Chapter-2
Infrared Spectra of Various Types of Polyanilines
1. INTRODUCTION

The polyaniline (PANI) exists in a variety of forms which differ in the chemical and physical properties (1-3). Leucoemeraldine is a fully reduced form and is yellow in color. Protoemeraldine is brown. Emeraldine is green. Nigraniline is blue. Pernigraniline is violet. Various oxidizing agent/monomer ratios have been used in the literature (4). Ammonium peroxydisulfate is commonly used as oxidizing agent. There are benzenoid and quinonoid resonances according to amine and imine structures. Changing ratio of amine to imine, various structures are formed (5). Emeraldine, nigraniline and pernigraniline in highly crystalline forms were produced by oxidation with hydrogen peroxide, perchloric acid and potassium dichromate respectively (6). Polyaniline has good environmental stability (7).

The polyaniline of ideal emeraldine base form contains alternating amine and imine repeat units (8, 9). Polyaniline has a chemically flexible –NH group in its backbone which is responsible for interesting chemistry and physics (10). It was found that IR spectrum of emeraldine contained three Gaussian bands, nigraniline spectrum showed two Gaussian band and pernigraniline spectrum had one Gaussian band. This was consistent with stacking of benzenoid and quinonoid rings along one direction and with coupling of electrons with ring puckering vibrations of benzenoid rings (11).
2. EXPERIMENTAL PROCEDURE

Emeraldine was prepared in the form of green crystalline (needle crystals) material by oxidation of aniline with hydrogen peroxide in the presence of copper sulfate. Nigraniline was prepared as large blue-indigo crystals by oxidation of aniline with perchloric acid in the presence of copper sulfate. Pernigraniline was prepared as violet flakes by oxidation of aniline by potassium dichromate in the presence of copper sulfate. These crystalline forms of polyanilines were not reproducible. Probably these were low molecular weight polyanilines and were therefore crystalline. Second time these polyanilines were prepared by replacing copper sulfate with sulfuric acid. The spectra contained Gaussians and were reported (11).

This study proved orientation of benzenoid and quinonoid rings perpendicular to linear polymer direction, i.e. stacking of rings. Once more the three polyanilines were prepared but giving heat treatment. The stretching of polymers led to fading of colours and observation of Gaussians which were resolved, broadened and red-shifted (12). Bipolarons showed symmetric structures. In the present study, we carry out detailed investigation and try to standardize methods of preparation of various forms of polyaniline. We prove that certain features of the FTIR spectra are invariant with respect to methods of preparation.

In a standard method, aniline hydrochloride was formed by mixing aniline and hydrochloric acid in 1:1 proportion. This was oxidized by ammonium peroxydisulfate. This particular reagent contains ammonia for deprotonation, peroxy group for oxidation and sulfate group for choosing
particular path of oxidation. The precipitates were washed with ammonia solution and acetone. Spectra were obtained both before and after washing with ammonia solution. The method is standardized for emeraldine form of polyaniline.

When aniline hydrochloride was oxidized with potassium dichromate dilute solution in water first yellow colored leucoemeraldine was formed. It was separated and spectra were obtained. Further by adding more solution of \( \text{H}_2 \text{Cr}_2 \text{O}_7 \) brown colored protoemeraldine was formed. Finally ammonia solution was mixed for precipitation. It was verified with solubility in water that copper dichromate (when copper sulfate was mixed) - a brown powder showed different spectra than that of protoemeraldine (water insoluble) which was also brown.

In an arbitrary mixing of reagents, low-molecular weight emeraldine was produced by HCl drops and \( \text{H}_2\text{O}_2 \) as oxidizing agents. Sulfuric acid and ammonia solutions were added. FTIR spectra were obtained. Pernigraniline (violet) was prepared by drops of HCl in aniline and \( \text{H}_2\text{Cr}_2\text{O}_7 \) – concentrated solution. Ammonia solution was finally mixed. The IR spectra were obtained for this arbitrary mixing.

The standard method of forming aniline hydrochloride and subsequent oxidation with ammonium persulfate was modified by putting \( \text{H}_2\text{O}_2 \) also before adding ammonia solution. This also generated emeraldine form of polyaniline. Similarly nigraniline was also prepared by using ammonium persulfate and perchloric acid both simultaneously as oxidizing agents.
A low molecular weight emeraldine was prepared by using copper sulfate to choose path of oxidation only. H$_2$O$_2$ was used as oxidizing agent. HCl was used as a few drops only. Low molecular weight nigraniline was prepared by using perchloric acid as an oxidizing agent. Copper sulfate was used pernigraniline was also prepared by potassium dichromate as an oxidizing agent and copper sulfate was added. It was also prepared by replacing copper sulfate by sulfuric acid.

