Preparation and Characterization of Polyaniline–1-Hydroxyethane 1,1-Diphosphonic Acid Salt and Its Application as a Catalyst for the Synthesis of *N*-Benzylidine-2-Phenyl Imidazo[1,2-a]pyridines

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ABSTRACT: A novel, efficient, and easily synthesizable catalyst, an emeraldine form of polyaniline (PANI)−1-hydroxyethane 1,1-diphosphonic acid salt (HEDP), was successfully synthesized and demonstrated as a reusable polymer-based solid acid catalyst in the synthesis of *N*-benzylidine-2-phenyl imidazo[1,2-a]pyridines with 2-aminopyridine with aromatic aldehydes and trimethyl silylcyanide at room temperature. PANI–HEDP was characterized by Fourier transform infrared spectroscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, field emission scanning electron microscopy, and conductivity measurements. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2995–3000, 2013

INTRODUCTION

Polyaniline (PANI) is one of the most interesting conducting polymers because of its good environmental stability, interesting redox properties, optoelectronic features, and controllable electrical and electrochemical properties.[1,2] As a result, many technological applications have been demonstrated, with PANI widely used as a base material in the development of pH sensors, biosensors, rechargeable batteries, supercapacitors, electrochromics, electromagnetic shielding, light emitting devices, photovoltaics, electrostatic discharges, and corrosion-protecting coatings.[3–6] Despite the vast bibliography devoted to PANI, new studies focusing on the polymerization process are reported each year.[7–10]

Recently, PANI has received considerable attention as a catalyst and support in catalytic reactions because of its highly conducting and redox properties.[11] Furthermore, its easy preparative protocol from nonexpensive starting material (aniline), controllable doping levels through an acid doping/base dedoping process, inert nature, nonsolubility in most organic solvents, and water make it an idle support in heterogeneous catalysis. Through the exploitation of these properties, PANI-supported acid catalysts were developed by our group for various organic transformations.[12] PANI salt contains a repeating aniline backbone with protic acid groups as the dopant. Thus, PANI chains containing protic acid as the dopant give hydrogen ions easily during the reaction and act as a catalyst. Hence, PANI salt plays a vital role in polymer-based solid acid catalysts.

The synthesis of imidazo[1,2-a]pyridines with a three-component condensation involving aminoazine, formaldehyde, and sodium cyanide[13] were reported; this synthesis suffered from a limited diversity of products. Many reports[14–16] are available on the synthesis of imidazo[1,2-a]pyridines with isocyanide-based chemicals, for example, montmorillonite K-10,[14] microwaves,[15] and ionic liquids.[16] However, this approach involves a very hazardous chemical, that is, the isocyanide. In 2005, Hulme et al.[17] replaced isocyanide with trimethylsilyl cyanide (TMSCN); this gave 3-aminoimidazo[1,2-a]pyridines. Subsequently, several people[18–20] have synthesized 3-amino imidazo[1,2-a]pyridines with different catalysts.

Very recently, Voskressensky et al.[20] and Vittal Rao et al.[21] reported the synthesis of *N*-benzylidene-2-phenyl imidazo[1,2-a]pyridines instead of 3-amino imidazo[1,2-a]pyridines. Some drawbacks of these methods include the nonreusable, toxic, and expensive nature of the catalysts; separation techniques (column chromatography); and the formation of byproducts. Hence, there is still a great demand for a new catalytic system with a high efficiency and low catalytic loading.

