

# Polyaniline-Supported Acid Catalyst: Esterification of Cinnamic Acid with Alcohols

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Received 14 June 2004; accepted 22 October 2004

DOI 10.1002/app.21601

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polyaniline-supported acid salts such as polyaniline-hydrochloride, polyaniline-sulfate, and polyaniline-nitrate were prepared by oxidation of aniline using benzoyl peroxide and ammonium persulfate as oxidizing agents. Polyaniline salts were used as catalysts in the esterification of cinnamic acid with alcohols. Polyaniline-sulfate salt was found to be the best catalyst for the esterification of cinnamic acid. The reusability, handling, and recovery of the

catalyst were found to be good. The yield of the ester depended on the type of the polyaniline salt, amount of the catalyst, amount of alcohol, and both the time and the temperature of the reaction. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1584–1590, 2005

**Key words:** conducting polymers; esterification; FTIR; catalysts; supports

## INTRODUCTION

Polymer-supported catalysts<sup>1,2</sup> have gained importance in organic synthesis because they offer high economical prospects in developing reusable catalysts. The use of polymer-supported catalysts facilitates the postreaction process; also, because the polymer is insoluble, the catalysts can be recovered by a simple filtration process and can easily be recycled. In polymer-supported catalysts, the fixed position of the metal ion on the polymer matrix may contribute to greater isolation of catalytically active sites and therefore can increase the catalytic activity. Recently, the air-stable, infusible, intractable organic conducting polymers have gained importance in catalytic applications. In earlier studies, polyaniline doped with metal ions or heteropoly acids were used as catalysts in the preparation of amino acid derivatives,<sup>2</sup> dehydration of alcohols,<sup>3</sup> synthesis of methyl tertiary butyl ether,<sup>4</sup> and in the hydrogenation of 2-ethylanthraquinone.<sup>5</sup> The polyaniline doped with metal ions or heteropoly acids was prepared by doping the polyemeraldine base with an appropriate reagent, and in some cases the heteropoly acid was doped onto the polyaniline chain during the polymerization of aniline.

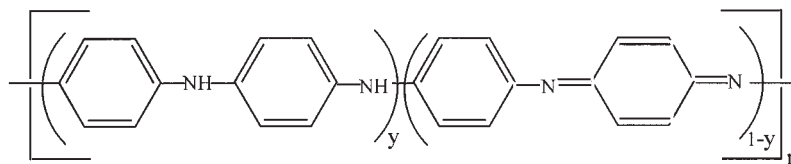
Esters are useful compounds that are used in such diverse industries as perfumes, plasticizers, fragrances, coatings, and adhesives. Several methods have been used to prepare esters of different acids.<sup>6</sup> The general procedure to prepare an ester is to treat a

carboxylic acid with an alcohol in the presence of a catalyst. A wide variety of catalytic systems have been used in the esterification process, including zeolytic molecular sieves,<sup>7</sup> aluminophosphate molecular sieves,<sup>8</sup> hydrated zirconium sulfate,<sup>9</sup> solid acid catalysts,<sup>10</sup> tin phosphate,<sup>11</sup> cation-exchange resins,<sup>12</sup> polymer-supported sulfonic acid catalyst,<sup>13</sup> iodine,<sup>14</sup> and tungstophosphoric and molybdophosphoric acids supported on zirconia.<sup>15</sup>

Most of the reported procedures for the synthesis of esters require the use of sulfuric acid, hydrochloric acid, and toxic chemicals, such as dimethyl sulfate, methyl iodide, or unsafe reagents such as diazomethanes, which are environmentally hazardous and unacceptable. Chemicals such as trifluoro acetic acid, *p*-toluene sulfonic acid, metal chlorides (AlCl<sub>3</sub>), and chloroaluminate ionic liquids should be used in excess and lead to increasing environmental pollution. Also, the above catalyst systems involve recovery, reusability, and handling problems. Replacement of acids by solid acid catalyst, such as zeolite, with clay sulfonic acid resin would result in simplified product recovery and a reduction in undesirable waste streams. Also, solid acid catalysts are highly susceptible to deactivation because of pore blocking and hydration. Ion-exchange resins are not resistant enough to high temperature (>120°C) and also the efficiency decreases because of a leaching problem. Considering the impact of the above catalysts, there is an urgent need to develop a more ecofriendly and economical method for the production of esters.

