Polyaniline salts and complexes as catalyst in bisindole synthesis

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Polyaniline salts are prepared by doping of polyaniline base with different Bronsted acids (H_2SO_4, HNO_3 and H_3PO_4), organic acid — *p*-toluene sulfonic acid (PTSA) and Iodine (I_2). Polyaniline complexes are also prepared using Lewis acids (BF_3, $AlCl_3$ and $SnCl_2$). Polyaniline salts and polyaniline complexes are characterized by physical, electrical and spectral methods. Polyaniline salts and polyaniline complexes are used as catalyst for the first time in bisindole synthesis. Bisindole (3,3′-bis(indolyl)phenylmethane) is obtained in excellent yields with simple and more environmental benign procedure. The use of polyaniline catalysts are feasible because of their easy preparation, easy handling, stability, easy recovery, reusability, good activity and eco-friendly.

KEY WORDS: polyaniline catalyst; reusable catalyst; bisindole; carbonyl compound.

1. Introduction

In recent years considerable attention has been paid to the potential of polymer-supported catalysts to act as heterogeneous and regenarable catalysts in organic transformations. The tunability of many properties such as easy preparation, recovery, economical, simple work-up procedures and eco-friendly make polymer-supported catalysts interesting alternatives for conventitional non-regenarable catalysts. In this paper, we report the results on a series of polyaniline catalysts for 3,3′-bis(indolyl)phenylmethane synthesis.

The biologically active indoles and their derivatives have long been of interest as pharmaceuticals. Bisindolylalkanes and their derivatives have received more attention because of their existence in bioactive metabolites of terrestrial and marine origin [1]. The simple method for the synthesis of this class of compounds involve with aldehydes and ketones in the presence of either protic or Lewis acids. Recently, $LiClO_4$ [2], $In(OTf)_3$ [3] and I_2 [4] were also found to catalyzed these reactions. However, some of these catalysts have some limitations, disadvantages and poor regeneration. In this letter, we have prepared polyaniline salts and polyaniline complexes as polymer based catalyst and used in bisindole synthesis. To the best of our knowledge, polyaniline complexes were prepared for the first time using Lewis acids such as aluminium chloride and stannous chloride.

2. Experimental

2.1. Preparation of polyaniline catalysts

Polyaniline salt and its base were prepared by aqueous polymerization pathway by reported procedure [5].

2.1.1. Polyaniline salt

In a 2 L round-bottomed flask, 700 mL of water was taken and 30 mL of H_2SO_4 was added slowly with stirring. To this mixture, 10 mL of aniline was added and the solution was kept under constant stirring at 5–10 °C. To this solution, 250 mL aqueous solution containing sodium persulfate (23.8 g) was added for 15–20 min duration. The reaction was allowed to continue for 4 h at 5–10 ^{0}C. The precipitated polyaniline powder was filtered and washed with 5 L distilled water followed by 500 mL acetone. The polyaniline powder was dried at 100 °C till a constant weight was reached.

2.1.2. Polyaniline base

Polyaniline salt powder (1.0 g) synthesized above was stirred in 100 mL aqueous sodium hydroxide solution (1.0 M) for 8 h at ambient temperature. Polyaniline base powder was filtered, washed with water and finally with acetone and dried at 100 °C till a constant weight was reached.

2.1.3. Redoped polyaniline salt

An amount of 50 mL of 1.0 M solution of HNO_3, H_2SO_4, H_3PO_4 in water, 0.1 M solution of PTSA, BF_3, $AlCl_3$, Iodine (I_2) in acetone, $SnCl_2$ in ethyl acetate was prepared separately. Polyaniline base (0.5 g) was added to each of the above solution and kept under constant stirring at ambient temperature for 4 h. Solid was filtered, washed with ample of respective solvents and the solid was dried at 100 °C till a constant weight was reached.

