

## Electron localization in substituted derivatives of poly(aniline)

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Aromatic ring substituted and N-substituted derivatives of poly(aniline) have been synthesized. Their electronic spectra, magnetic properties, ESR and electrical conductivity data have been presented and discussed in terms of electron localization due to substituent in the ring of poly(aniline).

Polyaniline (PANI) has emerged as an interesting conducting material. In addition to the electrical properties of the conducting polymers related to the doping level (oxidation level), PANI exhibits fascinating behaviour as a function of both the protonation level and the dehydration level. It has been shown that PANI undergoes a large conductor-to-insulator transition as a function of pH of the solution in which it has been equilibrated<sup>1-3</sup>; as a result, the conductivity can change by ten orders of magnitude while the number of electrons of the polymer chain remains the same<sup>4</sup>. It has also been proposed that the transition to conducting state is accompanied by an increase in spin susceptibility<sup>1</sup>, based on which, a granular polymeric metal model<sup>5</sup> has been proposed. According to this model, the conducting state is made of metallic particles embedded in an unprotonated insulating sea. Recently<sup>6</sup>, it has been confirmed by spin dynamics technique with magnetic resonance that this insulator to conductor transition is percolative in origin, consistent with the granular model. But 'the conducting island' consists of only a single or very few polymer chains<sup>4-7</sup>. Substituted PANI, with substituents either on the aromatic ring or the N-atom, have been synthesized and studied<sup>9-13</sup> in order to understand the effect of substituents on the crystal structure and the solubility of PANI.

In this paper we report UV-visible spectra, ESR, magnetic and conductivity data with a view to understanding the effect of the substituents in terms of the electron localization in PANI.

### Materials and Methods

#### Preparation of polymer

Oxidized poly(substituted aniline) was prepared by peroxodisulphate oxidation in a manner similar to that described earlier<sup>9-12</sup>. Usual chemical analy-

sis of the products showed the presence of sulphate and perchlorate anions.

Elemental C, H and N analyses of all the polymer samples were carried out by micro-analytical techniques using a Carlo Erba Strum DP 200 instrument at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow.

UV-visible spectra of all the polymer samples were recorded at room temperature in dimethylformamide in 200-700 nm range using a UV 240 Shimadzu automatic recording double beam spectrophotometer.

#### Measurement of electrical conductivity

Electrical conductivities of the samples were measured at different temperatures in terms of resistivity by two probe method. Powdered samples were made into pellets under a pressure of 5 metric tons cm<sup>-2</sup>. The pellets thus prepared were crack-free, hard and smooth. The resistance was measured on a DC resistance bridge in the range 28 ohm-3.5 × 10<sup>8</sup> ohm. The measured resistance was converted to conductivity using the dimensions of the pellet.

#### Measurement of susceptibility

The magnetic susceptibilities of the samples were determined by Gouy's method at room temperature at varying magnetic fields between 0.23 and 0.98T. Mercury tetrakis(thiocyanato)cobaltate (II), Hg[Co(CNS)<sub>4</sub>] was used as the reference material to calibrate the sample holder. Magnetic susceptibility values per two ring unit mole were computed from the change in mass of the sample under applied magnetic field. Diamagnetic corrections for the polymer and the counterions were applied to get corrected magnetic susceptibilities and magnetic moments.

### ESR studies

Electron spin resonance measurements were carried out using a Bruker EPR spectrometer [ESP 300 X-band]. The polymer samples were placed in the ESR tube and measurements were carried out under the following conditions: scan range 100 gauss, time constant 200, modulation amplitude 0.4 gauss, field set 3350 gauss, receiver gain 1250, microwave power 200 mW, modulation frequency 100 kHz, microwave frequency 9.75 GHz and temperature 25°C. DPPH was used as the standard.

