

# Mannich-type reaction in solvent free condition using reusable polyaniline catalyst

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## Abstract

Polyaniline salts are prepared by doping of polyaniline base with different Bronsted acids (H<sub>2</sub>SO<sub>4</sub>, HCl, HClO<sub>4</sub>, and HBF<sub>4</sub>) and organic acid [5-sulfosalicylic acid (SSA), *p*-toluene sulfonic acid (PTSA)]. Polyaniline complexes are also prepared by using Lewis acids (ZnI<sub>2</sub> and FeCl<sub>3</sub>). Polyaniline salts and polyaniline complexes are characterized by physical, electrical and spectral methods. Polyaniline salts and polyaniline complexes are used as catalyst for the Mannich-type reaction under solvent free condition. β-Amino carbonyl compounds obtained in high 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.

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**Keywords:** Polyaniline catalyst; Reusable catalyst; Mannich-type reaction; β-Amino carbonyl compound

## 1. Introduction

Much attention has been focused on organic processes in water and without use of harmful organic solvents, which is an environmentally friendly methodology. A totally new family of materials is in development to contribute important aspects to solve many different technical and ecological problems—the conducting polymers known as the organic metals. The synthesis, characterization and application of conducting polymers have brought a great deal of scientific attention to polymer and material science during the past two decades. Among those polymers, the polyaniline have been of particular interest due to their environmental stability, controllable electrical conductivity and interesting redox properties. Polymer supported catalyst are gaining more importance as efficient heterogeneous catalyst in a variety of organic transformation [1,2].

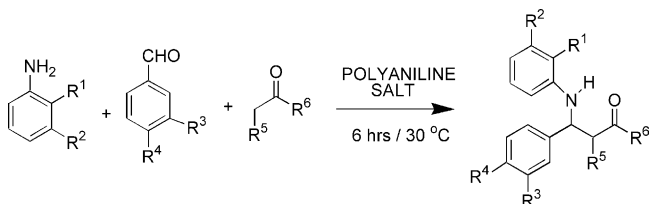
In this paper, we report the results on a series of polyaniline catalysts for Mannich-type reaction. Mannich-type reactions are an important carbon–carbon bond formation reactions widely used in the synthesis of secondary and tertiary amine derivatives and applied as a key step in the synthesis of many bioactive, natural products and versatile synthetic intermediates. Conventional protocols for proton-catalyzed three component Mannich-type reactions of aldehydes, amines and ketones in organic solvents include some severe side reactions and have some substrate limitations, especially for enolisable aliphatic aldehydes [3]. Bronsted acids, Lewis acids and lanthanide triflate in organic solvents like dichloromethane and acetonitrile catalyzed these kinds of reactions [4–7]. Some modern variants of Mannich reactions have been developed to avoid substrate limitations and environmental problems using catalyst in combination with surfactant in aqueous medium. Catalysts used in the above reactions are scandium triflate, copper triflate, scandium tris(dodecylsulfate) and scandium tris(dodecanesulfonate) [8], InCl<sub>3</sub> [9] and HBF<sub>4</sub> [10,11]. These processes afford good yields with the aid of surfactant only.

Herein, we wish to disclose our results on solvent free three components Mannich-type reactions using series of

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polyaniline salt catalyst at 30 °C for 6 h.



## 2. Experimental

### 2.1. Materials

Aniline (reagent grade) from E. Merck was distilled prior to use. Reagent grade acids, solvents, sodium persulfate, benzaldehyde and cyclohexanone (BDH, India) were used without further purification.

### 2.2. Sample preparation

#### 2.2.1. Polyaniline salt

Polyaniline salt was prepared by aqueous polymerization pathway by reported procedure [12]. In a 2 l round-bottomed flask, 700 ml of water was taken and 30 ml of H<sub>2</sub>SO<sub>4</sub> 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 °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.

#### 2.2.2. 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 excess water and finally with acetone and dried at 100 °C till a constant weight was reached.

