Emulsion polymerization pathway for preparation of organically soluble polyaniline sulfate

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In this work, aniline was polymerized directly to polyaniline sulfate salt without using protic acid. Polyaniline sulfate salt was prepared by an emulsion polymerization pathway using surfactants such as anionic surfactant (sodium lauryl sulfate), cationic surfactant (cetyltrimethylammonium bromide) and non-ionic surfactant (polyethylene glycol octadecyl ether). Anionic/cationic surfactants yield polyaniline sulfate salt in organic phase and non-ionic surfactant yields polyaniline sulfate in powder form. The dopant, *i.e.* sulfate ion, in polyaniline sulfate salt was generated from ammonium persulfate which was used to oxidize aniline. Ammonium persulfate acts both as an oxidizing agent and as a doping agent in the polymerization process of aniline to polyaniline sulfate salt. The spectral and electrical properties of the polyaniline salt synthesized by the emulsion polymerization pathway are compared with those of the polyaniline salt prepared by an aqueous polymerization pathway using sulfuric acid as protic acid.

Introduction

Aniline can be polymerized by chemical or electrochemical methods.[1] The synthesis of polyaniline is commonly performed by the method of chemical oxidative polymerization using protic acids based upon an aqueous solution polymerization system. Typical examples of protic acids in the prior art are hydrochloric,[2] sulfuric,[3] perchloric,[4] fluoroboric acids[5] (inorganic acids), *p*-toluenesulfonic,[6] benzenesulfonic,[6] *p*-styrenesulfonic acids[7] (organic acids), polyamic,[8] polyacrylic,[9] polyvinylsulfonic acid[10] (polymeric acids) and bis(2-ethylhexyl)hydrogen phosphate,[11] *etc.* Materials synthesized by this approach were predominately amorphous, intractable, and insoluble in most organic solvents.[12]

Several investigators have developed methods to improve the processability of polyaniline by a post-processing step, *i.e.* converting the salt to emeraldine base and reprotonating the emeraldine base with another protic acid. Tzou and Gregory[13] used this approach and reported that polyaniline salts containing carboxyl and amino substituents were soluble in *N*-methylpyrrolidone and dimethylsulfoxide. Cao *et al.*[14] reported the same method to prepare polyaniline salts with a number of protic acids including DBSA (4-dodecylbenzenesulfonic acid) and DNNSA (dinonylnaphthalenesulfonic acid). The polyaniline salts thus produced were reported to be soluble in non-polar solvents, however, the solubility was low.

An emulsion polymerization process for preparing a polyaniline salt of a protic acid has been reported,[15] wherein the protic acid acts as dopant. Smith *et al.*[16] reported the 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 a functionalized protic acid such as dodecylbenzenesulfonic acid, which simultaneously acts as a surfactant and protonating agent.

In the present work, aniline was oxidized to polyaniline salt by ammonium persulfate *via* an emulsion polymerization pathway, wherein the polyaniline salt is in an organic carrier solvent. To the best of our knowledge, this is the first report of the following: (i) aniline being polymerized to polyaniline sulfate salt without using protic acid and (ii) the preparation of polyaniline sulfate in an organic carrier solvent.

Polyaniline salt was prepared by (i) an aqueous polymerization pathway using water, aniline and ammonium persulfate and (ii) an emulsion polymerization pathway using water, aniline, chloroform, ammonium persulfate and surfactants such as sodium lauryl sulfate (anionic) or cetyltrimethylammonium bromide (cationic) or polyethylene glycol octadecyl ether (non-ionic).

Experimental

Materials

Aniline (reagent grade) from E. Merck was distilled prior to use. Reagent-grade sodium lauryl sulfate (SLS), cetyltrimethylammonium bromide (CTAB), polyethylene glycol octadecyl ether (BRIJ 76) (Fluka), ammonium persulfate, sulfuric acid (BDH, India) were used without further purification.

Syntheses

Method 1: Preparation of polyaniline salt by aqueous-polymerization pathway without protic acid. Aniline (2.3 ml) was dissolved in 100 ml of distilled water. 100 ml water containing 5.71 g of ammonium persulfate was added dropwise to the above solution over a period of approximately 20 minutes. The reaction was allowed to proceed for 4 hours at 30 °C. A green coloured precipitate was formed at the end of the reaction. The precipitate was filtered from the reaction mixture and washed three times with 300 ml water followed by 300 ml acetone. The powder was dried at 100 °C until it attained constant weight.