2.2. Reaction procedure

Typical procedure for 3,3′-bis(indolyl)phenylmethane synthesis: Indole (8 mmol), benzaldehyde (4 mmol) and

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powder form of polyaniline salts or polyaniline complexes (20 wt.% with respect to indole), methanol (40 mL) were taken in 50 mL round bottomed flask and stirred the reaction mixture at room temperature for 1 h or 4 h. The reaction mixture was washed with methanol to separate the catalyst and concentrated in vacuum. The crude mixture was treated with hexane and water to remove the unreacted reactants for affording the 3,3′-bis(indolyl)phenylmethane. The isolated product was characterized by ^{1}H NMR analysis.

2.3. *Analyses*

Polyaniline sample in the form of cylindrical pellet (16 mm diameter, 2–3 mm thickness) was obtained by subjecting the sample to a pressure of 400 MPa. Resistance measurement of the pellet was carried out using Fluke-45 digital multimeter. Pellet density was measured from mass per unit volume of the pressed pellet. Amount of acid group present in the polyaniline chain was calculated based on the weight of redoped polyaniline-salt obtained and weight of polyaniline-base used. Fourier transform infrared spectra were recorded using GC-FTIR spectrometer (MODEL 740 Nicolet, USA spectra). Wide angle X-ray diffraction (XRD) spectra for the polyaniline powder samples were obtained using a Siemens / D –5000 X-ray diffractometer using Cu, K∝ radiation of wave length 1.54×10^{-10} m and continuous scan speed of 0.045°/min. The NMR spectra for the obtained bisindole were recorded using Gemini–Varian 200 MHz equipment with $CDCl_3$ as solvent and TMS as internal reference.

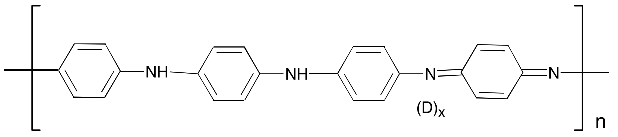
3. Results and discussion

The excellent processability, the presence of a number of intrinsic redox states and reasonable conductivity has enhanced polyaniline in potential practical applications in electronics field [6]. Polyaniline supported metals (Pd, Pt etc.) [7], and polyaniline doped hetero poly acids (12-tungstosilicic acid, 12-molybdophosphoric acid) [8] are exhibiting catalytic activity in organic synthesis. In this work, polyaniline-salts and polyaniline complexes are used as catalyst for 3,3′-bis(indolyl)phenylmethane synthesis in methanol medium.

3.1. *Characterization of polyaniline*

Polyaniline salts are prepared by doping of polyaniline base with different Bronsted acids (H_2SO_4, HNO_3 and H_3PO_4), organic acid (PTSA) and I_2. Polyaniline complexes are prepared using Lewis acids (BF_3, $AlCl_3$ and $SnCl_2$). Polyaniline systems are characterized by physical, electrical and spectral methods and the results are discussed here.

Polyaniline emeraldine salt form is generally represented by the following structure, where D is dopant group.



Amount of acid group (dopant – ‘D’ in structure) present in the polyaniline chain was calculated based on the weight of redoped polyaniline salt obtained and the weight of polyaniline base used (table 1). Amount of dopant present in polyaniline system such as PANI-H_2SO_4, PANI-H_3PO_4 and PANI-BF_3 was found to be 23.3, 29.5 and 31.5 wt. %, respectively. Higher amount of dopant was obtained in the case of PANI-$AlCl_3$, PANI-$SnCl_2$, PANI-I_2 and PANI-PTSA (38.6 – 43.5 wt.%) and lower amount of dopant was observed in PANI-HNO_3 (18.7 wt. %). Acid group (dopant) per aniline unit (‘x’ – in structure) was calculated from the amount of dopant present in the polyaniline chain and the values are included in table 1. Acid group per aniline unit was depended upon the dopant used and it varied from 0.25 to 0.44 (table 1). Density of the PANI-H_2SO_4, PANI-HNO_3, PANI-H_3PO_4, PANI-PTSA and PANI-BF_3 was found to be nearly the same (1.21–1.29 g/cm^3). However, density of the polyaniline complexes depends upon the density of dopant (table 1). Conductivity of PANI-H_2SO_4, PANI-H_3PO_4, PANI-HNO_3, PANI-PTSA and PANI-BF_3 systems was found to be nearly the same (10^{-2} S/cm). Lower conductivities were observed in the case of PANI-$SnCl_2$ (2.5×10^{-3} S/cm), PANI-$AlCl_3$ (6.0×10^{-4} S/cm) and PANI-I_2 (1.8×10^{-6} S/cm).

