

# Synthesis of Novel Optically Active Pyrrolidine-Containing Polyaniline: A New Heterogeneous Organo Polymeric-Base Catalyst for Direct Aldol Reaction

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**ABSTRACT:** An optically active pyrrolidine containing polyaniline, poly-(2-anilinomethylpyrrolidine) (PANiMp) is synthesized for the first time. PANiMp material is synthesized by simple one-pot synthetic route and is characterized by circular dichroism, NMR, FTIR, and electronic absorption spectral techniques. This novel polyaniline base is eval-

uated as new heterogeneous organo polymeric-base catalyst for direct Aldol reaction in water medium. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2536–2540, 2010

**Key words:** chiral; catalyst; UV-Vis spectroscopy; synthesis

## INTRODUCTION

Research concerning conducting polymers, such as polyacetylene, polypyrrole, polyphenylene, polythiophene, and polyaniline, has attracted much attention because of the various potential applications.<sup>1</sup> Polyaniline is one of the most promising electrically conducting polymers because of its chemical stability and reasonably good conductivity.<sup>2,3</sup> Polyaniline has been widely investigated due to several potential applications, including their use as organic lightweight batteries, microelectronics, optical displays, antistatic coatings, electromagnetic shielding materials,<sup>4</sup> and catalysts.<sup>5</sup> In recent years, there has been increased interest in synthesizing chiral conducting polymers because of their potential use in diverse areas such as surface-modified electrodes,<sup>6</sup> electrochemical asymmetric synthesis, chiral chromatography, molecular recognition, and membrane separation technology.<sup>7,8</sup> Chirality in conjugated polymers was first demonstrated with polypyrrole<sup>9</sup> and then polythiophene.<sup>10</sup> In polyaniline family, the chirality was introduced by polymerization of aniline monomer in the presence of a chiral dopant acid, chiral amines,<sup>11,12</sup> enzyme,<sup>13</sup> or doping of emeraldine base with chiral dopant.<sup>8,14,15</sup> Earlier

report demonstrated that chiral counter-ion dopant can induce optical activity in achiral polyaniline chain. The polyaniline backbone is believed to adopt a helical conformation in the presence of chiral dopants.<sup>14</sup> Moreover, the chiral chain conformations induced by the dopants are retained<sup>16,17</sup> when the dopants are removed from the polymers. As far as our knowledge is concerned, synthesis method for the preparation of chiral polyaniline base from chiral monomer is not available in the literature. On the basis of the earlier background investigation on chiral conducting polymers, we became interested in the synthesis of chiral polyaniline base, which is prepared from chiral aniline monomer<sup>18</sup> bearing a pyrrolidine moiety with aniline unit. This article explores the synthesis, characterization of novel optically active polyaniline, and its application in Aldol reaction.

The Aldol reaction is a key C–C bond forming reaction, which creates the  $\beta$ -hydroxy carbonyl structure unit found in many natural products and drugs.<sup>19</sup> Several efficient methodologies for this reaction using chiral metal catalyst<sup>20,21</sup> and organocatalysts<sup>22–29</sup> have recently been developed, of which catalysis by proline<sup>22–26</sup> and its derivatives<sup>27–29</sup> have been extensively explored. In recent years, the development of environmental friendly conversion process is gaining interest in the chemical community. The tunability of many properties such as easy preparation, recovery, economical, simple work-up procedure, and eco-friendly make polymer-supported catalysts interesting alternatives for conventional nonregenerable catalysts. In this article, PANiMp base is used as new heterogeneous organo

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polymeric-base catalyst for direct Aldol reaction in water medium.

## EXPERIMENTAL

### Materials and equipments

Aniline (reagent grade) was distilled before use, ammonium peroxydisulfate, aqueous ammonia solution, cycloketones, potassium hydroxide, dichloro methane are purchased from SD-fine chemicals, India. Reagent grade benzaldehyde, derivatives, and L-glutamic acid (ALDRICH, USA), methanol, acetone, sulfuric acid, dry THF, and lithium aluminum hydride (SPECTROCHEM, India) were used without further purification.

