



# Benzoyl peroxide oxidation route to polyaniline salt and its use as catalyst in the esterification reaction

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## Abstract

Aniline was oxidized to polyaniline salt using benzoyl peroxide as an oxidizing agent in the presence of sulfuric acid and sodium lauryl sulfate surfactant. The polymer sample was characterized using infrared, X-ray diffraction, particle size, resistance and density measurements. Polyaniline salt was used as catalyst for the esterification reaction of carboxylic acids with methanol. The process is being reported for the first time. Preparation of catalyst, recovery and reusability of the catalyst are found to be good.

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## 1. Introduction

In view of environmental mandate, there is a global effort to replace the conventional catalysts by eco-friendly catalysts. Esterification is one of the most fundamental and important reactions in organic synthesis [1–3] (references cited therein).

Recently, extensive research work is being carried out in esterification of acid with alcohol using catalysts such as enzyme [4], ceric ammonium nitrate [5], ruthenium salt [6], titanium salt [7], heteropolyacids [8], triphenyl phosphene-carbon tetrabromide [9], solid acid catalyst [10], hydrated ferrous sulfate [11], scandium triflate-dimethylaminopyridine [12], and sodium hydrogen sulfate-silica [13], etc.

Electrically conducting organic polymers are a new class of 'synthetic metals' that combine the chemi-

cal and mechanical attributes of polymers with the electronic properties of metals and semiconductors. Among them, polyaniline is one of the most interesting material because of its moderately high conductivity upon doping with acids, well behaved electrochemistry, easy preparation, possible processability and good environmental stability [14].

In chemical polymerization method, the synthesis of polyaniline was commonly performed by chemical oxidative (mostly using ammonium persulfate as an oxidizing agent) polymerization of aniline using protonic acids, viz. aqueous polymerization pathway [15,16]. Pron et al. [17] have compared the use of different oxidizing agents, such as ammonium persulfate, potassium dichromate, hydrogen peroxide and potassium iodate. Materials synthesized by this approach were predominately amorphous, intractable, and insoluble in most organic solvents [18].

Several investigators have developed methods to improve the processability of polyaniline by a post processing step, i.e. converting the salt to emeraldine

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base and reprotonating the emeraldine base with another protonic acid. Tzou and Gregory [19] used this approach and reported that polyaniline salts containing carboxyl and amino substituents were soluble in *N*-methyl pyrrolidone and dimethyl sulfoxide. Cao et al. [20] reported the same method to prepare polyaniline salts on a number of protonic acids including 4-dodecylbenzenesulfonic acid and dinonylnaphthalenesulfonic acid. The polyaniline salts thus produced were reported to be soluble in non-polar solvents, however, the solubility was low. Emulsion polymerization process for preparing a polyaniline salt of a protonic acid has been reported [21], wherein, protonic acid acts as dopant. Smith and coworkers [22] reported that polymerization of aniline in an emulsion of water and a non-polar or weakly polar organic solvent. This polymerization was carried out in the presence of functionalized protonic acid such as dodecylbenzenesulfonic acid, which simultaneously acts as a surfactant and protonating agent.

In this work, polyaniline salt was prepared by benzoyl peroxide and to the best of our knowledge, this is the first report that aniline was polymerized to polyaniline salt using benzoyl peroxide as an oxidizing agent. The polyaniline salt was used as catalyst in the esterification reaction of mono-carboxylic acids with methanol.

## 2. Experimental

### 2.1. Instrumentation

Fourier-transform infrared spectrum of the polymer sample was recorded using a Bomem MB 100 FT-IR spectrometer in the range 400–4000  $\text{cm}^{-1}$ . The KBr pellet technique was used for recording the infrared spectrum.