To find a relation between deprotonation and color of polyaniline, ammonia solution was added to all forms of polyanilines. Yellow leucoemeraldine became brown, brown protoemeraldine became green, green emeraldine became blue, and blue nigraniline became violet. Similarly when hydrochloric acid was added to polyanilines, violet pernigraniline became blue, blue nigraniline became green, green emeraldine became brown, and brown protoemeraldine became yellow. Thus deprotonation was found to be equivalent to oxidation and protonation was found to be equivalent to reduction. A dichroism is expected in the intermediate state of oxidation.

The polyanilines were grinded to fine homogeneous powder after drying the precipitates. The materials were regrinded with 95% KBr powder and circular pellets were prepared by manual compressing machine. These pellets were placed in dark chamber of perkin-Elmer single beam spectrophotometer.

The spectra in the range 400-4000 cm$^{-1}$ were recorded using GXFTIR spectrophotometer. The spectrometer has resolution of 0.15 cm$^{-1}$, a scan range of 15,600-30 cm$^{-1}$, a scan time 0.20 scan sec$^{-1}$ and an
OPD velocity of 0.20 cm sec$^{-1}$. MIRTGS and FIRTGS detectors were used. A beam splitter of opt KBr type was used, having a range of 7800-370 cm$^{-1}$. The spectra were recorded in purge mode.

3. RESULTS AND DISCUSSION

As mentioned above emeraldine was prepared by four different methods (1) standard method of using aniline hydrochloride and ammonium peroxydisulfate (2) modified standard method in which H$_2$O$_2$ was also used (3) Old method of using HCl drops only and copper sulfate (4) One more old method of using HCl drops only and sulfuric acid. In both of the old methods only H$_2$O$_2$ was used as oxidizing agent. The FTIR spectra of emeraldine form of polyaniline by these methods are shown (Figure 1 a-d).
Figure (1b): Emeraldine (APS)

Figure (1c): Emeraldine (CuSO₄)
Emeraldine prepared by standard method and modified standard method both showed three Gaussian bands in the FTIR spectra marked as G in the original spectra (Fig. 1 a, b). Both of them also showed a nature of transition which fitted $A=A_0 (hv-E_g)^{1/2}$ – a function for allowed direct transition. This shows by comparison with the results of a long chain molecule like β-carotene (13) and a metal chain semiconductor such as nickel dimethylglyoxime that it is a long chain polymer with large molecular weight. So emeraldine form of polyaniline behaves like other one dimensional semiconductors. There is not much change by adding H$_2$O$_2$ in a modified standard method. The maximum absorption at 2900 cm$^{-1}$ for standard method is about 30% and remains same by putting H$_2$O$_2$ but shifted to 2200 cm$^{-1}$. A few
more bands below 1000 cm\(^{-1}\) become visible by the addition of H\(_2\)O\(_2\). The Gaussians are fitted by plotting \(\ln A \text{ vs } (K-K_0)^2\) (Fig. 2 a-c and fig. 3a-c) because the Gaussian is described by

\[
A = A_0 \exp \left(\frac{(K-K_0)^2}{2m_2}\right)
\]

where \(A_0\) is maximum absorption, \(K_0\) is central wavenumber and \(m_2\) is the second moment of the distribution. The nature of transitions are fitted by plotting \((Ah_\nu)^2\) vs \(h_\nu\) which is found to be a straight line (Fig. 2d and 3d).
Figure 2: Gaussian distributions fitted

(A) First Gaussian
(B) Second Gaussian
(C) Third Gaussian and
(D) Allowed direct transition in emeraldine (standard method)
3(a) \[ \ln A \text{ vs } (K-K_o)^2 \]

3(b) \[ \ln A \text{ vs } (K-K_o)^2 \]

3(c) \[ \ln A \text{ vs } (K-K_o)^2 \]
Figure 3: Gaussian distributions fitted
(A) First Gaussian
(B) Second Gaussian
(C) Third Gaussian and
(D) Allowed direct transition in emeraldine (modified standard method)

