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Chemical and electrochemical polymerization of aniline using tartaric acid

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Abstract

Polyaniline–tartaric acid (PANI–TA) salts were prepared by chemical polymerization of aniline using four different concentrations of tartaric acid (TA). The polymer salts were characterized by infrared, electronic absorption, electron paramagnetic resonance spectral and conductivity measurements. Both the conductivity and yield of the PANI–TA salts were found to be dependent on the concentration of the TA employed. The conductivity and yield of the PANI–TA salt were found to be 0.2 $S\,cm^{-1}$ and 47% respectively. The values of density (1.20 $g\,cm^{-3}$) and water absorption (15–16%) were found to be independent of the concentrations of the acid used. Further, cyclic voltammetry was applied to electro polymerize aniline in aqueous TA solution using platinum as the working electrode. The results of the PANI–TA salt were compared with those of polyaniline-*p*-toluenesulfonic acid (PANI–TSA) salt. PANI–TA salt is slightly more soluble than PANI–TSA salt. The emeraldine salt may contain major amount of salt and little amount of emeraldine base and the emeraldine base may contain little amount of leucoemeraldine along with major amount of emeraldine base.

Keywords: Polyaniline–tartaric acid; Chemical polymerization; Electrochemical polymerization; Spectral studies

1. Introduction

Conducting polymers have been extensively studied due to their interesting electrical and electrochemical properties. Polyaniline (PANI) is a very attractive conducting polymer because it exhibits good stability and the redox mechanisms involving the exchange of protons and electrons are well characterized [1]. Also, it has attracted much attention because of fundamental interest and for possible applications such as batteries, electrochromic displays, Schottky diodes [2–8].

Mostly aniline has been polymerized by chemical and electrochemical methods using acids such as hydrochloric [9], sulfuric [10], perchloric [11], fluoboric acids [12] (inorganic acids), *p*-toluenesulfonic (TSA) [13], benzenesulfonic [13], *p*-styrenesulfonic acids [14] (organic acids), polyamic [15], polyacrylic [16], polyvinylsulfonic acid [17] (polymeric acid) and bis(2-ethylhexyl)hydrogen phosphate [18], etc.

PANI has often been categorized as an intractable polymer, in particular in its conducting emeraldine salt form. However, significant progress has been reported during recent years. PANI was processed [19] from a solvent, *N*-methyl-2-pyrrolidinone, in the nonconductive form of emeraldine base and then doped into the conductive form of emeraldine salt by protonic acids. Recently, Cao et al. [20,21] found that, by using functionalized protonic acids as dopants, the resulting emeraldine salt was soluble in common nonpolar or moderately polar organic solvents. The solubility of PANI salts depends on the choice of both the counterion and the solvent and the conductivity of the solution cast PANI films can be significantly enhanced compared with that of initial PANI powder [20].

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In this paper, the preparation and basic spectral properties of polyaniline–tartaric acid (PANI–TA) salts are described. Aniline was polymerized with tartaric acid by chemical oxidative polymerization using ammonium persulfate as an oxidizing agent. The polymer samples were characterized by infrared, electronic absorption, electron paramagnetic resonance (EPR) spectral and conductivity measurements. Further, cyclic voltammetry was applied to electropolymerize aniline in aqueous TA solution using platinum as the working electrode.

2. Experimental

2.1. Materials

Aniline, reagent grade from E. Merck, was vacuum distilled under nitrogen prior to use. All other reagents were used as received.

2.2. Chemical synthesis

Chemical synthesis of PANI–TA salt was carried out in aqueous acid solution. Aniline was dissolved in aqueous solution containing TA. The aqueous solution of ammonium persulfate was introduced dropwise into the above solution at room temperature. The mixture was stirred for 4 h at 25°C and the precipitated PANI 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 achieved. The concentrations of the reaction mixture are given in Table 1.

The polymer yield was calculated, for reasons of simplicity, assuming that the products were completely protonated, 50% oxidized poly(*p*-phenyleneamineimine) $[4(C_6H_4NH)^+(2HA^-)]_n$ (where A is the counter-anion, i.e. TA) and the values are included in Table 1.