In this work, polyaniline salts of hydrochloric, sulfuric, or nitric acid were used as polymer-supported catalysts for the esterification of cinnamic acid. Cin-

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Scheme 1

amic acid is an important precursor for its derivatives such as the esters, which have pleasant long-lasting aromas. Methyl cinnamate enjoys the greatest usage and is found in flavor and fragrance compositions created for products, which include soaps and cosmetics as well as beverages, baked goods, and convenience foods. Reported applications for cinnamic acid and its derivatives include use as a light-penetration inhibitor in sunscreen formulations.

The advantages of using polyaniline-supported acid catalysts are (1) a straightforward synthetic route and can easily be prepared in larger quantities, (2) easy handling, (3) good stability, (4) easy recovery, (5) does not lose its activity during thermal and recyclable treatments, and (6) they are ecofriendly.

## EXPERIMENTAL

### Materials

#### Preparation of polyaniline salts

Polyaniline salts such as polyaniline–hydrochloride (PANI–HCl), polyaniline–sulfate (PANI–H<sub>2</sub>SO<sub>4</sub>), and polyaniline–nitrate (PANI–HNO<sub>3</sub>) were prepared according to the procedure reported earlier by using two different oxidizing agents, benzoyl peroxide<sup>16</sup> and ammonium persulfate.<sup>17</sup>

*Preparation of polyaniline salts by benzoyl peroxide.*<sup>16</sup> Benzoyl peroxide (4.85 g) was dissolved in 60 mL acetone. To this solution, 2.0 g sodium lauryl sulfate in 30 mL distilled water was added. Aniline (2.4 mL) in 100 mL aqueous solution containing 1.0N [H<sub>2</sub>SO<sub>4</sub>, HCl, (or) HNO<sub>3</sub>] acid was introduced dropwise into the above solution at 40°C. The mixture was stirred for 8 h at 40°C and the precipitated polyaniline salt was filtered, washed with 3 L of distilled water, followed by methanol and acetone. The resulting polymer salt was finally dried at 100°C until reaching a constant mass.

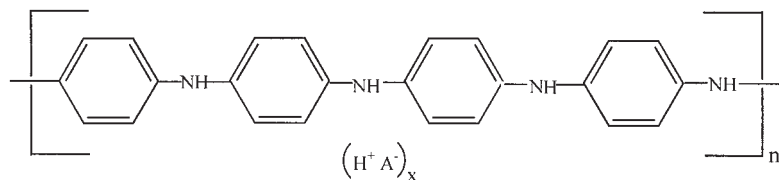
#### *Preparation of polyaniline salts by ammonium persulfate.*<sup>17</sup>

The polymerization was carried out in aqueous protic acid solution. An aqueous solution of ammonium persulfate (0.1M) was added very slowly into 1.0N acid solution containing 0.1M aniline at a temperature of 0–5°C. After all the oxidant was added, the reaction mixture was stirred at a constant temperature for 4 h. The oxidation of aniline is highly exothermic and thus the rate of addition of the oxidant was adjusted to prevent any increase in the temperature of the reaction mixture. The precipitated polyaniline was recovered from the polymerization vessel by filtration and then washed with distilled water until the washing liquid was colorless. To remove oligomers and other organic by-products, the precipitate was washed with methanol until the methanol solution was colorless. Finally, the resulting polymer salt was washed twice with acetone and subsequently dried at 100°C until it achieved a constant mass.

*Preparation of polyaniline base.* Polyaniline salts were dedoped to polyaniline bases by taking 1.0 g of polyaniline salt in 100 mL (1N) aqueous sodium hydroxide solution, the solution was kept for 12 h, after which the solution was filtered and washed with water; the product was dried at 100°C until it achieved a constant mass.

