



Synthesis of 7-hydroxy-4-methyl coumarin using polyaniline supported acid catalyst

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Abstract

Polyaniline-sulfate salts were prepared using four different oxidizing agents such as benzoyl peroxide, ammonium persulfate, sodium persulfate and potassium dichromate. Polyaniline-sulfate salts were characterized by spectral, physical and electrical methods. Polyaniline base was redoped to different polyaniline salts using various acids. Polyaniline salts are used as polymer supported acid catalysts for the preparation of 7-hydroxy-4-methyl coumarin. The efficiency of the catalyst may depend upon the amount of acid present on the polymer chain and also the strength of the acid used. The catalytic use of polyaniline salts is feasible because of their easy preparation, stability, easy handling, less toxic, recovery, reusability and eco-friendly.

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1. Introduction

Coumarins are an important group of naturally occurring compounds widely distributed in the plant kingdom and has been produced synthetically for many years for commercial uses [1]. Members of this group display a broad range of applications, as fragrances, pharmaceuticals, additives to food, cosmetics, agrochemicals, optical brightening agents, dispersed fluorescent, tunable dye lasers, biological activities like anthelmintic, hypnotic, insecticidal and anticoagulant properties.

Coumarin and some of its derivatives have been identified in plants and many of them have been synthesized and studied for their physiological activity. 7-Hydroxy-4-methyl coumarin (β -methylumbelliferone) is used as fluorescent brightener, efficient laser dye for pulsed and SW operation, standard for fluorometric determination of enzymatic activity, as a starting material for the preparation of an insecticide (hymerocromone), as precursor for furano coumarins and many other derivatives of substituted coumarins and analytical reagents.

Coumarin and its derivatives can be synthesized by various methods, which include Perkin reaction [2], Knoevenagel reaction [3], Wittig reaction [4], Pechmann reaction [5], and Reformatsky reaction. Among these reactions, Pechmann reaction is the most widely used method for the preparation of substituted coumarins since it proceeds from very simple starting materials and gives good yields of various substituted coumarins. Substituted coumarins can be prepared by using various reagents such as H_2SO_4 , $POCl_3$ [6], $AlCl_3$ [7], Cation exchange resins, trifluoro acetic acid [8], Montmorillonite clay [9], solid acid catalysts [10], W/ZrO₂ solid acid catalyst [11], Chloroaluminate ionic liquid [12] and Nafion-H catalyst [13].

Usually, these reactions occur by electrophilic substitution reaction and generally employ non-regenerable catalysts such as acids (H_2SO_4 , $POCl_3$, trifluoro acetic acid, *p*-toluene sulfonic acid), metal chlorides ($AlCl_3$), chloroaluminate ionic liquids, also these catalysts should be used in excess and lead to increasing environmental pollution. Replacement of acids by solid acid catalyst such as zeolite, clay, sulfonic acid resin would result in simplified product recovery and reduction in undesirable waste streams. Solid acid catalysts are highly susceptible to deactivation due to pore blocking and hydration. Cation exchange resins are not resistant enough to high temperature (>120 °C).

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In a method of replacing the conventional catalysts with eco-friendly catalysts, in this work, polyaniline supported acid catalysts are used in the preparation of 7-hydroxy-4-methyl coumarin by Pechman reaction.

The advantages of using polyaniline supported acid catalysts are (i) straight forward synthetic route and can be prepared in larger quantities easily, (ii) good stability, (iii) easy recovery, (iv) easy handling, (v) good activity, (vi) does not lose its activity during thermal and recyclable treatments, and (vii) eco-friendly.

2. Experimental

2.1. Materials

Aniline (reagent-grade) from E. Merck was distilled prior to use. Reagent-grade sodium lauryl sulfate, ammonium persulfate, sodium persulfate, potassium dichromate, methyl acetoacetate, ethyl acetoacetate, resorcinol, acids, solvents (BDH, India) was used without further purification. Reagent-grade benzoyl peroxide (BDH, India) was recrystallized from chloroform/methanol system.

