<table>
<thead>
<tr>
<th>Chapter 3.</th>
<th>MATERIALS AND METHODS</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Materials</td>
<td>40</td>
</tr>
<tr>
<td>3.2</td>
<td>Purification</td>
<td>41</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Water</td>
<td>41</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Aniline</td>
<td>41</td>
</tr>
<tr>
<td>3.3</td>
<td>Methods of synthesis</td>
<td>42</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Chemical synthesis</td>
<td>42</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Interfacial polymerization</td>
<td>45</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Electrochemical synthesis</td>
<td>46</td>
</tr>
<tr>
<td>3.4</td>
<td>Methods of characterization</td>
<td>47</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Chemical analysis</td>
<td>47</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Instrumental characterization</td>
<td>47</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>54</td>
</tr>
</tbody>
</table>
3.1. Materials

All the chemicals used in the present work were of commercially available analytical or guaranteed reagent (AR/GR) grade. Names of the chemicals, their make and grade/purity are given below in the following table.

<table>
<thead>
<tr>
<th>Name of the chemical</th>
<th>Grade/ Purity</th>
<th>Make</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monomer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aniline</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td>Aniline hydrochloride</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td><strong>Oxidant</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium persulfate</td>
<td>GR</td>
<td>Merck, India</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td><strong>Templates/Dopants</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl pyrrolidone) (MW 40000)</td>
<td>Pure</td>
<td>SRL, India</td>
</tr>
<tr>
<td>Sodium dodecylbenzenesulfonate</td>
<td>Tech. Grade</td>
<td>Aldrich, USA</td>
</tr>
<tr>
<td>Sodium dodecysulfate</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td><em>para</em>-toluene sulfonic acid</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td>β-Cyclodextrin</td>
<td>Pure</td>
<td>Lancaster, England</td>
</tr>
<tr>
<td><strong>Acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>GR</td>
<td>Merck, India</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>GR</td>
<td>Merck, India</td>
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### Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Grade</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>GR</td>
<td>Merck, India</td>
</tr>
<tr>
<td>Chloroform</td>
<td>GR</td>
<td>E-Merck, India</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td>Methanol</td>
<td>AR</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>AR</td>
<td>Qualigens, India</td>
</tr>
<tr>
<td>N-methylpyrrolidone</td>
<td>AR</td>
<td>SRL, India</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
</tbody>
</table>

### Other chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Grade</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium dichromate</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>AR</td>
<td>SD Fine-Chem., India</td>
</tr>
<tr>
<td>Anthrone</td>
<td>Pure</td>
<td>Loba Chemie, India</td>
</tr>
<tr>
<td>Potassium bromide</td>
<td>IR-Spectral Grade</td>
<td>Merck-Germany</td>
</tr>
</tbody>
</table>

### 3.2. Purification

#### 3.2.1. Water

All the experiments were carried out using double-distilled water (DDW). First the tap water was distilled with stiller distillatory plant and then it was distilled over alkaline potassium permanganate in an all-glass-setup. The DDW was collected and stored in amber-color glass bottles and used throughout the experiment.

#### 3.2.2. Aniline

Aniline was doubly distilled over zinc dust to eliminate the oxidation impurities formed during storage [1]. Aniline distillation with zinc dust was carried out with a water condenser. The initial and final fractions were discarded while the middle portion...
containing the colorless aniline boiling constantly at 185 °C was collected and stored in an air-tight bottle prior to use.

All other solvents, acids and solid chemicals, which are of AR/GR grade, were used as such without further purification.

3.3. Methods of synthesis

3.3.1. Chemical synthesis

PANI (method-1)

PANI was synthesized by *in situ* chemical oxidative polymerization of aniline hydrochloride using FeCl$_3$ as the oxidant in aqueous 1.0 M HCl medium. In a typical procedure, a mixture of 2g of aniline hydrochloride and 5g of FeCl$_3$ in the molar stoichiometric ratio of 1:2 was prepared. Polymerization was effected by drop wise addition of 1.0 M HCl over a period of 1 h with constant stirring for about 2 h. Then it was allowed to proceed further for 48 h with constant stirring. The polymer mass that settled was filtered, washed several times with 0.1 M HCl until the filtrate became colorless and dried in an air oven at 120 °C for about 5 h. The dried polymer samples were ground into fine powder and kept in air-tight polythene packets to avoid moisture absorption.