### Results and Discussion

The analytical data are given in Table 1. These are consistent with the empirical formula

$$\left[ \text{C}_6\text{H}_4\text{N} - \underset{\substack{| \\ \text{R}}}{\text{R}} \right]_4 \cdot 2\text{HSO}_4$$

in most of the cases indicating the presence of two anions for every four aromatic ring units. The discrepancy in the calculated and the experimental values is due to different counter

ion levels. In the above calculations, we have assumed complete protonation, but it may not be true in all the cases. Only a few  $\text{SO}_4^{2-}$  or  $\text{HSO}_4^-$  may be substituted and linked to N-atom.

Polymers derived from substituted aniline may be considered as mixture of repeat units characterized by the state of N atom whose relative concentration will depend on oxidation state of N atom and the degree of counter ion level. N atom may be present as<sup>14,15</sup>



For example, the unprotonated reduced form of PANI (leucoemeraldine base) is essentially composed of NH units while unprotonated first oxidation level form (like emeraldine base) is a mixture of NH (reduced) and N= (oxidized) units. The protonated forms of the reduced  $\text{NH}_2^+$  and the oxidized  $\text{NH}^+ =$  are related to the unprotonated ones NH and N= through acid base equilibria. The repeat unit  $\text{N}^+$  or  $=\text{N}^+ =$  is produced only in the second oxidation level of PANI, which occurs at a potential higher than the redox potential of the polymerization<sup>3</sup>. Thus the prepared polymer samples consist of reduced (NH and  $\text{NH}_2^+$ ) and oxidized (N= or  $\text{NH}^+ =$ ) units. The proportion of protonated and unprotonated units depends on the protonation level of the polymer.

### UV-visible spectra

UV-visible spectra of substituted derivatives of PANI were recorded in DMF solution and the corresponding bands are recorded in Table 2. There are two absorption bands in the electronic spectra of substituted derivatives. The band around 280-310 nm (4.44-4.00 eV) is assigned to  $\pi \rightarrow \pi^*$  (band gap) and the band above 400 nm (less than 3.1 eV) is due to inter band charge transfer associated with the excitation of benzenoid to quinoid moieties (formation of an exciton)<sup>9,13,15</sup>. As compared with the electronic spectrum of PANI, where  $\pi \rightarrow \pi^*$  transition occurs at 320 nm, the spectra of substituted polyanilines show hypsochromic shift in this band. This trend indicates an increase in band gap brought about by an increase in the torsion angle between adjacent rings on substitution, as also reported by Ginder *et al.*<sup>16</sup> A twist in the torsion angle is expected to increase the average band gap in the ensemble of the conjugated polymer system. Similar results have been reported by Ghosh *et al.*<sup>17</sup> and Wei *et al.*<sup>18</sup> due to steric repulsion by the bulkier substituents in the ring.

Table 1—Analytical data of the substituted derivatives of polyaniline

Polymer	Found (Calc.), %		
	C	H	N
Poly( <i>o</i> -methylaniline) sulphate	58.17 (55.02)	4.82 (4.90)	8.09 (9.1)
Poly( <i>o</i> -methylaniline) perchlorate	59.37 (54.45)	4.61 (4.86)	8.32 (9.07)
Poly( <i>m</i> -methylaniline) sulphate	59.33 (55.02)	4.53 (4.90)	8.21 (9.15)
Poly( <i>m</i> -methylaniline) perchlorate	62.12 (54.45)	4.89 (4.86)	9.46 (9.07)
Poly( <i>o</i> -ethoxyaniline) sulphate	63.75 (52.31)	5.35 (4.90)	6.24 (7.6)
Poly( <i>o</i> -ethoxyaniline) perchlorate	58.70 (51.96)	5.21 (4.87)	5.98 (7.5)
Poly( $\alpha$ -naphthylamine) perchlorate	74.21 (62.49)	4.08 (3.67)	5.86 (7.3)
Poly( <i>o</i> -methoxyaniline) sulphate	62.13 (59.17)	4.01 (4.68)	8.67 (9.84)
Poly(N-phenylaniline) sulphate	69.69 (66.82)	5.11 (4.17)	7.12 (6.49)
Poly(N-phenylaniline) perchlorate	65.28 (66.43)	4.90 (4.15)	6.67 (6.44)
Poly(N-acetylaniline) sulphate	65.28 (53.89)	3.90 (3.85)	8.07 (7.71)
Poly(N-acetylaniline) perchlorate	63.32 (52.23)	4.00 (3.83)	8.05 (7.66)