#### 2.2.3. Redoped polyaniline salt

Fifty millilitre of 1.0 M solution of HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, HBF<sub>4</sub> in water and C<sub>7</sub>H<sub>6</sub>O<sub>6</sub>S (SSA), C<sub>7</sub>H<sub>8</sub>SO<sub>3</sub> (PTSA), ZnI<sub>2</sub>, and FeCl<sub>3</sub> in acetone 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.

#### 2.2.4. Procedure for preparation of $\beta$ -amino carbonyl compound

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 5 ml round bottomed flask, 0.14 g of polyaniline salt catalyst (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 and the catalyst was recovered from the reaction mass by filtration. Acetone solvent was distilled off completely and the oil layer was added to 25 ml of hexane. The precipitated solid product was separated by simple filtration. The products were authenticated by <sup>1</sup>H NMR spectra. Diastereoselectivity of the catalyst was also found out from NMR spectra.

### 2.3. Characterization

#### 2.3.1. Resistance measurement

Polyaniline samples were pressed into disks of 16-mm diameter and ca. 2-mm thickness under a pressure of 400 MPa. Resistance measurement of the pellets was carried out on a two probe connected to a Keithley constant current source (MODEL—2010) and digital voltmeter (MODEL—195A). Resistance was calculated based on the average of at least three pairs of consistent readings at different points on the pressed pellet. Since, the mean value was used in the calculation of resistance, the total error involved is <1%.

#### 2.3.2. 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.

#### 2.3.3. Amount of dopant (acid group)

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.

#### 2.3.4. Infrared spectra

The polyaniline sample was mixed with KBr powder and compressed into pellet, wherein; the polyaniline powder was evenly dispersed. Fourier transform infrared spectra were recorded using GC-FTIR spectrometer (MODEL 740 Nicolet, USA spectra).

#### 2.3.5. X-ray diffraction spectra

Wide angle X-ray diffraction spectra for the polyaniline powder samples were obtained using a Siemens/D-5000 X-ray diffractometer using Cu K $\alpha$  radiation of wave length  $1.54 \times 10^{-10}$  m and continuous scan speed of 0.045°/min.

#### 2.3.6. NMR

The NMR spectra for the obtained  $\beta$ -amino ketones were recorded using Gemini-Varion 200 MHz equipment with CDCl<sub>3</sub> as solvent and TMS as internal reference.

### 3. Results and discussion

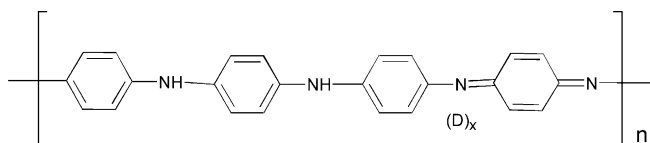
The excellent processability, the presence of a number of intrinsic redox states and reasonable conductivity have enhanced polyaniline in potential practical applications, such as in corrosion protection of metals, light emitting devices, organic field transistors, electro magnetic interference shielding, antistatic material, secondary batteries different sensors, etc. [13]. Polyaniline supported metals (Pd, Pt, etc.) [14], and polyaniline doped hetero poly acids (12-tungstosilicic acid, 12-molybdophosphoric acid) [15] are exhibiting catalytic activity in organic synthesis. In this work, polyaniline salts and polyaniline complexes are used as catalyst for Mannich-type reaction under solvent free condition.

#### 3.1. Characterization of polyaniline

Polyaniline salts are prepared by doping of polyaniline base with different Bronsted acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HClO}_4$ , and  $\text{HBF}_4$ ) and organic acid (SSA, PTSA). Polyaniline complexes are prepared by using Lewis acids ( $\text{ZnI}_2$  and  $\text{FeCl}_3$ ). Polyaniline systems are characterized by physical, electrical and spectral methods and the results are discussed here.