When all of aniline was not converted in aniline hydrochloride acid and when H$_2$SO$_4$ or CuSO$_4$ was used to choose path of oxidation, only low-molecular weight polyaniline of emeraldine form was produced. The maximum absorption in the high frequency range did not exceed 15-20% (Fig. 1c,d). Although three Gaussian bands were observed, their intensities remained low. The gaussians are fitted by plotting lnA vs (K-Ko)$^2$ (Fig. 4a-c and fig. 5a-c). In both of these methods, nature of transition was found to be allowed indirect type. This was confirmed by plotting $(Ahv)^{1/2}$ vs hv. (Fig. 4d and 5d). This reveals a long macromolecular which is finite and the intermolecular transition which is usually indirect. Nature of low-molecular substances were also confirmed by several non-degenerate stretching vibration of N-H group in the high frequency range. Also the bands due to HSO$_4^-$ group or SO$_4^{2-}$ group are also found in the IR spectra which indicate presence of sulfate groups in the precipitated polyaniline.
4(a) 

4(b) 

4(c) 

lnA vs (K-Ko)^2
Figure 4: Three Gaussian distributions fitted (a-c) and (d) allowed indirect transition in emeraldine (using CuSO₄).
Figure 5 : Three Gaussian distributions fitted (a-c) and (d) allowed indirect transition in emeraldine (using arbitrary mixing)
Nigraniline was prepared by two methods (1) using drops of HCl, ammonium persulfate and perchloric acid both as oxidizing agents (2) using drops of HCl and using only HClO₄ followed by sulfuric acid treatment. The FTIR spectra are shown (Fig. 6a). Two gaussians were observed in both of the cases which are analyzed (Fig. 7a,b). The absorption function obeyed $A= A_0 (\nu-E_g)^{1/2}$ which is a direct allowed transition and is verified by plotting $(A\nu)^2$ vs $\nu$ which is a rectilinear plot (Fig.7c).
Pernigraniline was prepared by three different methods (1) arbitrary amount in mixing HCl, H$_2$Cr$_2$O$_7$ and NH$_4$OH (2) by using copper sulfate also and (3) by using sulfuric acid in the place of copper sulfate. The FTIR spectra are shown (Fig. 8a-c). In all of the three methods, spectra contained only one Gaussian (Fig. 9a-c). All of the three
spectra contained three nature of transition regions marked by NT-1, NT-2 and NT-3 in the original spectra (Fig. 8a-c). These regions are analyzed. Various direct or indirect transitions from spin-orbit split valence sub bands to conduction band are observed and best fits are shown (Figs. 10, 11 and 12).
Figure 8: FTIR spectra of pernigraniline using
   (A) Arbitrary mixing
   (B) Using CuSO₄ and
   (C) Using H₂SO₄

![FTIR spectra of pernigraniline](image)

Figure 9(a): InA vs (K-K₀)²
Figure 9: Gaussian distributions fitted for pernigraniline using

(A) Arbitrary mixing
(B) Using CuSO$_4$ and
(C) Using H$_2$SO$_4$
Figure 10: Nature of transitions in pernigraniline using arbitrary mixing (a-c)
Figure 11: Nature of transitions in pernigraniline using CuSO₄ (a-c).
Figure 12: Nature of transition in pernigraniline using $\text{H}_2\text{SO}_4$ (a-c).
Apart from the above well known forms of polyaniline, protoemeraldine were prepared by using dilute solution of \( \text{H}_2\text{Cr}_2\text{O}_7 \) in water as oxidizing agent. The FTIR spectra are shown (Fig. 13a). Protoemeraldine contained four gaussian bands which are fitted (Fig. 14 a-d) and one nature of transition which is allowed direct type (Fig. 14e).
14(b) $\ln A$ vs $(k-k_0)^2$

14(c) $\ln A$ vs $(k-k_0)^2$

14(d) $\ln A$ vs $(k-k_0)^2$
4. CONCLUSIONS

It was found in this comparative study of various forms of polyaniline that leucoemeraldine, protoemeraldine, emeraldine, nigraniline and pernigraniline spectra contained five, four, three, two and one gaussians consistent with their resonance structures and protonation. The gaussians were found to be independent of their methods of preparation. Nature of transition was allowed direct type for long linear polymers and allowed indirect type for low molecular weight macromolecular-type polyaniline. Pernigraniline was found to be semiconducting with spin-orbit splitting of valence band. Three transitions were observed from three valence subbands to conduction band.
REFERENCES