### Characterization

The polyaniline sample was mixed with KBr powder and compressed into a pellet, wherein the polyaniline powder was evenly dispersed. FTIR spectra were recorded using a GC-FTIR spectrometer (Model 740, Nicolet Instrument Technologies, Madison, WI). An electronic absorption spectrum of the polyaniline sample was recorded at ambient temperature using a GBC Cintra 10e UV/V spectrophotometer (GBC Scientific Equipment, Mumbai, India). The solution for the absorption spectrum of polyaniline base was prepared



Scheme 2

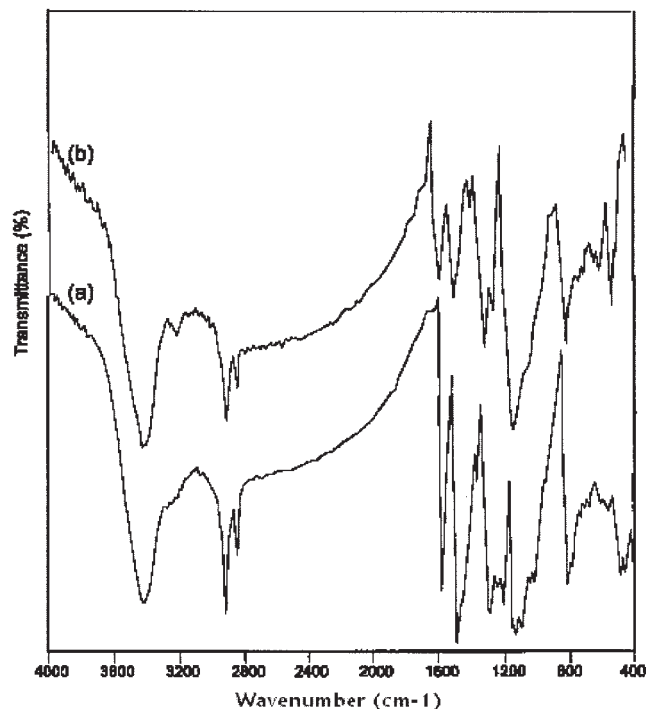


Figure 1 Infrared spectra of (a) PANI-BASE ( $\text{H}_2\text{SO}_4$ ) and (b) PANI- $\text{H}_2\text{SO}_4$ .

by dissolving the samples in dimethyl sulfoxide (DMSO) and filtered through Whatman (Clifton, NJ) 41 filter paper. An absorption spectrum of the dilute solution was recorded in the range 950–200 nm using a pair of matched 3-mL stoppered silica cells of 10 mm path length. Surface area measurement of the polymer powder was determined using an Autosorb-1 gas sorption system (Model ASIC-3; Quantichrome Corp., Syosset, NY). Particle size measurement of the polymer powder was determined using a Mastersizer 2000 (Malvern Instruments, Worcestershire, UK) by dispersing polymer powder in distilled water.

#### Procedure for the esterification of cinnamic acid

In a typical experiment, esterification of cinnamic acid (1 g) and methanol (5 mL) was carried out in a 10-mL round-bottom flask with 200 mg (20 wt % with respect to acid) of polyaniline salt powder. The reaction mixture was constantly stirred at  $70^\circ\text{C}$  in ambient atmosphere for 24 h. The reaction mixture was filtered and washed with methanol to recover the catalyst. Methanol was removed by vacuum and the crude ester was purified by column chromatography.

## RESULTS AND DISCUSSION

The polyanilines refer to a very important class of electronic/conducting conjugated polymers because of their good environmental stability, possible proces-

sibility, ease of preparation, redox properties, and conductivity. They can be considered as derived from a polymer, the base (emeraldine base) form of which has the general formula given in Scheme 1.

The imine nitrogen atoms can be protonated, in whole or in part, to give the corresponding salts, the degree of protonation of the polymeric base depending on its oxidation state and pH of the aqueous acid. Complete protonation of the imine nitrogen atoms in an emeraldine base by aqueous acid results in the formation of delocalized polysemiquinone radical cation and is accompanied by an increase in conductivity of about 10 orders of magnitude. The partly protonated emeraldine salt can be prepared easily either by chemical or electrochemical oxidative polymerization of aniline, which is shown in Scheme 2.

