Oxidative synthesis and properties of poly(2-ethylaniline)

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Poly(2-ethylaniline), a π-electron conjugated conducting polymer, has been prepared under different polymerization conditions in nitrogen atmosphere. The structure of the prepared polymer has been elucidated by infrared spectra and elemental analyses. The electrochemical studies of the polymerization of 2-ethylaniline and its film at a platinum electrode have been performed in 1,2-dichloroethane using different dopants. The electrical conductivities of these polymers are found to be in the range of $10^{-4}$ to $10^{-7}$ S cm$^{-1}$. Thermal studies of the polymer were carried out by thermogravimetric analysis. The DTG curves of ClO$_4^-$ and SbCl$_4^-$ doped polymer reveal the maximum weight loss at 400 and 500°C respectively. The magnetic susceptibility of the prepared polymer shows paramagnetic behaviour. Surface morphology of the polymer film is also described.

Research on highly conducting polymers has increased exponentially in the last twenty years$^{1-11}$. In the series of conducting organic polymers, polyaniline and polypyrrole have been recognized as interesting and unusual members of the class of π-conjugated conducting polymers$^{12-14}$. Polyaniline has shown potential for large scale applications due to its simple synthesis, good environmental stability and adequate levels of electrical conductivity. In view of the above, it was thought worthwhile to study in detail the synthesis of poly(2-ethylaniline) by oxidative polymerization using some novel dopants like SnCl$_4$ and SbCl$_4$. The present paper also emphasizes the electrochemical properties of the polymerization process and the polymer film. The thermal, morphological and electrical properties of the prepared polymer have also been studied.

Materials and Methods

2-Ethylaniline (Aldrich, b.p. 210°C) was purified by distillation under reduced pressure. 1,2-Dichloroethane (Glaxo) and water were used after two distillations. Tetra-$n$-butylammonium pentachlorostannate$^6$ (TBAPCS, m.p. 206°C), tetra-$n$-butylammonium perchlorate (TBAP, Fluka, m.p. 210°C), tetra-$n$-butylammonium tetrafluoroborate (TBAHFB, Aldrich, m.p. 244°C), tetra-$n$-butylammonium hexachloroantimonate$^6$ (TBAHCA, m.p. 200°C), tetra-$n$-butylammonium chloride (TBAC, m.p. 74°C) and tetra-$n$-butylammonium hexafluorophosphate (TBAHFP, m.p. 244°C) were used as supporting electrolytes. All other chemicals used were of A.R. grade.

(a) Electrochemical polymerization

In a typical electrolysis, a solution of 2-ethylaniline (0.1M) and tetra-$n$-butylammonium perchlorate (0.1M) in 1,2-dichloroethane (100 ml) was taken in one-compartment cell containing platinum foil (6.25 cm$^2$) as anode and cathode. The solution was purged with nitrogen and electrolysis was carried out under constant current ($I$=20 mA, c.d.$=3.2$ mA cm$^{-2}$) with D.C. regulated power supply. The temperature of the reaction mixture was maintained at 15±2°C. At the time of electrolysis the anode got heavily covered with black coloured polymer mass which was removed at the interval of 25-30 minutes by a sharp blade. After obtaining sufficient amount of product (about 5 hr) the electrolysis was terminated.

(b) Chemical polymerization

Chemical polymerization was performed by persulphate oxidation. A solution (0.12M) of K$_2$S$_2$O$_8$ in 0.1M acid (HCl, HClO$_4$, CH$_3$COOH, H$_2$C$_2$O$_4$, CCl$_3$COOH, 5-sulphosalicylic acid, p-toluene sulphonic acid or sulphamic acid)$^7$ was...
added to solution of the monomer (0.1M) in the same acid. The reaction mixture was stirred for 4-5 hr under nitrogen atmosphere to get the polymer mass.