2.2. Preparation of polyaniline supported acid catalysts

2.2.1. Preparation of polyaniline-sulfate salt using benzoyl peroxide [14]

An amount of 4.85 g of benzoyl peroxide was dissolved in 150 ml acetone taken in round bottomed flask. 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 drop wise into the above solution at 35 °C for 8 h under constant stirring. The precipitated polyaniline salt was filtered off, and then washed with 3 l of distilled water, followed by methanol. The resulting polymer salt was finally dried at 100 °C until a constant mass was reached.

2.2.2. Preparation of polyaniline-sulfate salt using different oxidizing agents [15]

In a typical experiment, aqueous solution of 0.1 M oxidizing agent (ammonium persulfate, potassium dichromate or sodium persulfate) was added very slowly into 1.0 N H₂SO₄ solution containing 0.1 M aniline at a temperature of 0–5 °C. After all the oxidant was added, the reaction mixture was left stirring at constant temperature for 4 h. The oxidation of aniline is highly exothermic and, therefore, 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, filtered and then washed with distilled water until the washing liquid was colorless. In order 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 with

acetone and subsequently dried at 100 °C till a constant mass.

2.2.3. Preparation of redoped polyaniline salts

Polyaniline base was prepared by dedoping the polyaniline-sulfate salt. Polyaniline-sulfate salt (10 g) prepared by the procedure given in Section 2.2.1 was constantly stirred at ambient temperature in 1 l sodium hydroxide solution (0.1N) for 12 h, filtered, washed with water, followed by acetone and finally dried at 100 °C till a constant mass.

Redoped polyaniline salts were obtained by doping of the polyaniline base with 1.0 M acid solution such as sulfuric acid, hydrochloric acid, nitric acid, perchloric acid, sodium bisulfate, *p*-toluene sulfonic acid or 5-sulfosalicylic acid. The dedoped polyaniline (0.5 g) was constantly stirred in 50 ml acid solution (1 M) at ambient temperature for 12 h. The polyaniline powder was filtered, washed with distilled water and finally with acetone. The resulting polyaniline salt was dried at 100 °C till a constant mass.

2.3. Characterization of polyaniline supported acid catalyst

2.3.1. Resistance measurement

Polyaniline samples were pressed into disks of 8 mm-diameter and ca. 2 mm-thickness under a pressure of 400 MPa. Resistance measurement of the pellets was carried out on a two probe connected to a Keithley constant current source (Model 230) and digital voltmeter (Model 195A). Resistance was calculated based on the average of at least three pairs of consistent readings at different points on the pressed pellet. Since, the mean value was used in the calculation of resistance, the total error involved is <1%.

2.3.2. Pellet density

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.

2.3.3. Amount of dopant (acid group)

Amount of acid group present in the polyaniline chain was calculated based on the weight of polyaniline base obtained after dedoping the known weight of the polyaniline salt.

2.3.4. Particle size analysis

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

2.4. Spectral characterization

2.4.1. Infrared spectra

The polyaniline sample was mixed with KBr powder and compressed into pellet, wherein, the polyaniline powder was evenly dispersed. Fourier transform infrared spectra were

recorded using GC–FTIR spectrometer (Model 740 Nicolet, USA).

2.4.2. Electronic absorption spectra

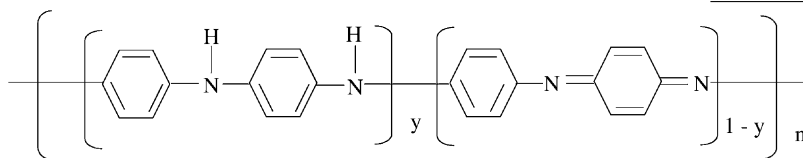
Electronic absorption spectrum of the polyaniline sample was recorded at ambient temperature using GBC cintra 10e UV/V spectrophotometer. The solution for the absorption spectrum of polyaniline base was prepared by dissolving the samples in dimethyl sulfoxide (DMSO) and filtered through Whatman 41 filter paper. 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.

