Polaron lattice-spinless defects in conducting organic polymers

Mool C Gupta* & D C Sindheshram
Chemistry Department, Nagpur University, Nagpur 440 010
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Organic π-electron conjugated conducting polymers of aniline and pyrrole have been prepared under different polymerization conditions in nitrogen gas. The results of magnetic susceptibility and electrical conductivity measurements have been explained on the basis of polaron-polaron interaction between neighbouring chains leading to the formation of spinless charged states and spinless dipolar charge carrier, or bipolarons.

In recent years much attention has been directed to electrically conducting organic polymers. In the series of conducting organic polymers, poly(pyrrole) and poly(aniline) have been recognized as interesting and unusual members of the class of π-conjugated conducting polymers. In poly(pyrrole) the conducting behaviour can be understood by considering its conjugated carbon backbone, while in poly(aniline) a nitrogen heteroatom incorporated between phenyl rings in the backbone provides the chemical flexibility. These conducting organic polymers could be synthesized by electrochemical as well as chemical peroxodisulphate oxidation methods and can be doped with either electron acceptor or donor to yield conducting polymers. The structure of poly(aniline) is known as para-linked phenyleneaminimine (structure I) whereas the constitutional units of poly(pyrrole) are linear to each other via α-carbon atom of pyrrole ring (structure II).

In these polymers, it has been suggested on the basis of experimental and theoretical work that polaron and bipolaron play a dominant role in electrical conduction in the initial stage of the doping. The conducting state has also been described in terms of a polaron-lattice model giving rise to metal-like bond structure. Besides, the role of disorder has been pointed out and a description in terms of a Fermi glass has been suggested. Magnetic methods enable one to probe spin concentration and since the spin carriers are also charge carriers (polaron) the magnetic susceptibility can be analyzed at the scale of polymer chains.

In this paper, we report magnetic susceptibility and electrical conductivity data on poly(aniline) and poly(pyrrole) which have been prepared under different conditions.

Materials and Methods

Pyrrole was purified before use by passing it through alumina column. First few ml were disregarded and thereafter purified pyrrole was collected and stored in dark.

Aniline was purified by distillation with zinc dust and then stored in dark.

Chemical polymerization

Oxidized poly(aniline) was prepared through a chemical method by peroxodisulphate oxidation. A 0.12 M solution of K₂S₂O₈ in 0.1 M acid (HClO₄ or H₂SO₄) was added to 0.1 M solution of aniline in the same acid. The resulting material was a dark bluish black powder. The polymerization was carried out under nitrogen gas.

Electrochemical polymerization

Poly(aniline) and poly(pyrrole) could be polymerized electrochemically and conducting films were grown from 0.1 M solution of monomer in 0.1 M aqueous acid (H₂SO₄, HClO₄, oxalic acid, or acetic acid). The polymerization was conducted under nitrogen gas on stainless steel plate in an electrolytic cell at 2
volt and 25 mA current at 25°C. The film on the stainless steel plate was washed with absolute alcohol and dried.

**Chemical analysis**

The presence of counterions (SO₄²⁻, ClO₄⁻, CH₃COO⁻, C₂O₄²⁻) in polymer powder and film was confirmed by usual analytical methods. However SO₄²⁻ and C₂O₄²⁻ ions were quantitatively estimated by usual BaCl₂ precipitation and titration with acidified permanganate solution respectively.

**Electrical conductivity**

Electrical conductivity of polymer samples was determined by two probe method by using BPL-megohmmeter and Universal Bridge TF-2700 at room temperature. The polymer powder was pressed to form a pellet and placed between electrodes in a cell. The measured resistance was converted to conductivity from sample dimensions.

**Magnetic susceptibility**

Magnetic susceptibility of polymer samples was determined by Gouy’s method at room temperature using mercury tetrathiocyanato cobaltate (II), Hg[Co(CNS)₄] as reference material. The sample tube was suspended from balance in a magnetic field of different strengths between 2300 and 9800 × 10⁻⁴ T. Diamagnetic corrections for the compounds and counterions were applied.

**Results and Discussion**

Magnetic susceptibility Xm per two ring unit mole and the electrical conductivity of polymer samples are given in Table 1.

The magnetic susceptibility data reveal that poly(aniline) whether prepared by electrochemical or chemical oxidation method in H₂SO₄ or HClO₄ in nitrogen gas exhibits paramagnetism whereas poly(pyrrole) behaves differently. However, both show measurable conductivity. The difference in these properties also reveals that method of synthesis and the dopant also influence these properties in extended conjugated π-electron systems.

