Electron spin resonance spectroscopy and electrical conductivity studies on some polyaniline salts and their bases

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Received 25 March 2004

Four different polyaniline salts have been prepared by chemical oxidative polymerization of aniline with benzyol peroxide as a novel oxidant employing inverse emulsion method at ambient temperature using different protic acids (HCl, H2SO4, H3PO4 and sulphosalicylic acid). Their corresponding bases have been obtained by dedoping the salts with aqueous ammonium hydroxide. The polyaniline HCl salt exhibits the highest room temperature conductivity ($2.31 \text{ S cm}^{-1}$). Temperature dependent EPR studies reveal Curie-Weiss and thermally activated paramagnetism for the polyaniline salts. No correlation between the magnetic properties and conductivity could be found.

IPC Code: Int. Cl.7 G01J 3/06; G01R

Among the family of conducting polymers, polyaniline and its derivatives have been the focus of attention due to their unique magnetic, optical and transport properties and high environmental stability$^1$. Different forms of polyaniline varying only in the degree of oxidation are known, among them the most important one being the emeraldine form containing equal amount of the oxidized and the reduced units in the polymer chain. The conductivity of polyaniline could reversibly be controlled by both redox and protonation methods$^2$. A striking feature of polyaniline is that the insulating emeraldine base form of polyaniline can be rendered conducting on protonation by treatment with aqueous acids$^3$ (Fig. 1). The conductivity increases by over six orders of magnitude. Protonated polyaniline is a highly disordered material. It is known to be inhomogeneously doped showing protonated regions

![Fig. 1—Scheme of protonation and polaron formation in polyaniline](image-url)
called conductive islands, distributed sparsely in the bulk of the unprotonated matrix\textsuperscript{4}.

Heavily doped conducting polymers are a class of quasi one-dimensional materials. It is generally assumed that the electron transport occurs primarily along the polymer chains\textsuperscript{5}. Conductivity\textsuperscript{6,7}, optical reflectance\textsuperscript{8} and magnetoconductivity\textsuperscript{9,10} of oriented "metallic" polymers have been found to be highly anisotropic. Models have been proposed based on the assumption that each polymer chain is an isolated one-dimensional conductor to account for many experimental observations\textsuperscript{11-13}.

Electrically conducting polymers contain a large number of unpaired electrons due to the defects in the polymer chains. These defects are caused mainly by the protonation induced spin unpairing mechanism, which causes a rearrangement in the structure of polyaniline having the following repeat unit,

\[
\begin{align*}
\text{(A-)} &-\text{-NH-} &\text{NH}^- &+ (A^+) \\
\end{align*}
\]

where A\textsuperscript{-} denotes the counter anion and \(A^+\) an unpaired spin and a positive charge in the repeat unit\textsuperscript{11,14}.

Significant increase in the paramagnetism arises chiefly due to the protonation of the polymer. Self-trapped carriers arising due to protonation of the conjugated polyaniline chains generate polarons and bipolarons. Two polarons under certain conditions couple to form a bipolaron. Polaron and bipolarons are localized excitations in non-degenerate conducting polymers. Bipolarons are spinless while polarons with spin of \(\pm 1/2\) are EPR active.

EPR spectroscopy has been used to obtain information on spin localization and mobility and also to understand the interaction of the polaron spin with the environment\textsuperscript{15-18}. Studies have revealed the highly paramagnetic nature of polyaniline with spin concentrations of about \(10^{19}-10^{21}\) spins/g\textsuperscript{9}. The magnetic properties of polyaniline have been interpreted by Epstein and MacDiarmid\textsuperscript{20} in two ways. One is concerned with the presence of two kinds of spins, namely, the Curie and Pauli spins as noted by the variation of magnetic susceptibility of polyaniline with temperature. The second concept is concerned with the presence of conducting metallic islands in a less conducting material in the bulk of polyaniline\textsuperscript{21}. EPR spectra of chemically synthesized polyaniline show a single signal of either Gaussian or Lorentzian shape\textsuperscript{21}. EPR spectra of electrochemically synthesized polyaniline have also been investigated\textsuperscript{22-24}. At higher doping levels, the spin concentration decreases due to pairing of polarons to bipolarons. Only at lower doping levels the identity between the spins and charge carriers, i.e. polarons, is valid as shown by the earlier EPR and conductivity studies. Spin susceptibility may decrease in some cases due to crossover from Curie to Pauli susceptibility\textsuperscript{25-28}.