2.3. Electrochemical synthesis

The electrochemical study was carried out from 1.0 M TA solution containing 0.1 M aniline on platinum electrode by sweeping the potential between −0.2 V and 1.6 V vs. SCE using a potentiostat/galvanostat model 273 A (EG&G Princeton Applied Research).

2.4. Measurements

Fourier-transform infrared (FTIR) spectra (from KBr disc) of the samples were recorded using a Bomem MB 100 FT IR spectrometer in the range 400–4000 cm^{-1}. Electronic absorption spectra of the sample were recorded using a Hitachi U3400 spectrophotometer. Solutions for the absorption spectra were prepared by dissolving the samples in *N*,*N*-dimethylformamide (DMF) and filtered through the filter paper. Absorption spectra of the dilute solution were recorded in the range 350–840 nm at room temperature using a pair of matched 3 ml stoppered silica cells of 10 mm path length. EPR spectra of the sample were obtained on a Varian E109 spectrometer operating in the X band. The sample was kept under vacuum when the spectrum was recorded. The *g* value and spin concentration were estimated using charred dextrose as a standard. The EPR spectra of the sample and charred dextrose were recorded under identical conditions. That is, the microwave frequency (9.05 GHz), microwave powder (2 mW), modulation frequency (100 kHz), field set (3280 G), scan range (40 G), modulation intensity (1 Gpp), modulation time (0.064 s) and scan time (200 s) were kept constant. The spin concentration for the sample was calculated by comparing the area under the EPR signal of the sample with that of charred dextrose whose spin concentration is known. Electrical conductivity (DC) of the samples was measured at room temperature using the four-probe method on pressed pellets. The pellets were obtained, by subjecting the polymer sample to a pressure of 950 $kg\,cm^{-2}$. Resistance measurements were carried out using a Keithley Model 220 programmable current source

Table 1
Concentrations of aniline, tartaric acid, ammonium persulfate used for polymerization (4 h) and yield, conductivity, water absorption of PANI–TA salts

System	Concentration (M)			Yield (%)	Conductivity ($S\,cm^{-1}$)	Water absorption (%)
	Monomer	Acid	Oxidant			
PANI–TA1	0.1	1.0	0.1	47.0	2.0×10^{-1}	15.3
PANI–TA2	0.1	0.5	0.1	45.8	1.0×10^{-1}	13.1
PANI–TA3	0.1	0.2	0.1	44.0	7.1×10^{-3}	15.2
PANI–TA4[a]	0.1	0.2	0.1	43.4	7.5×10^{-3}	14.7
PANI–TA5	0.1	0.1	0.1	38.7	8.6×10^{-4}	14.4
PANI–TSA	0.1	1.0	0.1	58.0	8.0	16.0

[a] The polymerization was carried out for 24 h at room temperature.

and a Keithley Model 195A digital voltmeter. The reproducibility of the results 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 values were used in the calculation of resistance, the total error involved is <3%. Percentage of water absorption and density of the polymer sample were measured at room temperature on pressed pellets obtained by subjecting the samples to a pressure of 950 $kg\,cm^{-2}$.

3. Results and discussion

3.1. Chemical polymerization

3.1.1. Infrared spectra

The infrared spectra of all the four PANI–TA salt are similar. As representative systems, the IR spectra of PANI–TA1 and polyaniline-*p*-toluenesulfonic acid salt (PANI–TSA) recorded in the range 2000–400 cm^{-1} are shown in Fig. 1. The vibrational bands observed for PANI–TA1 salt can be explained on the basis of the normal vibrational modes of PANI; a band at 3280–3400 cm^{-1} assigned to the NH stretch of an aromatic amine, a 2930 cm^{-1} band to an aromatic CH stretch, 1585 and 1490 cm^{-1} bands to benzene and or quinone ring deformations, a 1310 cm^{-1} band to the CN stretch of a secondary aromatic amine, and a 820 cm^{-1} band to an aromatic CH out-of-plane bending. In the region of 1010–1170 cm^{-1}, aromatic CH in-plane-bending modes are usually observed. For PANI–TA1, 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 base 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. Similar observations have been reported for PANI base [22]. When compared to the PANI base, PANI–TA1 showed bands at 1035, 1010, 755, 685, 570 cm^{-1}. These bands may be due to the presence of TA in the PANI–TA salt. The bands at 1035 and 1010 cm^{-1} are assigned to aliphatic C–H deformation modes. The IR spectrum of PANI–TA closely matches with that of PANI–TSA (Fig. 1).