The polymer mass obtained by the above method was filtered, washed thoroughly with distilled water and methanol and dried under controlled temperature at 70°C for 5-6 hr. For measuring conductivity the dried polymer mass was pressed in the form of a pellet and conductivity was measured with the help of a Keithly electrometer. The presence of dopant anion was confirmed by the usual analytical methods. Magnetic susceptibility of polymer samples was determined by Gouy's method at room temperature using mercury (tetraethylcyano)cobaltate (II), Hg[Co(CNS)]₄ as reference material. Cyclic voltammogram was recorded using an EG & G Par Model-362, scanning potentiostat and Servogor 733, X-y(t) recorder; scanning electron micrograph was recorded with a JSM 840-A SEM unit with the film deposited on platinum foil. IR spectrum of the poly(2-ethylaniline) was recorded with a JASCO FTIR-5300 infrared spectrophotometer using KBr pellet. The IR spectral data of some polymer samples are given below:

Poly(2-ethylaniline) ClO₄⁻, IR (KBr, cm⁻¹): 3450-3350, 2950, 2880, 1600, 1520, 1310, 1230, 1140, 1080, 840, 640; Poly(2-ethylaniline) CT, IR (KBr, cm⁻¹): 3475-3380, 2950, 2880, 1600, 1510, 1480, 1310, 1222, 1170, 838, 638; Poly(2-ethylaniline) BF₄⁻, IR (KBr, cm⁻¹): 3450-3370, 2950, 2880, 1600, 1520, 1480, 1300, 1225, 1180, 1040, 940, 838; Poly(2-ethylaniline) CH₃COO⁻ IR (KBr, cm⁻¹): 3500-3400, 2950, 2880, 1600, 1560, 1525, 1478, 1350, 1305, 1240, 1170, 840, 680; Poly(2-ethylaniline) CCl₃COO⁻, IR (KBr, cm⁻¹): 3500-3400, 2950, 2880, 1600, 1560, 1508, 1480, 1360, 1305, 1220, 1170, 840, 680; Poly(2-ethylaniline) NH₄SO₄⁻, IR KBr, cm⁻¹): 3500-3400, 2950, 2880, 1600, 1518, 1480, 1310, 1225, 1137, 835, 635; Poly(2-ethylaniline) p-CH₃C₆H₄SO₃⁻, IR (KBr, cm⁻¹): 3500-3400, 2950, 2880, 1600, 1520, 1480, 1310, 1250, 1170, 838, 640; Poly(2-ethylaniline) salicylic acid-5-sulphonate, IR (KBr, cm⁻¹): 3325-3250, 2950, 2880, 1600, 1518, 1390, 1305, 1240, 1222, 1139, 840, 612; Poly(2-ethylaniline) SnCl₄⁻, IR (KBr, cm⁻¹): 3375-3200, 2960, 1600, 1495, 1285, 1060, 820; Poly(2-ethylaniline) SbCl₅⁻, IR (KBr, cm⁻¹): 3430-3390, 2925, 1600, 1510, 1280, 1150, 810.

Results and Discussion

The anodic polymerization of 2-ethylaniline was carried out in different supporting electrolytes and solvents (Table 1). The results suggest that the solvent and electrolyte have pronounced effect on the yield as well as conductivity of polymer possibly due to variation of the chain length of the polymer. Magnetic susceptibility of the polymer per two ring unit mole of samples is also given in Table 1 which shows that the polymers are paramagnetic. The origin of the magnetic properties has been an unsolved problem in the study of conducting polymers. Earlier studies and theoretical calculations applied to conjugated chains have suggested that for such polymers, oxidation creates hole defect state in the band gap. Such a hole defect or charge state is localized to form a polaron. This is the main species generated by p-type doping in the polymer chain. A polaron has a localized energy level occupied by one electron and has a spin of 1/2. The interaction between polarons in the polaron lattice would lead to the formation of a half-filled band. This would change spin concentration in the sample and hence the magnetic susceptibility. The dopant oxidation level and method of synthesis may produce the variation in electrical conductivity of π-electron conjugated polymers. Polymers derived from 2-ethylaniline may be considered as a mixture of repeat units characterized by the redox state of N-atom such as NH, NH₂, N =, NH= and N or (=N=); the relative concentrations of these species depend on the nature, percentage of doping and the oxidation state of N atom which may affect the concentration of polaron and bipolaron and so the electrical conductivity of the polymer.

