Synthesis and Optical Characterization of Polymetatoluidine (PMT) doped with Complex of Cu$^{+1}$Salt

Gita Rani
Department of Chemistry, Chaudhary Devi Lal University, Sirsa (India).

Abstract
Polymetatoluidine (PMT) prepared after doping of PMT with Brown-red complex of copper with 2,9-dimethylphenanthroline [Cu (DMPhen)$_2$] ClO$_4$. The brown-red complex was dissolved in 1:1 ratio of water and THF. PMT were separately dissolved in THF and doped with the complex in different ratio of 2%, 4% and 6%. Optical studies of Polymetatoluidine (PMT) prepared after doping of PMT with Brown-red complex of copper have been studied at different concentration of dopant. UV-vis spectra and band gaps were used for optical and electrical characterization of the prepared doped PMT. The UV-vis spectra shows appreciable decrease in band gap after doping which is also confirmed by increase in DC conductivity with increase in concentration of dopant. These types of measurements of complex of copper complex doped polymetatoluidine system will be helpful for the development of conducting polymeric materials.

Keywords: UV-vis, Optical, Band gap and Polymers.

1. INTRODUCTION
Polymers are basically thought to be insulators till two and a half decades ago and then a new class of polymers was synthesized known as conducting polymers. Much of the interest in conducting polymers arises from their potential applications in many areas especially fabrication of electronic devices like rechargeable battery, sensors, LEDs etc. [1, 2]. Due to diversified use of conducting polymers [3], researchers are now focusing towards development of lightweight materials in advanced technological applications. Now days, the most extensively studied conducting polymer systems are polythiophene [4, 5 and 6], polypyrrole, and polyaniline. Conjugated semiconducting polymers are made conductive by reacting them with an oxidizing agent, a reducing agent or a protonic acid resulting in highly delocalized polycations or polyanions. The evidence and possibility of structural formation of hybrid materials of PANI with some metal salts has been illustrated [7]. π-conjugated backbone of organic polymers favour the chemical doping mechanism. Conjugated polymers have relatively large band gap, the concentration of free carriers is very low at normal temperature. In the present work, chemical doping of synthesized polymetatoluidine (PMT) has been done with different concentration of dopant in aqueous tetrahydrofuran(THF) solution. In the present investigation, we have studied the complex of Cu$^{+1}$ salt doped polymetatoluidine and also observed the influence of different concentration of dopant in terms of optical properties in doped PMT.

2. EXPERIMENTAL DETAILS

2.1 Chemicals

2.2 Synthesis and Doping of Polymetatoluidine(PMT)
The polymetatoluidine (PMT) was synthesized by the method suggested by A G Mac Diarmid et al. [8]. Doping agent has been used with different concentrations in the solvent mixture of water and tetrahydrofuran (THF) solution (4: 6 v/v) for doping of synthesized polymetatoluidine.
2.3 Synthesis of (tetraacetonitrile copper (I) perchlorate) \([Cu (AN)_4]ClO_4\)

\([Cu (AN)_4]ClO_4\) was prepared by following two steps as reported by Gill and R. Gupta [9].

1. **Preparation of copper (II) perchlorate hexahydrate \([Cu (ClO_4)_2, 6 H_2O]\)** from cupric carbonate

\([Cu (ClO_4)_2, 6 H_2O]\) was prepared by suspending cupric carbonate \((CuCO_3)\) in small amount of water. This was warmed at a temperature of 40°C and stirred. Now perchloric acid \((HClO_4)\) was added dropwise till the clear blue solution was obtained. The solution was filtered, concentrated and kept overnight. Blue crystals of copper (II) perchlorate hexahydrate \([Cu (ClO_4)_2, 6 H_2O]\) were obtained.

