Polyaniline supported indium chloride: A reusable catalyst for organic transformations in water☆

M. Lakshmi Kantam [a,*], Moumita Roy [a], Sarabindu Roy [a], M.S. Subhas [a],
Bojja Sreedhar [a], B.M. Choudary [b], Rajib Lal De [c]

[a] *Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India*
[b] *Ogene Systems (I) Pvt. Ltd., Moosapet, Hyderabad 500037, India*
[c] *Department of Chemistry, Jadavpur University, Kolkata 700032, India*

Abstract

Polyaniline supported indium(III) trichloride (PANI-In) catalyst was prepared and thoroughly characterized by using FTIR, XPS, scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) and ICP-AES. Thus, the synthesized catalyst was efficiently used in the aza-Michael reaction of amines with electron-deficient olefins and aza-Diels-Alder reaction of cyclic enol ethers with aromatic amines in water. Moreover, the catalyst was easily recovered by simple filtration and reused for several cycles with consistent activity.
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1. Introduction

In recent years, indium trichloride has gained wide spread application as an efficient Lewis acid catalyst for various important organic transformations, such as transmetallation with organotin compounds [1], Mukaiyama aldol reactions [2], Diels-Alder reactions [3], aza-Michael reactions [4], ring opening of epoxides with nucleophilies [5], etc. As most of these catalytic systems are homogeneous in nature, they suffer from product contamination with catalyst and it required cumbersome catalyst separation procedure. So it is highly desirable to develop a heterogeneous catalytic protocol, which allows easy recovery and recyclability of the precious indium catalyst [6]. From the standpoint of green chemistry, the development of more environmentally benign reaction conditions, which allows the use of water instead of organic solvents, would be desirable.

Polyaniline (PANI) is one of the most widely studied conducting polymers for electronic and optical applications [7]. It is also getting considerable attention in modern organic synthesis as a support and also as a promoter for metal catalyzed organic transformations for its easy preparative protocol from inexpensive starting material, high environmental stability, easy acid–base doping–dedoping and redox properties [8]. Herein, we wish to report the preparation, characterization and catalytic properties of polyaniline supported indium chloride in two important organic reactions namely aza-Michael reactions of amines with electron-deficient olefins [9] and aza-Diels-Alder reactions aromatic amines with cyclic enol ethers in water [3,10]. First, we have chosen aza-Michael reaction, as it is important for the synthesis of C−N heterocycles [11] containing the β-amino carbonyl functionality. Such functionality not only constitutes a component of biologically active natural products, but also serves as an essential intermediate in the synthesis of β-amino ketones, β-amino acids and β-lactam antibiotics, in addition to its use in the fine chemicals and pharmaceutical sectors [12]. Later, we have chosen aza-Diels-Alder reaction of aromatic amines with cyclic enol ethers for the synthesis of 1,2,3,4-tetrahydroquinoline derivatives, which are present as an important moiety in various natural products, and many of these tetrahydroquinoline derivatives also exhibit a broad range of biological activity [13].

2. Experimental

2.1. Materials and methods

IR spectra were recorded on BIORAD 175C FTIR spectrometer for samples as KBr pellets. ^{1}H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. Chemical shifts (δ) are reported in ppm, using TMS as internal standard for ^{1}H NMR. Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species were first determined by using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within ±0.1 eV. ACME silica gel (100–200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60–F$_{254}$ plates. ICP-AES analyses were performed on IRIS Intrepid II XDL ICP-AES (Thermo Electron Corporation). Anhydrous InCl$_3$ was purchased from Alfa Aesar. Aniline and other solvents were distilled before use. All other chemicals were procured from commercial sources and used as such without further purification.

2.2. Preparation of polyaniline base

Freshly distilled aniline (4.9 g, 53 mmol) was added to the aqueous solution (350 mL) containing H$_2$SO$_4$ (15 mL) and the solution was kept under continuous stirring at 0 °C. To this solution ammonium per sulfate (12 g, 53 mmol) in water (125 mL) was added drop-by-drop over 4 h. The precipitated polyaniline-sulfate salt was recovered by filtration and the precipitate was washed with copious amount of water followed by acetone. Thus, obtained polyaniline-sulfate salt was stirred for 12 h at ambient temperature with sodium hydroxide solution (1N, 500 mL). Then the deprotonated polyaniline base was filtered off, and washed with water, followed by acetone. PANI was first purified off oligomers in a Soxhlet apparatus by acetonitrile and then purified off low molecular weight fractions of the polymer using tetrahydrofuran.