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Table 1 Theoretical and experimental values of the percentages of carbon, hydrogen, nitrogen and sulfur of polyaniline sulfate salt

	Theoretical values				Experimental values				Sulfate per aniline unit	Dopant (%)
Sample	% C	% H	% N	% S	% C	% H	% N	% S		
Aqueous polymerization										
Without acid	70.7	5.1	13.7	3.5	69.1	5.5	13.8	3.4	0.11	10.6
With sulfuric acid	60.3	4.7	11.7	7.8	59.1	5.0	10.8	7.6	0.29	24.0
Emulsion polymerization										
With SLS	66.9	5.0	13.0	5.1	68.1	5.2	12.8	5.3	0.17	15.5
With CTAB	66.9	5.0	13.0	5.1	67.4	5.1	12.5	5.2	0.17	15.5
With BRIJ76	66.3	4.9	12.9	5.3	65.8	5.1	12.7	5.3	0.18	16.2

Method 2: Preparation of polyaniline salt by aqueous-polymerization pathway using sulfuric acid. Aniline (2.3 ml) and sulfuric acid (9 ml) were dissolved in 90 ml of distilled water. 100 ml water containing 5.71 g of ammonium persulfate was added dropwise to the above solution over a period of approximately 20 minutes. The reaction was continued for 4 hours at 30 °C. The isolation of the sample was carried out as in method 1.

Method 3: Preparation of polyaniline salt by emulsion-polymerization pathway using SLS surfactant with different amounts of chloroform. 2.3 ml of aniline was dissolved in a known amount of chloroform (30, 60, 90 or 120 ml). Then 40 ml aqueous solution containing 1.44 g of SLS surfactant was added slowly while stirring which resulted in an emulsion. To this emulsion, 100 ml aqueous solution containing 5.75 g of ammonium persulfate was added dropwise (15–20 min intervals). The mixture was stirred constantly for 4 h at 30 °C. The organic layer, which contained the polyaniline salt, and aqueous layers were separated from the reaction mixture. Polyaniline salt in solution form was isolated by keeping the organic layer in sodium sulfate for 8 h and filtered the solution. Polyaniline salt was precipitated in acetone and the salt was filtered, washed with water, acetone and finally with methanol. The sample was dried at 100 °C till constant weight.

Method 4: Preparation of polyaniline salt by emulsion-polymerization pathway using surfactants. 2.3 ml of aniline was dissolved in 60 ml of chloroform. 40 ml aqueous solution containing surfactant (see Table 1 for details) was added slowly while stirring which gave an emulsion. To this emulsion, 100 ml aqueous solution containing 5.75 g of ammonium persulfate was added dropwise (15–20 min intervals). The mixture was stirred continuously for 4 h at 30 °C. Anionic surfactant (SLS)/cationic surfactant (CTAB) produced polyaniline in organic solvent and the product was isolated as explained in method 3, whereas the non-ionic surfactant (BRIJ 76) yielded the salt in powder form and the product was isolated as detailed in method 1.

Dedoping

Polymer samples were dedoped with 1.0 M aqueous sodium hydroxide (NaOH) solution. A known quantity of the polymer salt was taken in 1.0 M aqueous NaOH solution and stirred overnight. The product was filtered, washed with aqueous NaOH solution followed by water and dried at 100 °C until it registered constant mass.

Aqueous saturated barium chloride was added to the above filtrate followed by concentrated hydrochloric acid. A white precipitate was formed indicating the presence of sulfate anion. This indicates that polyaniline salt contains sulfate groups as dopant ions, and sulfate ions were generated from ammonium persulfate, which was employed to oxidize aniline to polyaniline salt.

Measurements

Infrared spectra. Fourier-transform infrared spectra of the samples were recorded using a Bomem MB 100 FT IR spectrometer in the range 400–4000 cm^{-1}. The KBr pellet technique was used to prepare the samples for recording the infrared spectra.