UV-Vis spectrum of PANiMp sample in acetonitrile solvent was recorded at ambient temperature using LABOMED INC (USA) spectro UV-Vis double beam PC (8-Scanning Auto cell) spectrophotometer. CD spectrum was acquired using JASCO-810 spectrometers at room temperature in MeOH solvent using a 2-mm path length CD cell. Spectrum represent the average of two scan (100 ms time constant, 2-nm bandwidth) and were background corrected and smoothened over 2–5 data points by binomial method. The scans are carried out from 600 nm to 190 nm, at 0.0015 mol/L concentration. Fourier transform infrared spectrum of PANiMp dispersed in KBr pellet was recorded using GC-FTIR spectrometer (MODEL 670 Nicolet Nexus, USA). PANiMp was dissolved in  $d_6$ -DMSO solvent and heated up to 60°C, then cool down to room temperature and recorded NMR spectrum using VARIAN UNITY (INOVA)-500 MHz instrument. All Aldol products were analyzed by  $^1\text{H-NMR}$  (VARIAN-Gemini-200 and BRUKER-Avance-300 MHz) Spectrometer using  $\text{CDCl}_3$  solvent and TMS as an internal standard. Chiral-High performance liquid chromatography (HPLC) was performed using an LC-10AT-liquid chromatograph (Shimadzu, Japan) equipped with SPD-10A-UV-Vis detector using a chiralpak-AD-H columns with 2-propanol/hexane as eluting agent. Mass spectra were recorded on VG Micromass 7070H (EI) using  $\text{Cs}^+$  ion gun, *m*-nitro benzyl alcohol (MNBA) as a matrix and are given in mass units (*m/z*). SEM was carried out using Hitachi 3000N (Japan).

### Synthesis of poly(2-anilinomethylpyrrolidine) (PANiMp) base

In a typical experiment, 1 mL of (S)-2-anilinomethylpyrrolidine was added to 70-mL aqueous solution containing 3 mL  $\text{H}_2\text{SO}_4$  taken in 250-mL round bottomed flask. The solution was kept under constant stirring at room temperature for 10 min. To this solution, 2.3 g of ammonium peroxydisulfate in

25 mL of water was added immediately at once. The reaction was allowed to continue for 4 h. Then, whole reaction mixture was treated with aqueous ammonia solution (100 mL) and kept in static condition for 12 h. The precipitated PANiMp was recovered by filtration, washed with distilled water (500 mL), and then dried in an oven at 50°C for 12 h. The solid polymer was again purified using 50-mL acetone and dried the sample in an oven at 50°C for 2 h.

### Aldol reaction

*p*-nitro benzaldehyde (75 mg), acetone (2 mL), 15 mg PANiMp (20 wt % with respect to *p*-nitro benzaldehyde), and distilled water (0.5 mL) were taken in 10-mL round bottomed flask. The reaction mixture was stirred constantly for 36 h at ambient temperature. After 36 h of reaction, ethyl acetate (10 mL) was added to the reaction mixture and separated the catalyst by filtration. Organic layer was washed with distilled water (10 mL) in separating flask. Then organic layer was treated with brine (5 mL) solution, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum. The crude mixture was purified by column chromatography (10 : 90 EtOAc : hexane). All the isolated products were characterized by NMR and EI-MS analysis.

### 4-Hydroxy-4-(4-nitrophenyl)-butan-2-one

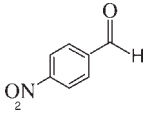
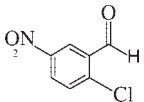
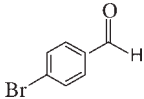
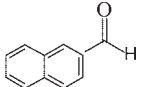
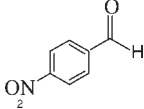
$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.20 (3H, s), 2.77–2.80 (2H, m), 3.50 (1H, s, br), 5.19–5.23 (1H, q), 7.49–7.52 (2H, d,  $J = 8.3$  Hz), 8.17–8.20 (2H, d,  $J = 8.3$  Hz);  $^{13}\text{C-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  30.5, 51.4, 68.7, 123.5, 126.3, 147.1, 150.0, 208.3; EI-MS: *m/z* 209 ( $\text{M}^+$ ) (Table I, entry 1).

## RESULTS AND DISCUSSION

Our investigation began with the polymer preparation via oxidative polymerization of (S)-2-anilinomethylpyrrolidine monomer by simple procedure (Scheme 1).

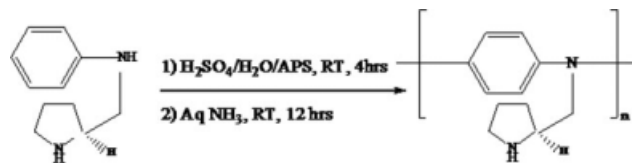
Generally, polyaniline base is being prepared by two steps (i) synthesis of polyaniline salt and (ii) its conversion to base by dedoping process. The oxidative polymerization of (S)-2-anilinomethylpyrrolidine monomer using ammonium peroxydisulfate oxidant by usual procedure<sup>30</sup> did not yield the polymer in solid form. We followed a different procedure, i.e., one-pot synthesis, which was carried out by adding ammonium peroxydisulfate oxidant immediately to the reaction mixture containing monomer and acid, the reaction was allowed for 4 h at ambient temperature and treated with aqueous ammonia for 12 h, finally the polymer was isolated by filtration.