Studies on temperature dependent EPR spectra and ambient temperature conductivity on some polyaniline salts and their bases are reported here. The polyaniline salts were synthesized using benzoyl peroxide as a novel organic oxidizing agent instead of conventional ammonium persulphate, with four different protic acids, namely, hydrochloric (HCl), sulphuric (H\textsubscript{2}SO\textsubscript{4}), \(\alpha\)-phosphoric (H\textsubscript{3}PO\textsubscript{4}) and sulphasaliclic (SSA) acids. The salts were converted to their corresponding bases using ammonium hydroxide. The polyaniline salts and bases have been characterized by electronic, FT-IR, FT-Raman and EPR spectroscopic techniques and also by conductivity studies.

**Materials and Methods**

**Preparation of polyaniline salts and bases**

Sodium lauryl sulphate in 50 ml of water (0.1 M) was added to a solution of benzoyl peroxide (0.2 M) in chloroform with stirring to obtain a milky white emulsion. Aniline (Merck) (0.1 M) was added to it followed by the dropwise addition of 100 ml of an aqueous solution of the dopant acid (HCl/H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{3}PO\textsubscript{4}/sulphasaliclic acid) over a period of 1/2 h. As the reaction proceeded, the colourless emulsion turned green. The reaction was allowed to proceed for 24 h. The organic phase was separated and washed repeatedly with water. The dark green polyaniline solution in chloroform was treated with anhydrous sodium sulphate to remove the excess of water. The viscous organic solution was then added to 1.5 l of acetone in order to break the emulsion. The precipitated polyaniline salt was recovered by filtration as a dark green powder. It was washed with acetone and dried in vacuum for 36 h.

Part of the polyaniline salt synthesized was converted into the emeraldine base by overnight treatment with 0.5 M NH\textsubscript{4}OH. The base obtained was filtered, washed with 0.5 M NH\textsubscript{4}OH and dried in vacuum for 36 h.
Physical measurements

The dc conductivity of the samples was measured at ambient temperature using the four probe method (pressure contact) on pressed pellets obtained by subjecting the powder to a pressure of 50 kN/m². The error in the resistance measurements under galvanostatic condition using a Keithley model 220 programmable current source and a Keithley model 195A digital voltmeter is less than 2%. The consistency in the measurements was checked by measuring the resistance twice for each pellet and for a batch of two pellets for each sample. The error in measuring the length and area of the pellet using Vernier calipers is 2-3%. The error in the conductivity value is expected to be < 3%.

EPR spectra were recorded using a Varian E109 spectrometer operating in the X-band. The sample tube was evacuated to remove the moisture before recording the spectrum. The spectra were recorded at different temperatures from room temperature to 200°C at regular intervals. To obtain the g value and spin concentration, the EPR spectra of the sample and charred dextrose as a standard were recorded under identical conditions of microwave frequency (9.05 GHz), microwave power (2 mW), modulation frequency (100 kHz), field set (3280 G), scan range (100 or 200 G), modulation intensity (1 Gpp), modulation time (0.064 s) and scan time (200 s). The spin concentration was determined by comparing the area under the EPR signal of polyaniline with that of charred dextrose. The calculated areas are likely to be within 5% of the true value.

The UV-visible absorption spectra of the samples in dimethylsulphoxide (DMSO) were measured using a Hitachi U-3000 spectrophotometer. FT-IR spectra were recorded with a Bruker Equinox 55 instrument by the KBr pellet technique. FT Raman spectra were obtained with a Bruker RFS100/S spectrometer using Nd³⁺: YAG laser with 30-40 mW power at the sample.

Table I—Absorption maxima for the polyaniline salts and their bases in DMSO

<table>
<thead>
<tr>
<th>Polyaniline</th>
<th>UV-visible spectra (λ, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pani-HCl salt</td>
<td>326 433 630 820</td>
</tr>
<tr>
<td>Pani-H₂PO₄ salt</td>
<td>332 436 625</td>
</tr>
<tr>
<td>Pani-H₂SO₄ salt</td>
<td>330 435 621 840</td>
</tr>
<tr>
<td>Pani-SSA salt</td>
<td>330 440 635 930</td>
</tr>
<tr>
<td>Pani-HCl base</td>
<td>330 — 625 —</td>
</tr>
<tr>
<td>Pani-H₂PO₄ base</td>
<td>327 — 632 —</td>
</tr>
<tr>
<td>Pani-H₂SO₄ base</td>
<td>320 — 624 —</td>
</tr>
<tr>
<td>Pani-SSA base</td>
<td>325 — 625 —</td>
</tr>
</tbody>
</table>

Results and Discussion

Absorption spectra

Table 1 gives the absorption maxima for the polyaniline salts and bases in DMSO solution. As representative of the systems, the absorption spectra of polyaniline-sulphosalicylic acid salt and its base are given in Fig. 2. The spectrum of the polyaniline base exhibits two bands near 325 and 625 nm, whereas that of the salt shows four bands around 330, 440, 630 and 825 nm. The electronic absorption spectrum thus helps to detect the presence or otherwise of the polyaniline salt and its base.