Electronic absorption spectrum of the sample was recorded at ambient temperature on a GBC cintra 10e UV/V spectrophotometer. Solution for the absorption spectrum of polyaniline base was prepared by dissolving the samples in *N*-methyl pyrrolidone (NMP) and filtering through Whatman 41 filter paper. Absorption spectrum of the dilute solution were recorded in the range 300–1000 nm using a pair of matched 3 ml stoppered silica cells of 10 mm path length.

X-ray diffraction spectrum of the polymer sample was recorded using D5000 Siemens equipment.

Particle size measurement of the polymer powder was determined using Malvern Mastersizer 2000 by dispersing polymer powder in distilled water.

The percentage of carbon, hydrogen, nitrogen and sulfur in the polyaniline sample was estimated using Elementar Vario EL analyzer.

Resistance measurement of the sample was measured at room temperature using the four probe method on pressed pellet. The pellet was obtained, by subjecting the polymer sample to a pressure of 400 MPa. Resistance measurement was carried out using Keithley Model 220 programmable current source and Keithley Model 195A digital voltmeter. The reproducibility of the result was checked by (i) measuring the resistance value thrice for each pellet, (ii) measuring the resistance for a batch of three pellet of each sample, (iii) measuring the length and area five times. Since the mean value were used in the calculation of resistance, the total error involved is <3%.

Polymer 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.

### 2.2. Materials

Reagent grade aniline from Merck was vacuum distilled under nitrogen prior to use. Benzoyl peroxide (BDH, India) was recrystallized from chloroform/methanol. Analar grade methanol (SD fine chemical, India) was purified by distillation. Analar grade reagents such as sulfuric acid (BDH, India), sodium lauryl sulfate (BDH, India), acids (BDH, India), dioxane (BDH, India) and all other reagents were used as received.

### 2.3. Preparation of polyaniline salt

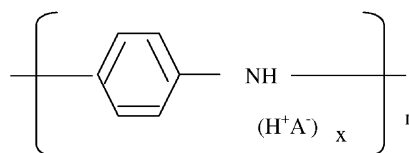
4.85 g of benzoyl peroxide was dissolved in 150 ml dioxane. To this solution, 1.44 g of sodium lauryl sulfate in 25 ml distilled water was added. 2.4 ml aniline in 30 ml aqueous solution containing sulfuric acid (9.0 ml) was introduced dropwise into the above solution at 35 °C. The mixture was stirred for 24 h at 35 °C and the precipitated polyaniline salt was recovered from the polymerization vessel, filtered, and

then washed with 3 l of distilled water and followed by methanol. The resulting polymer salt was finally dried at 100 °C until a constant mass was reached. Yield of the polyaniline salt: 1.43 g.

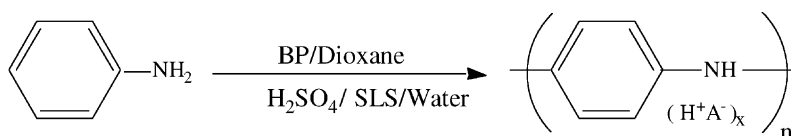
#### 2.4. Procedure for esterification

Esterification of lauric acid (1 g) and methanol (4 ml) was carried out in 10 ml round bottom flask with polyaniline salt (200 mg) powder. The reaction mixture was refluxed at 70 °C for 24 h. The reaction mixture was filtered and washed with chloroform to recover the catalyst. The chloroform solvent and unreacted methanol were evaporated off. The compound was loaded a column containing silica gel of finer than 200 mesh and eluted with 20:80 chloroform and hexane mixture (400 ml). The solvent mixture was recovered to get the pure ester. The details of the experimental conditions are given in tables.

i.e.  $(1 - y) = 0.5$ , is of special importance and is termed the emeraldine oxidation state or the emeraldine base. Pristine and partially oxidized leucoemeraldine and emeraldine base is shown to be an alternating copolymer of reduced and oxidized repeat units. The value of  $y$  varies from 0 to 1, but the percentages of carbon, hydrogen and nitrogen will be almost the same. Taking the above points into consideration, the following formula of polyaniline salt is considered for simplicity:

