 DOI: 10.1002/masy.201300141

Synthesis and Characterization of Polyaniline by Using Weak Oxidizing Agent

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Summary: Polyaniline was synthesized by using weak oxidizing agent $CuCl_2$ and characterized with FTIR, UV-vis, and XPS spectroscopic techniques. The composition of products was calculated from elemental analysis. The results show the presence of polyaniline in the emeraldine base (EB) form doped with $[CuCl_4]^-$. An increase in the yield and decrease in the final pH was observed when the oxidant to monomer ratio was increased. The increase in the yield was attributed to increase in the oxidation potential of oxidant with increase in its molar concentration.

Keywords: $CuCl_2$; emeraldine base; polyaniline; weak oxidizing agent

Introduction

The conducting polymers like polypyrrol, polythiophene, polyacetylene, polyaniline etc have received great attention during the last three decades. The conducting polymers were extensively studied by the scientists from all over the world soon after the discovery of polyacetylene by Shirakawa et al.[1] in 1975. Polyaniline (PANI) being unique in properties, structure, easy synthesis, low cost monomer and easy characterization is therefore of particular interest among the conducting polymers.[2] The industrial applications of PANI include its corrosion protection ability in paints, mercury removal from waste water, an important component of solar cells, light weight batteries, surgical instruments and light emitting diodes.[3]

In comparison to pure PANI the composites of PANI with other materials such as metals are gaining attentions due to unique properties and applications. Blinova et al[4] synthesize PANI-silver nanocomposites and reported higher conductivity of the nanocomposites as compared to pure PANI. Kinyanjui et al[5] chemically synthesize PANI-gold composites in high yield by using potassium tetrachloroaurate as oxidizing agent. The formation of short chains and gold colloids were reported. The metal was encapsulated in the polymer which results in composite formation with polycrystalline gold particles. The diameter of the gold particles was found to be in range of 0.8-1 μm. However, no significant change in the conductivity of composite has been reported. Mallick et al[6] synthesized PANI-Cu composite by using copper (II) sulfate as an oxidant. The morphology of resulting composite was reported to be flower like with a chemical structure similar to the conventionally synthesized PANI. The copper (II) sulfate was reduced to copper nano particles (2–5 nm) during the course of polymerization and the composites thus formed have comparable conductivity with emeraldine salt form of PANI.

In the present work polymerization of aniline under nitrogen atmosphere was investigated by using $CuCl_2$ as oxidizing agent in the presence of paratoluenesulfonic acid.

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Experimental Part

Materials

Aniline (99.5% Sigma Aldrich) was twice distilled under vacuume before use. Synthesis grade para toluene sulfonic acid (p-TSA) was used as received from Scharlau. Anhydrous copper II chloride (97%) was purchased from Sigma Aldrich and used as received.

Procedure

10 mL (0.2 M p-TSA and 0.2 M aniline) solution was prepared in deionized water. The initial pH of the solution was 4.80. This solution was kept in a refrigerator for 10-15 minutes. 10 mL (3 M copper II chloride) precooled solution was added to the aniline p-TSA solution. The reaction mixture was left undisturbed at room temperature under the nitrogen atmosphere for 24 h. The final pH of reaction mixture was measured to be 1.70. The precipitate was separated and washed with deionized water followed by acetone to remove unreacted material. The product obtained was dried for 24h at room temperature in a vacuum oven and was labeled as b-PANI. The b-PANI samples were washed HCl solution (1M) and labeled as h-PANI. The oxidant: monomer ratio from 1 to 15 were investigated by changing the concentration of $CuCl_2$.

Dedoping of h-PANI

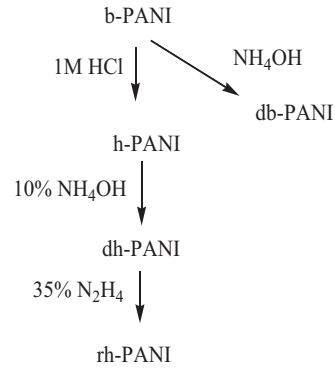
10% NH_4OH solution was used for the dedoping of h-PANI samples according to the method mentioned in literature.[7] After dedoping the samples were labeled as dh-PANI.

Reduction of dh-PANI

The reduction of dh-PANI samples were carried out with 35% aqueous hydrazine.[8] The reduced samples were labeled as rh-PANI see Scheme 1.

Characterization

The amount of product for various oxidant: monomer ratios ranging from 1-15 were calcualted. The initial and final pH for the various oxidant: monomer ratios in the reaction mixture was recorded..



Scheme 1.

FT-IR spectra were obtained by using Perkin Elmer spectrophotometer series 400 FT-IR. The spectra were recorded in the spectral region ranging from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were collected in ATR mode with 10 numbers of scans for each sample.