2.5. Procedure for preparation of 7-hydroxy-4-methyl coumarin

In a typical experiment, resorcinol (1 g, 9 mmol) was taken in 10 ml round bottom flask and added ethylacetoacetate (2.36 g, 18 mmol) followed by 200 mg of polyaniline-sulfate salt catalyst powder (20 wt.% with respect to resorcinol). Polyaniline salt was heated at 100 °C for 2 h and used in the reaction. The reaction mixture was heated at 150 °C for 6 h. At the end of the reaction, the reaction mixture was washed with acetone, filtered and acetone was evaporated under vacuum. The product obtained was washed with water, filtered and dried at 100 °C. The product was purified by dissolving in 20 ml 1 M NaOH and then regenerated with 10 ml 2 M H₂SO₄ solution. The product was characterized by melting point and ¹H NMR spectrum.

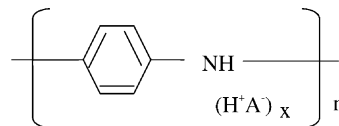
3. Results and discussion

Polyaniline has received wide interest due to its high potential in variety of applications as conducting polymer [16]. Polyanilines are particularly attractive based on their excellent electrical properties, easy preparation, possible processability and stability. 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, 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.



3.1. Characterization of polyaniline supported acid catalysts

Polyaniline-sulfate salt was prepared using four different oxidizing agents such as benzoyl peroxide, ammonium persulfate, sodium persulfate and potassium dichromate. Polyaniline-sulfate salts were characterized by spectral, physical and electrical methods and the results are presented here.

3.1.1. Infrared spectra

Generally, similar infrared spectral behavior was observed for the polyaniline bases prepared from their corresponding polyaniline salts. As a representative system, the infrared spectrum of polyaniline base [PANI-BASE (H₂SO₄)] is shown in Fig. 1b. 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 3420–3460 cm⁻¹ assigned to the N–H stretching vibration. The bands at 2920 and 2850 cm⁻¹ are assigned to vibration associated with the N–H part in C₆H₄NHC₆H₄ group or sum frequency. 1565 and 1480 cm⁻¹ bands due to quinonoid ring (Q) and or benzenoid ring (B). Bands at 1370 and 1300 cm⁻¹ assigned to C–N stretching vibration in QBQ and QBC, QBB, BBQ, a 1240 cm⁻¹ band to the C–N stretch vibration of aromatic amine. In the region of 1015–1175 cm⁻¹, aromatic C–H in-plane-bending modes are usually observed. For polyaniline, a strong band

characteristically appears at 1140 cm⁻¹, which has been explained as an electronic band or a vibrational band of nitrogen quinone. A band at 705 cm⁻¹ is assigned to ring C=C bending vibration and the band at 580 cm⁻¹ due 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 820 cm⁻¹, which fell in the range