When the data are compared for the N- and ring substituted derivatives of PANI, it is noted that substitution in the ring affects the torsion angle more than the substitution at N-atom in aniline. This may cause more electron localization in the ring substituted derivatives than in N-substituted PANI.

The interband transition may lead to the formation of molecular exciton (positive charge on the benzenoid unit bound to the negative charge centre on quinoid unit). This interchain charge transfer from HOMO to LUMO may lead to the formation of positive and negative polarons.

Such observations have been analysed using a model based on Valence Effective Hamiltonian (VEH) calculations by Stafstrom *et al.*<sup>19</sup>, which envisages the formation of polaron lattice from extended interaction of semi-quinone units. Thus the results indicate that a polaron band is created in the band gap of polyaniline by oxidation and that

an increase in the torsion angle (the angle by which the ring is twisted out of the plane of C-N bond) will affect the band width as well as average band energies<sup>15</sup>.

#### Magnetic susceptibility

The magnetic susceptibility per two-ring-unit mole (after applying diamagnetic correction for the compound and the counterion) and the magnetic moment data are recorded in Table 3. The data show that, except *o*-OCH<sub>3</sub> and *o*-OC<sub>2</sub>H<sub>5</sub> ring substituted derivatives, all substituted derivatives are paramagnetic. The N-substituted derivatives have large magnetic moments (3 to 4 unpaired electrons or holes per chain unit) as compared to the ring substituted derivative (1 to 2 unpaired electrons or holes per chain unit). This is equal to 0.25 to 0.5 electrons/holes per monomer unit in case of ring substituted derivatives as reported for PANI.

Thus the change in magnetic susceptibility of the substituted derivatives may be due to change in unpaired spin concentration in the chain units. Mizoguchi<sup>20</sup> in the study of the spin dynamics of PANI has proposed that polaron-polaron reaction or polaron ionization to bipolaron (spin-less charge defects) could change the spin concentration in the sample and hence the magnetic susceptibility. In  $\pi$ -conjugated systems polarons probably interact with each other or with neighbouring chains leading to spin-less charged states or hole states<sup>5,7,16</sup>. The state may be free or delocalized depending on the Coulomb interaction between the interacting moieties. They can also remain localized in the vicinity of a charged counterion formed in inter- or intra-molecular chains.

The change in the magnetic susceptibility can also be understood in terms of the disorder states in the band gap which are occupied. The disorder-induced states and interchain interaction may result in the formation of dipolar charge carriers. Therefore, in systems such as N-substituted PANI, the magnetic susceptibility and the magnetic moment will be higher compared to the values for the ring substituted derivatives due to delocalized spin or presence of disorder-induced states.

#### ESR studies

Recently, a number of ESR studies of conducting polymers have been performed to verify the suggested conduction mechanism and to confirm the existence of paramagnetic state/unpaired electron. The ESR spectra of substituted PANI salts at room temperature show a single peak like that of other conjugated conducting polymers. The