2.3. Preparation of polyaniline supported indium(III) chloride (PANI-In)

PANI (1000 mg) was charged into a RB flask containing an acetonitrile solution (25 mL) of indium trichloride (221 mg, 1.0 mmol) and stirred under nitrogen atmosphere for 48 h. The resultant catalyst was filtered off and washed with acetonitrile followed by acetone. The residue was dried in air for 24 h to afford the black catalyst. The amount of indium was measured by ICP-AES (In: 0.67 mmol/g).

2.3.1. General procedure for aza-Michael reaction of amines with electron-deficient olefins

In an oven dried 10 mL round-bottom flask, amine (1 mmol), olefin (1.2 mmol), PANI-In (10 mol%) and water (2 mL) were taken and stirred at room temperature. After the completion of the reaction as monitored by TLC, the catalyst was filtered off. The filtrate was diluted with ethyl acetate and washed with saturated aqueous NaCl solution. The organic layer was dried with Na$_2$SO$_4$ and concentrated to get the crude product. The crude product was column chromatographed using hexane:ethyl acetate (7:3) as eluent. All the products were characterized by using NMR and mass spectroscopy and compared with the literature data [9].

2.3.2. General procedure for aza-Diels-Alder reaction of aromatic amines with cyclic enol ethers

In an oven dried 10 mL round-bottom flask, aromatic amine (0.5 mmol), cyclic enol ether (1.5 mmol), PANI-In (10 mol%) and water (2 mL) were taken and stirred at room temperature. After the completion of the reaction as monitored by TLC, the catalyst was filtered off. The filtrate was diluted with ethyl acetate and washed with saturated aqueous NaCl solution. The organic layer was dried with Na$_2$SO$_4$ and concentrated to get the crude product. The crude product was column chromatographed using hexane:ethyl acetate (6:4) as eluent. All the products were characterized by using NMR and mass spectroscopy and compared with literature data [3,10].

3. Results and discussion

3.1. Preparation of PANI-In

PANI was doped with indium(III) trichloride from acetonitrile solution of indium chloride to give an air stable black colored PANI-In catalyst (Scheme 1).

3.2. Characterization of the PANI-In catalyst

3.2.1. FTIR spectroscopy

PANI has quinoid (Q) and benzenoid (B) units along with amine and imine functional moieties, which can hold the metal complexes. The characteristic vibrational absorbance of PANI and PANI-In (Fig. 1) are shown in Table 1. The most important bands in the spectrum of PANI are located at 1584, 1488, 1376, 1308, 1156 and 824 cm^{-1} and are attributed to the stretching
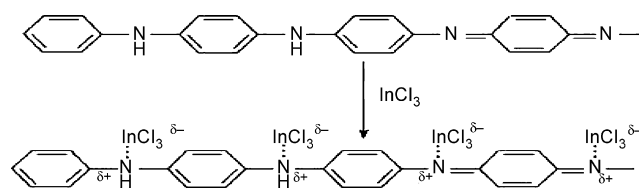
Scheme 1. Doping of polyaniline with InCl$_3$.

Table 1
FTIR spectroscopic data of PANI and PANI-In

Catalyst	N=Q=N (cm^{-1})	N—B—N (cm^{-1})	CH$_{in-plane}$ bending of PANI (cm^{-1})	Other important band (cm^{-1})
PANI	1584	1488	1156	1376, 1308, 824
PANI-In	1578	1494	1136	1374, 1300, 820
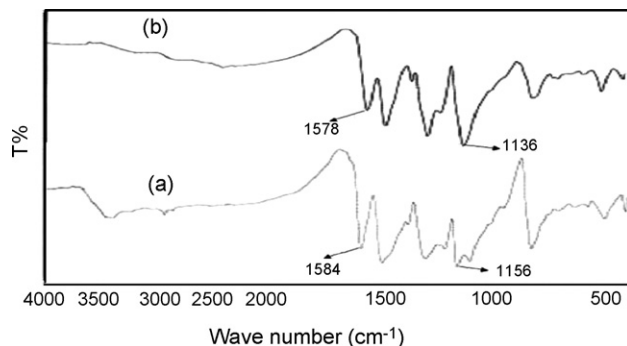
Fig. 1. FTIR spectra of: (a) PANI and (b) PANI-In.

Fig. 2. XPS narrow scan of PANI-In for In 3d and N 1s.

vibrations of quinoid ($\nu_{C=N} + \nu_{C=C}$), benzenoid ($\nu_{C=C}$) units of the polymer, deformations of the C—N bond, stretching vibrations of the C—N bond, in plane deformations of CH bonds present in the aromatic rings of the undoped polymer and the out of plane deformations of CH bonds in 1,4-substituted aromatic ring, respectively [14]. PANI-In shows a new peak at 1136 cm^{-1} that indicates the presence of charged polyaniline chain (CH$_{in-plane}$ bending) [15]. Moreover the characteristic peak for N=Q=N at 1584 cm^{-1} red shifted to 1578 cm^{-1} indicating the weakening of the N=Q=N bond.