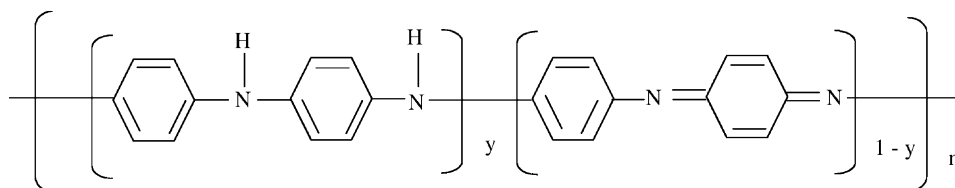


Polyaniline salt was prepared by chemical oxidative polymerization of aniline using benzoyl peroxide as an oxidizing agent in presence of sulfuric acid and sodium lauryl sulfate surfactant:



### 3. Results and discussion

The structure of polyaniline is known as *para*-linked phenylene amineimine. The base form of polyaniline can, in principle, be described by the following general formula:



In the generalized base form,  $(1 - y)$  measures the function of oxidized units. When  $(1 - y) = 0$ , the polymer has no such oxidized groups and is commonly known as a leucoemeraldine base. The fully oxidized form,  $(1 - y) = 1$  is referred to as a pernigraniline base. The half-oxidized polymer, where the number of reduced units and oxidized units are equal,

#### 3.1. Yield, conductivity, density and surface area

The yield of the polyaniline salt (58.4%) was calculated based on the amount of aniline used in the reaction. The value of conductivity and density of the polyaniline salt are found to be 0.04 S/cm and 1.26 g/cm<sup>3</sup>, respectively (Table 1). The surface area

of polyaniline salt was found to be very less (42 m<sup>2</sup>/g). The polyaniline salt was dedoped to polyaniline base using aqueous potassium hydroxide solution. Known amount of the polyaniline salt was added in to 0.5 M aqueous potassium hydroxide solution and stirred over night. Filtered the solution, washed with potassium hydroxide solution, water and finally with acetone.

Table 1  
Properties of polyaniline salt sample as prepared and after subjecting esterification reaction

Properties	Polyaniline salt	
	As prepared	After subjecting esterification
Amount of acid (%)	28.0	27.6
Density (g/cm <sup>3</sup> )	1.26	1.23
Particle size (μm)	0.3–300	0.2–285
Conductivity (S/cm)	0.04	0.02

The sample was dried at 100 °C till a constant mass. The amount of acid group present in the polyaniline salt was calculated from the weight of the polyaniline salt and polyaniline base and it was found to be 28%.

### 3.2. Infrared spectra

The infrared spectrum of polyaniline salt is shown in Fig. 1. The vibrational bands observed for the polyaniline salt are reasonably explained on the basis of the normal modes of polyaniline; a band at 3270–3400 cm<sup>-1</sup> assigned to the NH stretching vibration of  $-\text{C}_6\text{H}_4\text{NHC}_6\text{H}_4-$  group. The 2935 cm<sup>-1</sup> is assigned to vibration associated with the NH<sub>2</sub><sup>+</sup> part

in  $-\text{C}_6\text{H}_4\text{NH}_2^+\text{C}_6\text{H}_6-$  group. 1585 and 1490 cm<sup>-1</sup> bands to benzene and or quinone ring deformations, a 1315 cm<sup>-1</sup> band to the CN stretch of a secondary aromatic amine, and a 820 cm<sup>-1</sup> band to an aromatic CH out-of-plane bending. In the region of 1015–1175 cm<sup>-1</sup>, aromatic CH in-plane-bending modes are usually observed. For polyaniline, a strong band characteristically appears at 1150 cm<sup>-1</sup>, which has been explained as an electronic band or a vibrational band of nitrogen quinone. The CH out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. For the polymer salt, this mode was observed as a single band at 820 cm<sup>-1</sup>, which fell in the range 800–860 cm<sup>-1</sup> reported for a 1,4-substituted benzene. A similar observation was observed for the polyaniline salt prepared using ammonium persulfate as an oxidizing agent [16].