Polyaniline salts such as PANI-HCl, PANI- $\text{H}_2\text{SO}_4$ , and PANI- $\text{HNO}_3$  were prepared by chemical oxidative polymerization of aniline with two different oxidizing agents, ammonium persulfate and benzoyl peroxide. These polyaniline salts were characterized by infrared, electronic absorption spectral, surface area, and particle size analysis.

Generally, similar infrared spectral behavior was observed for the polyaniline bases prepared from their corresponding salts. As a representative system, the infrared spectrum of polyaniline base PANI-BASE ( $\text{H}_2\text{SO}_4$ ) is shown in Figure 1(a). 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  $3415\text{--}3460\text{ cm}^{-1}$  attributed to the N-H stretching vibration; the bands at  $2920$  and  $2850\text{ cm}^{-1}$  are attributed 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

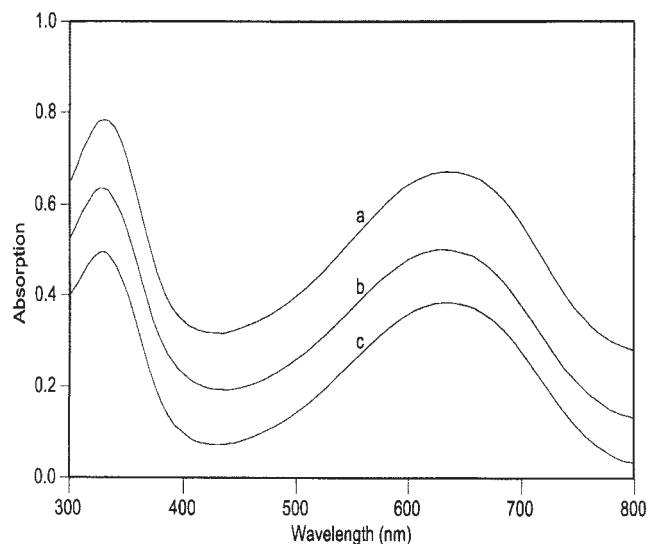


Figure 2 Electronic absorption spectra of (a) PANI-BASE (HCl), (b) PANI-BASE ( $\text{H}_2\text{SO}_4$ ), and (c) PANI-BASE ( $\text{HNO}_3$ ).

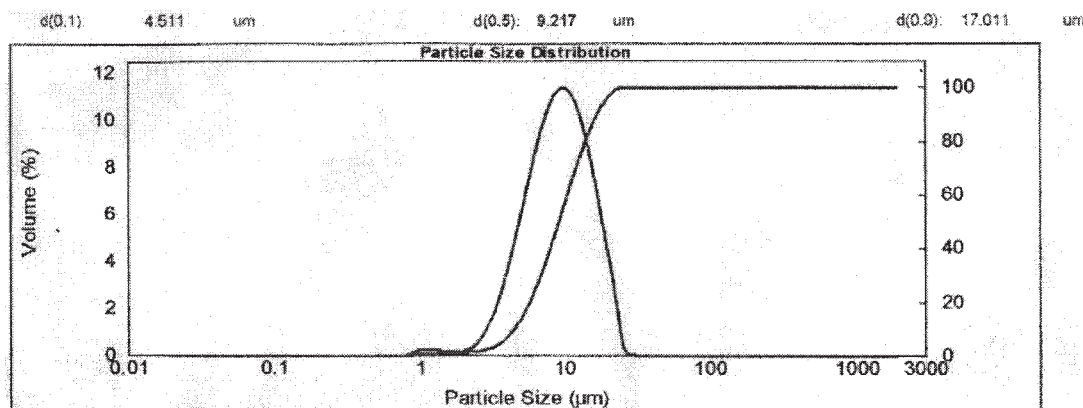


Figure 3 Particle size distribution pattern of PANI-H<sub>2</sub>SO<sub>4</sub> salt sample.