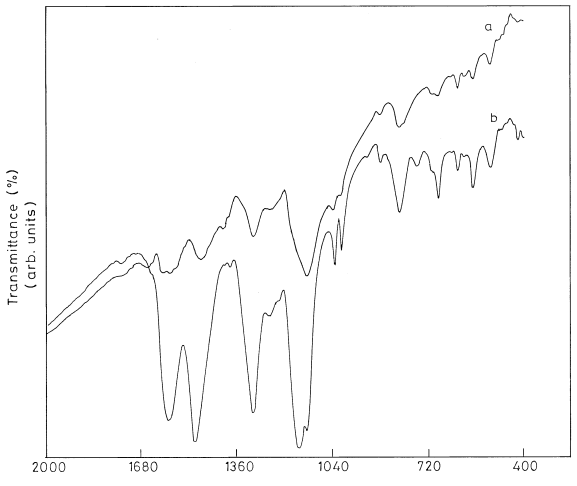

Fig. 1. Infrared spectra of (a) PANI–TA1 and (b) PANI–TSA.

3.1.2. Electronic absorption spectra

PANI–TA salt was dissolved in DMF and only a very small quantity of the sample was soluble in DMF. The electronic absorption spectrum of the solution was recorded. The absorption spectra of PANI–TA1 and PANI–TSA are shown in Fig. 2. The electronic absorption spectra of all the four PANI–TA salts showed a broad band around 580 nm, whereas, the PANI–TSA salt showed a broad band around 630 nm (Table 2).

The electronic absorption spectra of base [22,23] and PANI salt [22,24] have been reported in the literature. The PANI base in DMF/dimethylsulfoxide showed a

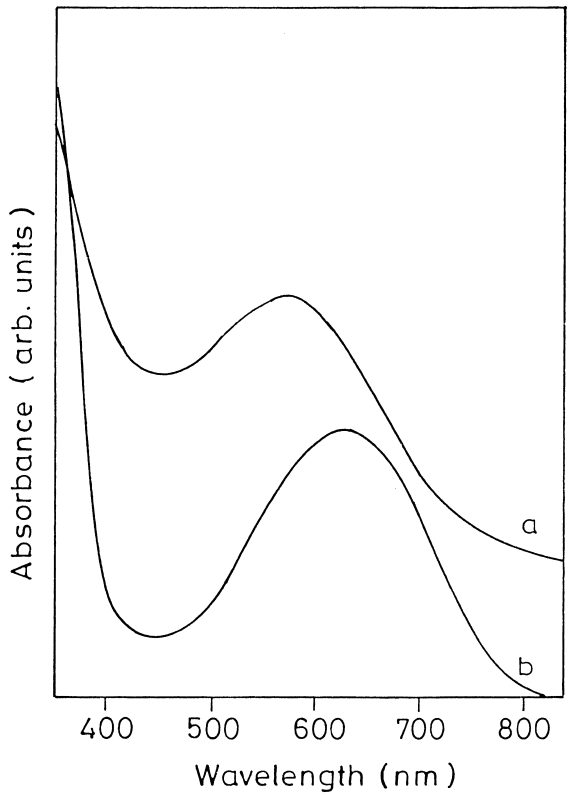

Fig. 2. Electronic absorption spectra of (a) PANI–TA1 and (b) PANI–TSA.

Table 2
Band maxima, g values, line width and spin concentrations of PANI–TA salts

System	λ_{max} (nm)	g value	Line width (G)	Spin concentration ($\times 10^{20}$ spins g^{-1})
PANI–TA1	575	2.0033	1.7	3.5
PANI–TA2	575	2.0033	1.8	2.4
PANI–TA3	575	2.0037	1.7	2.6
PANI–TA4	580	2.0036	1.7	2.9
PANI–TA5	585	2.0034	1.8	2.3
PANI–TSA	630	2.0039	2.3	1.5

broad band around 630 nm and the PANI salt showed a band around 800 nm. In the present study, PANI–TA and PANI–TSA showed broad bands around 580 and 630 nm respectively and it should be noted that no change in the absorption spectra was observed even after the solution was left for 48 h. The conspicuous absence of an absorption band around 800 nm in the absorption spectra of PANI–TA and PANI–TSA indicates that these salts are not soluble in DMF and only the base part is soluble. Also, this result indicates that PANI salt contains little amount of PANI base.