Electronic absorption spectra. Electronic absorption spectra of the samples were recorded at ambient temperature on a GBC cintra 10 e UV/V spectrophotometer. Solutions for the absorption spectra were prepared by dissolving the samples in dimethylsulfoxide and filtering through Whatman 41 filter paper. Absorption spectra of the dilute solutions were recorded in the range 1100–300 nm using a pair of matched 3 ml stoppered silica cells of 10 mm path length.

Elemental analyses. The percentages of carbon, hydrogen, nitrogen and sulfur in the polyaniline sample were estimated using an Elementar Vario EL analyzer.

Resistance measurements. Resistance measurements of the samples in the form of compacted disk pellets were carried out on a two probe connected to a Keithley constant current source (Model 230 A) and digital voltmeter (Model 195 A). The pellets were prepared by subjecting the polymer samples to a pressure of 950 Kg cm^{-2}. Three pairs of consistent readings were taken at different points on the pressed pellet and the average value was reported on conductivity. Since the mean values were used in the calculation of resistance, the total error involved is $< 1\%$.

Viscosity measurements. Viscosity measurements of polyaniline sulfate salt (prepared by method 3 using 60 ml chloroform) were carried out by using a capillary viscometer and Schott gerate equipment system for automatic recording of flow time to the accuracy of 0.01 s. Viscosity was calculated using the formula[17]

$$\log[\eta] = \log[\eta_{\text{spc}}/C] - K\eta_{\text{spc}}$$

The limiting viscosity number of the polyaniline salt was found to be 0.4 dl g^{-1} and this low value of viscosity may be attributed to the low molecular weight of the polyaniline salt.

Results and discussion

Aniline was polymerized directly to polyaniline salt by ammonium persulfate without using acid. The polyaniline salts prepared by the aqueous/emulsion polymerization pathway were compared with polyaniline salt prepared by the aqueous polymerization pathway using sulfuric acid as protic acid.

Aqueous polymerization yielded polyaniline salt in powder form. In the emulsion polymerization pathway, the use of anionic/cationic surfactant yielded polyaniline salt in solution form; however, non-ionic surfactant resulted in polyaniline salt

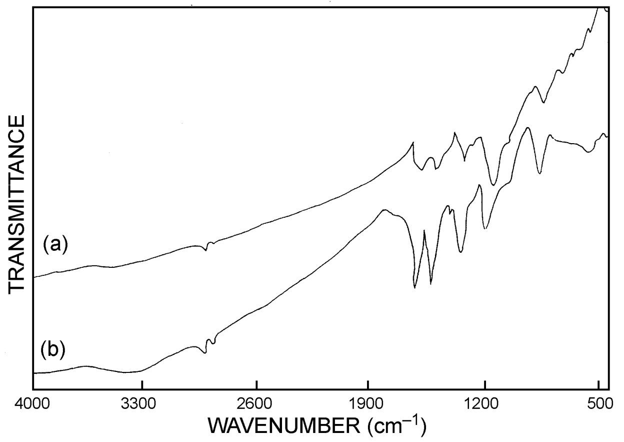

Fig. 1 Infrared spectra of (a) polyaniline salt and (b) its base prepared by the emulsion polymerization pathway using SLS surfactant.

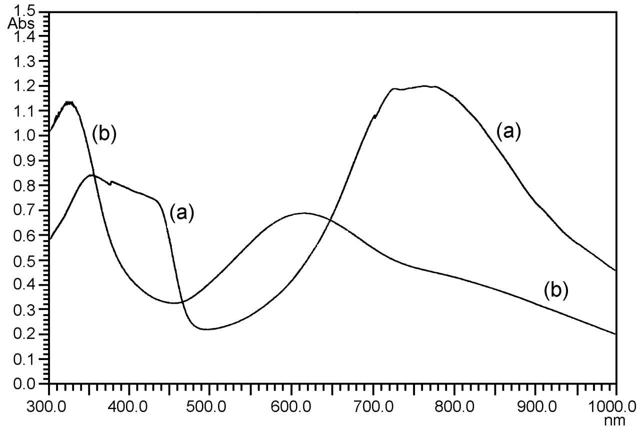

Fig. 2 Electronic absorption spectra of (a) polyaniline salt prepared by emulsion polymerization using SLS surfactant and (b) its base.

in powder form. The polyaniline salts prepared were dedoped by using aqueous sodium hydroxide solution. Spectral and electrical properties of the polyaniline salts and bases are reported here.