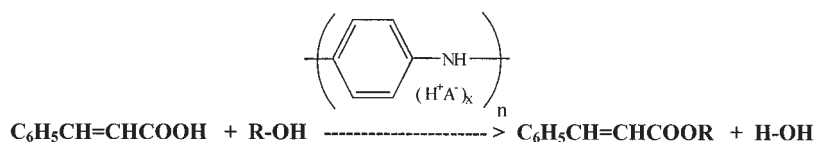
sum frequency; 1565 and 1490 cm<sup>-1</sup> bands attributed to the quinonoid ring (Q) and or benzenoid ring (B); the bands at 1370 and 1300 cm<sup>-1</sup> are attributed to C—N stretching vibration in QBQ, QBB, and BBQ; a 1240 cm<sup>-1</sup> band attributed to the C—N stretching vibration of aromatic amine. In the region of 1020–1170 cm<sup>-1</sup>, aromatic C—H in-plane bending modes are usually observed. For polyaniline, a strong band characteristically appears at 1140 cm<sup>-1</sup>, which has been explained as an electronic band or a vibrational band of nitrogen quinone. A band at 705 cm<sup>-1</sup> is attributed to ring C—C bending vibration and the band at 580 cm<sup>-1</sup> is attributed 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<sup>-1</sup>, which fell in the range 800–860 cm<sup>-1</sup> reported for 1,4-substituted benzene. The infrared spectra of polyaniline bases prepared are very close to the infrared spectrum of the polyaniline base system reported in the literature.<sup>17–20</sup>

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

The electronic absorption spectra of polyaniline bases and polyaniline salts have been reported in the literature.<sup>21–23</sup> An absorption spectrum of polyaniline base shows two distinct absorption bands located between 320 and 340 and 600–650 nm, depending on the method of preparation and/or processing of polyaniline. The band around 320–340 nm and the band around 600–650 nm are assigned to the excitation of the amine and imine segments of the polymer chain, respectively.

Polyaniline salt in the powder form is not soluble in most of the organic solvents. However, polyaniline base is sparingly soluble in dimethyl sulfoxide (DMSO). The electronic absorption spectra of the DMSO soluble fractions of the polyaniline bases prepared from their corresponding salts are very nearly the same (Fig. 2). The electronic absorption spectra of polyaniline bases showed a band around 320–330 nm and another broad band around 620–650 nm. These two peaks are assigned to the excitation of the amine and imine segments of the polymer chain, respectively, and are consistent with literature reports on polyaniline base. The absence of the peak above 725 nm, which is attributed to the polaron, shows that dedoping of the salt is complete.

Particle size distribution of the PANI-H<sub>2</sub>SO<sub>4</sub> sample prepared by benzoyl peroxide oxidizing agent is shown in Figure 3. It was found that 90% of the particles show less than 17 μm, whereas the PANI-H<sub>2</sub>SO<sub>4</sub> sample prepared by ammonium persulfate oxidizing agent shows less than 120 μm.



70°C, 24 h

Scheme 3

TABLE I  
Yield of Methyl Cinnamate Prepared Under Different Conditions

Entry	Amount of catalyst (%)	Amount of methanol (mL)	Reaction temperature (°C)	Time (h)	Isolated yield (%)
1	20	5.0	70	4	39
2	20	5.0	70	8	63
3	20	5.0	70	12	78
4	20	5.0	70	20	82
5	20	5.0	70	24	99
6	5	5.0	70	24	52
7	10	5.0	70	24	72
8	15	5.0	70	24	80
9	20	5.0	70	24	99
10	20	3.0	70	24	45
11	20	4.0	70	24	82
12	20	5.0	70	24	99
13	20	5.0	30	24	28
14	20	5.0	50	24	50
15	20	5.0	70	24	99

The polyaniline salts prepared using both oxidizing agents were used directly as catalysts in the esterification of cinnamic acid with different alcohols, as in Scheme 3.