##### 3.1.1. Physical characterization

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). Higher amount of dopant was obtained in the case of PANI–PTSA (43.5%). The amount of dopant present in polyaniline system was found to be almost the same in the case of PANI– $\text{H}_2\text{SO}_4$ , PANI– $\text{HBF}_4$ , and PANI– $\text{ZnI}_2$  (21.8–23.4%). In the case of PANI– $\text{HClO}_4$ , PANI–SSA and PANI– $\text{FeCl}_3$  (25.3–27.3%) amount of dopant was obtained and lower amount of dopant was ob-

served in PANI– $\text{HCl}$  (15.5%). Acid group 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 found to be almost the same in the case of PANI– $\text{H}_2\text{SO}_4$ , PANI– $\text{HBF}_4$ , PANI– $\text{ZnI}_2$ , and PANI– $\text{HClO}_4$  (0.29–0.32). Higher amount of dopant was observed in the case of PANI– $\text{HCl}$  (0.47) and PANI–PTSA (0.37) and lower amount of acid group was obtained with PANI–SSA (0.12). Density of the polyaniline salts was found to be nearly the same (1.2–1.3  $\text{g}/\text{cm}^3$ ). However, density of the polyaniline complexes depends upon the density of dopant (Table 1). Conductivity of PANI– $\text{H}_2\text{SO}_4$ , PANI– $\text{HBF}_4$ , PANI–PTSA and PANI–SSA salts were found to be nearly the same ( $2 \times 10^{-2}$  S/cm) and one-order of lower magnitude was observed in the case of PANI– $\text{FeCl}_3$ , PANI– $\text{HClO}_4$ . Lower conductivities were observed in the case of PANI– $\text{HCl}$  ( $5.0 \times 10^{-4}$  S/cm) and PANI– $\text{ZnI}_2$  ( $3.8 \times 10^{-6}$  S/cm).

##### 3.1.2. Infrared spectra

Infrared spectra of as synthesized polyaniline-sulfate (PANI– $\text{H}_2\text{SO}_4$ ) salt, its corresponding polyaniline base and redoped PANI– $\text{H}_2\text{SO}_4$  salt are shown in Fig. 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 Fig. 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  $3415\text{--}3460\text{ cm}^{-1}$  assigned to the N–H stretching vibration. The bands at  $2920$  and  $2850\text{ cm}^{-1}$  are assigned to vibrations associated with the N–H part in  $\text{C}_6\text{H}_4\text{NH}_2\text{C}_6\text{H}_4$  group or sum frequency.  $1565$  and  $1490\text{ cm}^{-1}$  bands due to quinonoid ring (Q) and or benzenoid ring (B). The bands at  $1370$  and  $1300\text{ cm}^{-1}$  are assigned to C–N stretching vibration in QBB, QBQ and BBQ, a  $1240\text{ cm}^{-1}$  band to the C–N stretch vibration of aromatic amine. In the region of  $1020\text{--}1170\text{ cm}^{-1}$ , aromatic C–H in-plane-bending modes are usually observed. For polyaniline, a strong band characteristically appears at  $1140\text{ cm}^{-1}$ , which has been explained as an electronic band or a vibrational band of nitrogen quinone. A band at  $705\text{ cm}^{-1}$  is assigned to ring C–C bending vibration and the band at  $580\text{ cm}^{-1}$  due to ring in plane deformation. The C–H out-of-plane bending mode has been used as a

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

Entry	System	Conductivity (S/cm)	Density ( $\text{g}/\text{cm}^3$ )	Dopant (%)	Dopant per aniline unit
1	PANI– $\text{H}_2\text{SO}_4$	$2.0 \times 10^{-2}$	1.22	23.3	0.29
2	PANI– $\text{HBF}_4$	$1.0 \times 10^{-2}$	1.30	21.8	0.29
3	PANI– $\text{HClO}_4$	$5.0 \times 10^{-3}$	1.21	25.7	0.32
4	PANI– $\text{HCl}$	$5.0 \times 10^{-4}$	1.16	15.5	0.47
5	PANI–PTSA	$1.0 \times 10^{-2}$	1.21	43.5	0.37
6	PANI–SSA	$1.0 \times 10^{-2}$	1.36	25.3	0.12
7	PANI– $\text{FeCl}_3$	$2.4 \times 10^{-3}$	0.96	27.3	0.22
8	PANI– $\text{ZnI}_2$	$3.8 \times 10^{-6}$	1.21	23.4	0.29