### 3.3. Electronic absorption spectra

The electronic absorption spectra of polyaniline base and polyaniline salt have been reported in the literature [14,16,23]. The electronic absorption spectrum of freshly prepared leucoeraldine in NMP reveals a strong band at 345 nm due to  $\pi-\pi^*$  transition

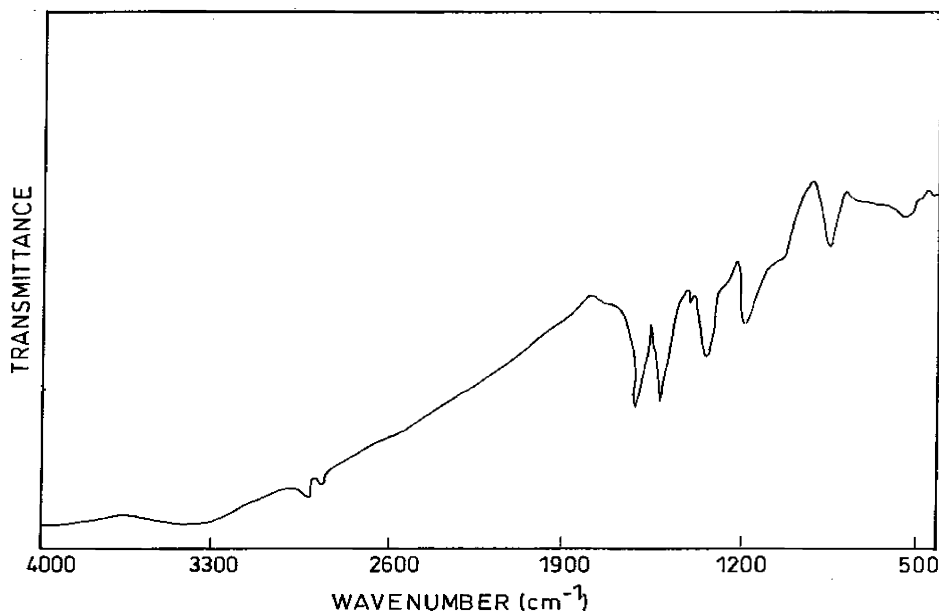


Fig. 1. Infrared spectrum of polyaniline salt.

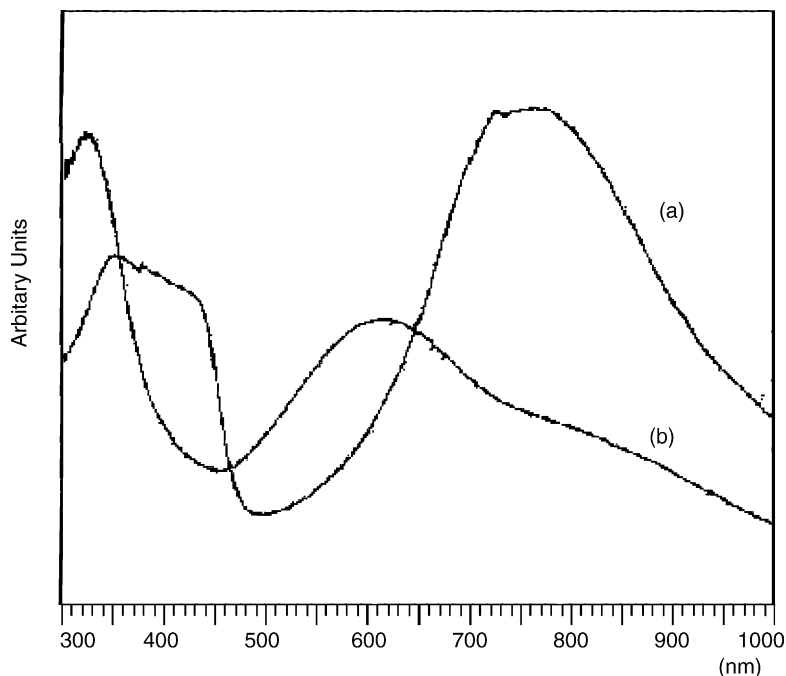


Fig. 2. Electronic absorption spectra of (a) polyaniline salt and (b) polyaniline base.