A Shimadzu UV-vis 1700 spectrophotometer was used to record the UV-vis spectra. The sampling interval was 0.5nm and the spectra were recorded in the spectral region ranging from 800 to 200 nm.

Elemental analysis was carried out by the Cambell Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand.

X-Ray photoelectron spectroscopy (XPS) data taken at photon energy of 710 eV at Australian synchrotron.

Results and Discussion

Table 1 shows the mass of product relative to the mass of aniline monomer and the oxidant to monomer ratio of the reactions. A decrease in final pH and the increase in the yield of reactions were observed as the concentration of $CuCl_2$ increases in the reaction mixture. This is consistant with the fact that the oxidation potential of $CuCl_2$ increses with the increase in its molar concentration[9] and thus the yield of reaction also increases.

Table 1.
Oxidant to monomer ratio and mass yield along with initial and final pH

Oxi/Mon	Initial pH	Final pH	Mass yield in grams
1	4.71	4.23	0.0170
2	4.86	3.73	0.0281
3	4.83	3.61	0.0341
4	4.73	3.18	0.0262
5	4.79	2.68	0.0373
6	4.71	2.70	0.0343
7	4.79	2.63	0.0376
8	4.83	2.37	0.0505
9	4.79	2.30	0.0506
10	4.82	2.19	0.0524
11	4.81	2.28	0.0538
12	4.76	2.14	0.0539
13	4.73	2.09	0.0573
14	4.76	1.88	0.0674
15	4.77	1.71	0.0764

Table 2.
%Weight lost in the b-PANI by washing with HCl, followed by dedoping with ammonia and reduction with hydrazine.

Sample	Mass yield in grams	%Weight lost in washing with HCl	%Weight lost in washing with NH_4OH	% weight lost in reduction NH_2-NH_2
b-PANI	$\sim$ 0.0776	82 ± 5	23 ± 5	24 ± 5

The % weight loss by b-PANI in washing with HCl is very large as shown in Table 2, which indicate the presence of $Cu_2(OH)_3Cl$[10] in large amount. The non-conductive behavior of b-PANI supports the presence of $Cu_2(OH)_3Cl$ in b-PANI products.. The mass yield of h-PANI after washing the b-PANI with HCl is 0.0157g. The h-PANI sample was dedoped with 10% NH_4OH and mass yield of dh-PANI is 0.0121g. The dh-PANI samples were reduced by hydrazine. The mass yield of the reduced samples rh-PANI is 0.0093g.

FT-IR Spectroscopy

All the informations in the following discussion are for the Oxi/Mon = 15 case

Figure 1 shows the FT-IR spectrum before washing of the initial product obtained when the mole ratio of Oxi/Mon = 15 in the reaction mixture. The Comparison of the spectrum of this product showed close similarities with that obtained by Le Cocq et al.[10]The bands at around 1601 and 1567cm^{-1} indicates that the initial product is a 1:2 complex of copper(II) chloride with aniline.[10] The presence of two narrow peaks in the region [3200-3600] cm^{-1} shows the existance of basic copper (II) chloride product similar to the $Cu_2(OH)_3Cl$ that was reported in previous literature.[10]

The mechanism for the formation of $Cu_2(OH)_3Cl$ in aqueous media is as follows:

$$C_6H_5NH_2 + H_2O \rightarrow C_6H_5NH_3^+ + OH^- \quad (1)$$

$$2CuCl_2 + 3OH^- \rightarrow Cu_2(OH)_3Cl + 3Cl^- \quad (2)$$

Extensive washing of the initial product with deionized water followed by acetone, removes the bands for the $CuCl_2$/aniline complex and those of the basic copper(II) chloride are shifted to 3512 and 3430 cm^{-1} which are close to the positions for $Cu_2(OH)_3Cl$,[10] as clear from the spectrum of the b-PANI product in Figure 2 (a).

In Figure 2 (a) b-PANI the bands at 1580 and 1488 cm^{-1} are attributed to the

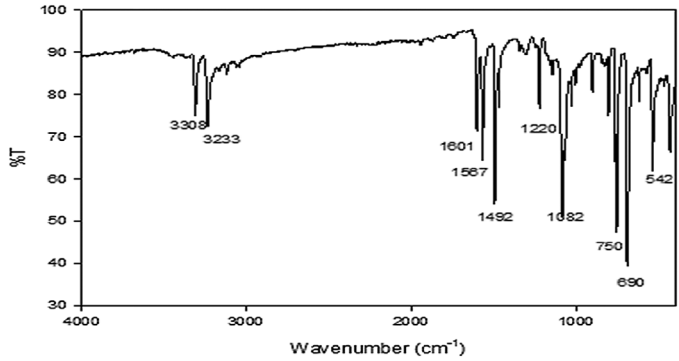


Figure 1.
FT-IR spectrum of the initial product (*Oxi/Mon* = 15) before washing.