In this study, a novel PANI salt containing 1-hydroxyethane 1,1-diphosphonic acid salt (HEDP) was successfully synthesized and characterized. This PANI–HEDP was used as an efficient and reusable catalyst in the reaction of 2-aminopyridine with aromatic aldehydes and TMSCN.
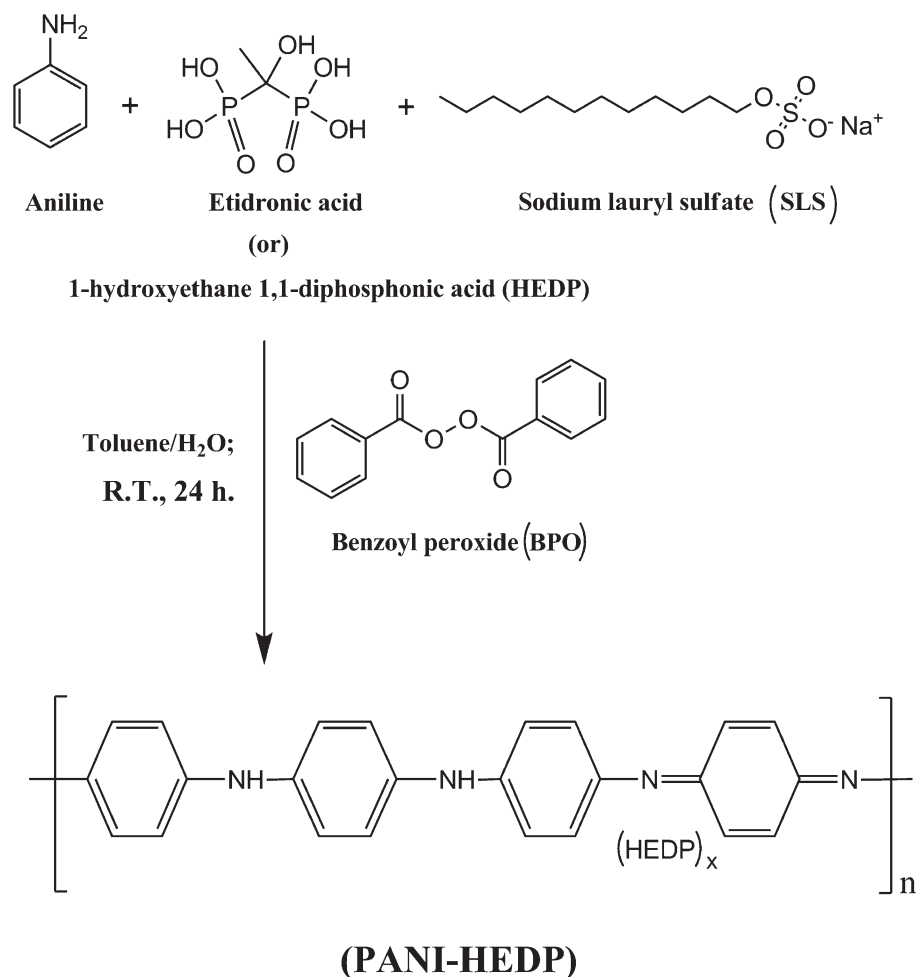
(PANI-HEDP)

Scheme 1. Synthesis of the PANI–HEDP catalyst by an emulsion polymerization pathway.

EXPERIMENTAL

Instruments and Characterization

PANI–HEDP powder was pressed into a disk 13 mm in diameter and with a thickness of about 1.5 mm under a pressure of 120 kg/cm^2. The resistance of the pellet was measured by a four-probe method with a 6220 constant current source and a 2182A voltmeter (Keithley, Cleveland, OH). The pellet density was measured from the mass per unit volume of the pressed pellet. Fourier transform infrared spectra of polymer samples were registered on a Fourier transform infrared spectrometer (Thermo Nicolet Nexus 670) with the KBr pressed pellet technique. X-ray diffraction profiles for the polymer powders were obtained on a Siemens/D-500 X-ray diffractometer with Cu Kα radiation at a scanning speed of 0.045°/min. Morphological studies of PANI salt powders were performed with a Hitachi 3000N scanning electron microscope (Tokyo, Japan) 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 the sample from possibly charging. Energy-dispersive X-ray spectroscopy (EDAX) was done with an EDAX detector (Oxford LINK-ISIS 300) with a Jest microscope. Thermogravimetric analysis (TGA) of the polymer samples were carried out with a TA Instruments TGA Q500 V20.8 up to 700°C at a heating rate of 10°C/min.
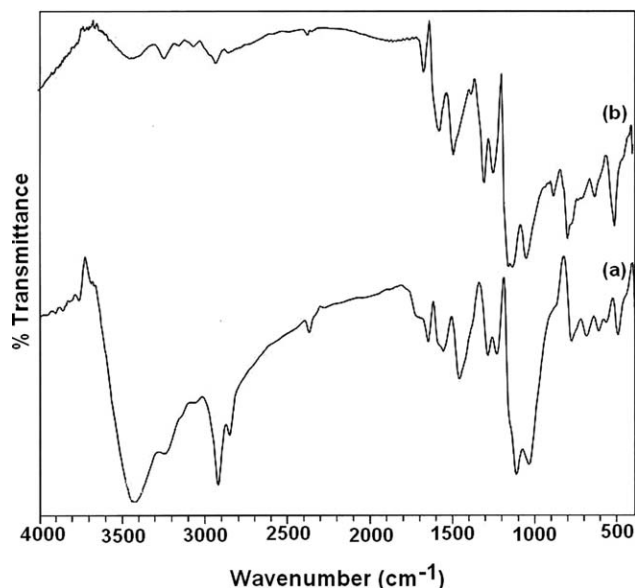