Infrared spectra

Generally, similar infrared spectral behavior was observed for the polyaniline systems prepared by different methods. As a representative system, the infrared spectra of polyaniline salt and its base (prepared by method 4 using SLS surfactant) are shown in Fig. 1.

The resolution of the polyaniline base spectrum is found to be better than that of its salt. The vibrational bands observed for polyaniline and its base are reasonably explained on the basis of the normal modes of polyaniline; a broad band at 3270–3400 cm^{-1} assigned to the NH stretching vibrations of $-C_6H_4NHC_6H_4-$ groups. The band at 2935 cm^{-1} is assigned to vibrations associated with the NH_2^+ part in $C_6H_4NH_2^+C_6H_4-$ groups, the 1585 and 1490 cm^{-1} bands to benzene and or quinone ring deformations, a 1315 cm^{-1} band to the CN stretch of a secondary aromatic amine, and the 820 cm^{-1} band to an aromatic CH out-of-plane bending. In the region of 1015–1175 cm^{-1}, aromatic CH in-plane-bending modes are usually observed. For polyaniline, a strong band characteristically appears at 1150 cm^{-1}, 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^{-1}, which fell in the range 800–860 cm^{-1} reported for a 1,4-substituted benzene. The infrared spectra of polyaniline salts prepared without acid are very similar to the infrared spectra of the polyaniline salt reported in the literature.[18,19]

Electronic absorption spectra

The electronic absorption spectra of polyaniline base and polyaniline salt have been reported in the literature. The absorption spectrum of polyaniline base[20,21] 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 a π–π^* transition and the band around 590–650 nm is due to the excitation of the imine segment of the polymer chain. Polyaniline salt[20,22] obtained from the base by treatment with acid showed three absorption bands at 325–360 nm, 400–430 nm and 780–825 nm.

Electronic absorption spectra of the chloroform solution isolated from the emulsion polymerization method (method 4 using SLS and CTAB surfactant) were recorded using chloroform as reference solvent and are shown in Fig. 2a. The electronic absorption spectra showed two bands: one band around 360 nm, another broad band around 760 nm and one hump around 430 nm corresponding to the polyaniline salt. This result indicates that polyaniline salt is in chloroform solvent.

Polyaniline salt (powder form) and its corresponding base are sparingly soluble in dimethylsulfoxide (DMSO). In order to find out the soluble portion, the electronic absorption spectra of the solution were recorded. The electronic absorption spectra of the DMSO soluble fractions of the polyaniline base prepared by all the methods are very nearly the same. As a representative system, the electronic absorption spectrum of polyaniline base (method 4 using SLS surfactant) is shown in Fig. 2b: it shows a broad band around 325 nm and another band around 625 nm. This is consistent with literature reports of polyaniline base.

The electronic absorption spectra of the DMSO soluble fractions of all the samples of polyaniline salt are very nearly the same irrespective of the method employed. As a representative system, the electronic absorption spectrum of polyaniline salt (method 4 using SLS surfactant) showed only two bands: a broad band around 330 nm and another band around 620 nm. It should be noted that no change in the absorption spectrum was observed even after aging the solution for 48 h. This indicates that the soluble fraction does not undergo any time dependent change. The electronic absorption spectrum of the polyaniline base is very nearly the same as the spectrum of the salt. This result indicates that (i) a small amount of base is present along with the salt, (ii) the salt is not soluble in DMSO, only the base part is soluble in this solvent.

Infrared, electronic absorption spectral and chemical analysis (barium chloride) of the polyaniline salts prepared without acid by the emulsion polymerization pathway are more or less similar to that of the polyaniline sulfate salt prepared using sulfuric acid as protic acid. These results show that the salt prepared by the emulsion polymerization pathway without using protic acid yield polyaniline sulfate salt. The dopant, *i.e.* sulfate ion, in polyaniline sulfate salt was generated from ammonium persulfate which was used for oxidizing aniline and ammonium persulfate acts both as an oxidizing agent and as a doping agent in the polymerization process of aniline to polyaniline salt.