and very weak absorption at 635 nm due to very small fraction of quinoid ring. Fully oxidized pernigraniline base in dimethyl formamide solution showed three bands at 280, 320 and 530 nm. Absorption spectrum of emeraldine base shows two distinct absorption bands located between 315–345 and 590–650 nm depending on the method of preparation and/or processing of polyaniline. The band around 315–345 nm may be assigned to  $\pi$ - $\pi^*$  transition and the band around 590–650 nm is due to the excitation of the imine segment of the polymer chain. Polyaniline salt (emeraldine salt) obtained from the base by treatment with acid showed three absorption bands at 325–360, 400–430 and 780–825 nm.

Polyaniline sulfate salt prepared in the present work was not soluble in most of the organic solvents. Electronic absorption spectrum of the salt in dilute sulfuric acid medium was recorded using sulfuric acid as reference and are shown in Fig. 2a. The electronic absorption spectrum showed two bands one band around 360 nm, another broad band around 760 nm and one hump around 430 nm and this result indicates the presence of emeraldine salt.

Polyaniline base was soluble in NMP solvent and the electronic absorption spectrum of the NMP solution of polyaniline base is shown in Fig. 2b and it showed a band around 325 nm and another broad band around 625 nm. This is consistent with literature reports of emeraldine base.

The electronic absorption spectral results indicate the formation of emeraldine base and emeraldine salt type of polyaniline.

### 3.4. X-ray diffraction spectra

X-ray diffraction pattern of polyaniline salt powder is shown in Fig. 3. It showed two peaks at around 20 and 25° angle and this is similar with the reported value in the literature [14] (references cited therein).

### 3.5. Particle size analysis

Particle size distribution of the polyaniline salt powder is shown in Fig. 4 and the particle size of the polyaniline salt was found to be in the range 0.3–300  $\mu\text{m}$ .

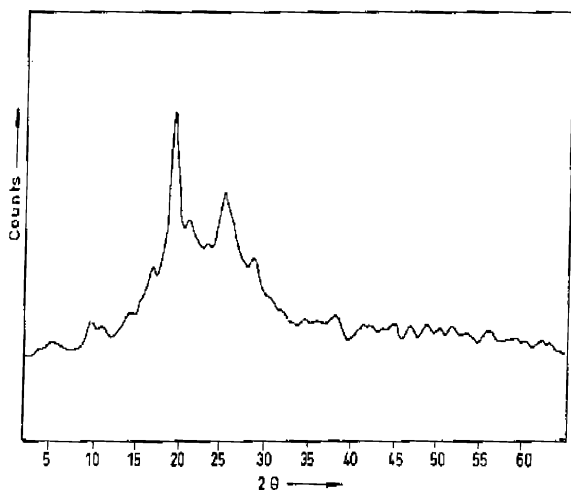


Fig. 3. X-ray diffraction pattern of polyaniline salt.