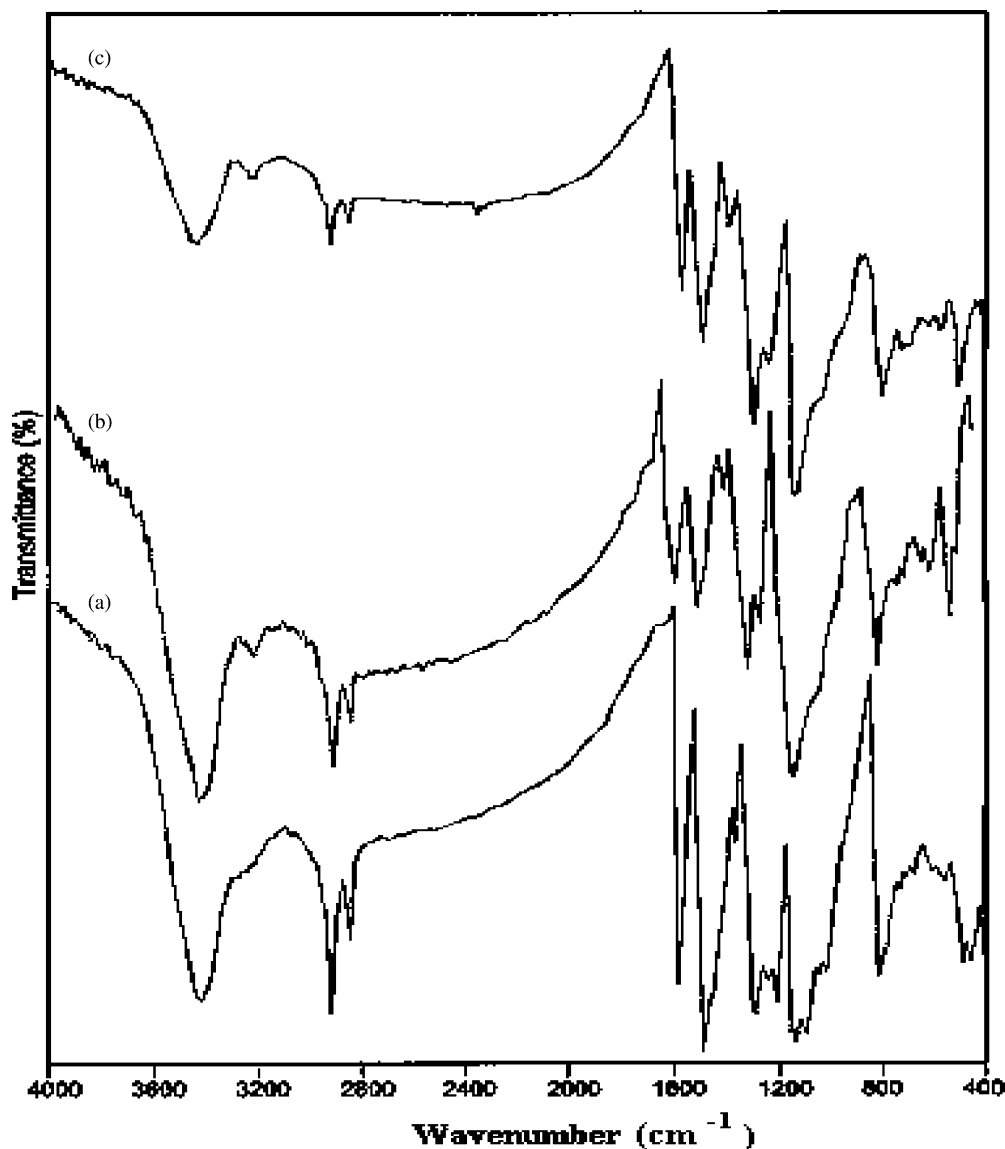


Fig. 1. Infrared spectra of (a) polyaniline base (b) as synthesized PANI-H<sub>2</sub>SO<sub>4</sub> salt and (c) redoped PANI-H<sub>2</sub>SO<sub>4</sub> salt.

key to identifying the type of substituted benzene. For the polyaniline base, this mode was observed as a single band at 825 cm<sup>-1</sup>, which fell in the range 800–860 cm<sup>-1</sup> 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 [16].

The infrared spectrum of as synthesized PANI-H<sub>2</sub>SO<sub>4</sub> salt is shown in Fig. 1b. The infrared spectrum of PANI-H<sub>2</sub>SO<sub>4</sub> salt is similar to that of polyaniline base except a band around 3230 cm<sup>-1</sup> that is assigned to the NH<sub>2</sub><sup>+</sup> group and indicates the formation of protonated polyaniline salt. The doublet band at 1140 cm<sup>-1</sup> and 1110 cm<sup>-1</sup> in the polyaniline base which is assigned to mode of Q=N<sup>+</sup>H-B or Q-NH-B becomes a singlet in the salt spectrum.

Infrared spectrum of redoped PANI-H<sub>2</sub>SO<sub>4</sub> salt prepared from polyaniline base (Fig. 1c) is similar to that of the as

synthesized PANI-H<sub>2</sub>SO<sub>4</sub> salt (Fig. 1b). This result indicates the formation of polyaniline in salt form. A similar infrared spectrum was observed for the redoped polyaniline salt using Bronsted, Organic and Lewis acids.

### 3.1.3. X-ray diffraction spectra

XRD of polyaniline base indicates amorphous nature (Fig. 2a). X-ray diffraction patterns of as synthesized PANI-H<sub>2</sub>SO<sub>4</sub> salt (Fig. 2b) shows peaks at  $2\theta = 14.5, 20,$  and 25 and these positions are in accordance with the earlier report [17]. A similar XRD pattern of redoped PANI-H<sub>2</sub>SO<sub>4</sub> salt (Fig. 2c) was observed with that of the as synthesized PANI-H<sub>2</sub>SO<sub>4</sub> salt (Fig. 2b). 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 salt using Bronsted, Organic and Lewis acids.