TABLE I  
PANiMp as an Organo Polymeric-Base Catalyst for  
Aldol Reactions

Entry No.	R	R'	t (h)	Yield (%)
1		CH <sub>3</sub>	36	73
2		CH <sub>3</sub>	36	68
3		CH <sub>3</sub>	36	50
4		CH <sub>3</sub>	48	20
5		-(CH <sub>2</sub> ) <sub>4</sub>	36	56 <sup>a</sup>

<sup>a</sup> Diastereomers ratio—38 : 62.

The UV-Vis spectrum of PANiMp base is shown in Figure 1 PANiMp base has an absorbance at 360 and 480 nm, which is the signature of the chiral PANiMp. Most significantly, its CD spectrum (Fig. 2) confirmed that it is optically active, showing negative peak at about 390 nm associated with the absorption band at 360 nm, then the positive peak at 470 nm associated with the absorption band at 480 nm. The positive peak at 470 nm is exclusively to chiral polyaniline and it can be used to monitor chirality in the polymer.<sup>31,32</sup> The chiral induction of



Scheme 1 Preparation of PANiMp base.

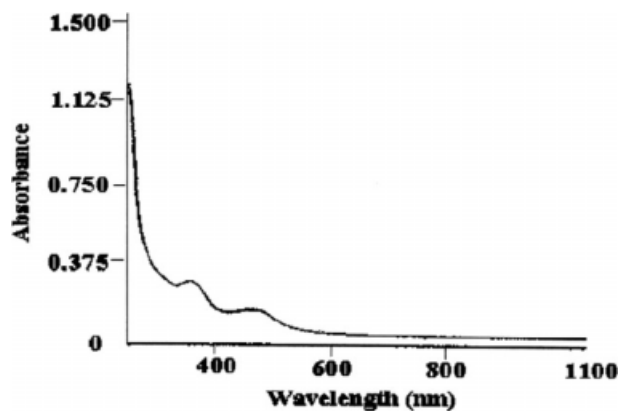


Figure 1 UV-Vis spectrum of PANiMp base.

optical activity in the polymer chain is believed to arise from the asymmetric center of the monomer.

The structure of the PANiMp was determined by <sup>1</sup>H-NMR spectrum (Fig. 3). Signals in the range 6.5 to 8.3 δ are attributable to the aromatic protons of the polyaniline moiety and peaks observed in the range 1.3 to 3.5 δ are due to aliphatic protons of the pyrrolidine moiety.

The FTIR spectrum of PANiMp (Fig. 4) shows the characteristic peaks at 3415 cm<sup>-1</sup> (N-H str.), 1605 and 1515 cm<sup>-1</sup> (C-C str. of polyaniline unit) and 1455 cm<sup>-1</sup> (C-N str. of pyrrolidine unit), 1280 cm<sup>-1</sup> (C-N str. of polyaniline unit), 1220 cm<sup>-1</sup> (C-N str. of nonaromatic ring), 1190 cm<sup>-1</sup> (C-C breathing vibration) and 1110 cm<sup>-1</sup> (ν<sub>as</sub>(CNC) ring breathing of pyrrolidine moiety). The presence of bands at 2925 and 2855 cm<sup>-1</sup> are assigned to asymmetric and symmetric aliphatic C-H stretching vibrations of alkyl substituent (pyrrolidine unit), respectively. The band of C-H and N-H in-plane deformation vibration is situated at 1035 cm<sup>-1</sup>. A single band at 815 cm<sup>-1</sup> indicating the presence of 1,4-disubstituted benzene ring in PANiMp structure. The bands at 750 cm<sup>-1</sup> (N-H wag of secondary amine of pyrrolidine moiety), 695 cm<sup>-1</sup> (C-C out-of-plane ring

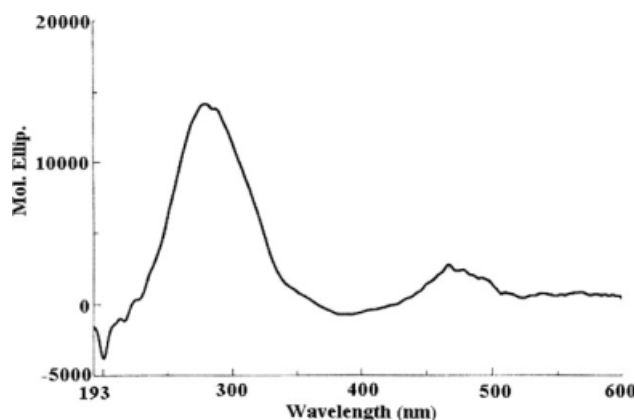


Figure 2 CD spectrum of PANiMp base.