2. **Preparation of tetraacetonitrile copper (I) perchlorate** from copper (II) perchlorate hexahydrate

\([Cu (AN)_4]ClO_4\) was prepared by dissolving \([Cu (ClO_4)_2, 6 H_2O]\) in acetonitrile \((AN)\) and the solution was heated and stirred. Now copper (metal) powder was added slowly till the solution became colorless. The hot solution was filtered and the filtrate was allowed to cool to get the crystals, which were covered with the layer of dry acetonitrile and a pinch of copper (metal) powder was added again. Heat it to reduce any oxidized form of the product, if present. The solution was again filtered and cooled to get white crystals, which are dried in a vacuum oven.

2.4 Synthesis of bis (2,9-dimethyl-1,10-Phenanthroline) copper (I) perchlorate \([Cu (DMPhen)_2]ClO_4\)

bis (2,9-dimethyl-1,10-Phenanthroline) copper (I) perchlorate \([Cu (DMPhen)_2]ClO_4\), was prepared by mixing warm solution of 2,9-dimethylphenanthroline ligand with \([Cu (AN)_4]ClO_4\) in AN in 2:1 ratio. The mixture was concentrated and then solution was allowed to cool at room temperature. The brown- red colored complex was precipitated out by adding excess of toluene. The complex was then filtered and dried at 70°C under vacuum for 6 h.

2.5 Doping with Brown-red complex of copper with 2,9-dimethylphenanthroline

\([Cu (DMPhen)_2]ClO_4\)

The brown-red complex was dissolved in 1:1 ratio of water and THF. Then PMT was separately dissolved in THF and doped with the complex in different ratio. PMT was doped with with 2, 4 and 6% concentration of complex.

All the samples prepared above were dried in oven and powdered by the application of a hydraulic pressure of about 9 tonnes.

3. RESULTS AND DISCUSSION

3.1 Optical Characterization

Modern absorption spectrophotometer can usually display the data as percentage transmittance, or absorbance. Experimental measurements are usually made in terms of transmittance \((T)\). The relationship between absorbance \((A)\) and transmittance \((T)\) is:

\[
A = - \log T = - \log \left(\frac{I_t}{I_0}\right)
\]

Where, \(I_t\) is the light intensity after passing through the sample and \(I_0\) is the initial light intensity.

The optical percentage transmittance spectra of undoped and doped PMT (Figure1a, b and c) were recorded at room temperature using a FTIR spectrophotometer (Spectrum RXI FTIR Perkin Elmer). The transmittance of undoped, 5.0% and 20.0% w/w doped PMT are used here to study the absorption coefficient \((\alpha)\) and the type of optical transitions/ interactions before and after doping. The absorption coefficient \((\alpha)\) can be derived from relationship of absorbance[10-12].

\[
\frac{(A)}{\log T} = \frac{\log (I_t/I_0)}{\log T} \quad \text{OR} \quad \log (I_t/I_0) = \text{Absorption Coefficient} \times T
\]

\[
\text{Absorption Coefficient} \times T = \frac{1}{t} \left(\frac{I_t}{I_0}\right) \quad \text{OR} \quad \alpha = \frac{1}{t} \left(\frac{I_t}{I_0}\right)
\]

The absorption spectra actually appeared due to transitions of charged carrier species of dopant. Attempts have been made to characterize the optical properties such as absorption coefficient \((\alpha)\) and photon energy. The absorption coefficient \((\alpha)\) is derived from percentage transmittance of FTIR signals of undoped and doped
PMT. Energy (hν) has been calculated by using Tauc equation [13]. According to semiconductor’s theory, the electronic transition between the valence and the conduction bands starts at the absorption edge corresponding to the minimum energy difference between the lowest energy of the conduction band and the highest energy of the valence band. The theory of electrical excitation for semiconductor and organic conductors was reported for the first time in anthracene single crystal [14]. It has been investigated in the theory that this excitation process generates electroluminescence, which requires ejection of electrons from one electrode and holes from the other. The capture of oppositely charged carriers (recombination) and the radiative decay of the excited states produced recombination process. Conjugated polymers carry out their semi conducting properties by having delocalized π electron bonding along the polymer chain.