A known quantity of dedoped sample of PANI–TA and a PANI–TSA sample were dissolved in known amount of DMF, the solution was filtered and the electronic absorption spectra recorded. The results are given in Table 3. Absorbance for PANI–TA sample are found to be more than that of the PANI–TSA sample. As a representative case, the absorbances observed for 5 mg samples of PANI–TA and PANI–TSA are 1.25 and 1.02 respectively. This result indicates that PANI–TA sample is slightly more soluble in DMF solution than PANI–TSA sample.

1 ml of the filtered solution of dedoped sample of PANI–TA and PANI–TSA sample was diluted with 2, 3 and 4 ml of DMF and the spectra recorded. The results are compared with values calculated using the Beer Lambert law and the results are reported in Table 4. It

Table 3
Optical density (OD) values for the dedoped polyaniline systems

System	Weight (mg)	OD
D PANI–TA	5.0	1.2517
	7.0	1.4244
	9.0	1.5798
	11.0	1.8322
D PANI–TSA	5.0	1.0201
	7.0	1.2912
	9.0	1.4430
	11.0	1.8242

Table 4
OD values for the dedoped polyaniline systems and calculated value from the Beer Lambert law

System	Dilution	Observed OD	Calculated OD
D PANI–TA	As prepared	1.8824	
	1 ml+2 ml	0.6067	0.6275
	1 ml+3 ml	0.4443	0.4706
	1 ml+4 ml	0.3449	0.3765
D PANI–TSA	As prepared	1.8835	
	1 ml+2 ml	0.6958	0.6278
	1 ml+3 ml	0.6099	0.4708
	1 ml+4 ml	0.4067	0.3767

was found that the absorbances of the solution are different from the calculated values and this indicates that the solution does not obey Beer Lambert law. This may be due to inhomogenous nature of the sample, i.e., the sample may contain little amount of leucoemeraldine base in addition to a major amount of emeraldine base.

PANI–TSA showed a broad absorption band around 630 nm where as PANI–TA showed around 580 nm and this result suggests that the use of TA as counterion to prepare PANI salt affects the conjugation in the PANI chain.

3.1.3. Electron paramagnetic resonance spectra

The EPR spectra of PANI–TA1 and PANI–TSA sample are shown in Fig. 3. The EPR spectra of all the four PANI–TA salt and PANI–TSA salt showed a single signal without fine structure. g value, line width and spin concentration of the salts are included in Table 2.

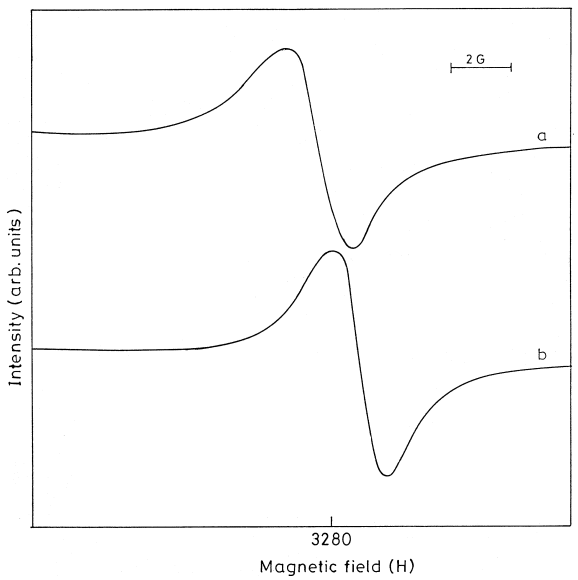

Fig. 3. EPR spectra of (a) PANI–TSA and (b) PANI–TA1.