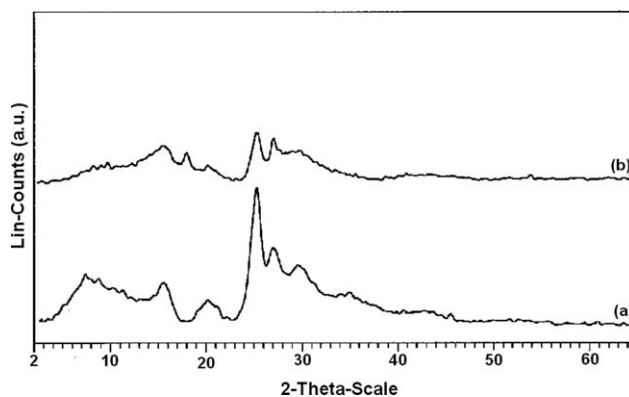**Figure 1.** IR spectra of the (a) PANI–HEDP and (b) recycled PANI–HEDP.

Figure 2. X-ray diffraction patterns of the (a) PANI–HEDP and (b) recycled PANI–HEDP.

General Procedure for the Preparation of the PANI–HEDP Salt

A 40-mL aqueous solution containing 1 g of sodium lauryl sulfate (SLS) was added to a 30-mL toluene solution containing 3 g of benzoyl peroxide (BPO) with stirring at ambient temperature; then, 5 mL of 1-hydroxyethane 1,1-diphosphonic acid (60% aqueous solution) followed by 30 mL of aqueous solution containing 1 mL of aniline were added. The mixture was stirred constantly for 24 h at ambient temperature. Two layers were obtained, the organic layer containing PANI salt and aqueous layers containing side products. The organic layer was separated, and PANI powder was precipitated with 300 mL of acetone. The precipitated PANI powder was filtered, washed with water, and finally washed with acetone. The sample was dried at 50°C until it reached a constant weight (Scheme 1).

General Experimental Procedure for the Synthesis of Imidazo[1,2-a]pyridine

In a typical experiment, a mixture of 2-aminopyridine (1 mmol), 4-chlorobenzaldehyde (2 mmol), TMSCN (1 mmol), and PANI–HEDP catalyst (20 mg, 7 wt % with respect to aldehyde) was stirred at ambient temperature for a particular period of time and monitored with thin-layer chromatography. Dichloromethane was added to the reaction mixture and filtered, and we separated the catalyst. The dichloromethane solution was washed with water, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude solid residue was crystallized with ethyl acetate to obtain the pure product. The products were authenticated with ^{1}H-NMR spectra of known compounds. The separated catalyst was washed with dichloromethane and dried in an oven at 50°C for 10 min and reused again.

RESULTS AND DISCUSSION

Preparation and Characterization of the PANI Catalyst

PANI–HEDP (Scheme 1) was prepared with an emulsion polymerization pathway through the oxidation of aniline with the BPO oxidant in the presence of 1-hydroxyethane 1,1-diphosphonic acid and SLS emulsifier.

Physical Properties of PANI–HEDP

PANI–HEDP was obtained at a yield of 1.05 g (with respect to the 1 mL of aniline used) with a pellet density of 1.32 g/cm^3 and a conductivity of 0.2 S/cm.