There was no appreciable reaction (3%) when cinnamic acid was allowed to react with methanol in the absence of catalyst. Encouraged by this result, we carried out further investigation on several variations using polyaniline salt catalyst. To standardize the esterification reaction of cinnamic acid, the reaction was conducted for different periods of time, with different amounts of PANI-H<sub>2</sub>SO<sub>4</sub> catalyst (prepared by Method I), different amounts of methanol, and at different temperatures (Table I). We first investigated the effect of time on the yield of the ester by carrying out the esterification reaction for different periods of time (4, 8, 12, 20, 24 h) with 1 g of cinnamic acid and 5 mL of methanol in the presence of 20 wt % of catalyst (with respect to cinnamic acid) at 70°C. The results are reported in Table I (entries 1–5). The yield of the ester was increased with reaction time and quantitative yield of the ester was obtained when the reaction was carried out for 24 h. To investigate the effect of amount of catalyst on the yield of the ester, the reaction mixture containing cinnamic acid (1 g) and methanol (5 mL) with different amounts of catalyst (5, 10, 15, and 20 wt %, with respect to acid) was heated at 70°C for 24 h (Table I, entries 6–9). The ester was obtained in quantitative yield when the reaction was conducted with 20 wt % of the catalyst. Comparatively fewer yields (i.e., 80, 72, and 52%) were obtained when the amount of catalyst used was 15, 10, and 5%, respectively. The esterification reaction of cinnamic acid (1 g) was carried out with different amounts of methanol (3, 4, and 5 mL) for 24 h using 20 wt % of catalyst to find the minimum amount of methanol required to obtain ester in good yield (Table I, entries 10–12). The ester

was obtained in quantitative yield when the amount of methanol used was 5 mL; the yield of the ester declined with a reduction in the amount of methanol used. The reaction temperature showed a marked effect on the yield of the ester when the reaction was performed with cinnamic acid (1 g), methanol (5 mL), and 20 wt % of the catalyst at different temperatures (30, 50, 70°C). The ester was obtained in quantitative yield when the reaction was carried out at 70°C (Table I, entries 13–15).

The above results show that the ester in quantitative yield can be obtained with the use of cinnamic acid (1 g), methanol (5 mL), polyaniline salt (20 wt % with respect to acid), temperature (70°C), and time (24 h).

The catalytic activities of the various polyaniline salts were explored by using the polyaniline salts prepared by two different methods. The esterification reaction of cinnamic acid (1 g) with methanol (5 mL) at 70°C for 24 h was carried out using 20 wt % of the polyaniline salt catalyst (Table II). Quantitative yield of the ester was obtained with the use of PANI-H<sub>2</sub>SO<sub>4</sub> prepared by both methods. However, lower yields were obtained with the use of PANI-HCl (50%) and PANI-HNO<sub>3</sub> (60%) catalysts. No marked difference in the yield of the ester was observed with (1) the use of polyaniline salts prepared by either method and (2) with particle size (benzoyl peroxide, 17 μm; ammonium persulfate, 120 μm).

The yield of the polyaniline salt was calculated on the basis of the amount of aniline used in the reaction. Generally, the yield of the polyaniline salts was found to be higher with ammonium persulfate oxidizing agent compared to that of benzoyl peroxide (Table II). However, yield of the ester was found to be independent of the oxidizing agents used.

Polyaniline salts were dedoped to polyaniline bases by taking a known amount of polyaniline salt in 1N

**TABLE II**  
Yield of Methyl Cinnamate Using Different Polyaniline Salts<sup>a</sup>

Method	Polyaniline salt	Yield of polyaniline salt (%)	Dopant (%)	Yield of ester (%)
I	PANI-HCl	80.9	40	50
	PANI-H <sub>2</sub> SO <sub>4</sub>	82.1	30	99
	PANI-HNO <sub>3</sub>	87.4	29	60
II	PANI-HCl	83.4	16	48
	PANI-H <sub>2</sub> SO <sub>4</sub>	90.6	25	99
	PANI-HNO <sub>3</sub>	89.1	27	58

<sup>a</sup> Yield of polyaniline salts and amount of dopant present in the polyaniline salt were taken from Palaniappan et al.<sup>16</sup> for method I and Palaniappan and Narayana<sup>17</sup> for method II.

aqueous sodium hydroxide solution. The solution was kept for 12 h, after which the solution was filtered and washed with water; the product was dried at 100°C until achieving a constant mass. The amount of acid present in the polyaniline salt was calculated based on the weight of polyaniline salt and its base.