Structural Studies

These polyaniline derivatives obtained by chemical and electrochemical methods were characterized by IR. The IR spectra of polymers with various dopants show a weak band between 3500 and 3250 cm⁻¹; characteristic of NH₂ and NH stretching vibrations. Presence of the dopant ClO₄⁻ anion was confirmed by absorption peak at 1110 or 1080 cm⁻¹ and the presence of sulphamate anion was confirmed
Oxidative synthesis of poly(2-ethylaniline)

Table I - Yield, electrical conductivity and magnetic susceptibility of poly(2-ethylaniline) formed in different electrolytic media by electrochemical [c.d. = 3.2 mA cm⁻², t = 15±2°C, volume of reaction mixture (100 ml), electrolysis time = 5 hr at Pt (6.25 cm²) electrode] and chemical methods

<table>
<thead>
<tr>
<th>No.</th>
<th>Solvent</th>
<th>Electrolyte</th>
<th>Magnetic susceptibility (emu/two ring unit)</th>
<th>μ eff (BM)</th>
<th>Yield (mg)</th>
<th>Conductivity (Scm⁻¹)</th>
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<tbody>
<tr>
<td>A</td>
<td>Electrochemical method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1,2-Dichloroethane</td>
<td>TBAP (0.1M)</td>
<td>2.270x10⁻³</td>
<td>2.347</td>
<td>276</td>
<td>0.48x10⁻⁷</td>
</tr>
<tr>
<td>2</td>
<td>1,2-Dichloroethane</td>
<td>TBAP (0.1M)</td>
<td>4.789x10⁻³</td>
<td>3.38</td>
<td>360</td>
<td>1.28x10⁻⁷</td>
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<tr>
<td>3</td>
<td>1,2-Dichloroethane</td>
<td>TBAPCS (0.05M)</td>
<td>3.486x10⁻³</td>
<td>2.90</td>
<td>270</td>
<td>3.80x10⁻⁷</td>
</tr>
<tr>
<td>4</td>
<td>1,2-Dichloroethane</td>
<td>TBATFB (0.02M)</td>
<td>0.220x10⁻³</td>
<td>0.73</td>
<td>300</td>
<td>2.08x10⁻⁷</td>
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<tr>
<td>5</td>
<td>1,2-Dichloroethane</td>
<td>TBATFB (0.02M)</td>
<td>1.160x10⁻³</td>
<td>5.27</td>
<td>390</td>
<td>7.60x10⁻⁷</td>
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<tr>
<td>6</td>
<td>1,2-Dichloroethane</td>
<td>TBAC (0.1M)</td>
<td>0.647x10⁻³</td>
<td>1.24</td>
<td>330</td>
<td>2.70x10⁻⁷</td>
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<td>7</td>
<td>1,2-Dichloroethane</td>
<td>TBHCA (0.005M)</td>
<td>3.591x10⁻³</td>
<td>2.19</td>
<td>280</td>
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<td>8</td>
<td>1,2-Dichloroethane</td>
<td>TBHF (0.05M)</td>
<td>8.754x10⁻³</td>
<td>4.60</td>
<td>230</td>
<td>5.60x10⁻⁷</td>
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<td>Chemical method</td>
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<td>10</td>
<td>Aqueous HClO₄ (0.1 M)</td>
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<td>6.219x10⁻³</td>
<td>3.88</td>
<td>480</td>
<td>0.37x10⁻⁷</td>
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<td>11</td>
<td>Aqueous CH₃COOH (0.1 M)</td>
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<td>9.423x10⁻³</td>
<td>4.75</td>
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<td>1.00x10⁻⁷</td>
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<tr>
<td>12</td>
<td>Aqueous HCl (0.1 M)</td>
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<td>1.535x10⁻³</td>
<td>1.91</td>
<td>630</td>
<td>0.31x10⁻⁷</td>
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<td>13</td>
<td>Aqueous H₂C₂O₄ (0.1 M)</td>
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<td>1.916x10⁻³</td>
<td>2.14</td>
<td>210</td>
<td>0.11x10⁻⁷</td>
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<td>14</td>
<td>Aqueous 3-sulphosalicylic acid (0.1 M)</td>
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<td>0.764x10⁻³</td>
<td>1.33</td>
<td>1260</td>
<td>0.63x10⁻⁷</td>
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<tr>
<td>15</td>
<td>Aqueous sulphamic acid (0.1 M)</td>
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<td>7.042x10⁻³</td>
<td>4.05</td>
<td>150</td>
<td>0.18x10⁻⁷</td>
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<tr>
<td>16</td>
<td>Aqueous p-toluene sulphonic acid (0.1 M)</td>
<td></td>
<td>3.691x10⁻³</td>
<td>2.04</td>
<td>300</td>
<td>0.31x10⁻⁷</td>
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<tr>
<td>17</td>
<td>Aqueous CCl₃COOH (0.1 M)</td>
<td></td>
<td>4.922x10⁻³</td>
<td>3.43</td>
<td>340</td>
<td>0.78x10⁻⁷</td>
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a=at Ni electrode, b=at stainless steel electrode