Table 2—UV-vis absorption bands, nm

Polymer	$\pi \rightarrow \pi^*$ Transition (band gap), nm	Exciton bands, nm
Poly( <i>o</i> -methylaniline) sulphate	272, 310	—
Poly( <i>o</i> -methylaniline) perchlorate	300	—
Poly( <i>m</i> -methylaniline) sulphate	270, 310	—
Poly( <i>m</i> -methylaniline) perchlorate	270, 310	—
Poly( <i>o</i> -ethoxyaniline) sulphate	285, 310 (s)	500
Poly( <i>o</i> -ethoxyaniline) perchlorate	282, 310 (tail)	—
Poly( $\alpha$ -naphthylamine) perchlorate	280, 335 (s)	520
Poly(N-phenylaniline) sulphate	310, 340	—
Poly(N-phenylaniline) perchlorate	290, 320	390
Poly(N-acetylaniline) sulphate	280	380
Poly(N-acetylaniline) perchlorate	270	440 (b)
Poly(N-ethylaniline) sulphate	300	—
Poly( <i>o</i> -methoxyaniline) sulphate	280, 300	480 (b)
Poly(aniline)	320	600

measured  $\Delta H_{pp}$  (linewidth), peak ratio A/B and  $g$ -values are recorded in Table 3 for different substituted PANI.

It is observed from Table 3 that the line-width varies with the substituents, specially when substitution is at the N-atom. This variation of line-width could be explained by the delocalization of spins. In N-substituted PANI, delocalization of spin is more effective through the participation of the phenyl or acetyl group. When phenyl group is replaced by ethyl group,  $\Delta H_{pp}$  becomes much less because ethyl group does not participate in delocalization of spins. Thus delocalization results in the line broadening caused by electron spin-spin dipolar coupling.

Further, substitution in the ring causes steric hindrance (ring is strained) whereas in N-substituted compounds aromatic ring maintains planarity and, hence, delocalization through N-atom is favoured. Thus, spin-spin relaxation time which is related to  $\Delta H_{pp}$  in inverse proportion is less where spin delocalization is greater<sup>21</sup>.

The studies of Mizoguchi *et al.*<sup>6</sup> on the spin dynamics of PANI based on the frequency dependence of ESR and NMR line-widths gave evidence of diffusive nature of spin in PANI. Thus, in the case of ring substituted PANI, spin can diffuse along the chain at a faster relaxation rate, then that in the case of N-substituted PANI in which spin delocalization is greater.

Thus, substitution of a group at N-atom which can participate in spin delocalization in a conjugated system, leads to spin diffusion along the chain at lower relaxation rate as compared to the same when the substituted group does not parti-

cipate in delocalization. In ring substituted product, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> groups do not participate in resonance delocalization; hence, the relaxation rate will be much faster. Further, similar observation can be made from the ESR line shape. From Table 3 it can be observed that A:B ratio is almost 1 in all sulphates whereas it is less than 0.95 in the case of perchlorates. The decrease in the ratio is probably because of a domination of mobile spins that are delocalized in the conjugated polymer network. The diffusive motion leads to inter-chain coupling causing asymmetry in the line shapes. In aromatic ring substituted compounds, spins remain localized and the ESR signals tends to become symmetrical. Thus, line shape also indicates the existence of mobile and fixed spins.

#### Electrical conductivity

The data on the electrical conductivity of the substituted derivatives have been fitted to Arrhenius type equation relating temperature and electrical conductivity. The measured values of  $\sigma(T)$  are plotted semi-logarithmically in Fig. 1. In the temperature range 298-330K, initially there is an increase in conductivity followed by a decrease. Above 335K, it increases continuously. This dip in the electrical conductivity may be due to loss of moisture by the sample since the conductivity depends on the moisture content and the environmental humidity<sup>3,22</sup>. The conductivity data of the samples are given in Table 3.

From Table 3, it is observed that the activation energy of conductivity varies between 0.16 and 0.36 eV for different substituted derivatives. It compares well with the values of polyaniline te-

Table 3—Magnetic, ESR and electrical conductivity data of substituted derivatives of polyaniline

