

Synthesis of Tri(hydroxyphenyl)methane using Polyaniline-*p*-toluenesulfonic Acid Salt

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ABSTRACT: Synthesis of tri(hydroxyphenyl)methane and tri(hydroxyphenyl)butane were achieved using polyaniline-*p*-toluenesulfonic acid salt as polymeric solid acid catalyst. This method provides several advantages such as easy preparation of the catalyst, its stability, recovery and

easy work-up procedure. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2760–2763, 2007

Key words: tri(hydroxyphenyl)methane; polyaniline-*p*-toluenesulfonic acid salt; polymer based solid acid catalyst

INTRODUCTION

Polymer-supported catalysts are important conceptually in linking catalyst in solutions and catalysts on supports. The polymer-supported catalysts have replaced acid solution in numerous processes because they minimize the corrosion, separation and disposal problems posed by conventional catalysts.

A totally new family of materials is in development to contribute important aspects to solve many technical and ecological problems—the conducting polymers known as organic metals. In recent years, there have been intense efforts to develop reusable heterogeneous catalysts. For example, polyaniline was employed as a catalyst support for the oxidation of a spectrum of organic compounds.^{1,2} Pron and coworkers have used heteropolyanions, which were incorporated into conjugated polymer matrices via chemical doping.^{3–5} Pielichowski and Iqbal⁶ have developed efficient catalysts for the oxidation of aromatic hydrocarbons, alcohols and alkenes with high efficiency at relatively low temperatures. Further research on application of catalysts based on polyaniline salts in oxidation reactions was continued by Das, Iqbal, and coworkers.^{7–10} As there is much interest in the use of these heterogeneous systems in chemical industry as an environmentally more acceptable alternative compared with the classical stoichiometric catalysts, recently, we have reported several organic transformations using polyaniline salts as polymer based solid acid catalyst.^{11–14}

Tri(hydroxyphenyl)methane is being used in the preparation of polyglycidyl ethers.¹⁵ Derivatives of tri(hydroxyphenyl)methane are used as photosensitizer¹⁶ particularly in color filter array for liquid crystal display device.¹⁷ In an attempt to replace the conventional catalysts with eco-friendly catalysts, in this work, polyaniline-*p*-toluenesulfonic acid salt was used as polymeric solid acid catalyst in the preparation of tri(hydroxyphenyl)methane. Tri(hydroxyphenyl)methane has been prepared earlier using *p*-toluenesulfonic acid,¹⁵ but the isolation of the product was quite tedious. However, using polyaniline salt catalyst, tri(hydroxyphenyl)methane can be isolated by simple filtration and washing.

EXPERIMENTAL

Materials

Aniline (reagent grade) from Merck was distilled prior to use. Analar grade phenol, 4-hydroxy benzaldehyde, crotonaldehyde and solvents (BDH, India) were used without further purification.

Preparation of polyaniline-*p*-toluenesulfonic acid salt catalyst

Synthesis and characterization of Polyaniline-*p*-toluenesulfonic acid (PANI-PTSA) has been reported.¹⁸

Preparation of polyaniline salt

In a typical reaction, 1.0 mL of aniline, 2.1 g of *p*-toluenesulfonic acid and 75 mL of distilled water were taken in 250 mL round bottomed flask. To the above solution 2.6 g of sodium persulfate in 35 mL water was added dropwise for 15–20 min, and

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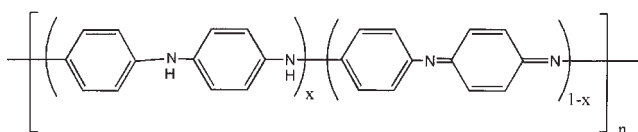


Figure 1 General structure of polyaniline base.

stirred at ambient temperature for 4 h. The precipitated polyaniline was isolated from the polymerization vessel by filtration and then washed with distilled water until the filtrate become colorless. To remove oligomers and other organic by-products, the precipitate was washed with acetone until the filtrate was colorless and subsequently dried at 100 °C till a constant mass.