Earlier studies and theoretical calculations applied to conjugated chains have suggested that for such polymers oxidation creates a hole defect state in the band gap. Such a hole defect or charge state is localized to form a polaron. The polaron states in poly(aniline) are shown in Fig. 1. A polaron gives rise to two levels (polaron bands) in the band gap due to the formation of polaron lattice defect state. The charge and the spin of the defect will depend on the occupancy of the mid gap state. It is singly occupied and has a spin 1/2. At the polaron site, the polymer structure locally deviates towards the high energy structure but never achieves it. If the gain in lattice distortional energy outweighs the cost of bringing like charges close together, two polarons will collapse to form a bipolaron. Bipolarons can have zero spin, yet carry charge. This would change spin concentration in the sample and hence the magnetic susceptibility.

The polaron in the extended π-conjugated systems such as poly(aniline) and poly(pyrrole) could interact with each other or with the polaron of neighbouring chains leading to spinless charged states or hole states. The state may be free or delocalized depending on the Coulomb forces between interacting moieties. They can also remain localized in the vicinity of charged counterions formed in inter or intramolecular chains.

However, the trends in the electrical conductivity may arise due to the dopant oxidation level and method of preparation. Since poly(aniline) has been considered as a mixture of repeat units characterised by the redox state of N-atom such as NH₂ NH₂ NH⁺ = and N⁺ or ( = N⁺ =), the relative concentration of these in polymer repeat unit depends on the oxidation

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Method of preparation</th>
<th>Magnetic susceptibility (emu/two ring unit)</th>
<th>μₑᶠ</th>
<th>Electrical conductivity, Ω⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(aniline)</td>
<td>Electrolysis in HClO₄</td>
<td>3.1 × 10⁻³</td>
<td>2.75</td>
<td>7.7 × 10⁻³</td>
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<tr>
<td></td>
<td>Electrolysis in H₂SO₄</td>
<td>1.4 × 10⁻³</td>
<td>1.85</td>
<td>4.0 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Chemical oxidation in HClO₄</td>
<td>2.7 × 10⁻³</td>
<td>2.57</td>
<td>8.8 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Chemical oxidation in H₂SO₄</td>
<td>0.51 × 10⁻³</td>
<td>1.12</td>
<td>0.31</td>
</tr>
<tr>
<td>Poly(pyrrole)</td>
<td>Electrolysis in HClO₄</td>
<td>-8.63 × 10⁻³</td>
<td>—</td>
<td>4.0 × 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>Electrolysis in H₂SO₄</td>
<td>6.19 × 10⁻³</td>
<td>3.88</td>
<td>1.66 × 10⁻⁴</td>
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<tr>
<td></td>
<td>Electrolysis in (COOH)₂</td>
<td>13.34 × 10⁻³</td>
<td>5.7</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Electrolysis in CH₃COOH</td>
<td>-13.1 × 10⁻³</td>
<td>—</td>
<td>3.46 × 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>Oxidation by UV in H₂SO₄</td>
<td>-4.50 × 10⁻³</td>
<td>—</td>
<td>7.8 × 10⁻⁸</td>
</tr>
</tbody>
</table>
Polaron and bipolaron state of poly(aniline)

of N-atom and the degree of counter ion level. An as prepared sample of poly(aniline) is experimentally found to be composed of reduced [NH and NH₃⁺] and oxidized (N = and NH⁺) units, and the distribution of these between protonated and unprotonated units depends on the equilibration pH. Thus, electrical conductivity depends on the pH of the equilibration solution. Therefore there will be difference in the electrical conductivity when PANI is produced in HClO₄ and H₂SO₄.

In the case of polypyrrole also the oxidation level and nature of anion produce a variation in the electrical conductivity. The results in the Table 1 suggest that the size of the anion affects the electrical conductivity and in the case of electrolysis in H₂SO₄ and oxidation by UV in H₂SO₄, the lower conductivity of the latter sample may be due to lower level of oxidation. The electrical conductivity of polypyrrole could be analyzed in terms of polarons and bipolarons. At low doping level polarons (radical cation) are produced best above 1% doping, these combine to form bipolarons or dication. These bipolarons are spinless and hence the material will be diamagnetic depending on the preparative conditions.

References