3.2.2. X-ray photoelectron spectroscopy

PANI-In was subjected to XPS analysis (Table 2 and Fig. 2) and after deconvoluting the N 1s signal from PANI-In, three peaks at 397.78 eV (share 19.4%), 399 eV (share 56.4%) and 400.14 eV (share 24.2%) are observed which are assigned to imine nitrogen (−N=), amine nitrogen (−NH−) and N$^+$, respectively [16]. In 3d$_{5/2}$ signal appears at 445.17 eV and Cl 2p peak is observed at 198.58 eV. Therefore, we postulate that indium chloride forms a bond with imine as well as amine nitrogen of polyaniline (Scheme 1). Similar kind of bonding is also reported for PANI doped with other strong Lewis acids, such as SnCl$_4$ and FeCl$_3$ [15a,b].

3.2.3. Scanning electron microscopy and X-ray energy dispersive analysis

The SEM images of PANI and PANI-In were almost similar indicating that after doping with InCl$_3$, morphology did not

change appreciably. The EDX analysis of PANI-In indicates the presence of indium in 0.68 mmol/g, which is almost comparable to ICP-AES analysis (0.67 mmol/g).

3.3. Catalytic activity of PANI-In in different organic transformations

3.3.1. Aza-Michael reaction of amines with electron deficient olefins using PANI-In catalyst in water

A variety of α, β-unsaturated carbonyl compounds, or nitriles, such as methyl acrylate, 2-cyclohexenone and acrylonitrile were reacted with a wide range of amines in the presence of 10 mol% of PANI-In in water at room temperature (Scheme 2) to afford the corresponding β-amino compounds in high yields within a very short time. The results are summarized in Table 1. In general the aliphatic amines reacted at a faster rate than the

Table 2
XPS analysis of PANI and PANI-In for N 1s

Sample	−N=		−NH−		−N$^+$	
	BE (eV)	Share (%)	BE (eV)	Share (%)	BE (eV)	Share (%)
PANI	398	45	399.4	45	402	10
PANI-In	397.78	19.4	399	56.4	400.14	24.2
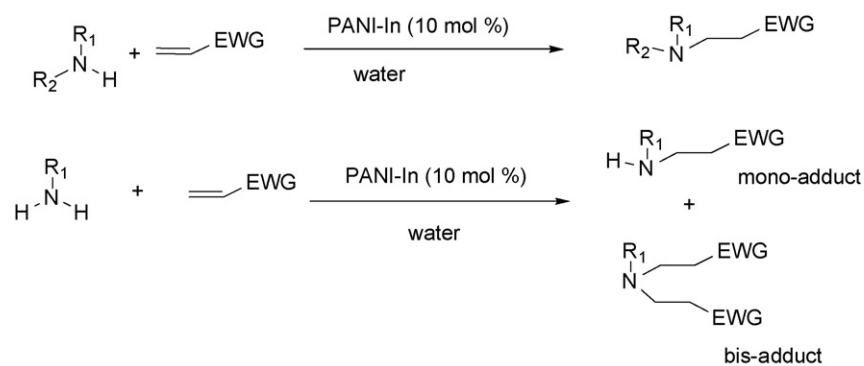
Scheme 2. Aza-Michael reaction of amines with electron-deficient olefins in water catalyzed by PANI-In.

aromatic amines (Table 3, entries 11–13), as their nucleophlicity is much higher. After the completion of the reaction, catalyst was separated by simple filtration washed with acetone, air-dried and reused for five cycles with consistent activity (Table 3, entry 1).

3.3.2. Aza-Diels-Alder reaction of aromatic amines with cyclic enol ethers using PANI-In in water

A variety of substituted anilines were reacted with 3,4-dihydro-2H-pyran (DHP) and 2,3-dihydrofuran (DHF) at 50 °C or at room temperature in presence of 10 mol% of PANI-

Table 3
Aza-Michael reaction of amines with olefins catalyzed by PANI-In in water

Entry	Amine	Olefin	Time (min)	Isolated yield (%)
1	C_6H_5—CH_2NH_2	—CN	20	95, 92[a]
2[b]	C_6H_5—CH_2NH_2	—CO_2Me	30	92
3	C_6H_5—CH_2NH_2	cyclohexenone =O	30	90
4	piperidine NH	—CN	20	95
5	piperidine NH	—CO_2Me	20	90
6	piperidine NH	cyclohexenone =O	30	95
7	morpholine O NH	—CO_2Me	30	92 (95)[c]
8	morpholine O NH	cyclohexenone =O	30	95
9	n-Bu, n-Bu NH	—CO_2Me	20	95
10	(iPr)HN(iPr)	—CO_2Me	10	92
11	MeO—C_6H_4—NH_2	—CO_2Me	24 h	65
12	MeO—C_6H_4—NH_2	—CN	24 h	66
13	Me—C_6H_4—NH_2	—CO_2Me	24 h	55