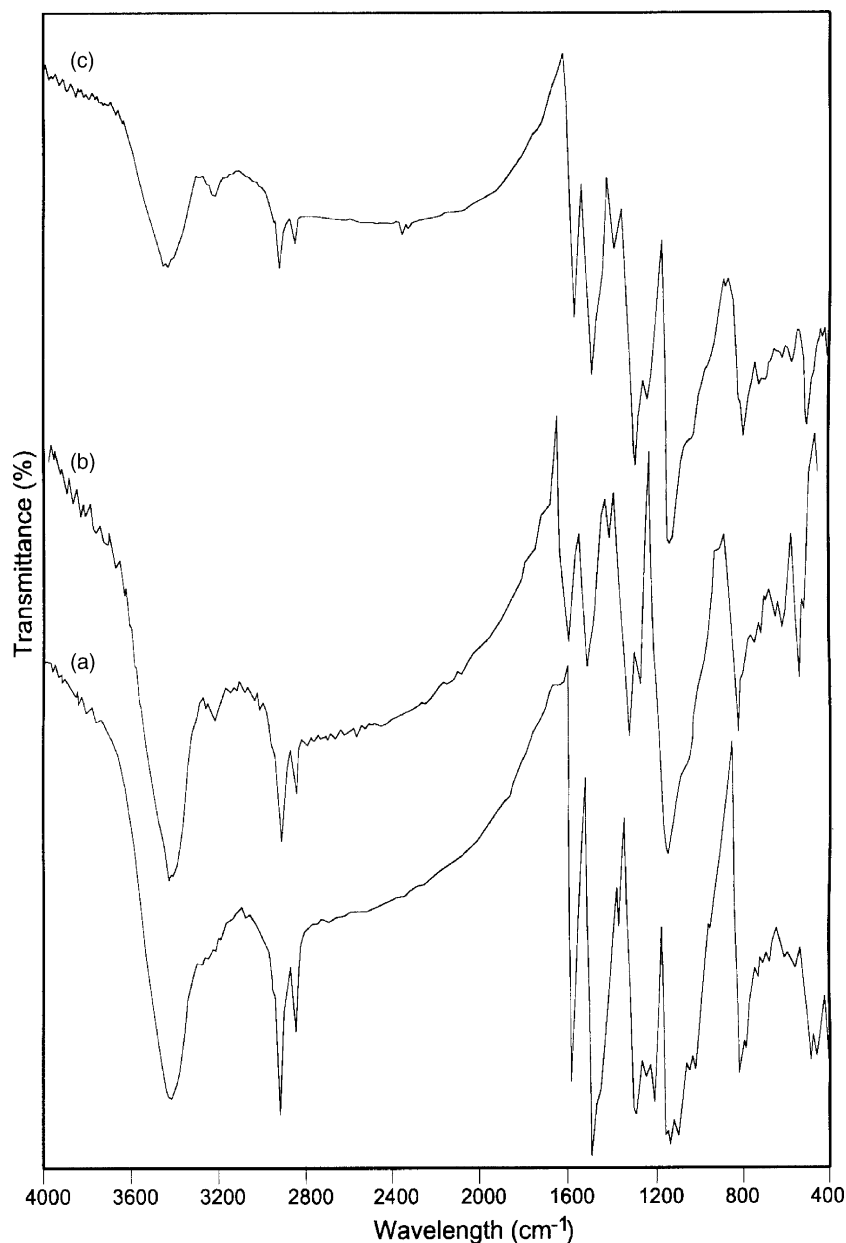


Fig. 1. Infrared spectra of (a) PANI-H₂SO₄, (b) PANI-BASE (H₂SO₄) and (c) PANI-RD-H₂SO₄.

800–860 cm⁻¹ reported for a 1,4-substituted benzene. The infrared spectra of polyaniline bases prepared are very close to the infrared spectrum of the polyaniline system reported in the literature [15,17–19].

A similar infrared spectral behavior was observed for the polyaniline salts prepared directly. As a representative system, the infrared spectrum of polyaniline salt (PANI-H₂SO₄) is shown in Fig. 1a. The infrared spectrum of PANI-H₂SO₄ is similar to that of the spectrum of PANI-BASE (H₂SO₄) except (i) a band around 3230 cm⁻¹ arises due to the NH₂⁺ group and this indicates the protonation of polyaniline base to polyaniline salt and (ii) the doublet band at 1140 and 1110 cm⁻¹ in the polyaniline base assigned to mode of Q = N⁺H–B or Q–NH–B becomes a singlet in the salt.