### 3.6. Elemental analysis

The elemental analyses of polyaniline base, polyaniline salt and the polyaniline salt prepared without using SLS are given in Table 2. The percentage of carbon, hydrogen and nitrogen of polyaniline base is found to be nearly the same to that of the theoretically calculated value. This result shows that the formation of polyaniline base and all the acid part has been removed from the salt by dedoping. The sulfur content of the polyaniline sulfate salt (due to the presence of  $\text{H}_2\text{SO}_4$  dopant.) prepared without

Table 2

Elemental analysis result of polyaniline base, polyaniline salt prepared with and without SLS

Polyaniline	C (%)	H (%)	N (%)	S (%)
Polyaniline base	78.4	5.3	15.1	
Polyaniline base (theoretical)	79.1	5.5	15.5	
Polyaniline sulfate (without using SLS)	58.9	4.3	11.5	3.2
Polyaniline sulfate (using SLS)	52.9	3.1	10.4	7.3

using SLS was found to be 3.2%. The value of sulfur content increased from 3.2 to 7.3% in the case of polyaniline salt prepared using SLS and this result indicates that both SLS and  $\text{H}_2\text{SO}_4$  dopants are present in the polyaniline salt. From the present study, it is difficult to calculate the amount of SLS or  $\text{H}_2\text{SO}_4$  dopant present in the polyaniline salt.

The results of the above analyses show that polyaniline salt (emeraldine salt) can be prepared by oxidizing aniline using benzoyl peroxide. This polyaniline salt was used in the esterification reaction and the results are presented here.

### 3.7. Esterification of acid with methanol

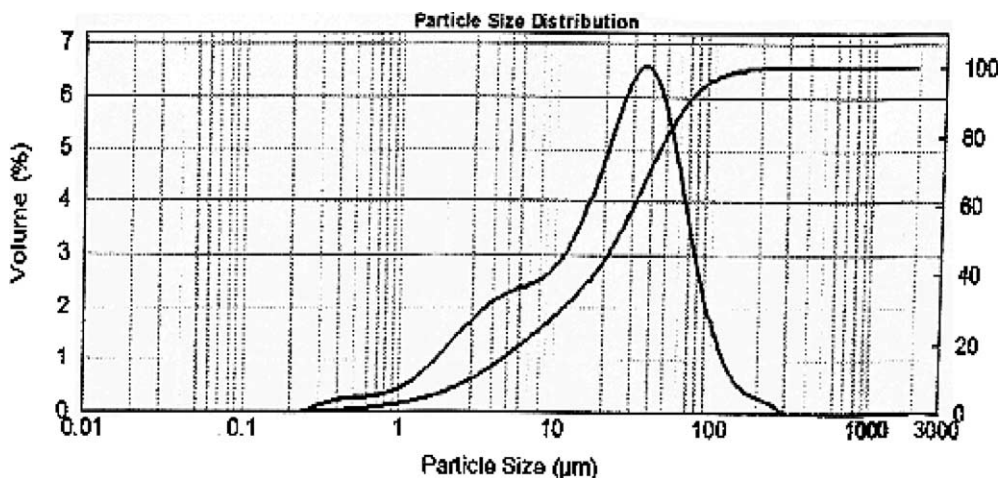
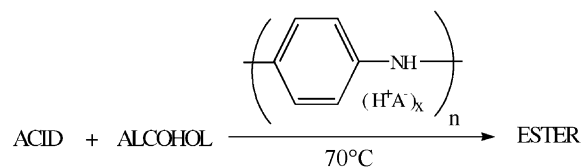


Fig. 4. Particle size distribution of polyaniline salt.

Table 3  
Esterification of lauric acid with methanol using polyaniline salt catalyst<sup>a</sup>

Entry	Amount of catalyst (mg)	Time (h)	Isolated yield (%)
1	100	4	Nil
2	100	8	5
3	100	12	25
4	100	16	44
5	100	20	85
6	100	24	94
7	200	4	Nil
8	200	8	63
9	200	12	80
10	200	16	87
11	200	20	98
12	200	24	98
13	300	24	98
14	150	24	98

<sup>a</sup> Reaction condition: acid (1 g), methanol (4 ml), polyaniline salt (varied), temperature (70 °C), time (h) (varied).