The 325 nm absorption band is assigned to the π–π transition of the phenyl rings. The absorption at 620 nm is attributed to the exciton transition (n−π*) from the HOMO of the benzenoid ring (non-bonding nitrogen lone pair) to the LUMO (π*) of the quinoid ring. The bands around 430 and 830 nm observed in the salts have been assigned as due to the polaron transition³. The absorption spectra of doped polyaniline (Table 1) exhibit bands at 840 and 440 nm demonstrating the presence of the salt form of polyaniline.

FT-IR and FT Raman spectra

The FT-IR spectra of polyaniline HCl salt and its base are given in Fig. 3. Changes in the infrared spectrum of the emeraldine base on protonation to the salt form may be expected due to changes in the dihedral angle between adjacent phenyl rings and the
changes in the electronic structure. The doping of polyaniline leads to the formation of \(-Q=N^+\)H\(^{+}\) groups. A positive charge on the polymer chain may lead to an increase in the dipole moment of the molecule, consequently resulting in increased intensity of the IR bands\(^{32}\). Most of the bands of the base are shifted towards lower frequencies in the spectra of the polyaniline salts due to the conversion of the quinoid rings to the benzenoid form. The bands at 1294 and 1234 cm\(^{-1}\) in the spectrum of the salt correspond to N–H bending and asymmetric C–N stretching mode of the benzenoid ring respectively. The band at 1573 cm\(^{-1}\) in the salt spectrum is assigned to the C=C ring stretching vibration. The band at 1475 cm\(^{-1}\) corresponds to the C–N stretching mode of the quinoid ring, which decreases in intensity on protonation of polyaniline by the dopant. In the IR spectrum of the salt, a band of medium intensity appears near 875 cm\(^{-1}\), which is absent in the spectrum of the base. It is assigned to the ring-breathing mode of the quinoid group. A medium intensity band at 3230 cm\(^{-1}\) is assigned to the NH stretching mode. The presence of \(SO_3^-\) and \(-COOH\) groups is shown by the appearance in the spectrum of the salt doped with sulphosalicylic acid of bands around 570 and 1693 cm\(^{-1}\) arising from the degenerate bending mode of the \(SO_3^-\) group and carbonyl stretching respectively.

The Raman spectrum of polyaniline base has an intense band near 1500 cm\(^{-1}\) assigned chiefly to the benzenoid C–C ring stretching vibration and a band near 1600 cm\(^{-1}\) attributed to the quinoid C=C stretching mode of the polymer chain. The bands at 1598, 1508 and 1376 cm\(^{-1}\) are strengthened and new bands appear on the high/low frequency side for each of these bands in the spectra of the polyaniline salts. Several new less intense bands also appear in the Raman spectra of the salts. The 1328 cm\(^{-1}\) band in the salt is assigned to the C–C stretching mode of the quinoid ring. Due to differences in the conformation of the polymer and the extent of doping, the frequency of the C–C stretching vibration varies. The C=C bond is strengthened in the protonation induced polaron lattice. In particular, the Raman band at 1173 cm\(^{-1}\) assignable to the out of plane –CH bending, which is of weak to medium intensity, appears upon doping with dramatically enhanced intensity as the strongest band in the spectrum and its intensity increases with protonation. It can be assigned to \(Q=N^+\)H structure which is formed on protonation.

**Room temperature conductivity**

The electrical conductivity of the polyaniline salts and their bases is presented in Table 2. The conductivity of Pani-HCl salt is the highest (2.31 S cm\(^{-1}\)), and that of Pani - \(H_2\)PO\(_4\) salt the lowest (7.33 \(\times\) 10\(^{-2}\) S cm\(^{-1}\)). The conductivity of polyaniline base (10\(^{-9}\)-10\(^{-10}\) S cm\(^{-1}\)) is much lower than that of the corresponding salt.
Room temperature EPR spectra

Ambient temperature EPR parameters of polyaniline salts and their bases are given in Table 2. The g value and the A/B ratio (that is, the ratio of the area of the positive to the negative peak) do not reveal unambiguously the nature of the polymer as to whether it is a salt or a base. The actual differentiation between the salt and the base is provided by the spin concentration and linewidth (ΔH). For a typical polyaniline salt, the spin concentration is around 10²⁰ spins g⁻¹ and the value of ΔH is smaller, 2.0-3.0 G. On the other hand, for the base, the spin concentration is lower, about 10¹⁸ spins g⁻¹ and the value of ΔH is greater, about 8.0-12.0 G⁻¹.