Three characteristic absorption bands are observed in the spectrum of PMT at 296, 410 and 544 nm wavelength, which are also attributed to π – π* conjugated ring systems, polaron-p*, and p-polaron benzenoid to quinoid exciton transition (n – π*), respectively. The first two bands are shifted to longer wavelength, called Bathochromic (red) shift with low intensity (hypochromic shift), which indicates that transitions require lesser energy than PANI in case of PMT which confirms the dominancy of the benzenoid ring [15]. PMT was doped with brown-red complex of copper with 2, 9-dimethyl-1, 10-phenanthroline ligand and then UV spectra of doped samples was noticed. There is decrease in intensity of absorption after doping which shows interaction of dopant with the polymers. The spectra are shown in Fig. 1.

![UV-Vis spectra of Pure PMT (A) and PMT doped with 2 % (B), 4% (C) and 6% (D) concentration of brown-red complex of copper.](image)

Fig. 1. UV-Vis spectra of Pure PMT (A) and PMT doped with 2 % (B), 4% (C) and 6% (D) concentration of brown-red complex of copper.

After doping with brown–red complex of Cu, it has been observed that there is decrease in values of both direct and indirect band gaps. Values of direct band gap in PMT(pure) and brown-red complex doped PMT are 3.38 eV and 3.31 eV, 3.28 eV and 3.40 eV respectively.

Indirect band gaps are also 1.88 eV, 1.80 eV, 1.74 eV and 1.77 eV respectively for undoped and brown–red complex doped PMT. It has to be noticed that in all cases values of doped form is less and indirect band gaps are even less than that of direct band gaps. All the values for PMT (both undoped and brown-red
complex of Cu doped forms) are shown in Table 1. along with values of absorption coefficient and extinction coefficient.

Table 1. Values of Band Gaps, Absorption coeff. and Extinction coeff. for PMT doped with brown–red complex of Cu.

<table>
<thead>
<tr>
<th>Dopant conc. in (w/w)</th>
<th>Direct band gap $E_g$ (eV)</th>
<th>Indirect band gap $E_g$ (eV)</th>
<th>Absorption coeff. $\alpha$ at $\lambda=280$ nm</th>
<th>Extinction Coeff. $k$ at $\lambda=280$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>3.38</td>
<td>1.88</td>
<td>4.56</td>
<td>101.55</td>
</tr>
<tr>
<td>2% doped</td>
<td>3.31</td>
<td>1.80</td>
<td>3.28</td>
<td>73.04</td>
</tr>
<tr>
<td>4% doped</td>
<td>3.28</td>
<td>1.74</td>
<td>4.13</td>
<td>91.97</td>
</tr>
<tr>
<td>6% doped</td>
<td>3.40</td>
<td>1.77</td>
<td>3.92</td>
<td>87.29</td>
</tr>
</tbody>
</table>

Fig. 2. Optical band gap (Indirect) of PMT (A) and PMT doped with 2 % (B), 4 % (C) and 6 % (D) concentration of brown-red complex of Cu.

4 Conclusion
Optical band gap PMT decreases with increasing content of the metal salts and hence optical conductivity increases.
Experimental results of optical absorption fit well by the Maxwell-Garnet model. Electrical conductivity of the conducting polymers can be increased by doping of suitable metal salts. So, this is a simple way by which optical and electrical properties of other conducting polymers may be enhanced by using different concentrations of dopant.

From the structural study it is found that PMT is highly cross linked in all the pure and doped states. The UV-Vis absorption peak at 375 nm reveals the formation of polaronic structure due to doping of metal salts. The optical band gap of the pure PMT is found to decrease in the doped PMT due to the formation of polaronic structure. The optical band gap of the PMT depends on the extended conjugation, oxidation level and doping.

REFERENCES