Thermal and conducting behaviour of emeraldine base (EB) form of polyaniline (PANI)

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Emeraldine base (EB) form of polyaniline (PANI) powder is prepared by chemical oxidative polymerization using different acidic media (HCl or CF₃COOH) at different temperatures (-15°C to +5°C). The chemical structure, thermal characterization and conducting behaviour are studied by means of Fourier transform infra-red (FTIR) spectroscopy, differential scanning calorimetry (DSC) and two-probe conductivity method. These polyanilines are soluble in N-methyl-2-pyrrolidone, dimethyl sulfoxide (DMSO) and dimethyl propylene urea (DMPU). The softening temperatures of different EB range from 87.8-116.4°C, which is believed to be an indication of cross-linking. Conductivity of emeraldine base of PANI is around (0.8-1.5) × 10⁻⁶ S/cm and energy band gap is approximately 0.5 eV, and no detectable crystallinity is observed. Wide-angle XRD technique indicates that PANI-EB base is amorphous in nature.

Keywords: Conducting polymer, Polyaniline-emeraldine base, Two-probe conductivity method, Differential scanning calorimetry

In the recent years, conductive polymers have received considerable attention worldwide due to their novel electronic and electrical properties. These polymers have diverse applications ranging from energy storage, sensors, anticrocorrosive materials, electromagnetic interference shielding, electrostatic charge dissipation, organic light emitting diodes, plastic solar cells and supporting material for catalysis. However, among other conducting polymers, polyaniline has been extensively studied not only because its electronic conductivity can easily be tuned by adjusting the oxidation state and degree of doping of the backbone, but also due to its environmental stability as well as economic feasibility. Polyaniline is a promising material for various techno-commercial applications, and hence the electrical properties, thermal and environmental stability of PANI films is highly dependent on the nature and the size of its dopant.

A comparative study of conductivity and thermal studies of different emeraldine base doped with inorganic acid (HCl)/organic acid (CF₃COOH) and further dedoped by ammonium hydroxide (NH₄OH) has been made here. These emeraldine bases were characterised by FTIR, DSC and their electronic conductivities have been measured by two-probe technique, where resistivity and conductivity varies with temperature.

Experimental Procedure

Sample preparation

Polymerization of aniline (0.05 mol) was carried out in a reaction vessel in temperature range from -15°C to 5°C (reaction condition are given in Table 1). Aniline was dissolved in 1M HCl/LiCl or 1M CF₃COOH and 11.5 g ammonium persulphate (APS) was added drop-wise. Then the reaction was continued for 2 h. The solution was filtered by

<table>
<thead>
<tr>
<th>Code</th>
<th>Monomer</th>
<th>Oxidant</th>
<th>Solvent</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>Aniline</td>
<td>(NH₄)$_₂$S₂O₈</td>
<td>Mixture of HCl/LiCl and 0.1M HCl</td>
<td>-15°C</td>
</tr>
<tr>
<td>A₂</td>
<td>Aniline</td>
<td>(NH₄)$_₂$S₂O₈</td>
<td>0.6M LiCl</td>
<td>-5°C</td>
</tr>
<tr>
<td>A₃</td>
<td>Aniline</td>
<td>(NH₄)$_₂$S₂O₈</td>
<td>0.1M HCl</td>
<td>+5°C</td>
</tr>
<tr>
<td>B₁</td>
<td>Aniline</td>
<td>(NH₄)$_₂$S₂O₈</td>
<td>1M CF₃COOH</td>
<td>-15°C</td>
</tr>
<tr>
<td>B₂</td>
<td>Aniline</td>
<td>(NH₄)$_₂$S₂O₈</td>
<td>1M CF₃COOH</td>
<td>-5°C</td>
</tr>
<tr>
<td>B₃</td>
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<td>+5°C</td>
</tr>
</tbody>
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vacuum filtration and the precipitate was washed with acetone to remove the unreacted aniline. PANI synthesized by this method was formed in its protonated state and it is dark green in colour. The precipitate was dried, washed and allowed to equilibrate with an appropriate amount of ammonium hydroxide overnight. This process converted (dedoped) the PANI to its EB form.

The mechanisms of formation of PANI-EB, PANI-LEB and PANI-PGB are given in Fig. 1.

Samples are compressed into pellets of $1.5 \times 10^{-1}$ cm diameter and $7.4 \times 10^{-2}$ cm thickness by applying a pressure of $\sim 700$ kgf/cm$^2$.

**Spectroscopic analysis**

IR spectra were recorded on Perkin Elmer-2000 spectrophotometer in KBr pellets.

