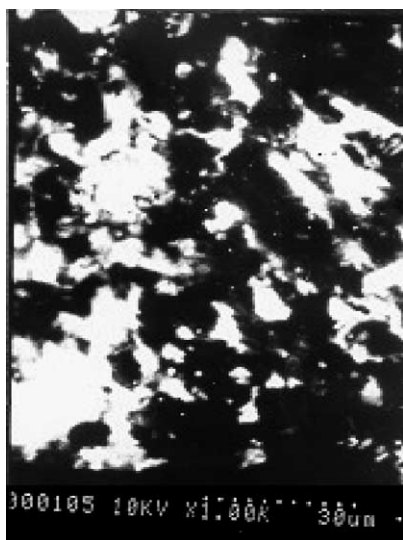

Fig. 4. Scanning electron micrograph of PANI–HBF₄–DHS salt.

### 3.9. PANI–HBF₄–DHS salt catalyst in organic transformations

In our earlier report, different polyaniline based solid acid catalysts were prepared by doping of polyaniline base (polyaniline base was prepared by dedoping of polyaniline–sulfate salt) with various acids. However, in this work PANI–HBF$_4$–DHS salt was prepared by single step and used as polymer based solid acid catalyst in organic transformations such as Mannich-type reaction, Biginelli reaction, Pechmann reaction, esterification and carbonyl protection. The products of various reactions were authenticated by ^{1}H NMR spectra (Gemini Varian 200 MHz and Avance 300 MHz) and mass spectra (VG-Auto Spec.). The results of all the reactions have been compared with the results obtained from other reported polyaniline based solid acid catalysts by our group [12–15].

3.9.1. Mannich-type reaction for the synthesis of β-amino ketone

Mannich-type reactions are among the most important carbon–carbon bond forming reactions in organic synthesis. They provide β-amino carbonyl compounds, which are important synthetic intermediates for various pharmaceuticals, natural products and versatile synthetic intermediates.

There was no appreciable reaction when aniline and benzaldehyde was allowed to react with cyclohexanone in the absence of catalyst. With the use of 25 wt.% of PANI–HBF$_4$–DHS salt catalyst gave 80% yield under solvent free condition at 30 °C in 6 h. The product was confirmed by NMR (300 MHz) in CDCl$_3$ which gave peaks at 1.5–2.7 (9H, m), 4.6 (0.82H, d), 4.7 (0.18H, d), 6.5–7.3 (10H, m).

We have reported earlier [12] the preparation of β-amino ketone with the use of different polyaniline based solid acid catalyst such as PANI–H$_2$SO$_4$ (65%), PANI–HClO$_4$ (74%), PANI–HCl (84%), PANI–PTSA (85%), PANI–SSA (72%), PANI–FeCl$_3$ (72%) and PANI–ZnI$_2$ (12%).
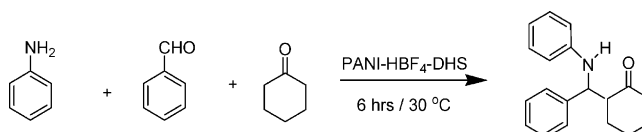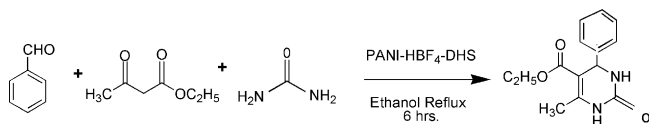

Reusability of the catalyst was checked by recovered PANI–HBF$_4$–DHS salt and reused for a further five consecutive reactions and obtained the yield 75–80%. This indicates that PANI–HBF$_4$–DHS does not lose its activity and can be recyclable.

3.9.2. Biginelli reaction for the synthesis of dihydropyrimidinone

The synthesis of dihydropyrimidinones is currently important because of their wide range of pharmaceutical and biological properties. The most simple and straightforward procedure reported by Biginelli in 1893 involves condensation of ethyl acetoacetate, benzaldehyde and urea under strongly acidic conditions.

Dihydropyrimidinone was synthesized by refluxing benzaldehyde, ethyl acetoacetate and urea with 5 wt.% of PANI–HBF$_4$–DHS salt in ethanol for 6 h and yielded 97% product and the product was authenticated by NMR (300 MHz) in CDCl$_3$ gave peaks at 1.1 (3H, t), 2.3 (3H, s), 4.0 (2H, m), 5.4 (1H, d), 5.6 (1H, br), 7.3 (5H, m), 7.77 (1H, br). In our earlier work, we have reported 94% yield with the use of polyaniline–bismoclite complex [13].
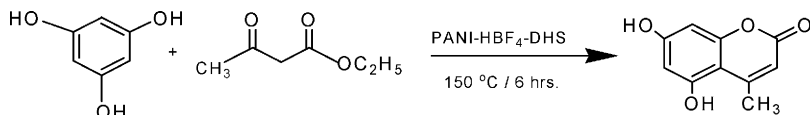

The reusability of the catalyst was checked by conducting three consecutive reactions with recovered PANI–HBF$_4$–DHS salt catalyst and obtained yield in 82–80%.

3.9.3. Pechmann reaction

Coumarins are an important group of naturally occurring compounds which display a broad range of applications as fragrances, pharmaceuticals, additives to food, cosmetics, agrochemicals, optical brightening agents, dispersed fluorescent, tunable dye lasers, biological activities like anthelmintic, hypnotic insecticidal and anticoagulant properties. Pechmann reaction is the most widely used method for the preparation of substituted coumarins since it proceeds from very simple starting materials and gives good yields of various substituted coumarins.