Preparation of polyaniline base

Polyaniline salt was dedoped by aqueous sodium hydroxide solution. Polyaniline salt (1.0 g) was stirred in 100 mL of 1.0*N* sodium hydroxide solution for 12 h at ambient temperature. The solution was filtered, washed with sodium hydroxide (1.0*N*) solution followed by distilled water. The sample was dried at 100°C till a constant weight was reached.

Preparation of redoped polyaniline salt from polyaniline base

Polyaniline base (1.0 g) was stirred with 3.8 g (0.2*M*) of *p*-toluenesulfonic acid solution in 100 mL of dry acetone for 12 h at ambient temperature. The reaction mixture was filtered, washed with ample amount of acetone. The sample was dried at 100°C till a constant weight was reached.

Preparation of tri(hydroxyphenyl)methane

Polyaniline salt was heated at 100°C for 2 h and it was used as catalyst in the reaction. In a typical experiment, phenol (2.82 g, 30 mmol) was taken in a 10-mL round bottom flask, and 60 mg of polyaniline-*p*-toluenesulfonic acid salt powder (20 wt % with respect to 4-hydroxy benzaldehyde) was added and the mixture was heated at 70°C then 305 mg of 4-hydroxy benzaldehyde (2.5 mmol) was added. The reaction mixture was heated at 90°C for 24 h, filtered, washed with acetone and acetone was evaporated under vacuum. The obtained product was washed thrice with hexane followed by chloroform, finally filtered and dried at 100°C. The authenticity of the product was confirmed by ¹H NMR spectrum and mass spectrum.

Tri(hydroxyphenyl)butane was also prepared by following a similar procedure for the synthesis of tri(hydroxyphenyl)methane, using crotonaldehyde in place of 4-hydroxy benzaldehyde.

Characterization

Polyaniline sample was pressed into disks of 16 mm diameter and ca. 2 mm thickness under a pressure of 400 MPa. Resistance measurement of the pellet was carried out by two probes connected to a digital multimeter (Keithley model-2010). Resistance value was taken based on three consistent readings and conductivity was calculated using the formula, $\sigma = L/AR$ (R is the resistance, L the thickness, and A the area of the pellet). The polyaniline sample was mixed with KBr powder and compressed into pellet; the polyaniline powder was evenly dispersed. Fourier transform infrared spectrum was recorded using GC-FTIR spectrometer (MODEL 670 Nicolet Nexus, USA spectra).

RESULTS AND DISCUSSION

The structure of polyaniline (PANI) is known as a *para*-linked phenylene amineimine. The base form of polyaniline can, in principle, be described by the following general formula (Fig. 1).

In the generalized base form, $(1 - x)$ measures the function of oxidized units. When $(1 - x) = 0$, the polymer has no such oxidized groups and is commonly known as a leucoemeraldine base. The fully oxidized form, $(1 - x) = 1$, is referred to as a pernigraniline base. The half-oxidized polymer, where the number of reduced units and oxidized units are equal, i.e., $(1 - x) = 0.5$, is of special importance and is termed as the emeraldine oxidation state or the emeraldine base. Partially oxidized emeraldine base is shown to be an alternating copolymer of reduced and oxidized repeat units (Fig. 2).

Physical Properties of PANI-PTSA salt

Aniline was oxidized to PANI-PTSA salt using sodium persulfate as oxidizing agent in presence of *p*-toluenesulfonic acid. PANI-PTSA salt was dedoped to polyaniline emeraldine base using aqueous sodium hydroxide solution. Polyaniline base was redoped to polyaniline salt using *p*-toluenesulfonic acid (Fig. 3).

Physical properties and infrared spectrum of PANI-PTSA salt have been reported.¹⁸ The amount of acid group present in the polyaniline chain was calculated based on the weight of redoped polyani-

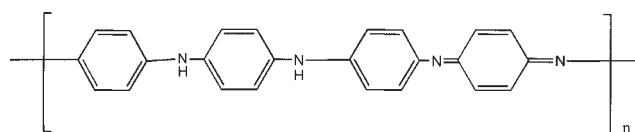


Figure 2 Structure of emeraldine base.