IR Spectra of PANI–HEDP

The IR spectrum of PANI–HEDP [Figure 1(a)] showed major characteristic peaks of PANI at 3425, 2920, 2855, 1565, 1495, 1290, 1235, 1115, and 790 cm^{-1}. A broad band at 3425 cm^{-1} was assigned to free N—H stretching vibrations.[22] In addition to these peaks, a peak appeared at 3225 cm^{-1}, and this peak indicated the formation of the PANI salt. The PANI salt showed peaks around 1715, 1655, and 1040 cm^{-1} due to PO$_3$H groups; this indicated the presence of HEDP on the PANI salt. The IR spectrum of the recycled PANI–HEDP salt is shown in Figure 1(b); it was similar to the IR spectrum of the as-synthesized PANI–HEDP shown in in Figure 1(a).
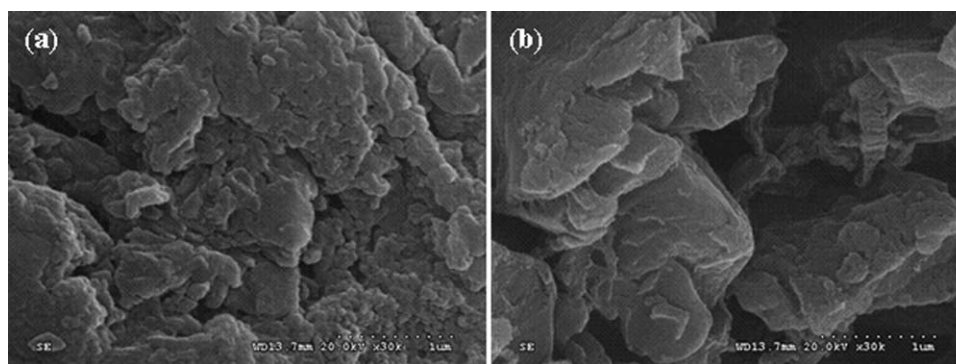

Figure 3. FESEM pictures of the (a) PANI–HEDP and (b) recycled PANI–HEDP.
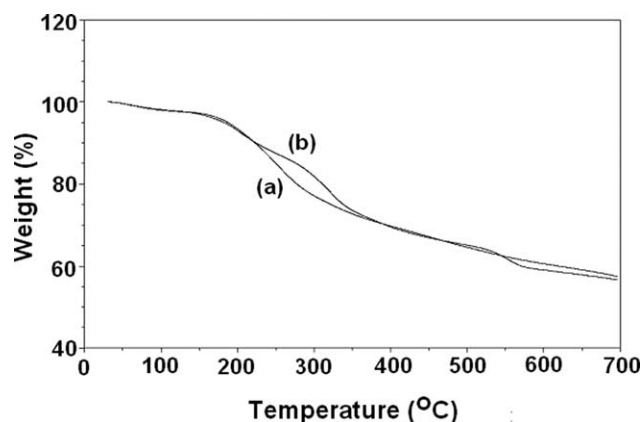
Figure 4. TGA thermograms of the (a) PANI–HEDP and (b) recycled PANI–HEDP.

XRD Patterns of PANI

The X-ray diffraction profiles registered for PANI–HEDP [Figure 2(a)] showed three broad peaks around $2\theta = 7.2$, 15.5, 20, 25, 27, and 30° with corresponding d-spacings of 12.3, 5.7, 4.4, 3.5, 3.3, and 3.1; these indicated its semicrystalline nature.[23] The X-ray diffraction pattern of the recycled PANI–HEDP salt [Figure 2(b)] showed a broad peak around $2\theta = 15.5$, 18, 20, 25, and 27° similar to that of PANI–HEDP [Figure 2(a)].

Field Emission Scanning Electron Microscopy (FESEM) of PANI–HEDP

The morphological structure of the as-synthesized PANI–HEDP was carried out by scanning electron microscopy [Figure 3(a)], and it showed agglomerated small spheres, whereas the recycled PANI–HEDP showed a flakelike structure [Figure 3(b)]. EDAX spectroscopy of PANI–HEDP indicated the presence of elements such as nitrogen and phosphorous. This result supported the fact that the PANI salt contained the HEDP dopant.

Thermogravimetry of PANI–HEDP

The TGA thermogram of PANI–HEDP is shown in Figure 4(a). The TGA thermogram showed a two-step weight loss process; the first weight loss (4%) was due to water molecules, and the polymer was stable up to 190°C. Then, the second weight loss occurred because of the degradation of the polymer chain. Similar weight loss behavior was observed for the recycled PANI–HEDP sample [Figure 4(b)].