A similar infrared spectrum was observed for the redoped polyaniline salts from polyaniline base. As a representative system, the redoped (PANI-RD-H₂SO₄) is shown in Fig. 1c. Redoped polyaniline salt spectrum (Fig. 1c) is very similar to as prepared polyaniline salt spectrum (Fig. 1a). In comparison with polyaniline base, a band at 3230 cm⁻¹ is observed and the doublet became a singlet after doping the base using acid. This result supports the formation of polyaniline salt that on redoping from polyaniline base.

3.1.2. Electronic absorption spectra

The electronic absorption spectra of polyaniline base and polyaniline salt have been reported in the literature.

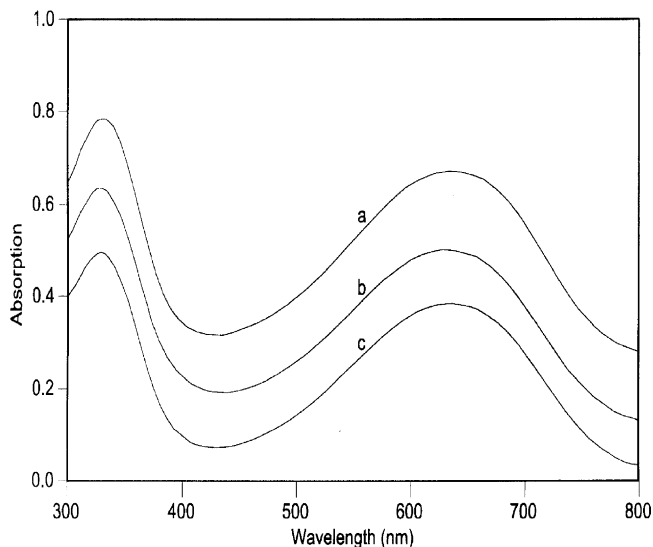


Fig. 2. (a) Electronic absorption spectra of (a) PANI-BASE (HCl), (b) PANI-BASE (H₂SO₄) and (c) PANI-BASE (HNO₃) recorded in DMSO.

Absorption spectrum of polyaniline base [20–22] 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 and the band around 590–650 nm may be assigned to the excitation of the amine and imine segment of the polymer chain. Fully protonated polyaniline in the salt form, the peak at 630 nm disappears except for an absorption at 325 nm, whereas a new peak at about 725 nm occurred. This new

peak is due to the polaron has been demonstrated [20,23–25].

Polyaniline salts prepared by four different methods are 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 broad band around 320–330 nm and another band around 620–650 nm. These two peaks are assigned to the excitation of the amine and imine segment of the polymer chain respectively and this is consistent with literature reports of polyaniline base.

3.1.3. Physical characterization

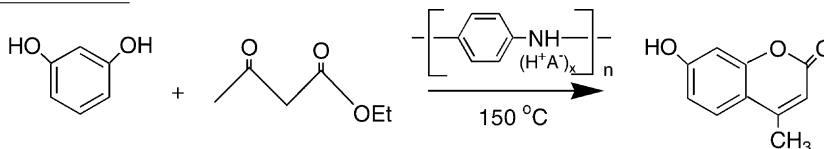
Yield of the polyaniline-sulfate salt (prepared by four different oxidizing agents) was calculated based on the amount of aniline used in the reaction. Yield of the polyaniline salt

was found to be nearly the same (99.7, 99.0 and 97.2%) with the use of ammonium persulfate, sodium persulfate, potassium dichromate and however, lower yield was obtained with the use of benzoyl peroxide (82%). Conductivity of the polyaniline salts decreased as 5, 0.5, 0.1 and 0.04 S/cm with ammonium persulfate, sodium persulfate, potassium dichromate and benzoyl peroxide respectively. Particle size of the polyaniline-sulfate salt prepared using benzoyl peroxide was found to be lower (45 μm) when compared with that of the salt prepared using ammonium persulfate, sodium persulfate and potassium dichromate (120–130 μm). Density of the polyaniline salts (1.15–1.22 g/cm³) was found to be independent of the oxidizing agents used. Amount of sulfuric acid present in the polyaniline-sulfate was found by de-doping method and 30, 25, 24 and 23 wt.% of sulfuric acid (dopant) was obtained with benzoyl peroxide, ammonium persulfate, sodium persulfate and potassium dichromate, respectively.