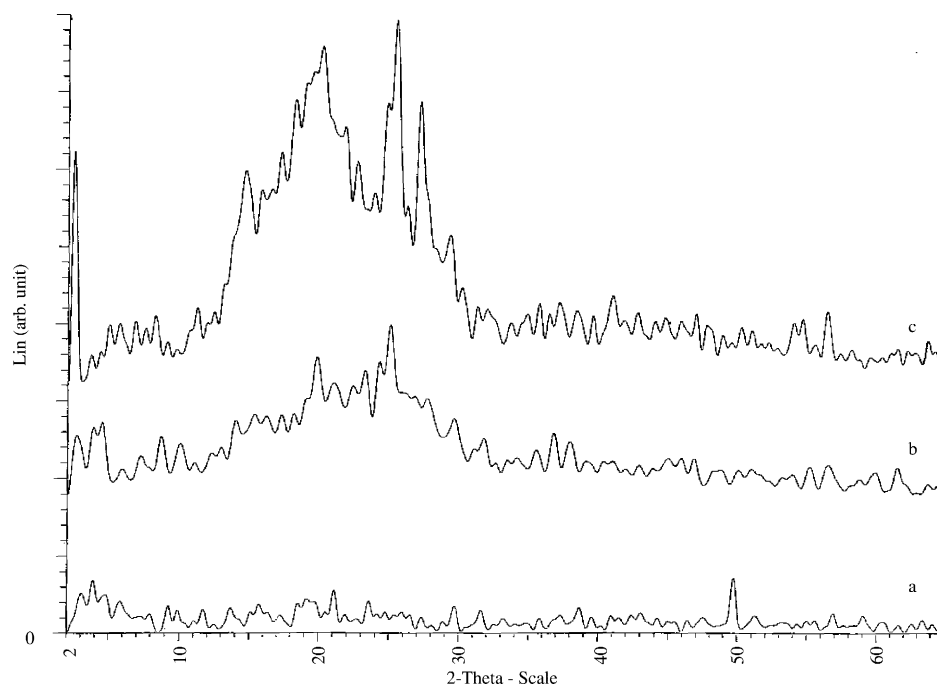


Fig. 2. XRD pattern of (a) polyaniline base (b) as synthesized PANI-H<sub>2</sub>SO<sub>4</sub> salt and (c) redoped PANI-H<sub>2</sub>SO<sub>4</sub> salt.

### 3.2. Preparation of $\beta$ -amino carbonyl compound using polyaniline salts

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 5 ml round bottomed flask, 0.14 g of polyaniline salt catalyst (25% with respect to weight of benzaldehyde) was added into the reaction mass. In order to avoid polyaminoalkylation 5 eq. of ketone was taken [3].

There is no appreciable reaction when aniline and benzaldehyde was allowed to react with cyclohexanone in the absence of catalyst. However, high yield of  $\beta$ -amino carbonyl compound was obtained with the use of polyaniline salts. This result gave us impetus to carry out the Mannich type reaction using polyaniline-based catalyst.

Table 2  
The yield and diastereoselectivity of  $\beta$ -amino carbonyl compound using polyaniline salts and polyaniline complexes

Entry	System	$\beta$ -Amino ketones	
		Yield (%)	d:l ratio
1	PANI-H <sub>2</sub> SO <sub>4</sub>	65	63:37
2	PANI-HBF <sub>4</sub>	86	62:38
3	PANI-HClO <sub>4</sub>	74	63:37
4	PANI-HCl	84	71:29
5	PANI-PTSA	85	63:37
6	PANI-SSA	72	63:37
7	PANI-FeCl <sub>3</sub>	72	64:36
8	PANI-ZnI <sub>2</sub>	12	88:12

#### 3.2.1. Effect of the solvent on yield

Three component Mannich-type reaction was carried out with polyaniline-*p*-toluenesulfonic acid salt under solvent free condition, which yields the product 85%. For comparison, the same reaction was carried out using dichloromethane as a solvent at ambient temperature, which yields the product 85%. Since both methods offered same yield, solvent free protocol employed for the remaining course of work.

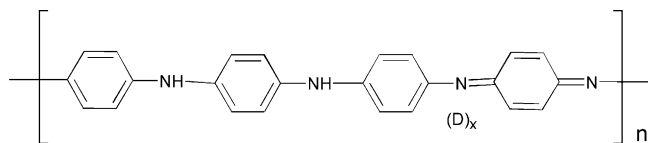
#### 3.2.2. Effect of time and temperature on yield

Three component Mannich-type reaction was carried with aniline (0.5 g, 5.3 mmol), benzaldehyde (0.56 g, 5.3 mmol), cyclohexanone (2.6 g, 26.0 mmol) and 25 wt.% of PANI-H<sub>2</sub>SO<sub>4</sub> by varying the reaction time and temperature. The reaction was carried out at 30 °C as well as 40 °C for 4, 6, 8, 12, and 16 h. The yields of the products at 30 °C are 55, 65, 66, 62, and 64%, respectively which are slightly higher than that of the reaction at 40 °C (40, 61, 60, 62, and 61%, respectively). This may be due to the thermal instability of the imine at higher temperature. Based on these results, the Mannich-type reaction is carried out 30 °C for 6 h.