Composition of polyaniline sulfate salt

The base form of polyaniline can, in principle, be described by the following general formula (Fig. 3)

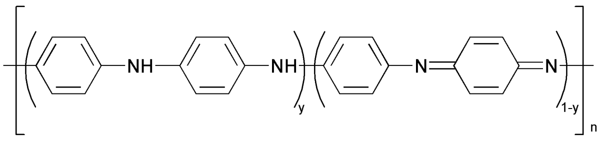

Fig. 3

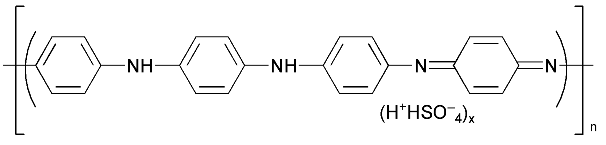

Fig. 4

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 is equal, *i.e.* $(1-y)=0.5$, is of special importance and is termed as the emeraldine oxidation state or the emeraldine base. The corresponding emeraldine salt can be represented by the following formula (Fig. 4)

The dopant sulfate group (H_2SO_4) per aniline unit present in the polymer chain was calculated from elemental analysis results. The percentages of carbon, hydrogen, nitrogen and sulfur were calculated theoretically by varying the amount of sulfate group from $x = 0.1$ to 0.5 in steps of 0.01. The number of sulfate groups per aniline unit was found out by comparing the experimental value with the theoretical value and the results are reported in Table 1.

Conductivity

Conductivity of the polyaniline salt can be controlled by adjusting two independent variables, namely the degree of oxidation and the degree of protonation.

The number of dopant groups (H_2SO_4) per aniline unit, dopant (weight percentage), the percentage yield of polyaniline salt (calculated based on the formula—Fig. 4) and conductivity of polyaniline salts prepared by different methods are given in Table 2.

The conductivity of the polyaniline sulfate salt prepared by the aqueous polymerization pathway without protic acid was found to be 1.2×10^{-5} S cm^{-1}. The conductivity of the polyaniline sulfate salt prepared by the emulsion polymerization pathway using ionic surfactants was found to be around 3.0×10^{-3} S cm^{-1} which is two orders of magnitude higher than that of the salt prepared using the aqueous polymerization pathway. The higher conductivity of the polyaniline salt in the case of the emulsion polymerization pathway compared to the aqueous polymerization pathway is may be due to the higher dopant content (15.5%) compared to that (10.6%) in the case of aqueous polymerization pathway. This can be attributed to the fact that the polymerization occurs at the water/chloroform interface, the polyaniline formation occurs in the chloroform solvent and the polyaniline salt precipitates out from the reaction mixture. This result indicates that the efficiency of ammonium persulfate in oxidizing aniline to polyaniline salt is increased by the use of surfactant.

The conductivity of the polyaniline sulfate salt prepared by the aqueous polymerization pathway using sulfuric acid as protic acid was found to be 4.0 S cm^{-1} which is six orders of magnitude higher than that of the salt prepared without using sulfuric acid as protic acid. This higher conductivity can be attributed to the higher dopant content (24%) in the polyaniline salt. This shows that the efficiency of ammonium persulfate in oxidizing aniline to polyaniline salt is further increased by the use of sulfuric acid as protic acid.

The conductivity of the polyaniline sulfate salt prepared without using acid was found to be low when compared to that of the salt prepared using acid. This may be due to the low doping level and/or maybe over-oxidation due to the present polymerization conditions.

The effects of the amount of chloroform solvent and surfactants on the polymer separation, yield and pellet conductivity of the polyaniline product were investigated and the results are tabulated in Table 3.

The yield (calculated based on the amount of aniline used) of the polyaniline salt prepared with varying amount of chloroform increased and then decreased. The conductivity of the polyaniline salt increased and attained a maximum. Good separation of the organic layer, maximum yield and conductivity were observed with the use of 60 ml chloroform (Table 3,Method 3). As 60 ml of chloroform gave the best result, 60 ml of chloroform was used in the experiment where the amount of surfactant was varied. Polyaniline salt did not separate out when 0.36 and 3.60 g of SLS were employed and good separation, yield (78.1%) and reasonable conductivity (3.0×10^{-3} S cm^{-1}) were obtained when 2.16 g of SLS was used (Table 3, Method 4). In the case of cationic surfactant (CTAB), better separation, reasonable yield and conductivity of the polyaniline salt were achieved with the use of 0.9 g CTAB (Table 3, Method 4). However, non-ionic surfactant (BRIJ76) yielded polyaniline salt in powder form. The yield and conductivity were found to be independent of the amount of non-ionic surfactant used (Table 3, Method 4).