The g value of the polyaniline salts and their bases lies in a very narrow range 2.0008-2.0025. It indicates that the radical electron spin is localized on or near the nitrogen atom and on the π system of the polyenes and aromatics. A shift in the g value of at least 10⁻³ occurs when the radical spin is localized on or near the heteroatom.

In the EPR spectra of the polyaniline salts the observed linewidth ranges from 2.25 to 5.75 G. The smaller linewidth suggests mobility of the spins and there may also be strong exchange coupling. The observed linewidth for the corresponding polyaniline bases is greater, ~9.50 and 12.50 G.

The spin concentration of the polyaniline salts varies from 7.6x10¹⁹ to 3.23x10²⁰ spins g⁻¹ while that of the polyaniline bases is lower, ~10¹⁸ spins g⁻¹. When polyaniline is doped with a protonic acid, the quinone imine nitrogens are protonated first forming bipolarons which are EPR inactive. An internal redox mechanism converts the bipolarons formed on protonation into two polarons which migrate successively to reduce the Coulombic repulsions. A decrease in the spin concentration in the base is attributed to the formation of bipolarons by spin pairing mechanism.

The EPR spectra of the polyaniline salts and their bases exhibit a single signal without hyperfine splitting. The calculated skin depth for the polyaniline salts and their bases is given in Table 2. The skin depth δ is defined as the depth at which the current decays to 1/e (= 0.369) of its value at the surface. It is given by the relation,

\[
\delta = \frac{\pi \sigma \mu_0 \nu}{\sigma \mu_0} \frac{1}{m}
\]

where \( \mu_0 \) denotes the permeability of vacuum \( (4\pi \times 10^{-7} \text{ Hm}^{-1}) \), \( \sigma \), the electrical conductivity \( (\text{S m}^{-1}) \) and \( \nu \) the microwave frequency \( (9.05 \times 10^9 \text{ Hz}) \). The calculated value of \( \delta \) for the polyaniline salts is of the order of 10⁻⁴ m which is greater than that of a good conductor such as copper which has a value of 6.6 \times 10⁻⁷ m at a typical EPR frequency. In a good conductor, the conductivity is very high and no free charges are present. Free charges generated in a good conductor move to the surface with a time constant \( \tau = \sigma / \varepsilon \) (\( \varepsilon \) = permittivity and \( \sigma \) = conductivity), which is extremely small. For the bases, however, the value of \( \delta \) varies from 11.83 to 30.58 m (Table 2) which is typical of an insulator. For thin samples, the absorption curve is symmetrical and the line shape is Lorentzian since no Dysonian effect is expected. The characteristic effect of electron diffusion is to change the shape of the EPR signal rather than to broaden it.

Variable temperature EPR spectra

Temperature dependent EPR studies carried out on polyaniline salts and their bases have shown the g