by the absorption bands at 1310 and 1137 cm⁻¹. The other dopants like acetate and p-toluene sulphonate anion were observed to absorb at 1560 and 1250 cm⁻¹ respectively. The peak at 1525 cm⁻¹ is attributed to C=N bonds of the benzenoid units, and the peak at 1600 cm⁻¹ is attributable to C=N bonds of quinoid units. The absorption peak around 840 cm⁻¹ is assignable to 1,2,4-trisubstituted benzene.

The elemental data of carbon, hydrogen and nitrogen in the poly(2-ethylaniline) are presented in Table 2. The empirical formula of these polymers are (2-EtC₆H₄NH-)₄ suggesting the presence of two dopant anions in most of the cases for every four aromatic ring units. The presence of different counter ion levels possibly causes the discrepancy observed in the calculated and experimental values. The percent doping levels of poly(2-ethylaniline) with different anion are given as P2-EtAnClO₄⁻ (26.4%), P2-EtAnSnCl₄⁻ (51.2%), P2-EtAnCl⁻ (11.7%), P2-EtAnSbCl₅⁻ (52.7%), P2-EtAn p-CH₃C₆H₄SO₄⁻ (15.3%). The proposed structure for the polymer chain is shown in Scheme 1.

Cyclic voltammetric studies

In the CV run, all studies were carried out using platinum microelectrode (0.16 cm²) very cautiously avoiding the potential values beyond the range of E = -0.4 to 1.0 V vs SCE under nitrogen atmosphere. The cyclic voltammogram of 2-ethylaniline obtained in 0.02 M Bu₄NSnCl at scan rates, 20, 50, 100 and 200 mV/s are shown in Fig. 1. The first potential sweep is characterized by a strong narrow anodic peak at approximately 580 mV with the corresponding cathodic peak at 420 mV. The oxidation reaction involves a charge of 151 mC/cm² at 20 mV/s. During different scan sweeps (Fig. 1) the anodic current peak is increased and shifted towards positive potentials and the corresponding cathodic current peak shifted...
Towards negative potentials. The $I_p$ values vary linearly with sweep rate and $I_p/I_n$ ratio is found to be unity between 20 and 200 mV/s as expected for the reaction of surface localized material. The linear plot of anodic peak current vs scan rate appears to show that the polymerization is reversible and diffusion controlled.

The cyclic voltammogram for 2-ethylaniline in 0.1M Bu$_4$NCIO$_4$ is depicted in Fig. 2 and has two anodic peaks with corresponding cathodic peaks. The broad current peaks for the redox reaction of the polymerization process were centered at $E_p=680$ mV and $E_n=180$ mV vs SCE and the coulombic charge passed during the reaction was calculated as 207 and 190 mC/cm$^2$ respectively at 20 mV/s. The plot of anodic peak current vs scan rate is linear and peak current ratio found to be unity. Although the redox reaction must involve the electrons in the extended $\pi$-system of the polymer, the broadness of the peaks together with the fact that $E_p$ does not equal $E_n$ suggests that the reaction has some kinetic limitation. The polymer deposited on the electrode surface was found to be quite stable and could be cycled repeatedly without any evidence of decomposition of the material. As expected, the reaction is slow with thicker film and peaks broaden considerably.