Conclusions

Polyaniline sulfate salt was prepared directly by oxidation of aniline without protic acid using ammonium persulfate as oxidizing agent, *via* aqueous or emulsion polymerization pathways. Only the sulfate salt of polyaniline can be prepared without using protic acid by ammonium persulfate. Anionic/cationic surfactants gave polyaniline salt in organic phase and non-ionic surfactant yielded polyaniline in the form of a

Table 2 Conductivity and yield of polyaniline sulfate salt prepared by different methods

Method	Sulfate group per aniline unit	Dopant (wt%)	Yield[a] (%)	Conductivity/S cm^{-1}
Aqueous polymerization				
Without acid	0.11	10.6	79.1	1.2×10^{-5}
With sulfuric acid	0.29	24.0	90.2	4.0×10^{0}
Emulsion polymerization				
With SLS	0.17	15.5	67.3	3.0×10^{-3}
With CTAB	0.17	15.5	71.3	1.0×10^{-3}
With BRIJ76	0.18	16.2	53.6	6.2×10^{-3}

[a] Yield of polyaniline salt—calculated based on the formula in Fig. 4.

Table 3 Yield and conductivity of polyaniline sulfate salt

Method	Reaction conditions	Variation	Yield (%)	Conductivity/S cm^{-1}
3	Aniline = 2.3 ml	$CHCl_3$/ml		
	SLS = 1.44 g in 40 ml water	30	56.8^{N}	3.7×10^{-4}
	Variable = $CHCl_3$	60	73.1^{Y}	8.9×10^{-4}
		90	56.4^{N}	9.0×10^{-4}
		120	54.6^{N}	4.2×10^{-3}
4	Aniline = 2.3 ml	SLS/g		
	$CHCl_3$ = 60 ml	0.36	—	
	Variable = SLS in 40 ml water	0.72	25.8^{Y}	3.3×10^{-4}
		1.44	73.1^{Y}	8.9×10^{-4}
		2.16	78.1^{Y}	3.0×10^{-3}
		2.88	60.6^{Y}	4.2×10^{-3}
		3.60	—	
4	Aniline = 2.3 ml	CTAB/g		
	$CHCl_3$ = 60 ml	0.45	55.9^{Y}	3.9×10^{-4}
	Variable = CTAB in 40 ml water	0.90	71.3^{Y}	1.0×10^{-3}
		1.80	65.4^{Y}	8.5×10^{-4}
4	Aniline = 2.3 ml	BRIJ/g		
	$CHCl_3$ = 60 ml	1.20	61.1^{S}	6.2×10^{-3}
	Variable = BRIJ 76 in 40 ml water	2.40	62.8^{S}	6.2×10^{-3}

SLS = sodium lauryl sulfate, CTAB = cetyl trimethylammonium bromide, BRIJ 76 = polyethylene glycol octadecyl ether, $CHCl_3$ = chloroform, APS = ammonium persulfate, Y = soluble in chloroform; N = not soluble in chloroform, S = solid product

powder. Infrared and electronic absorption spectra of the polyaniline salt prepared with or without acid are almost similar. Ammonium persulfate acts both as an oxidizing agent and as a doping agent in the polymerization process of aniline to polyaniline salt. The efficiency of ammonium persulfate is enhanced by the use of surfactant. The activity of ammonium persulfate is further increased by the use of sulfuric acid as protic acid. The conductivity of the polyaniline sulfate salt prepared by the emulsion polymerization pathway without acid was found to be two orders of magnitude higher than that of the salt prepared by the aqueous polymerization pathway. The conductivity of the polyaniline sulfate salt prepared using sulfuric acid was found to be six orders of magnitude higher than that of the salt prepared by the aqueous polymerization pathway without using acid. The conductivity is almost independent of the concentration of the surfactant used. However, the yield increased when the amount of surfactant was increased and attained a maximum. In the oxidation process of aniline to polyaniline salt by ammonium persulfate in the presence of acid *via* either the aqueous or the emulsion polymerization pathway, it may be necessary to study the effect of sulfate ion which is generated during the oxidation process.

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