<table>
<thead>
<tr>
<th>System</th>
<th>Conductivity (S cm⁻¹)</th>
<th>g value</th>
<th>Linewidth (G)</th>
<th>Spin conc. (spins g⁻¹)</th>
<th>Skin depth δ (m)</th>
<th>λ = 0/δ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pani-HCl</td>
<td>2.31</td>
<td>2.0005</td>
<td>5.75</td>
<td>7.6290x10¹⁹</td>
<td>3.4840x10⁻⁴</td>
<td>8.6108</td>
</tr>
<tr>
<td>Pani-H₂PO₄</td>
<td>7.33x10⁻¹²</td>
<td>2.0018</td>
<td>2.25</td>
<td>3.2370x10⁻²⁰</td>
<td>1.5951x10⁻³</td>
<td>1.5352</td>
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<tr>
<td>Pani-H₂SO₄</td>
<td>1.48</td>
<td>2.0012</td>
<td>2.75</td>
<td>2.6003x10⁻²⁰</td>
<td>4.3473x10⁻⁴</td>
<td>6.9008</td>
</tr>
<tr>
<td>Pani-SSA</td>
<td>5.90x10⁻¹⁴</td>
<td>2.0025</td>
<td>2.25</td>
<td>3.1872x10⁻²⁰</td>
<td>6.8876x10⁻⁴</td>
<td>4.3557</td>
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<td>Base</td>
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<tr>
<td>Pani-HCl</td>
<td>2.00x10⁻⁹</td>
<td>2.0001</td>
<td>11.00</td>
<td>6.3515x10¹⁸</td>
<td>11.8299</td>
<td>2.5399x10⁻⁴</td>
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<td>2.99x10⁻¹⁰</td>
<td>2.0023</td>
<td>10.25</td>
<td>9.0043x10¹⁸</td>
<td>30.5752</td>
<td>9.8119x10⁻⁵</td>
</tr>
<tr>
<td>Pani-H₂SO₄</td>
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<td>2.0001</td>
<td>12.50</td>
<td>1.0957x10¹⁸</td>
<td>18.5236</td>
<td>1.6196x10⁻⁴</td>
</tr>
<tr>
<td>Pani-SSA</td>
<td>5.24x10⁻¹⁰</td>
<td>2.0001</td>
<td>9.50</td>
<td>4.9766x10¹⁸</td>
<td>23.1048</td>
<td>1.2984x10⁻⁴</td>
</tr>
</tbody>
</table>
value and the A/B ratio to be temperature independent. However, the linewidth (ΔH) and the spin concentration vary. The behaviour of both PaniiH₂SO₄ (Fig. 4a) and Panii-SSA salts is similar i.e. ΔH decreases up to 353 K and then increases with temperature. For Panii-H₃PO₄ salt, ΔH is nearly constant (2.25 G) up to 403 K and then increases with temperature up to 473 K. On the other hand, Panii-HCl salt shows a decrease in ΔH with rise in temperature.

If the hopping rate for the spins is faster than the relaxation time (inverse of EPR time scale), the spins would experience an averaged magnetic environment leading to narrowing of the EPR line profile. Both Panii-H₃PO₄ and Panii-H₂SO₄ bases show a steady decrease in ΔH from room temperature up to 473 K (Fig. 4b) and Panii-SSA base also shows a similar trend as the Panii-HCl base. For Panii-HCl salt, Wang et al. have reported that at T > 100-200 K, ΔH increases with temperature while at lower temperatures, ΔH decreases with increase in temperature and a minimum occurs between 150 and 200 K.

The spin concentrations of polyaniline salts and bases under investigation also show different variations with temperature.

i) The spin concentration of Panii-H₃PO₄ (Fig. 5a), Panii-H₂SO₄, and Panii-SSA salts decreases with temperature indicating paramagnetism of the Curie-Weiss type.

ii) The bases of Panii-SSA, Panii-H₃PO₄ and Panii-HCl show enhanced spin concentration with temperature. This kind of behaviour is known as thermally activated paramagnetism through super exchange generally show thermally activated paramagnetism.

iii) The Panii-HCl salt initially, up to 383 K, exhibits paramagnetism of the Curie-Weiss type, and from 383 K onwards it displays thermally activated paramagnetic behaviour (Fig. 5c), that is, the spin concentration increases with temperature. On the other hand, the Panii-H₂SO₄ base shows thermally activated paramagnetic behaviour up to 403 K and then
as the temperature is raised further, it shows
the Curie-Weiss type of paramagnetism, that is,
the spin concentration decreases with

The different variations in the spin concentration
with temperature for different polyaniline salts may
arise due to the different characteristics, such as the
molecular shape, molecular motion and polarity of the
counter ions. Thus the properties of polyaniline
arise due to the different characteristics, such as the

The spin dipole-dipole interaction contributes to
1/T_2' in the case of isolated spins. The spin dipole-dipole interaction \( \omega_d \) is given by,
\[ \omega_d = \gamma H_d \]
where \( H_d = 5.1 \times (g \mu_B n)^2 S(S+1) \)

Here \( n \) denotes the spin concentration, \( \mu_B \) is the
Bohr magneton and \( S = 1/2 \)

The hyperfine interaction \( \omega_h \) can be obtained from the Eqs (5) and (6)
\[ \omega_h = \gamma H_h \]
and \[ H_h = (1/3) A^2 I (I+1) \]
where \( A \) is the hyperfine splitting constant (for amine
nitrogen NH\(^+\), \( A = 30 \text{ G} \)) and \( I \) is the nuclear spin (for
\(^{14}\text{N}, I = 1)\)

On substituting the values, we obtain \( H_h^2 = 600 \text{ G}^2 \).