3.2. Synthesis of 7-hydroxy-4-methyl coumarin

We found that polyaniline-sulfate salt could be used for condensation reaction of resorcinol with ethyl acetoacetate without using any solvent. A background reaction was examined with resorcinol and ethyl acetoacetate in the absence of catalyst and no product was observed. The presence of polyaniline-sulfate salt (20 wt.% with respect to resorcinol) provided 72% yield of product.

7-Hydroxy-4-methyl coumarin was prepared using polyaniline supported acid catalyst and can be shown as



3.2.1. Effect of time, amount of catalyst, mole ratio and temperature on the yield

Preparation of 7-hydroxy-4-methyl coumarin was carried out with resorcinol (one equivalent) and ethyl acetoacetate (two equivalent) by varying the reaction time, catalyst amount (PANI-H₂SO₄ salt prepared using benzoyl peroxide), molar ratio and temperature of the reaction and the yield of the product is reported in Table 1. The preparation of 7-hydroxy-4-methyl coumarin was carried out by varying the reaction time between 6 and 24 h and maximum yield (72%) was obtained around 6 h (entries 1–4). The catalyst amount was varied as 10, 15, 20 and 30 wt.% catalyst with respect to resorcinol. 65% yield (entry 5) was obtained with the use of 10% catalyst and obtained 70–72% yield with the use of more than 15% catalyst (entries 6–8). The reaction was carried using different molar ratios of resorcinol: ethyl acetoacetate (1:1.0, 1:1.2, 1:1.5, 1:2.0 and 1:3.0). The yield increased as 41, 54, 62, 72 and 72% (entries 9–13) with increasing the amount

Table 1

Yield of 7-hydroxy-4-methyl coumarin carried out at different reaction time, molar ratio, catalyst concentration and temperatures

Entry	Time (h)	Catalyst (mg) PANI-H ₂ SO ₄	Molar ratio ^a	Temperature (°C)	Yield (%)
1	4	200	1.0:2.0	150	54
2	6	200	1.0:2.0	150	72
3	9	200	1.0:2.0	150	72
4	24	200	1.0:2.0	150	72
5	6	100	1.0:2.0	150	65
6	6	150	1.0:2.0	150	70
7	6	200	1.0:2.0	150	72
8	6	300	1.0:2.0	150	72
9	6	200	1.0:1.0	150	41
10	6	200	1.0:1.2	150	54
11	6	200	1.0:1.5	150	62
12	6	200	1.0:2.0	150	72
13	6	200	1.0:3.0	150	72
14	6	200	1.0:2.0	110	4
15	6	200	1.0:2.0	130	34
16	6	200	1.0:2.0	150	72
17	6	200	1.0:2.0	170	74

^a Molar ratio of resorcinol:ethyl acetoacetate.

of ethyl acetoacetate and maximum yield was obtained with the use of two equivalent of ethyl acetoacetate. The yield increased from 4 to 74% with increasing the temperature from 110 to 170 °C (entries 14–17). Based on the above results, the preparation of 7-hydroxy-4-methyl coumarin with reasonable yield (72%) could be prepared using one equivalent of resorcinol and two equivalent of ethyl acetoacetate, catalyst amount 20% with respect to resorcinol, reaction time: 6 h, reaction temperature: 150 °C.