Substituted coumarin was synthesized by heating phloroglucinol and ethyl acetoacetate with 20 wt.% of PANI–HBF$_4$–DHS salt at 150 °C for 6 h and yielded 98%. The product was confirmed by NMR (300 MHz) in CDCl$_3$ + DMSO d$_6$, spectrum shows peaks at 2.2 (3H, s), 5.7 (1H, s), 6.2 (2H, d), 10.0 (2H, br). In our earlier report, we have obtained 92% yield with polyaniline–sulfate against 98% obtained in the present study [14].
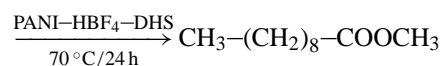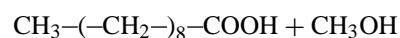

The reusability of the catalyst was checked with two consecutive synthesis of coumarin by using recovered PANI–HBF$_4$–DHS, and desired product obtained in 94–97% yield.

3.9.4. Esterification

Esterification is one of the most fundamental and important reactions in organic syntheses. Most of the reported procedures for the synthesis of esters require the use of sulfuric acid, hydrochloric acid, and toxic chemicals like dimethyl sulfate, methyl iodide or unsafe reagents such as diazomethanes, which are environmentally hazardous and unacceptable. Chemicals like triflouroacetic acid, *p*-toluenesulfonic acid, metal chlorides, chloroaluminate ionic liquids are used in excess and lead to the environmental

pollution. Also, the above catalyst systems involve recovery reusable and handling problems. Replacement of acids by solid acid catalysts such as zeolite, clay, or sulfonic acid resin would result in simplified product recovery and reduction in undesirable waste streams. Also, solid acid catalysts are highly susceptible to deactivation due to pore blocking and hydration. Ion exchange resins are not resistant enough to high temperature and also the efficiency is reduced because of leaching problems. Considering the impact of the above catalysts, there is an urgent need to develop a more eco-friendly and economical method for the production of esters [20].

The esterification of capric acid was performed by refluxing the capric acid in methanol with 20 wt.% of PANI–HBF$_4$–DHS salt for 24 h, yielded 95% and the product shows NMR peaks (200 MHz) in CDCl$_3$ at 0.8–2.2 (19H, m), 3.5 (3H, s).

$$CH_3-(-CH_2-)_8-COOH + CH_3OH$$

$$\xrightarrow[70\,°C/24\,h]{PANI-HBF_4-DHS} CH_3-(CH_2)_8-COOCH_3$$

The reusability of PANI–HBF$_4$–DHS catalyst was checked with two consecutive reaction of esterification of capric acid and resulted in 95–93% yields.

3.9.5. Protection of carbonyl compounds

Protection of carbonyl compounds is the frequently encountered synthetic steps for the preparation of many important compounds. The protective reaction may be catalyzed by protic acids, Lewis acids, iodine, *N*-bromosuccinamide, lanthanides, metal catalysts, zeolites, montmorillonite clay and graphite [15].

PANI–HBF$_4$–DHS used as catalyst to protect the carbonyl group as its acetals by using ethanediol with more clean and green procedure. The protection of acetophenone with 1,2-

ethanediol using 20 wt.% of PANI–HBF$_4$–DHS salt was performed in dry toluene medium, which results in 64% yield and the product was authenticated with NMR (300 MHz) spectrum in CDCl$_3$ solvent 3.9–4.1 (4H, m), 1.8 (3H, s), 7.2–7.4 (3H, m), 7.8 (2H, m). In the present study, we have obtained lower yield (64%) against our earlier report (94–97%) with the use of polyaniline–sulfate salt [15].
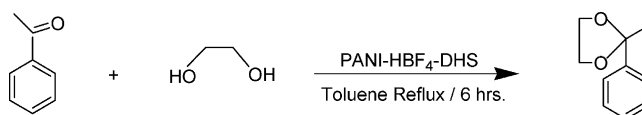
The recovered PANI–HBF$_4$–DHS salt was reused for two times and resulted in 62–64% yield.

At the end, the catalyst was recovered and subjected for analysis. A similar infrared pattern was observed for the PANI–HBF$_4$–DHS salt as prepared and the sample subjected after the reaction. Similarly, pellet density (1.20 g/cm^3), conductivity (0.03 S/cm), elemental analysis (carbon: 61.6%, hydrogen: 7.1%, nitrogen: 7.4%, sulfur: 5.2%) is almost the same. The above result shows that the catalyst does not lose its activity and can be reused.

The presence of acid groups such as fluoroboric acid and dodecyl hydrogen sulfate present in the polyaniline salt may take part in organic transformation. It is difficult to find out the role of fluoroboric acid and dodecyl hydrogen sulfate from the present study.

4. Conclusion

The results in this paper show that it is possible to prepare polyaniline salts with excellent yield (1.1 g) and reasonable conductivity (0.03 S/cm) by chemical oxidative polymerization using BP as an oxidizing agent. This process leads to incorporation of both acid and dodecyl hydrogen sulfate as dopant in the polyaniline system. The optimum reaction condition for polymerization of aniline by BP in chloroform is aniline 1.0 ml, BP 3.0 g, SLS 1.0 g, reaction temperature 40 °C, reaction time 8 h, dopant fluoroboric acid (5.5 ml).

PANI–HBF$_4$–DHS was used as catalyst for various organic reactions such as Mannich-type reaction, Biginelli reaction, Pechmann reaction, esterification and carbonyl protection with excellent yield. The ease of preparation, easy handling, simple work-up procedure and reusability of the catalyst makes all process more economical and industrially important.

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