If the spins are movable or if there is exchange
interaction \( \omega_e \), then the
\[ 1/T_2' = [(10/3) \omega_d^2 + \omega_h^2] / \omega_e \]

The exchange interaction \( \omega_e \) is given by \( \gamma H_e \) where
\( \gamma \) defined above is the gyromagnetic ratio.

Equation (2) can be rewritten as,
\[ \Delta H_{1/2} = \gamma^4 (1/T_2') \] (8)
when the contribution from \( T_1 \) is negligible (as \( T_1 \to 0 \)). Equation (7) can also be rewritten as,
\[ H_e = [(10/3) H_d^2 + H_h^2] / \Delta H_{1/2} \] (9)

The values of \( \Delta H_{1/2} \), \( H_d^2 \), \( H_e \) and \( \omega_e \) for the
polyaniline salts and bases under investigation have
been calculated. The exchange interaction rate is a
function of i) the interchain exchange integral \( t_2 \),
ii) mean free time \( \tau \) for the electron moving along the
chain and iii) the interchain mean free time \( \tau_2 \). When
\( \omega_e \) is much smaller than \( 1/2 \tau \), localization occurs. It is
observed that the value of \( \omega_e \) is much smaller (\( 10^8 \) to
\( 10^9 \text{ Hz} \)) than the scattering rate (\( 1/\tau \sim v_f / l_i \sim 10^{15} \text{ Hz} \)
where, \( l_i \) is the mean free path and \( v_f \) is the electron
transverse velocity). The electrons are therefore in
localized regions and hopping conduction mechanism
is assumed in the amorphous region.37

EPR and conductivity

i) The spin concentration of Pani-HCl salt, \( 10^{19} \)
spins \( \text{ cm}^{-3} \), is an order of magnitude lower than
that of Pani-H_3PO_4 salt, \( 10^{20} \) spins \( \text{ cm}^{-3} \).
However, the conductivity of the former is
much higher (2.31 S cm\(^{-1} \)) than that of the latter
(7.33 \( \times 10^{2} \) S cm\(^{-1} \)).

ii) The spin concentrations of Pani-H_2SO_4 and
Pani-H_3PO_4 salts are comparable (\( 10^{20} \) spins
\( \text{ cm}^{-3} \)). However, the conductivity of the latter is
nearly two orders of magnitude lower than that of the former (Table 2). These results do not lend
support to the assumption that the EPR signal is due to the same species that carry the
electric current as discussed above.

iii) For the polyaniline salts, the variation in EPR
linewidth is small although there is a large
variation in their conductivity (Table 2). The
carrier mobility apparently is also not related to
the linewidth.

From the above observations, it may be said that the
paramagnetic centers alone do not contribute to the
conductivity, since no correlation seems to exist
between conductivity and spin concentration. The
observed thermally activated paramagnetism suggests
the formation of bipolarons from polaronas. A polaron
that is present on a positively charged nitrogen, by
polarization of the electron on the adjacent carbon
atom, induces spin polarization in succession until an
unpaired electron is encountered on a nitrogen atom.
It leads to two unpaired electrons that are coupled antiferromagnetically. It involves the interaction of a number of polaron spins that are present along the polymer chain. The polarons or radical cations are EPR active. The presence of polarons in polyaniline salts and their bases is evident from the EPR studies. In polyaniline both polarons and bipolarons exist, while polarons are spin carriers, the charge carriers are polarons as well as bipolarons. Similar observations have been made from studies on polypyrroles and poly(4,4'-methyleneedianiline).

**Conclusion**  
The EPR spectroscopic studies have revealed for the polyaniline salts of HCl, H2SO4, H3PO4 and sulphosalicylic acid paramagnetism of Curie-Weiss type. However, the bases display predominantly thermally activated paramagnetism. The EPR line shape is Lorentzian and Dysonian effect is not observed. In polyaniline the presence of both polarons and bipolarons is suggested from EPR studies. There appears to be no relationship between conductivity and spin concentration. Thus the charge transport cannot be explained solely in terms of the migration of the paramagnetic species. The electrons are present in a localized region and hopping conduction is assumed in the amorphous regions of polyaniline.

*Supplementary material available*  
Tables 3-6 listing the values of spin concentration, g factor, ΔH, Hν2, Hν, and Ω, of the polyaniline salts and their bases are available from the authors.

**Acknowledgement**  
The authors thank Mrs. Prathima Srinivasan, Materials Research Center of the Institute for her help in recording the EPR spectra.

**References**