No direct correlation was observed between the yield of the ester and the amount of acid present in the polyaniline salt (Table II), which is evident from the following results:

1. Amount of acid dopant present in the polyaniline salts (H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) prepared by Method I was found to be nearly the same (~ 30 wt %). However, the ester was obtained in quantitative yield with the use of PANI-H<sub>2</sub>SO<sub>4</sub> and lower yield was observed with the use of PANI-HNO<sub>3</sub>.
2. Quantitative yield of the ester was obtained with PANI-H<sub>2</sub>SO<sub>4</sub> (Method I), which contains 30 wt % of H<sub>2</sub>SO<sub>4</sub> group, whereas PANI-HCl gave lower yield (50%), which contains a greater amount of HCl groups (40 wt %).
3. Yield of the ester was found to be independent of the oxidizing agents used, whereas the amount of HCl present in the PANI-HCl was found to be 40 and 16 wt % with the use of benzoyl peroxide and ammonium persulfate, respectively.

The esterification of cinnamic acid with various alcohols was examined and the results are given in Table III. The esterification of cinnamic acid (1 g) and alcohol (5 mL) was carried out with 20 wt % of PANI-H<sub>2</sub>SO<sub>4</sub> catalyst. The reaction mixture was refluxed at 70°C for 24 h. The yield of the ester was found to decrease in going from primary to secondary and tertiary alcohols, which is in accordance with the reactivity of the alcohols.

Polyaniline-supported acid catalysts such as PANI-H<sub>2</sub>SO<sub>4</sub>, PANI-HCl, and PANI-HNO<sub>3</sub> exhibited surface areas of 42, 35, and 40 m<sup>2</sup> g<sup>-1</sup>, respectively. Such surface area values must imply the existence of micro-

porosity in which the size of pores is of a molecular level. These results are in accordance with the surface area of the polyaniline-supported system reported in the literature.<sup>24</sup> Dopants in the polyaniline salt such as hydrochloric, sulfuric, or nitric acid present in the polyaniline chain take part in the esterification reaction.

Reusability of the catalyst was verified by the esterification of cinnamic acid with methanol catalyzed by PANI-H<sub>2</sub>SO<sub>4</sub>. The reaction was carried out with cinnamic acid (1 g), methanol (5 mL), and recovered PANI-H<sub>2</sub>SO<sub>4</sub> (20 wt %) catalyst at 70°C for 24 h. The ester was obtained in good yield. The experiment was repeated five times with the same filtered and washed catalyst. In all cases, the yield of the ester was found to be good (96–98%). After the recyclability experiment, the catalyst was analyzed by infrared, electronic absorption, and particle size analysis and similar results for the catalyst were obtained before and after the esterification reaction. These results indicate that there is only a negligible change in the activity of the catalyst.

## CONCLUSIONS

Polyaniline salts were used as catalysts in the esterification of cinnamic acid with alcohols. Polyaniline-sulfate salt was found to be a better catalyst. The method of preparation of the polyaniline salt has no significant effect on the yield of the ester. Preparation

**TABLE III**  
Esterification of Cinnamic Acid with Different Alcohols<sup>a</sup>

Alcohol	Yield (%)
Methanol	99
Ethanol	95
Propanol	90
Butanol	91
Isopropanol	14
Tertiary butanol	5

<sup>a</sup> The authenticity of the product was established by <sup>1</sup>H-NMR.

of polyaniline salt catalyst is by a straightforward synthetic route and the catalyst can be handled easily. The catalyst can be separated from the reaction mixture by a simple filtration process and can be reused.

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