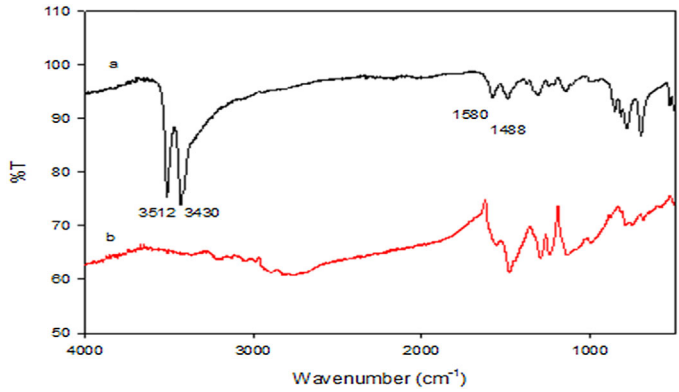


Figure 2.
FTIR spectra of (a) b-PANI, (b) h-PANI.

N=Q=N and N−B−N (where Q is quinoid and B is benzenoid) segments of polyaniline. The C−N and C=N stretching modes are shown by bands at 1315 and 1243 cm^{-1}. The C-H in-plane and out-of-plane bending modes are shown by bands at 1142 and 819 cm^{-1}.[11] The O-H stretching modes of $Cu_2(OH)_3Cl$ are shown by peaks at 3512 and 3430 cm^{-1}.[10]

The FT-IR spectrum of h-PANI obtained after washing the b-PANI product with 1M HCl is shown in Figure 2 (b), in which the peaks at 3512 and 3430 cm^{-1} are disappeared. The reason for the disappearance of these bands is the formation of soluble $CuCl_2$ by the dissolution of $Cu_2(OH)_3Cl$ in the HCl.

Figure 3 (a) and (b) show the FT-IR spectra of dh-PANI and rh-PANI products which are obtained by washing of h-PANI with 10% ammonium hydroxide solution, followed by reduction with 50% hydrazine solution for 24 hours respectively. The reduction of sample is confirmed by the decrease in the intensity of band for N=Q=N unit at 1594 cm^{-1}.[8] This is due to the addition of hydrogen from hydrazine and evolution of nitrogen gas from the reaction mixture to convert the N=Q=N units into N-B-N units of polyaniline.

UV-vis Spectroscopy

Figure 4(a), (b) and (c) show the UV-vis of b-PANI, h-PANI and dh-PANI

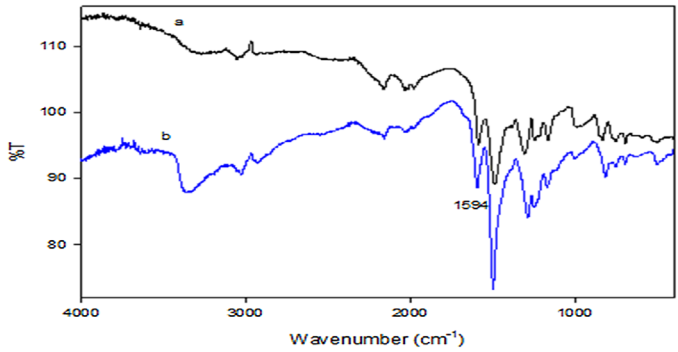


Figure 3.
(a) dh-PANI and (b) rh-PANI.

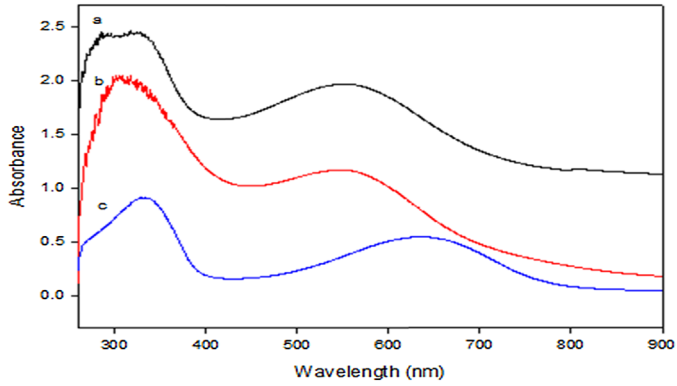


Figure 4.
UV-vis spectra of (a) b-PANI, (b) h-PANI, (c) dh-PANI.

respectively. The $\pi - \pi^*$ transition of the N-B-N unit is shown by band at 325–330 nm.[12] In b-PANI and h-PANI the N=Q=N band is blue shifted. The shifting of this peak is attributed to the presence of Cu II chloride in the emeraldine base (EB) form of PANI.[5] This type of behavior is also reported for the presence of TiO_2 in PANI.[13]