**DC conductivity measurements**

Temperature dependent DC conductivity measurements were carried out with the samples in the temperature range from 30°C to 90°C. The resistivities of different PANI EB samples were measured by two-probe measurements, as their resistances are relatively high. A Keithley electrometer 6517-A was used in two-probe measurements. Electrical contacts were made using silver paste. It has two spring load contact probes. These probes moved in a pipe and are insulated by teflon washers. This probe arrangement is mounted in a suitable stand, which also holds the sample plate and RTD sensor. The stand also serves as the lid of PID controlled oven. Teflon coated leads are provided for connecting with High Voltage Power Supply EHT-11 and Digital Pico ammeter DPM-111. In the set-up, maximum voltage was equal to 1500 V; current $100 \times 10^{-12}$ A (max) and thickness of sample was 1 mm. The resistivity of the sample could be measured up to $10^{14}$ ohm.cm.

**Thermal analysis**

Phase transitions were investigated over the range of 50-300°C in N$_2$ atmosphere using a Perkin-Elmer diamond differential scanning calorimetry (DSC).

**Results and Discussion**

The FTIR spectra of polyaniline films ($A_1$, $A_2$, $A_3$, $B_1$, $B_2$ and $B_3$) were obtained. All polyanilines were found in their emeraldine base form. The peak near 800 cm$^{-1}$ is due to the N-H out of plane bending. The strongest band observed near 1100 cm$^{-1}$ and 1235 cm$^{-1}$ are due to C-C stretching and C-C twisting of the alkyl chain, respectively. The presence of quinoid ring is also suggested by the peak at 1163 cm$^{-1}$, which is

![Chemical structures and mechanisms of formation of PANI-EB, PANI-LEB and PANI-PGB](image)

**Fig. 1** – (a) A general scheme for polymerization of aniline and (b) different oxidation state of PANI
characteristic of the electronic like absorption of the [N=Q=N] vibration. The peak at 1300 cm\(^{-1}\) is due to the C-N stretching of the polymer.

The spectra are very similar displaying a vibrational peak at 1591 cm\(^{-1}\) assigned to the stretch of the quinoid (Q) ring and a peak at 1496 cm\(^{-1}\) assigned to the stretch of the benzenoid (B) ring. According to results reported previously, these bands are of almost equal intensity indicating that the polymer backbone contains equal population of quinoid and benzenoid rings. The C=C stretch absorption of aromatic compound generally present in the range of 1475-1600 cm\(^{-1}\). In the present study, this peak was obtained at 1496 cm\(^{-1}\). The peaks due to N-H bending can be seen in the range of 1560-1640 cm\(^{-1}\). The peak near 3000 cm\(^{-1}\) in due to the C-H stretching absorption. The stretching peak of N-H appeared in the range of 3390-3400 cm\(^{-1}\). The C-Cl stretching peak arises in the range of 590-700 cm\(^{-1}\).

Polyaniline acts as an electrically conductive material only in the protonated form of emeraldine salt. Arrhenius relation-gives the relationship between the activation energy \(E_a\) and the conductivity:

\[
\sigma T = A \exp\left(-\frac{E_a}{kT}\right) \quad \ldots (1)
\]

Where, \(A\) is pre-exponential constant, \(k\) is Boltzmann constant (1.38 \times 10^{-23} \text{ J/s and } E_a\) is activation energy (eV).

\(\sigma_{dc}\) is related with Nernst-Einstein equation:

\[
\sigma_{dc} = q^2 ND / kT \quad \ldots (2)
\]

Where, \(q\) is charge of the ion, \(N\) is number density of mobile ion and \(T\) is temperature in Kelvin.

In case of conducting polymers, the total conductivity is a function of inter-chain conducting. For completely doped polyaniline, the number of charge carrier \((n)\) is usually maximized; thus, conductivity depends on the charge mobility. The intra-chain mobility primarily depends on the conjugation length (extent of conjugation) and the number of defects. The inter-chain mobility depends on the degree of crystallinity, which is a function of the proximity and orientation of neighbouring chains\(^{10,11}\). In addition, the counter ions are capable of introducing defects by causing significant charge polarization in neighbouring chains. The major contributor to the overall conductivity of polyaniline is inter-chain charge transport\(^{12}\). Charge transport mechanism depends on a number of factors including temperatures and protonation (doping) level. The interaction between polyaniline and polar molecule is strong and this interaction induces a redistribution of charge, resulting in enhanced conductivity\(^{13}\). Water acts as a proton carrier from one side of the chain to another increasing the interaction, mobility, and delocalizing the electrons along the chain\(^{14}\). Transport properties (d c electrical conductivity), was measured for a series of conducting polyaniline films using the Eq. (3).

\[
\rho = \frac{1}{AT^{3/2} \exp\left(\frac{E_g}{2kT}\right) e^{\left(\frac{\mu_n + \mu_p}{\mu}\right)}} \quad \ldots (3)
\]

Where \(\rho\) is resistivity(ohm.cm) , \(E_g\) is energy gap (eV), \(e\) is charge on electron (e.s.u.), \(\mu_n\) is hole mobility \((\text{m}^2\text{V}^{-1}\text{s}^{-1})\), \(\mu_e\) is electron mobility \((\text{m}^2\text{V}^{-1}\text{s}^{-1})\) and \(A\) is pre-exponential factor (independent on temperature).