Infrared spectra of as synthesized polyaniline-sulfate (PANI-H_2SO_4) salt, its corresponding polyaniline base and redoped PANI-H_2SO_4 salt are shown in figure 1. Generally, similar infrared spectral behavior was observed for the polyaniline base prepared from the corresponding salt. The infrared spectrum of polyaniline base is shown in figure 1a. The vibrational bands observed for the polyaniline base 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 $C_6H_4NH_2C_6H_4$ group or sum frequency. 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}

Table 1
The physical and electrical properties of polyaniline salts and polyaniline complexes

Entry	Polyaniline System	Conductivity (S/cm)	Density (g /cm^3)	Dopant (wt %)	Dopant per aniline unit
1	PANI-H_2SO_4	2.0×10^{-2}	1.22	23.3	0.29
2	PANI-HNO_3	1.2×10^{-2}	1.21	18.7	0.34
3	PANI-H_3PO_4	2.0×10^{-2}	1.23	29.5	0.32
4	PANI- PTSA	1.0×10^{-2}	1.21	43.5	0.37
5	PANI- BF_3	4.5×10^{-2}	1.29	31.5	0.30
6	PANI-$AlCl_3$	6.0×10^{-4}	1.45	38.6	0.44
7	PANI- $SnCl_2$	2.5×10^{-3}	1.76	39.1	0.26
8	PANI-I_2	1.8×10^{-6}	1.71	40.6	0.25

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 base, 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 base prepared is very close to the infrared spectrum of the polyaniline base system reported in the literature [9].

The infrared spectrum of as synthesized PANI-H_2SO_4 salt is shown in figure 1(b). The infrared spectrum of PANI-H_2SO_4 salt is similar to that of polyaniline base except a band around 3230 cm^{-1} that is assigned to the NH_2^+ group and indicates the formation of protonated polyaniline salt. The doublet band at 1140 and 1110 cm^{-1} in the polyaniline base which is assigned to mode of Q$=$N$^+$H-B or Q-NH-B becomes a singlet in the salt spectrum.