The emulsion polymerization of aniline gave PANI salt containing protic acid groups in excellent yield with an agglomerated small-sphere morphology and a semicrystalline nature having stability up to 190°C. By considering the presence of protic acid on PANI, we used the PANI salt as a catalyst in imidazo[1,2-a]pyridines, and the results are discussed here.

Synthesis of Imidazo[1,2-a]pyridines with the PANI–HEDP Catalyst

In continuation of our work on the use of conjugated conducting polymers containing sulfate group dopants as reusable catalysts for carrying out organic transformations, in this study, we carried out the synthesis of imidazo[1,2-a]pyridines with PANI–HEDP, wherein the phosphate group acted as a protonic acid dopant.

In a typical procedure, the reaction was carried out with 2-aminopyridine (1 mmol), 4-chlorobenzaldehyde (1 mmol), TMSCN (1.5 mmol), and the PANI–HEDP catalyst (20 mg) under solvent-free conditions at room temperature (RT) for 1 h. This gave N-(4-chlorobenzylidene)-[2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl]amine in a 42% yield and 3-amino-4-chlorobenzyl imidazo[1,2-a]pyridines in a 16% yield (Scheme 2). To get one product, the reaction was carried out with 2 mmol of 4-chlorobenzaldehyde instead of 1 mmol under the same conditions, and this reaction gave only N-(4-chlorobenzylidene)-[2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl] amine in an 84% yield in 20 min (Scheme 2). To optimize the amount of catalyst, the reaction was carried out with increasing amounts of catalyst, that is, 1.75–14 wt % (with respect to aldehyde). The yield of the product was found to increase with the amount of catalyst, and we obtained a maximum yield with the use of 7 wt % catalyst (Table I). Vittal Rao et al.[21] reported the synthesis of N-(4-chlorobenzylidene)-{2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl}amine in 91% yield in 10 h with 5 mg of bromodimethylsulfonium bromide catalyst, and this catalyst could not be reused. Voskressensky et al.[20] carried out a similar reaction with amino-azine (1 mmol), toluadehyde (3 mmol), and 2-hydroxy-2-methyl propanenitrile (3 mmol) with 130 mg of a silica–sulfuric acid catalyst and obtained a yield of 70% in 2–3 days' time.

To address the effect of solvents on this methodology, the standard reaction was carried out in various solvents (Table II). Among these, the reaction in solvents such as dichloroethane, hexane, ethyl acetate, and acetonitrile favored the formation of a product with low yields in comparison with the reaction
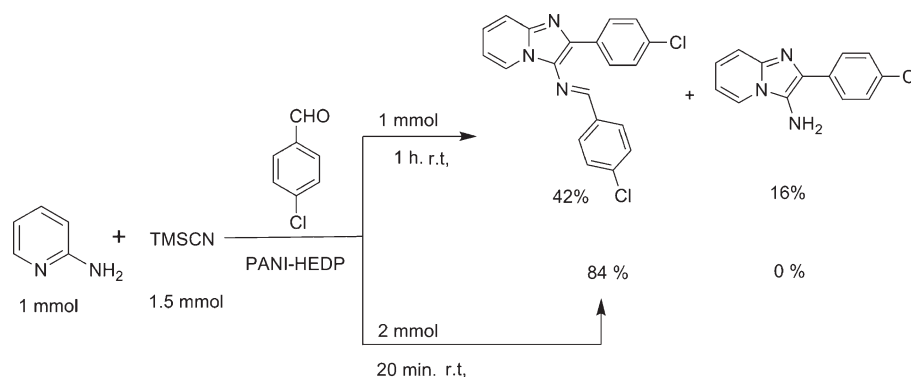
Scheme 2. Synthesis of the imidazo[1,2-a]pyridines with a PANI–HEDP catalyst.