The UV-vis spectra of dh-PANI and its reduced form r-PANI are shown in Figure 5 (a) and (b) respectively. In the r-PANI (Figure 5 (b)) the band at around 620-650 nm for the N = Q = N unit tends to disappear as compared to that of dh-PANI (Figure 5 (a)), which shows that the sample has been reduced.[14]

Elemental Analysis

Table 3 show the elemental composition of dh-PANI and h-PANI. The C, H and N contents were found to be 53.68%, 3.79% and 9.92% respectively in dh-PANI and in case of h-PANI the C, H and N contents were found to be 52.84%, 4.30% and 10.06% as shown in Table 3. The C/N ratio was calculated to be 6.3 and 6.1 for dh-PANI and h-PANI respectively. The results for the composition of dh-PANI suggest that the product is EB form of PANI doped with $[CuCl_4]^{-2}$ which was further investigated by the XPS analysis. However, such type of results are reported for the presence of water molecule in the EB form of PANI by Zeng et al.[8]

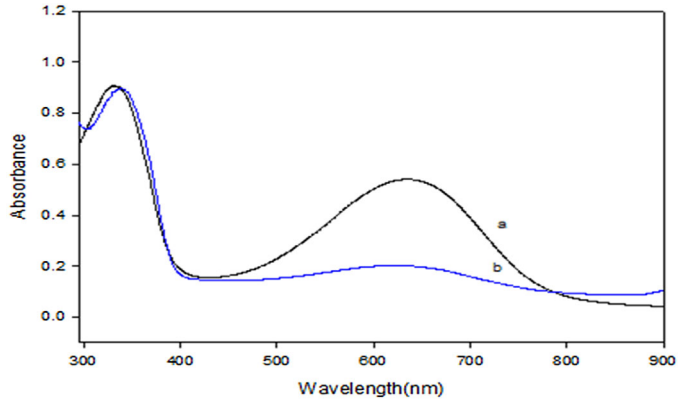


Figure 5.
UV-vis spectra of (a) dh-PANI, (b) r-PANI.

Table 3.
Compositions of dh-PANI and h-PANI

Sample	Oxi/Mon	%C	%H	%N	Composition	C/N ratio
dh	15	53.68	3.79	9.92	$C_{24}H_{20.23}N_{3.80}.[CuCl_4]^{-2}$	6.3
h	15	52.84	4.30	10.06	$C_{24}H_{23.44}N_{3.91}.H_2CuCl_4$	6.1

X-Ray Photoelectron Spectroscopy

Figure 6 show the Cu 2p X-ray photoelectron spectroscopy (XPS) for h-PANI and db-PANI. A strong signal of Cu 2p is shown by the spectrum of h-PANI. This signal is absent in the db-PANI product. This indicate that all of the copper(II) has been removed by washing the b-PANI with NH_4OH, whereas washing of the b-PANI with HCl did not. These results are in agreement with the above proposal of EB-PANI H_2CuCl_4 salt formation in the oxidative polymerization of aniline by $CuCl_2$. The NH_4OH treatement would remove this copper (II) as ($[Cu(NH_3)_4]^{2+}$ $2Cl^-$), as observed experimentally, so the Cu (II) would not be present in the db-PANI product. This is further supported by the fact that the XPS results also showed the presence of Cl, and in the db-PANI product the Cl content is reduced.

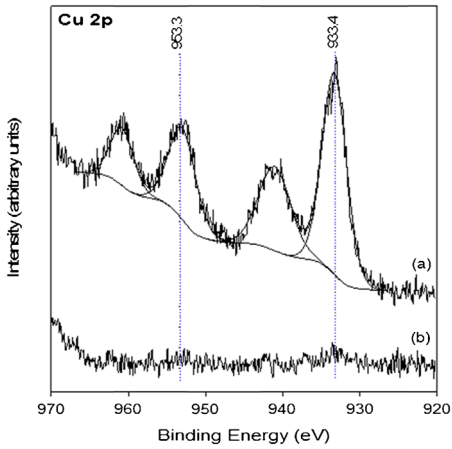


Figure 6.
Cu 2p XPS for (a) h-PANI, and (b) db-PANI.

Conclusion

The oxidative polymerization of aniline was investigated by using $CuCl_2$ as oxidant. The UV-vis, FTIR, XPS and elemental analysis showed that polyaniline was formed in the emeraldine base (EB) with $[CuCl_4]^-$ as dopant anion. With the increase of oxidant

to monomer ratio an increase in mass yield and decrease in the final pH was observed. The increase in the mass yield was attributed to an increase in the oxidation potential of $CuCl_2$ with an increase in its molar concentration. The co-formation of copper (II) chloride aniline complex in the reaction was responsible for the low mass yield. Although the mass yield of the reaction was less but, the present work shows that the oxidative polymerization of aniline can also be carried out by using weak oxidizing agent.

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