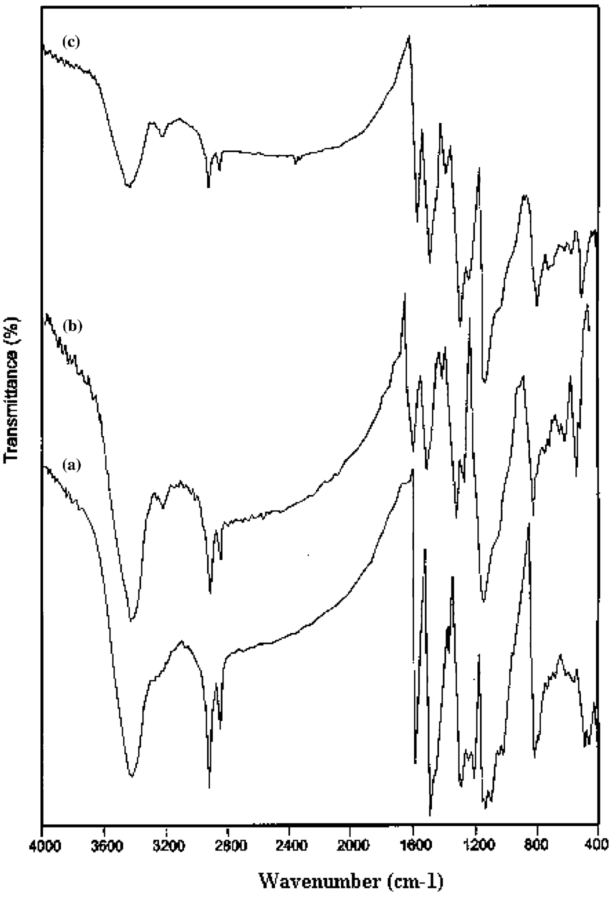


Figure 1. Infrared spectra of: (a) polyaniline base; (b) as synthesized PANI-H_2SO_4 salt; (c) redoped PANI-H_2SO_4 salt.

Infrared spectrum of redoped PANI- H_2SO_4 salt prepared from polyaniline-base (figure 1(c)) is similar to that of the as synthesized PANI- H_2SO_4 salt (Figure 1(b)). This result indicates the formation of polyaniline in salt form. A similar infrared spectrum was observed for the redoped polyaniline system using Bronsted, organic and Lewis acids.

XRD of polyaniline base indicates amorphous nature (figure 2a). XRD patterns of as synthesized PANI-H_2SO_4 salt figure 2(b) shows peaks at 2θ = 14.5, 20 and 25° and these positions are in accordance with the earlier report [10]. A similar XRD pattern of redoped PANI-H_2SO_4 salt figure 2(c) was observed with that of the as synthesized PANI-H_2SO_4 salt figure 2(b). This result indicates the formation of polyaniline in salt form by doping of polyaniline base with acid. A similar XRD spectrum was observed for the redoped polyaniline system using Bronsted, organic and Lewis acids.

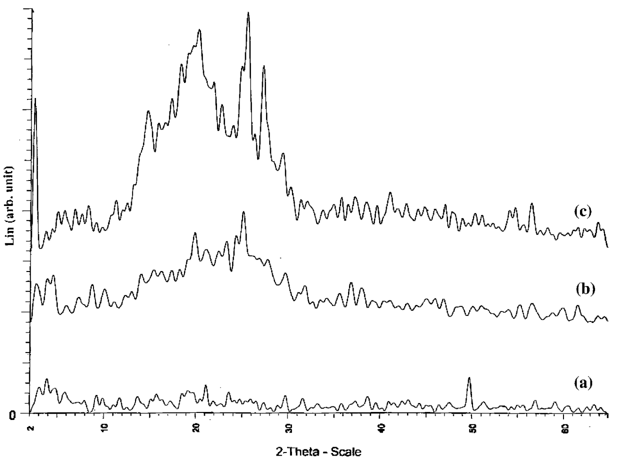
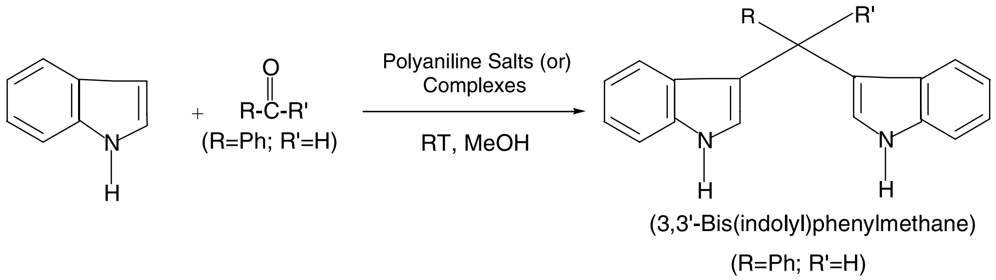


Figure 2. XRD pattern of: (a) polyaniline base; (b) as synthesized PANI-H_2SO_4 salt; (c) redoped PANI-H_2SO_4 salt.