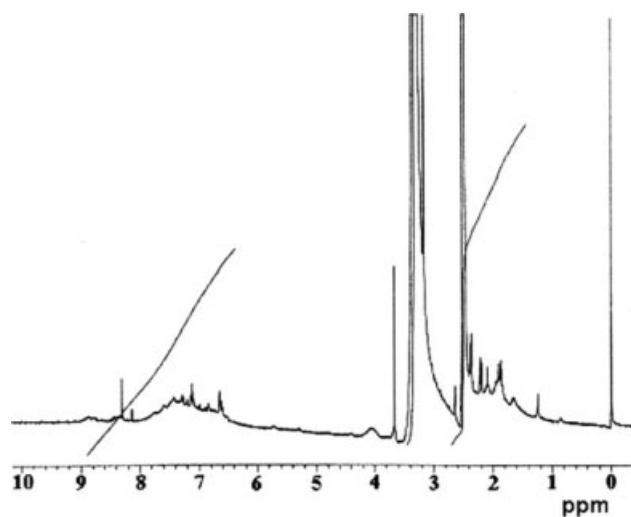


Figure 3  $^1\text{H-NMR}$  spectrum of PANiMp base in DMSO- $d_6$ .

deformation), and  $590\text{ cm}^{-1}$  (ring in-plane deformation) are also observed. The infrared spectrum of the PANiMp is very close to the infrared spectrum of the polyaniline<sup>33</sup> and pyrrolidine moiety<sup>34</sup> reported in the literature.

The morphology of synthesized PANiMp sample was analyzed in scanning electron microscopy (Fig. 5). Figure indicates that PANiMp is cauliflower-like structural morphology.

A background reaction was examined in water with *p*-nitrobenzaldehyde and acetone (acetone : water—4 : 1 ratio) for 2 days in the absence of catalyst and product was not formed. To our surprise, however, the presence of PANiMp (20 wt % with respect to carbonyl compound) provided 73% yield of Aldol product (Table I, Entry 1). The reaction was clean and the work-up procedure was simple. Encouraged by this result, we carried out further investigation on several carbonyl compounds and resulted in reasonably good yields (Table I, entries 2–4). The Aldol reaction was extended to cyclic ketone such as cyclopentanone (Table I, entries 5), which resulted diastereomers in the ratio 38 : 62.

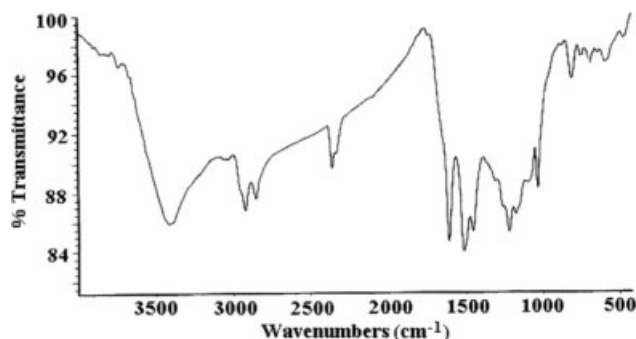


Figure 4 FTIR spectrum of PANiMp base.

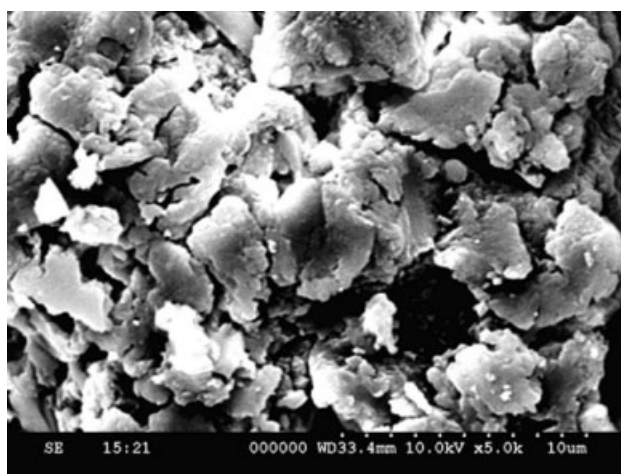


Figure 5 SEM picture of PANiMp base.

Enantioselectivity was not observed for the reaction of *p*-nitrobenzaldehyde and acetone (acetone : water—4 : 1 ratio) with PANiMp base catalyst. However, 3% enantioselectivity was observed when we change the solvent ratio from 4 : 1 to 1 : 2. Change of solvent from acetone to DMSO : water (1 : 1 ratio) yielded 5% enantioselectivity with 41% yield. The earlier results show that PANiMp base catalyst is useful for Aldol reaction, however, with this methodology we did not get enantioselectivity of the product.

## CONCLUSIONS

In summary, we have demonstrated the synthesis of novel optically active polyaniline base by simple one-pot synthetic route even in polyaniline synthesis. The use of polyaniline base was demonstrated as new heterogeneous organo polymeric-base catalyst in direct Aldol reaction. However, our present methodology does not give 100% chiral product and the work is under progress to modify the synthesis route. We hope the synthesis of PANiMp base catalyst may open up a new avenue for developing polyaniline-based chiral catalyst.

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