Polymer salt	$\chi_m \times 10^{-3}$ emu/2 ring unit mol	$\mu_{\text{eff}}$	$\Delta H_{pp}$	A/B	$g$	$\sigma \times 10^4$ , $\Omega^{-1}\text{cm}^{-1}$	$E_a$ , eV
Poly(N-ethylaniline) sulphate	2.29	4.25	—	—	—	0.007	0.0037
Poly(N-phenylaniline)perchlorate	6.04	3.83	366.1	0.98	2.6040	66.4	0.34
Poly(N-ethylaniline) sulphate	6.85	4.08	197	0.93	2.0038	47.8	0.36
Poly(N-acetylaniline) perchlorate	9.68	4.88	188.1	0.85	2.0038	30.4	0.19
Poly(N-acetylaniline) sulphate	11.20	5.23	65.8	0.84	2.0038	44.6	0.21
Poly( $\alpha$ -naphthylamine)perchlorate	5.66	3.77	460.8	1.00	2.0026	5.24	0.34
Poly( <i>o</i> -toluidine) perchlorate	1.03	1.60	112.8	0.93	2.0040	8.57	0.25
Poly( <i>o</i> -toluidine) sulphate	3.01	2.70	112.8	1.00	2.0040	0.284	0.34
Poly( <i>m</i> -toluidine) perchlorate	1.35	1.82	112.8	0.94	2.0039	0.251	0.16
Poly( <i>m</i> -toluidine) sulphate	1.60	1.98	112.8	1.00	2.0038	0.170	0.22
Poly( <i>o</i> -phenitidin) perchlorate	-1.36	Diamag.	197.5	0.90	2.0029	66.4	0.34
Poly( <i>o</i> -phenitidin) sulphate	-1.05	Diamag.	37.62	0.95	2.0038	47.8	0.36
Poly( <i>o</i> -anisidine) perchlorate	-109.0	Diamag.	—	—	—	1000	0.20
Poly( <i>o</i> -anisidine) sulphate	-112.0	Diamag.	—	—	—	0.27	0.05

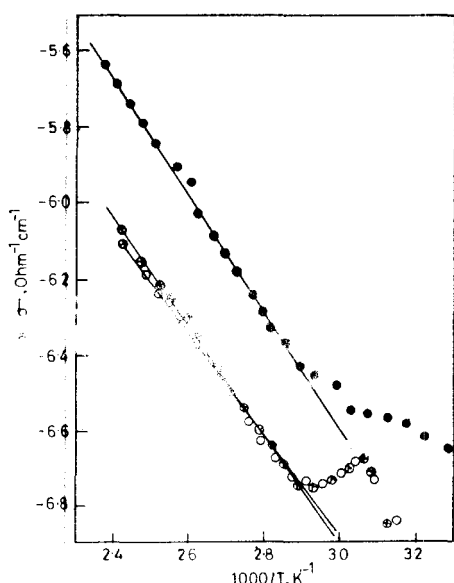


Fig. 1—Temperature dependence of electrical conductivities of substituted PANI (● poly(*o*-methoxyaniline) sulphate (●), poly(*N*-phenylaniline) perchlorate (⊗) and poly(*N*-phenylaniline) sulphate (○))

trafluoroborate (0.082 eV)<sup>23</sup>, polyacetylene (0.5 eV)<sup>12</sup> and polypyrrole (0.04 eV)<sup>24</sup>.

The lower conductivities of ring substituted derivatives as compared to those of *N*-substituted derivatives suggest that the electrons are more localized in the former than in the latter systems.

Data presented in Table 3 show that the conductivities of various substituted PANI decrease with the decrease in  $\Delta H_{pp}$ , *g*-value,  $\chi_m$ ,  $\mu_{eff}$  and with the increase in band width in a series of aromatic ring substituted salts. In the case of *N*-substituted derivatives also conductivity decreases with the decrease in  $\Delta H_{pp}$  and *g*-value. However, the ring substituted salts have lower conductivity, lower  $\chi_m$ , lower magnetic moment, smaller  $\Delta H_{pp}$  and larger band gaps compared to the *N*-substituted salts. These values indicate that electron delocalization and spin mobility is greater in *N*-substituted salts than in the ring substituted salts of PANI. Further, the size and the nature of the counterion affects these values.

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