3.2.2. Reusability of the polyaniline supported acid catalyst

Reusability of the catalyst was checked by the preparation of 7-hydroxy-4-methyl coumarin using polyaniline-sulfate salt catalyst (20 wt.%) at 150 °C for 6 h, which resulted in a conversion of 70%. Polyaniline salt catalyst was recovered and reused seven times for preparation of 7-hydroxy-4-methyl coumarin and obtained the conversion in 68–70%. At the end, the catalyst was recovered and subjected for analysis. Similar infrared patterns were observed for the polyaniline salt as prepared and the sample subjected after the reaction. Similarly, the value of the amount of acid group (30%), particle size (45 μm), density (1.15) and conductivity (0.04) for the polyaniline-sulfate salt samples (before and after the reaction) are almost the same. The above result shows that the catalyst does not lose its activity and can be reused.

3.2.3. Effect of keto ester

The preparation of 7-hydroxy-4-methyl coumarin was also carried out using resorcinol (one equivalent) with methyl acetoacetate (two equivalent), 20 wt.% of the catalyst with respect to resorcinol, at 150 °C for 6 h. Methyl acetoacetate resulted in higher yield (78%) when compared with that of ethyl acetoacetate (72%).

3.2.4. Effect of polyaniline-sulfate salt prepared by different oxidizing agents on the yield

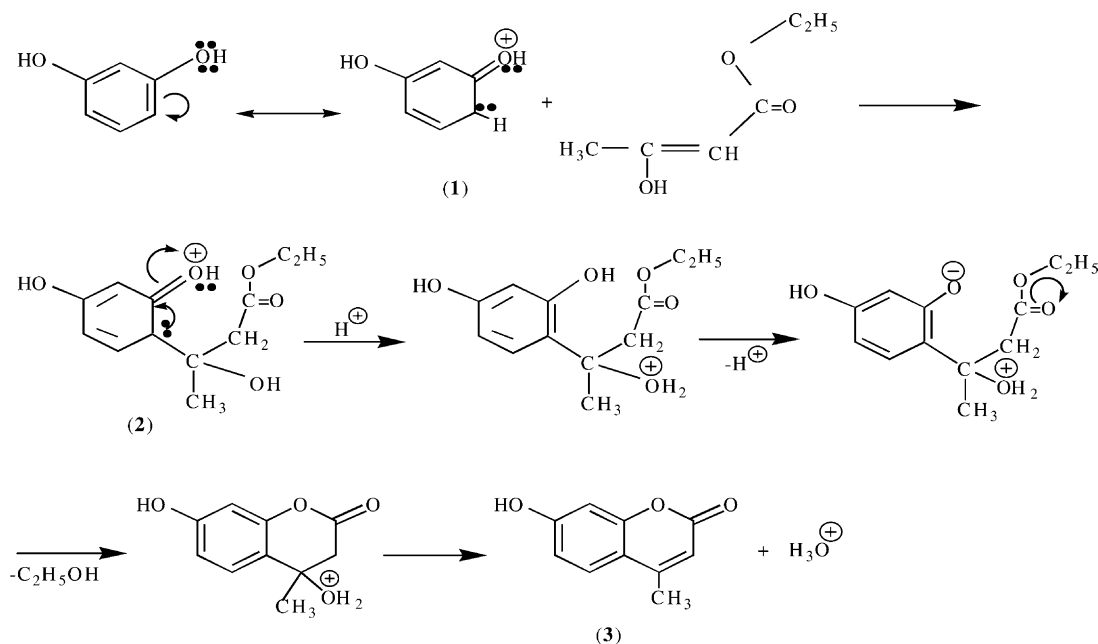
The preparation of 7-hydroxy-4-methyl coumarin was carried out with polyaniline-sulfate salts prepared using four different oxidizing agents. The yield of the product was found to be nearly the same, 72, 71, 67 and 66% with the oxidizing agents benzoyl peroxide, ammonium persulfate, sodium persulfate and potassium dichromate respectively. This result shows that the yield of the product is independent of the oxidizing agents used.