The cyclic voltammetry of 2-ethylaniline in 0.05 M Bu$_4$NBF$_4$ (Fig. 3) shows anodic peak at 460 mV (8.8 mC/cm$^2$) with the corresponding cathodic peak at 380 mV (6.5 mC/cm$^2$). The $I_p/I_n$ values vary linearly with sweep rate between 10 and 200 mV/s. The $I_p/I_n$ values obtained are approximately unity revealing the process to be diffusion controlled. The cyclic voltammogram of 2-ethylaniline with 0.005 M Bu$_4$NSbCl$_6$ in 1,2-dichloroethane (Fig. 4) shows oxidation peak at 760 mV (257 mC/cm$^2$) vs SCE at 20 mV/sec. The oxidation peaks are shifted towards positive potentials at higher scan rates. The comprehensive CV data of 2-ethylaniline with Bu$_4$NSnCl$_6$, Bu$_4$NClO$_4$ and Bu$_4$NBF$_4$ are given in Table 3.

The poly(2-ethylamine) film deposited on platinum microelectrode from the solution containing 2-ethylamine (0.01M) and Bu$_4$NSnCl$_6$ (0.02M) in 1,2-dichloroethane was washed thoroughly with 1,2-dichloroethane and then immersed in 1,2-dichloroethane containing Bu$_4$NSnCl$_6$ (0.02M) and its cyclic voltammogram was recorded (Fig. 5). The CV curve of the polymer film shows electroactive
Fig. 1—Cyclic voltammogram of 2-ethylaniline (0.01M) on a platinum microelectrode in 1,2-dichloroethene containing Bu4NHSOCl (0.02M) with different scan rates of (a) 20 mVs⁻¹, (b) 50 mVs⁻¹, (c) 100 mVs⁻¹ and (d) 200 mVs⁻¹.

Fig. 2—Cyclic voltammogram of 2-ethylaniline (0.01M) on a platinum microelectrode in 1,2-dichloroethene containing Bu4NBF4 (0.05M) with different scan rates of (a) 10 mVs⁻¹, (b) 20 mVs⁻¹, (c) 50 mVs⁻¹, (d) 100 mVs⁻¹ and (e) 200 mVs⁻¹.

Fig. 3—Cyclic voltammogram of 2-ethylaniline (0.01M) on a platinum microelectrode in 1,2-dichloroethene containing Bu4NSnCI (0.02M) with different scan rates of (a) 20 mVs⁻¹, (b) 50 mVs⁻¹, (c) 100 mVs⁻¹ and (d) 200 mVs⁻¹.

Fig. 4—Cyclic voltammogram of 2-ethylaniline (0.01M) on a platinum microelectrode in 1,2-dichloroethene containing Bu4NSbCl (0.0055M) with different scan rates of (a) 20 mVs⁻¹, (b) 50 mVs⁻¹ and (c) 100 mVs⁻¹.
Table 3—Cyclic voltammetric results: Polymerization of 2-ethylaniline (0.01 M) on platinum microelectrode in 1,2-dichloroethane containing \(n\)-Bu\(_3\)NStCl (0.02 M), \(n\)-Bu\(_3\)NClO\(_4\) (0.01 M) or \(n\)-Bu\(_3\)NBF\(_4\) (0.05 M), as a supporting electrolyte at different scan rates

<table>
<thead>
<tr>
<th>No.</th>
<th>Scan rate mVs(^{-1})</th>
<th>(n)-Bu(_3)NStCl (0.02 M)</th>
<th>(n)-Bu(_3)NClO(_4) (0.01 M)</th>
<th>(n)-Bu(_3)NBF(_4) (0.05 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(E_{pa}) (mV)</td>
<td>(E_{pc}) (mV)</td>
<td>(i_{pa}) (mA)</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>580</td>
<td>420</td>
<td>0.007</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>620</td>
<td>380</td>
<td>0.012</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>660</td>
<td>320</td>
<td>0.020</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>700</td>
<td>260</td>
<td>0.032</td>
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Table 4—Thermogravimetric analysis of poly(2-ethylaniline)