DC and AC electrical conductivity measurements on 1D conductor provide valuable information like nature of current carrier, 3D effects, scattering by defects, impurities and solution propagation. Therefore, the measurement of conductivity was performed over a wide range of temperature above room temperature as:

\[
\ln \rho = \ln K + \frac{E_g}{2kT} \quad \ldots (4)
\]

If the carrier, conductivity does not vary much with the temperature, then the second term in Eq. (4) is negligible. Then it becomes:

\[
\ln \rho = \ln K + \frac{E_g}{2kT} \quad \ldots (5)
\]

Where

\[
K = \frac{1}{Ae\left(\mu_n + \mu_p\right)}
\]

\[
\log_{10} \rho = \frac{1000E_g}{2.303 \times 10^3 \times 2kT} + \log_{10} K \quad \ldots (6)
\]

If graphs are plotted between \(\log_{10} \rho\) and 1000/T, (Fig. 2) then the slope \(m\) from Eq. (6) is

\[
m = \frac{E_g}{2.303 \times 2K \times 10^3} \text{ and band gap } E_g = 2K \times m \times 2.303 \times 10^3 \text{ Joule},
\]

where \(k = 1.38 \times 10^{-23}/1.6 \times 10^{-19} \text{ eV}\) = 8.6 \times 10^3 \text{ eV}

The plots of \(\log \sigma /\text{s} 1000/T\) were also drawn (Fig. 3). It was observed that the conductivity of PANI EB films increased with increase in temperature.
The band gaps of different PANI EB films were calculated. These are reported in Table 2.

Polyaniline consists two kinds of rings, quinoid ring with hybridized orbitals, which is resonance stabilized and it enables charge transport between chains, while benzenoid rings are non-conductive in nature. The electrical conductivity and mechanical properties of polyaniline increase with the decreasing reaction temperature and are optimum almost at stochiometric ratio of oxidant, dopant and aniline. The films obtained are compact in nature with good mechanical properties. The conductivity of polyaniline does not depend on the temperature of surroundings, which indicates a small energy gap. The endotherm height (half-vitrification) is the temperature ($T_{0.5}$), where the thermal transition has approximately reached the inflection point. According to ASTM-E 1356 and ASTM-D 3418, extrapolated temperature and half-vitrification temperature is specific for glass transition temperature of maximum slope (peak of derivative plot). It is called $T_p$, the temperature at which largest fraction of sample melts. The area under the degradation endothermic peak is directly proportional to heat of volatilization. The DSC thermograms were also recorded using Perkin Elmer model diamond and the data given in Table 3.
These plots show that the DSC heat flow as a function of sample temperature and endothermic response (heat absorbed by sample) is oriented towards the top of the graph. Irreversible heat flow curve indicates two major endothermic peaks that resemble those observed in the conventional DSC thermograph. Two major endothermic peaks are observed in temperature range 54-116°C. The first endothermic peak lies in the range of 25-60°C, which may be mostly likely due to the evaporation of sorbed water molecules. The second endothermic peak (90-115°C) might be due to cross linking reaction of the coupled quinoid rings in the polymer. The first heating peak among the samples of PANI EB-A was obtained for PANI EB-A, which melts at 116.36°C with total heat of melting of 727.69 J/g, while among samples of PANI EB - B, PANI EB-B melts at 103.45°C with total heat of melting of 87.87 J/g. PANI EB-A has maximum area (4780.985 mJ) under the degradation endothermic peak in PANI EB-A while PANI EB-B has maximum area (1625.87 mJ) under the degradation endothermic peak in PANI EB-B.

### Conclusions

All the PANI EB showed two redox couples. In each polyaniline, the benzenoid form was first oxidized to the emeraldine form, which was followed by its oxidation to the quinoid form. Conductivity varied from $10^{-5}$-$10^{-6}$ S/cm depending on the composition. The decrease in conductivity with increase in annealing temperature is related to moisture loss of dopant ions and polymer degradation. The cross-linking process of PANI-EB was also observed during heat treatment. Longer heat treatment time leads to more pronounced cross-linking, which reduces solubility of polymer and also the electrical conductivity.

### References