Reaction conditions: amine (1 mmol), olefin (1.2 mmol), PANI-In (10 mol%), water (2 mL) stirred at room temperature. usually the mono-adduct formed with 2–5% bis adduct unless other wise stated.
[a] Yield after sixth cycle.
[b] 2.5 equivalent olefin. Ninety-eight percent bis-adduct formed.
[c] Reaction conducted with 10 mol% InCl$_3$.
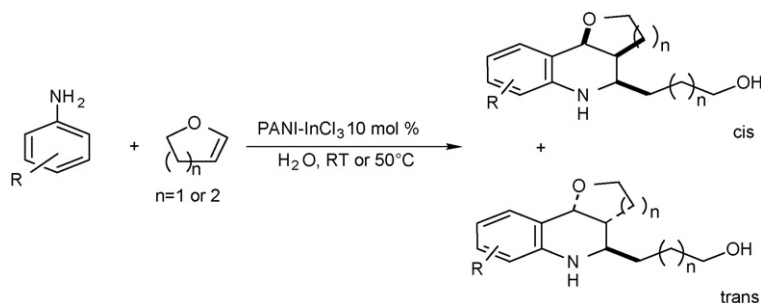
Scheme 3. Synthesis of pyrano- and furanoquinolines in water catalyzed by PANI-In.

In in water to generate the tetrahydroquinoline derivatives in excellent yields (Scheme 3) and the results are summarized in Table 4. In all the cases, the products were obtained as a mixture of *cis*- and *trans*-isomers and the product ratios were determined from the ^{1}H NMR spectra of the crude products [17]. Anilines bearing electron-donating groups found to be more active than the ones bearing electron-withdrawing groups. When we conducted the Diels-Alder reaction with 4-nitroaniline and 4-cyanoaniline, unfortunately, there was no reaction between 4-nitroaniline and 2,3-dihydrofuran/3,4-dihydro-2*H*-pyran. 4-Cyanoaniline reacted with 2,3-dihydrofuran at 45 °C and afforded 43% of the product with 75% *cis*-selectivity (Table 4,

entry 10). Anilines bearing electron-withdrawing group gave a better selectivity than the ones with electron donating group when reacted with DHP (Table 4, entries 3–5) but in the reaction with DHF, anilines bearing electron-donating group yielded better selectivity (Table 4, entries 7 and 8).

3.4. Reusability study of the catalyst

The catalyst was recovered by simple filtration and washed with acetone and air-dried. The recovered catalyst was reused and consistent activity was noticed even after fifth cycle (Table 3, entry 1; Table 4, entry 7). When a fresh reaction was conducted

Table 4
Reaction of anilines with 3,4-dihydro-2*H*-pyran and 2,3-dihydrofuran in water catalyzed by PANI-In

Entry	Amine	Olefin	Temperature/time (h)	Isolated yield (%)[a]	*Cis:trans*
1	NH$_2$	O	RT/16	95	45:55
2	NH$_2$	O	50 °C/5	95	35:65
3	Me—NH$_2$	O	50 °C/5	92	53:47
4	Cl—NH$_2$	O	50 °C/24	87	28:72
5	MeO—NH$_2$	O	50 °C/5	90	59:41
6	NH$_2$	O	RT/24	92	45:55
7	Me—NH$_2$	O	RT/2	90, (87)[b] (84)[c]	82:18 (81:19)[c]
8	MeO—NH$_2$	O	RT/2	90	90:10
9	Cl—NH$_2$	O	45 °C/5	88	62:38
10	NC—NH$_2$	O	45 °C/24	43	75:25

Reaction conditions: amine (0.5 mmol), enol ether (1.5 mmol), PANI-In (10 mol%), water (2 mL) stirred at RT or 50 °C.

[a] Isolated yields.
[b] Yield after sixth cycle.
[c] Reaction with 10 mol% InCl$_3$ and the results are cited from ref. [3b].

with the filtrate obtained at the end of the reaction, almost no catalytic activity of the filtrate was observed. Moreover, the absence of indium in the filtrate was determined by ICP-AES analysis.

4. Conclusion

In summary, polyaniline supported indium(III) catalyst was prepared, thoroughly characterized and employed in two important organic transformations in water to afford the corresponding products in good to excellent yield in shorter duration than the precursor $InCl_3$. The simple procedure of catalyst preparation, easy recovery and reusability of the catalyst is expected to contribute to the development of benign chemical processes and products.

Acknowledgements

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