#### 3.2.3. Effect of the catalyst

Three component Mannich-type reaction of aniline, benzaldehyde and cyclohexanone was carried out with different polyaniline salts under solvent free condition and the results are reported in Table 2.  $\beta$ -Amino carbonyl compound was obtained in high yield (84–86%) with the use of PANI-HCl, PANI-PTSA and PANI-HBF<sub>4</sub> catalyst and lower yield was

Table 3

Three component Mannich-type reactions catalyzed by polyaniline-*p*-toluenesulfonic acid catalyst

Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	Isolated yield (%)
1	H	H	H	H	–	–(CH <sub>2</sub> ) <sub>4</sub> –	85
2	Cl	H	H	H	–	–(CH <sub>2</sub> ) <sub>4</sub> –	66
3	H	Cl	H	H	–	–(CH <sub>2</sub> ) <sub>4</sub> –	75
4	OCH <sub>3</sub>	H	H	H	–	–(CH <sub>2</sub> ) <sub>4</sub> –	72
5	H	COOH	H	H	–	–(CH <sub>2</sub> ) <sub>4</sub> –	95
6	H	H	H	NO <sub>2</sub>	–	–(CH <sub>2</sub> ) <sub>4</sub> –	87
7	H	H	OCH <sub>3</sub>	OCH <sub>3</sub>	–	–(CH <sub>2</sub> ) <sub>4</sub> –	62
8	H	H	H	H	H	Ph	69

obtained with PANI–HClO<sub>4</sub> (74%) PANI–H<sub>2</sub>SO<sub>4</sub> (65%). 72% yield was obtained with PANI–SSA and PANI–FeCl<sub>3</sub>. However, very low yield was obtained with the use of PANI–ZnI<sub>2</sub> (12%). The yield of the product generally depends upon the strength of the acid dopant.

### 3.2.4. Effect of the catalyst on various substrates

The PANI–PTSA catalyzed process was extended to substituted aniline like 2-chloro aniline, 3-chloroaniline, *o*-anisidine, and amino benzoic acid (entries 2–5, Table 3). Amino benzoic acid and aniline gave excellent yield (entries 1 and 5). The reaction with substituted benzaldehyde like 4-nitrobenzaldehyde and 3,4-dimethoxy benzaldehyde was also investigated (entries 6 and 7). In the place of cyclohexanone, acetophenone was also investigated (entry 8) and the result shows that acetophenone is less reactive than cyclohexanone. These results are indicating that the effect of electronic behavior and nature of the substituents on the aromatic ring plays a vital role on this transformation.

### 3.2.5. Reusability of the catalyst

Reusability of the catalyst was checked by the reaction of aniline, benzaldehyde and cyclohexanone with 25.0% of the PANI–H<sub>2</sub>SO<sub>4</sub> salt catalyst for 6 h at 30 °C. The PANI–H<sub>2</sub>SO<sub>4</sub> salt was recovered and reused for a further five consecutive reactions, which gave the product in 60–65% yield. The recovered catalyst was subjected for infrared and XRD analysis. A similar infrared and XRD pattern were observed for PANI–H<sub>2</sub>SO<sub>4</sub> salt before and after catalytic reaction. These results indicate that PANI–H<sub>2</sub>SO<sub>4</sub> salt catalyst does not lose its activity and can be reused.

### 3.2.6. Diastereoselectivity of the catalyst

The diastereoselectivity of the catalysts are calculated from NMR spectroscopic technique and the results are included in Table 2. Only PANI–ZnI<sub>2</sub> shows better selectivity,

88:12, this may be due to the less reactivity of the catalyst. All other catalysts are showing around 65:35 selectivity.

## 4. Conclusion

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 X-ray diffraction techniques. Three component Mannich-type reaction of aniline, benzaldehyde and cyclohexanone are effectively catalyzed by polyaniline salt under solvent free condition at 30 °C. 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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