Esterification of lauric acid (1 g) with methanol (4 ml) was carried out using polyaniline salt (200 mg) for 24 h at three different temperatures (30, 50 and 70 °C). At 30 °C product was not obtained, 41% yield was observed at 50 and 70 °C, the reaction gave the ester in quantitative yield (99%).

The esterification reaction was carried out with different amounts of catalyst (Table 3). Use of 100 mg of catalyst, the yield increased with time and attained a maximum, i.e. 94% with 24 h (entries 1–6). Similarly, yield increased with time and attained a quantitative yield within 20 h (entries 7 to 12) with the use of 200 mg of catalyst. Quantitative yield was obtained with 300 mg (entry 13) and 150 mg (entry 14) of catalyst.

Reusability of the catalyst was checked by the esterification of lauric acid (1 g) with methanol (4 ml) catalyzed by 200 mg of polyaniline salt resulted stoichiometric quantity (98%). The experiment was repeated six times with the same filtered catalyst and it gave the corresponding ester in same yield (96–98%). After the seventh trial, the catalyst was recovered and characterized by infrared, X-ray diffraction, amount of acid present in the polymer, particle size and density measurements. A similar infrared and X-ray diffraction patterns was observed for the polyaniline salt as prepared and the sample subjected after esterification

Table 4  
Direct esterification of carboxylic acids with methanol catalyzed by polyaniline salt<sup>a</sup>

Carboxylic acid	Yield of the product (%) <sup>b</sup>
Lauric acid	99.1
Caproic acid	98.6
Stearic acid	99.0
Cinnamic acid	98.5
Phenyl acetic acid	69.3

<sup>a</sup> Reaction condition: acid (1 g), methanol (4 ml), polyaniline salt (200 mg), temperature (70 °C), time (24 h).

<sup>b</sup> The products were analyzed by <sup>1</sup>H NMR spectra and authenticity of the products was established.

reaction. Similarly, the value of the amount of acid group, particle size, density and conductivity for the polyaniline salt samples (before and after esterification reaction) are almost the same (Table 1).

To explore the generality and scope of the polyaniline salt catalyzed in the esterification reaction, we examined the reaction of carboxylic acids with methanol and the results are reported in Table 4. The esters of aliphatic carboxylic acids with methanol gave quantitative yields.  $\alpha$ -Substituted acid (phenyl acetic acid) gave the ester in low yield (69%).

Generally, esterification reaction has been carried out by Lewis acid, *p*-toluene sulfonic acid, solid acid catalyst, etc., as catalyst. In this work, polyaniline salt was tried out as polymer supported catalyst. Sulfuric acid present in the polymer chain takes part in the esterification reaction. The mechanism of the reaction would be similar to pyridinium *p*-toluenesulfonate promoted esterification reaction.

For comparison, the esterification reaction was carried out using commercially available Amberlyst IR 15 catalyst and polyaniline salt catalyst. Quantitative yield of the ester was obtained in 6 h with Amberlyst IR 15 and the esterification reaction takes a longer time (24 h) with polyaniline sulfate salt. Work is in progress to modify the polyaniline salt system and thereby increase the efficiency of the catalyst.

#### 4. Conclusion

Polyaniline salt can be prepared using benzoyl peroxide as an oxidizing agent. Polyaniline salt was used as catalyst in the direct esterification of carboxylic

acids with methanol. Ester was obtained in quantitative yield with use of 150 mg of polyaniline salt for 24 h at 70 °C. The use of polyaniline salt as catalyst may be quite practical because of its easy preparation, recovery, reusability, activity, toxicity of the catalyst. The advantages of the catalyst are (i) preparation of the polyaniline salts through a simple synthetic route (ii) quick regeneration of the catalyst and (iii) better reusability of the catalyst. However, the esterification reaction takes a longer time (24 h) and also require (15 wt.%) to obtain the ester in quantitative yield. Work is in progress to modify the polyaniline salt system and thereby increase the efficiency of the catalyst.

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