3.2. *Synthesis of 3,3′-bis(indolyl)phenylmethane using polyaniline catalysts*

There was no appreciable reaction when indole was allowed to react with benzaldehyde in the absence of catalyst. However, high yield of bisindole was obtained with the use of polyaniline catalyst (PANI-PTSA). This result gave us impetus to carry out the bisindole synthesis using polyaniline-based catalysts.

The yield of 3,3′-bis(indolyl)phenylmethane using polyaniline salts and complexes are represented in figure 3. Generally, the yield of the product was higher with 4 h reaction time when compared with 1 h reaction. As a representative case, 98% yield was obtained in 4 h against 50% yield in 1 h with the use of PANI-H_2SO_4. Excellent yield (98–99%) was obtained with the use of PANI-H_2SO_4, PANI-PTSA, PANI-$AlCl_3$ and PANI-I_2 in 4 h. Lower yield was obtained in the case of PANI-HNO_3 (74%), PANI-$SnCl_2$ (88%) and PANI-BF_3 (89%) and poor yield was observed with the use of PANI-H_3PO_4 (38%) in 4 h. Among the polyaniline catalysts, PANI-PTSA acts as a better catalyst, which yield 89% in 1 h. The above results indicate that the conversion of reactant is mainly depends on the nature of the catalysts involved and time of the reaction.

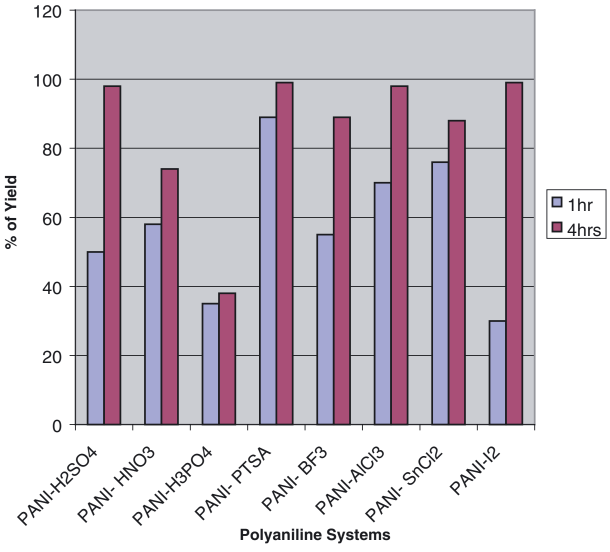


Figure 3. Catalytic activity of polyaniline salts and complexes.

3.3. *Reusability of the catalyst*

Reusability of the catalyst was checked by the condensation of indole with benzaldehyde using PANI-H_2SO_4 salt in methanol medium, which results in 98% yield. The PANI- H_2SO_4 salt was recovered and reused for a further seven times and resulted in 96–98% yields. The recovered catalyst was subjected for infrared, XRD analysis and determined the amount of H_2SO_4 present in polyaniline salt. A similar infrared and XRD pattern was observed for PANI-H_2SO_4 salt before and after catalytic reaction. The amount of H_2SO_4 present in polyaniline sulfate salt before (23.3 wt.%) and after the catalytic reaction (23.2 wt.%) was found to be almost the same. These results are indicate that PANI- H_2SO_4 salt catalyst does not lose its activity and can be reused.

4. Conclusions

Polyaniline salts and polyaniline complexes were prepared by post doping process of emeraldine base using Bronsted, organic and Lewis acids. The amount of acid group, acid group per aniline unit present in the polyaniline chain, pellet density and conductivity of the polyaniline system were found out. Formation of polyaniline salts and complexes were confirmed from infrared and XRD techniques. The synthesis of 3,3′-bis(indolyl)phenylmethane from indole and benzaldehyde catalyzed by regenarable polyaniline salts and complexes. This present protocol is noteworthy because polyaniline salts and complexes acts as catalyst and underwent smooth and clean reaction with simple work-up procedure. This method has several advantages; the catalytic use of polyaniline salt is quite feasible because of its easy preparation, easy handling, stability, easy recovery, reusability and eco-friendly nature.

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