Table I. Effect of the Amount of PANI–HEDP Catalyst in the Synthesis of *N*-(4-Chlorobenzylidene)-[2-(4-Chlorophenyl) Imidazo[1,2-a]pyridin-3-yl]amine Under Solvent-Free Conditions[a]

Entry	Catalyst (wt %)[b]	Isolated yield (%)
1	1.75	68
2	3.5	80
3	7	84
4	10.5	78
5	14	76

[a] 2-Aminopyridine (1 mmol), 4-chloro benzaldehyde (2 mmol), and TMSCN (1.5 mmol) PANI–HEDP.
[b] With respect to aldehyde.

under solvent-free conditions. However, the reaction did not proceed in solvents such as chloroform, diethyl ether, dimethyl sulfoxide, water, and acetone.

To determine the versatility of this catalyst, the standard reaction under solvent-free conditions was extended further by changes in the aromatic aldehydes, and the results are reported in Table III (entries 1–12). In all cases, the reaction proceeded smoothly to furnish the desired imidazo[1,2-a]pyridine derivatives in 66–84% yields. In all cases, neither electron-rich nor electron-deficient aldehydes affected the yield of product. The reaction with the use of aldehydes such as *p*-bromobenzaldehyde, *p*-hydroxy benzaldehyde, *p*-methyl benzaldehyde, and *m*-chlorobenzaldehyde gave good yields compared to other aldehydes. Vittal Rao et al.[21] reported higher yields with electron-donating substituents present on the aromatic aldehyde, and 2-aminopyridine, electron-withdrawing groups, and metasubstitutions had a negative impact and resulted in lower yields.

Recyclability

The reusability of the PANI–HEDP was verified for the standard reaction of 2-aminopyridine, 4-chlorobenzaldehyde, and TMSCN in the presence of the PANI–HEDP catalyst under solvent-free

Table II. Synthesis of *N*-(4-Chlorobenzylidene)-[2-(4-Chloro Phenyl) Imidazo[1,2-a]pyridin-3-yl] Amine Catalyzed by PANI–HEDP at Ambient Temperature[a] in Different Solvents

Entry	Solvent	Time (h)	Isolated yield (%)
1	No solvent	0.33	84
2	CH$_3$CN	2	53
3	Dichloroethane	4	30
4	Hexane	4	47
5	Ethyl acetate	4	44
6	Diethyl ether	4	[b]
7	Dimethyl sulfoxide	4	[b]
8	CHCl$_3$	4	[b]
9	H$_2$O	4	[b]
10	CH$_3$COCH$_3$	4	[b]

[a] 2-Aminopyridine (1 mmol), 4-chlorobenzaldehyde (2 mmol), TMSCN (1.5 mmol) solvent (5 mL), and catalyst (7 wt %).
No product.

Table III. PANI–HEDP-Catalyzed Synthesis of *N*-Benzylidine-2-Phenyl Imidazo[1,2-a]pyridines Under Solvent-Free Conditions at Ambient Temperature[a]

Entry	R_1	R_2	Time (min)	Isolated yield (%)
1	H	4-Cl	20	84
2	H	4-F	60	76
3	H	4-Br	120	78
4	H	4-OH	5	84
5	H	2-Cl,5-NO$_2$	90	69
6	H	4-CH$_3$	20	77
7	H	[b]	50	70
8	H	[c]	45	78
9	H	3-Br	30	68
10	4-CH$_3$	2-OH	15	60
11	5-CH$_3$	H	50	66
12	H	3-Cl	30	78

R_1, substituent in 2-aminopyridine; R_2, substitutent in benzaldehyde.
[a] 2-Aminopyridine derivative (1 mmol), aryl aldehyde (2 mmol), TMSCN (1.5 mmol), and PANI-HEDP (7 wt %).
[b] 2-Naphthaldehyde.
[c] Thiophene-2-aldehyde.

conditions at RT for 1 h. The yields of the product obtained in the subsequent cycles were 79, 70, 72, 71, and 70%. At the end of the recyclability experiments, the catalyst was isolated and analyzed by IR spectroscopy, X-ray diffraction, FESEM, and TGA. Similar results for the catalyst were observed before and after the recycling reaction (Figures 1–4). These results indicated that the PANI–HEDP catalyst showed good recyclability.

CONCLUSIONS

In summary, a novel, easily synthesizable, handleable, and cheaper catalyst, an emeraldine form of PANI–HEDP, was successfully synthesized and demonstrated as an efficient, green, versatile, reusable polymer-based solid acid catalyst for the synthesis of *N*-benzylidine-2-phenyl imidazo[1,2-a]pyridines.

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