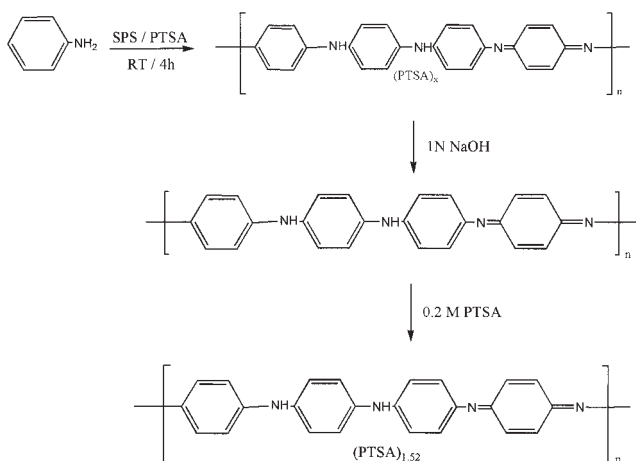


Figure 3 Synthesis of polyaniline-*p*-toluenesulfonic acid salt.

line salt obtained and weight of polyaniline base used. The amount of dopant was found as 43.5 wt %, which corresponds to 0.38 dopant per aniline unit (Fig. 3).

The yield of polyaniline was found to be 91.4% with respect to aniline used in the reaction or 51.4% based on PANI-PTSA formula. Conductivity of PANI-PTSA was found to be 1.0×10^{-2} S/cm.

Infrared spectrum

Infrared spectrum of redoped PANI-PTSA salt is shown in Figure 4. The spectrum showed the following five major vibrational bands: 1585, 1480, 1300, 1115, and 805 cm^{-1} . A broad band at 3440 cm^{-1} was assigned to the free N—H stretching vibration. The bands at 2920 and 2850 cm^{-1} was assigned to vibration associated with NH part in $\text{C}_6\text{H}_4\text{NH}_2\text{C}_6\text{H}_4$ group or sum frequency. The ring stretching of quinoid and benzenoid form was observed at 1585 and 1480 cm^{-1} respectively. The C—N stretching band of an aromatic amine appeared at 1300 and 1225 cm^{-1} . Polyaniline showed a strong band at 1115 cm^{-1} ,

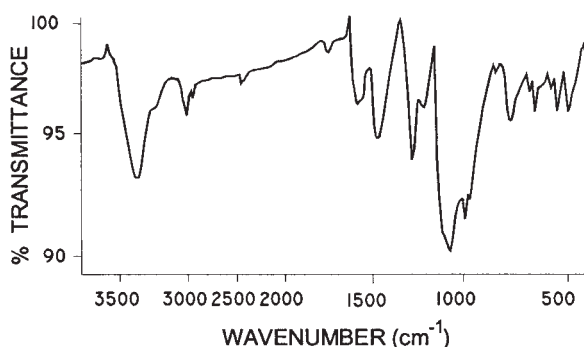
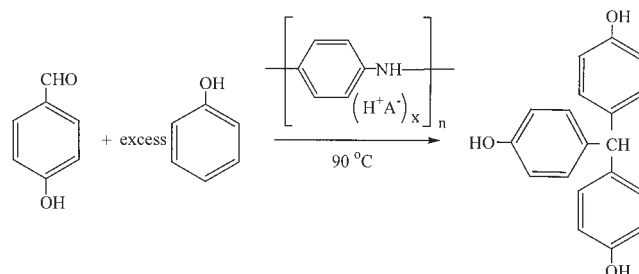


Figure 4 Infrared spectrum of redoped PANI-PTSA salt.¹⁸



Scheme 1 Preparation of tri(hydroxyphenyl)methane.

which has been explained as electronic like absorption of $\text{N}=\text{Q}=\text{N}$ (where Q denotes quinonoid ring). The C—H out-of-plane bending mode has been used as a key to identify the type of substituted benzene. For polyaniline salt, this mode was observed as a single band at 805 cm^{-1} , which was in the range 800–860 cm^{-1} reported for 1,4-substituted benzene. A band at 560 cm^{-1} was due to SO_3^- group of *p*-TSA. The bands at 695 and 580 cm^{-1} are assigned to ring C=C bending vibration and ring in plane deformation respectively.