The g value of all the salts lies around 2.0033–2.0039 compared to the free electron g value of 2.0023. A g shift of at least 10^{-3} has been observed when the radical is localized on or near a heteroatom, such as oxygen in carboxylic species or nitrogen in pyridines [25]. This result indicates that PANI salt exists primarily as polysemiquinone radical cation in which the electron is localized on or near nitrogen atom in PANI salts. The line width of all the four PANI–TA salt is around 1.7 G which is slightly smaller than that of PANI–TSA (2.3 G). The spin concentration of all the PANI–TA salt lies between 2.3 and 3.5×10^{20} spins g^{-1} and which are slightly higher than that of PANI–TSA salt (1.5×10^{20} spins g^{-1}).

Infrared, electronic absorption and EPR spectra of all the four PANI–TA acid salt are very nearly the same, and in turn similar to that of PANI–TSA salt. From the spectral studies on PANI–TA salt, it is clear that TA can be used as the counterion to prepare PANI salts.

3.1.4. Yield

The yield of all the four PANI–TA salts along with PANI–TSA are reported in Table 1. The value of yield increases, (i.e., 38.7%, 44.0%, 45.8%, 47.0%) when increasing the concentration of the TA 0.1, 0.2, 0.5, 1.0 M respectively. The value of yield in the case of PANI–TA is 47.0% which is less than that of PANI–TSA (58.0%).

3.1.5. Conductivity

The conductivity of PANI–TA salts depends on the concentration of the TA as shown in Table 1. The maximum conductivity of PANI–TA salt is 0.2 S cm^{-1} which is less than that of PANI–TSA (8 S cm^{-1}).

The yield and conductivity of PANI–TA are less when compared to that of PANI–TSA and this indicates that the efficiency of oxidation and protonation of aniline monomer to PANI salt by TA is less when compared to that of *p*-TSA.

3.1.6. Relationship of conductivity to electron paramagnetic resonance spin concentration

The conductivity of PANI–TA salts increases with increasing concentration of the TA. However, the spin concentration of all PANI–TA salts is similar. The conductivity of PANI–TA is 40 times lower than that of PANI–TSA salt. Whereas, the spin concentration of PANI–TA is twice as high as that of PANI–TSA salt. From the above results, it is clear that the paramagnetic species are not the sole charge carrier, since there is no direct correlation exists between conductivity and spin concentration.

3.1.7. Water absorption

PANIs have been found to contain water in substantial amounts (0.78 water molecules per monomeric unit) [26]. The amount of water present in PANI has been determined by several workers using thermogravimetric analyzer [27–29] and it was found that PANI contains up to 7% water. In the present work, the percentage of water absorbed was calculated by immersing the pellet in distilled water for 24 h at room temperature and then removing the excess water with tissue paper. The percentage of water absorption of PANI–TA varies from 13.1% to 15.2% which is slightly less than that of PANI–TSA (16%).

3.1.8. Density

The pellet density was measured as the mass per unit volume of the pressed pellets. The density of all the four PANI–TA and PANI–TSA before and after water absorption are found to be similar (around 1.20 g cm^{-3}).

It should be noted that the values of yield, conductivity, density and percentage of water absorption of the PANI–TA salts prepared at 4 and 24 h are all very similar.

3.2. Electrochemical studies

Cyclic voltammograms obtained for the oxidation of aniline (0.1 M) in 1.0 M TA solution by cycling between −0.2 and 1.6 V vs. SCE at a scan rate of 50 mV s^{-1} are shown in Fig. 4a. For the first positive sweep, a peak at about 1.24 V is observed (Fig. 4a) but in the subsequent sweeps, the current in that region decreases rapidly and the cyclic voltammogram shows a main reversible process centered at 0.43 and 0.30 V respectively (Fig. 4b). Continuous cycling does not change the reversible response and a film was not formed on the surface.

Dhavan and Trivedi [13] studied the electrochemical behavior of aniline in *p*-TSA by anodic polymerization of 0.1 M aniline by potential sweep between −0.2 and 1.0 V in 1.0 M *p*-TSA. In the first cycle one oxidation peak was observed at about 0.58 V vs. SCE which was related to the oxidation of aniline. In the subsequent cycles, new oxidation peaks appeared indicating that the radical cations generated at the electrode surface undergo further reaction to give oligomer species that are more readily oxidized and finally after a few couplings, the intensity of peak increased, an indication of the polymer growth.