<table>
<thead>
<tr>
<th>S No</th>
<th>Monomer</th>
<th>Solvent</th>
<th>Electrolyte</th>
<th>Percentage loss at 300°C</th>
<th>Percentage loss at 400°C</th>
<th>Residue percentage c</th>
<th>DTG(^d) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-Ethylamine</td>
<td>1,2-Dichloroethane</td>
<td>TBAP* (0.1 M)</td>
<td>34.04</td>
<td>84.90</td>
<td>9.93</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>2-Ethylamine</td>
<td>1,2-Dichloroethane</td>
<td>TBAHCA(^b) (0.005 M)</td>
<td>8.80</td>
<td>25.00</td>
<td>17.50</td>
<td>500</td>
</tr>
</tbody>
</table>

a = Measurement performed at 5°C/min under nitrogen atmosphere  
b = Measurement performed at 10°C/min under air  
c = Weight percentage residue at 900°C  
d = High rate of decomposition of polymers
Fig. 5—Cyclic voltammogram of poly(2-ethylaniline) film on a platinum microelectrode in 1,2-dichloroethane containing Bu4NSnCl4 (0.02M) at 50 mV s⁻¹.

Fig. 6a—TGA and DTG curves of ClO₄⁻ doped poly(2-ethylaniline) with a heating rate of 10°C/min.

Fig. 6b—TGA and DTA curves of SbCl₅ doped poly(2-ethylaniline) with a heating rate of 10°C/min.

\[
\begin{align*}
\text{Scheme 2}
\end{align*}
\]
properties which cycles at 1150 mV vs SCE. The
redox peak current of this film at multiple
scans (Fig. 5) is constant which shows that the electrochemically
prepared P2-EtAnSnCl₄ film is stable under
experimental condition.

**Thermogravimetric (TG) analysis**

The TG analysis of ClO₄⁻ (Fig. 6a) and SbCl₅⁻
(Fig. 6b) doped electrochemically synthesised
polymer (Table 4) shows that about 34 and 10 percent
weight of the polymer sample gets lost at 300 and
333°C respectively. This loss may be due to the
evolution of a low molecular weight compound, like
the dopant anion. The weight loss at 400 and 600°C
indicated about 85 percent loss either by evaporation
and/or by degradation on heating the ClO₄⁻ and
SbCl₅⁻ doped polymer. The derivative thermogrammetry
(DTG) curve of ClO₄⁻ (Fig. 6a) and
SbCl₅⁻ (Fig. 7a) doped polymer suggested that the
maximum rate of decomposition is at 400 and 500°C
respectively. The differential thermal analysis (DTA)
curve of poly(2-ethylamine) ClO₄⁻ (Fig. 7b) shows
one exotherm hump around 150°C and another two
exotherms around 250 and 350°C. The SbCl₅⁻ (Fig.
6b) doped polymer system also shows one exotherm
hump at 324°C and other two exotherms observed at
456 and 599°C. This exothermic decomposition
possibly corresponds to the branching and/or
crosslinking of the polymer at this point (Table 4).
Morphology

SEM photograph of poly(2-ethylaniline) doped with SnCl₄ (Fig. 8a) shows regular pattern of deposition with petal like morphology having minute cracks. On the other hand ClO₄ doped (Fig. 8b) poly(2-ethylaniline) shows chain like fibrous structure with broader cracks. The SbCl₅ doped (Fig. 8c) poly(2-ethylaniline) represents regular pattern of deposition with granular morphology without any cracks. Further, corroboration is provided by the fact that conductivity is affected by the pattern of deposition of polymers since poly(2-ethylaniline) SnCl₂ doped polymer with no cracks has a higher conductivity than SnCl₄ doped polymer and the conductivity of SnCl₄ doped polymer is higher than that of ClO₄ doped one which is also confirmed by the conductivity measurement presented in Table 1.

Mechanism

The chemical and electrochemical polymerization of 2-ethylaniline to poly(2-ethylaniline) is a straightforward reaction. The anodic oxidation of 2-ethylaniline in nonaqueous solution affords a radical cation which then dimerizes with the expulsion of 2H⁺. The process is repeated with involvement of 2e⁻ and 2H⁺ in each step favouring the polymerization process (Scheme 2).

Acknowledgement

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References