Synthesis of tri(hydroxyphenyl)methane

Polyaniline-*p*-toluenesulfonic acid salt was used as catalyst for condensation reaction of phenol with 4-hydroxy benzaldehyde without using any solvent. The background reaction was examined with phenol and 4-hydroxy benzaldehyde in the absence of catalyst and no product was observed. However, the use of polyaniline-*p*-toluenesulfonic acid salt (20 wt % with respect to 4-hydroxy benzaldehyde) provided 70.8% yield of product.

Preparation of tri(hydroxyphenyl)methane (Scheme 1) was carried out with phenol and 4-hydroxy benzal-

TABLE I
Yield of Tri(hydroxyphenyl)methane Obtained with Different Reaction Times, Molar Ratios, Catalyst Concentrations, and Temperatures

Entry	Time (h)	Catalyst (mg) PANI-PTSA	Molar ratio	Temperature (°C)	Yield (%)
1	1	60	1:12	90	10.4
2	4	60	1:12	90	34.0
3	8	60	1:12	90	52.3
4	16	60	1:12	90	61.8
5	24	60	1:12	90	70.8
6	40	60	1:12	90	49.3
7	24	60	1:12	75	48.3
8	24	60	1:12	105	48.6
9	8	75	1:12	90	27.7
10	24	45	1:12	90	45.0
11	24	30	1:12	90	37.5
12	24	15	1:12	90	20.1
13	24	60	1:4	90	24.0
14	24	60	1:8	90	32.3
15	24	60	1:16	90	35.2

dehyde by varying the reaction time, catalyst amount, molar ratio of the reactants and temperature of the reaction (Table I).

The preparation of tri(hydroxyphenyl)methane was carried out by varying the reaction time between 1 and 40 h and maximum yield (70.8%) was obtained around 24 h (entries 1–6).

The catalyst amount was varied as 5, 10, 15, 20, and 25 wt % catalyst with respect to 4-hydroxy benzaldehyde. The yield of the product was increased from 20.1% (entry 12) with the use of 5 wt % catalyst to 70.8% with the use of 20 wt % catalyst and then decreased to 27.7% (entry 9) with further increase of catalyst amount (25 wt %).

The reactions were carried out using different molar ratios of phenol : 4-hydroxy benzaldehyde (1:4, 1:8, 1:12, and 1:16). Increase in the yield was observed with increasing amount of phenol and reached maximum (70.8%) when 12 equivalents of phenol was used and thereafter decreased (entries 13, 14, 5, and 15).

The temperature of the reaction was varied and the yield increased from 48.3% to 70.8% with increasing temperature (entries 7 and 5) and decreased to 48.6% at 105°C (entry 8).

The results of this study indicate that polyaniline-*p*-toluenesulfonic acid salt could be used for the preparation of tri(hydroxyphenyl)methane. The better result (70.8% yield) could be obtained with the use of one equivalent of 4-hydroxy benzaldehyde, 12 equiv. of phenol, 20 wt % catalyst, reaction time: 24 h, reaction temperature: 90°C.

Polyaniline-*p*-toluenesulfonic acid salt was served as catalyst for the synthesis of tri(hydroxyphenyl)methane. This procedure was extended to prepare tri(hydroxyphenyl)butane in 85.4% yield.

CONCLUSIONS

In summary, synthesis procedure for tri(hydroxyphenyl)methane was optimized using polyaniline-*p*-

toluenesulfonic acid salt as polymeric solid acid catalyst. This method has several advantages: the catalytic use of polyaniline salt is quite feasible because of its easy preparation, stability, recovery and simple work up procedure.

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