However, the anodic polymerization of aniline in TA solution, a single well defined peak appears at a peak potential of 1.24 V vs. SCE due to loss of one electron to produce a cation radical and on the reverse and subsequent scans, the cyclic voltammogram shows a main reversible process centered at 0.44 and 0.27 V with no change in the current density. These results suggest that this may be due to either soluble or loosely surface bound products, which may be identified as a dimer from head-to-tail coupling.

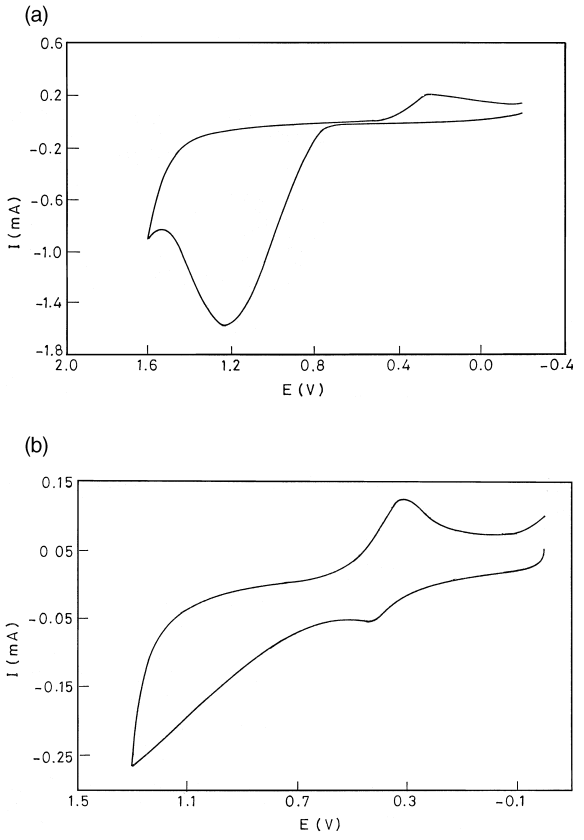

Fig. 4. Cyclic voltammograms of 0.1 M aniline in 1.0 M TA in aqueous solution (a) first cycle and (b) after 25th cycle.

3.3. Comparison between polyaniline–tartaric acid salt with polyaniline-p-toluenesulfonic acid salt

- Infrared, electronic absorption and EPR spectra of the PANI–TA salt closely match with those of the PANI–TSA salt.
- The conductivity of PANI–TA salt is 0.2 $S\,cm^{-1}$ which is less than that of PANI–TSA salt (8 $S\,cm^{-1}$). Also the yield of PANI–TA (47%) is lower than that of PANI–TSA (58%).
- The efficiency of oxidation and protonation of aniline monomer to PANI salt by TA is less when compared to that of *p*-TSA.
- The extent of conjugation of the PANI polymer chain was affected by tartaric acid counterion when compared to *p*-TSA.
- The values of density (1.20 $g\,cm^{-3}$) and percentage of water absorption (15–16%) of PANI–TA salts and PANI–TSA are nearly the same.
- Both PANI–TA salt and PANI–TSA salts are insoluble in DMF. However, PANI–TA salt is slightly more soluble than PANI–TSA salt.
- Electrochemical polymerization of aniline using *p*-TSA gave a polymer film. However, electrochemical polymerization of aniline using TA gave soluble or loosely bound dimer products.

4. Conclusions

Oxidation of aniline in presence of TA by ammonium persulfate yields a PANI–TA salt. The value of yield and conductivity increases with increasing the concentration of the TA used. However, the density of the polymer and the water absorption are independent on the concentration of the acid used. PANI–TA salt exists primarily as polysemiquinone radical cation. Paramagnetic species are not only the charge carrier. The PANI–TA salt is not soluble in DMF. Generally, PANI salt contains a major amount of emeraldine salt and a small amount of pernigraniline, emeraldine base, leucoemeraldine base. On the other hand the emeraldine base contains a major amount of emeraldine base and a small amount of leucoemeraldine base. Electropolymerization of aniline using TA is difficult.

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