3.2.5. Effect of redoped polyaniline salts on the yield

The preparation of 7-hydroxy-4-methyl coumarin was carried out using different redoped polyaniline salt catalysts and the results are reported in Table 2. Polyaniline-sulfate (70%) and polyaniline-perchlorate (72%) gave higher yield when compared with that of the polyaniline *p*-toluenesulfonate (62%) and polyaniline-sulfosalicylate (67%) (entries 6 and 8). However, lower yields were obtained with polyaniline-sodium bisulfate (26%), polyaniline-trifluoroacetate (20%), polyaniline-hydrochloride (12%), and polyaniline-nitrate (6%) salts. The activity of the catalyst may be depend upon the strength of the acid and the amount of acid present in the polymer chain. For comparison with polyaniline salts, the preparation of 7-hydroxy-4-methyl coumarin was carried using different anilinium salt catalysts such as aniline-sulfate, aniline-perchlorate, aniline-sulfosalicylate and aniline-toluene sulfonate salt and the results are included in Table 2. Almost same yield was obtained with the use of polyaniline salt and aniline salt in the case of salts such as *p*-toluene sulfonic acid, sulfosalicylic acid and perchloric acid (Table 2). The advantage of polyaniline salts when compared with that of aniline salts are easy recovery and reusability. However, polyaniline-sulfate salt gave 70% yield and only trace amount of product was observed (8%) with the use of aniline-sulfate salt.

3.2.6. Possible mechanism

Generally, preparation of 7-hydroxy-4-methyl coumarin was carried out by Lewis acid, *p*-toluene sulfonic acid, solid acid catalyst, etc., as catalyst. In this work, polyaniline salts were tried out as polymer supported catalyst. Acid (sulfuric acid, nitric acid or hydrochloric acid, etc.) present in the polymer chain takes part in the preparation of 7-hydroxy-4-methyl coumarin. The mechanism of polyaniline supported acid catalyzed reaction can be shown as



The use of polyaniline salts as catalysts provides the following advantages (i) separation of catalyst from a reaction mixture is easy, (ii) repeated use of catalyst is possible, (iii) there is no problem for the disposal of used catalyst as they are environmentally safe, though the disposal of mineral acid catalyst requires much money for treatment to make it environmentally safe, and (iv) the preparation of the catalyst is straight forward synthetic route and (v) good stability of the catalyst.

Table 2
Yield of 7-hydroxy-4-methyl coumarin catalyzed by various redoped polyaniline salts^a and anilinium salts^b

Entry	Salts	Yield (%)
Polyaniline salt		
1	Polyaniline-hydrochloride	12
2	Polyaniline-sulfate	70
3	Polyaniline-nitrate	6
4	Polyaniline-perchlorate	72
5	Polyaniline-sodiumbisulfate	26
6	Polyaniline- <i>p</i> -toluenesulfonate	62
7	Polyaniline-trifluoroacetate	20
8	Polyaniline-sulfosalicylate	67
Aniline salt		
9	Aniline-sulfate	8
10	Aniline-perchlorate	75
11	Aniline-toluene sulfonate	65
12	Aniline-sulfosalicylate	63

^a Reaction conditions: resorcinol, 9 mmol; ethyl acetoacetate, 18 mmol; polyaniline salt, 20 wt.% based on resorcinol; temperature, 150 °C; time, 6 h.

^b Reaction conditions: resorcinol, 9 mmol; ethyl acetoacetate, 18 mmol; anilinium salt, 20 wt.% based on resorcinol; temperature, 150 °C; time, 6 h.

4. Conclusion

Polyaniline supported acid salts serve as catalysts for the synthesis of 7-hydroxy-4-methyl coumarin. The efficiency of the catalyst is considered to be based on the amount of acid present on the polymer chain and also the strength of the acid used. This method has several advantages: the catalytic use of polyaniline salt is quite feasible because of its easy preparation, stability, recovery, reusability, and eco-friendly of the catalyst.

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