PANI (method-2)

PANI was also synthesized by *in situ* chemical oxidative polymerization technique [2]. In a typical procedure, 100 ml of 0.2 M distilled aniline in aqueous sulfuric acid medium of pH 1.0 was polymerized by drop-wise addition of 100 ml of pre-cooled 0.2 M ammonium persulfate (APS) with constant magnetic stirring for 1 h. The mixture was kept overnight in a refrigerator for completion of polymerization reaction. A dark green colored polymer mass obtained was filtered by suction, washed several times with DDW, acetone and 0.1 M sulfuric acid until the washings were colorless in each case.
The polymer sample was dried in an air oven at 120 °C for about 5 h, ground into fine powder and stored in air-tight polythene packets.

**PANI-PVP blend materials**

PANI-PVP blend materials were prepared by *in situ* chemical oxidative polymerization using FeCl₃ oxidant as described in method-1 with appropriate amount of PVP (less, equal and higher content based on monomer molecular weight with respect to ANI.HCl). The three different concentrations of aniline hydrochloride, PVP and FeCl₃ were in the molar ratios of 1:0.5:2, 1:1:2 and 1:3:2. Polymerization was effected by drop-wise addition of 1.0 M HCl with constant stirring for about 2 h. Then it was allowed to proceed further for 48 h. The polymer mass that settled was filtered, washed several times with 0.1 M HCl until the filtrate became colorless and dried in an air oven at 120 °C for about 5 h. The dried polymer samples were ground into fine powder and kept in air-tight polythene covers to avoid moisture absorption prior to use.

**PANI-PVP and/or HBA blend materials**

These materials were synthesized separately by adopting chemical synthesis as described in method-2. Appropriate quantities of PVP and HBA corresponding to the concentrations of 1 mM and 2 mM respectively in the final volume of the polymerization mixture (200 ml) were added initially to the aniline solution and the polymerization was continued. The two PANI-PVP+HBA blends were prepared with identical PVP and aniline concentrations but with two different [HBA] ([ ] represents concentration), namely 2 mM and 4 mM. After the addition of APS which continued for 1 h, the reaction mixture was kept overnight in a refrigerator at rest for the completion of polymerization reaction. The polymer sample was washed, dried and stored as described earlier.
**PANI-CPVP composite materials**

PANI-CPVP composites were synthesized by conventional precipitation polymerization method using APS oxidant. In a typical procedure, a suspension of aniline monomer and CPVP (stoichiometric ratio - 2:1) in aqueous sulfuric acid medium (100 ml) was prepared. 100 ml of 0.2 M APS was added to the above mixture drop-wise with constant stirring. The reaction mixture was left 2 h with constant stirring and kept overnight in a refrigerator for completion of polymerization reaction. A dark green colored polymer mass obtained was filtered by suction, washed several times with DDW, acetone and then with 0.1 M sulfuric acid until the washings became colorless in each case. The polymer sample was dried in air oven at 120 °C for about 5 h, ground into fine powder and stored in an air-sealed polythene cover.

**PANI-TSA/TSA+SDS composite materials**

Four different composite materials were synthesized separately by adopting chemical synthesis procedure (method-2) as described above. For PANI-TSA composite, appropriate quantity of TSA (2 mM) was added initially to the aniline solution (0.1 M) in aqueous H$_2$SO$_4$ (0.2 M), sonicated for 5 min and then stirred well with magnetic stirrer for more than 2 h to get homogeneous solution. For PANI-TSA+SDS 1 and 2 composites, synthesis was performed by keeping [aniline] and [TSA] fixed as above and using two different [SDS] of 0.1 mM (below CMC) and 10 mM (above CMC). When aniline and surfactant solutions were mixed, a suspension of precipitate was formed. This means that the sulfoxy group of the surfactant interacted with the anilinium cations to produce the suspension. By ultrasonic treatment, this suspension converted into a milky emulsion.

**PANI-CD and/or HBA composite materials**

The same procedure described in method-2 was adopted in PANI-CD and PANI-HBA composites preparation. Appropriate quantities of CD and HBA
(1.19 and 2.0 mM, respectively) were added initially to the aniline solution (200 ml) in aqueous H$_2$SO$_4$ (0.1 M) and stirred well for more than 2 h. For PANI-CD+HBA 1, 2 and 3 composites, the synthesis was performed by keeping [aniline] and [CD] fixed as above, and using three different [HBA] of 2.0, 4.0 and 6.0 mM respectively.

3.3.2. Interfacial polymerization

PANI

PANI and its blend materials were synthesized separately by interfacial polymerization method by adopting the literature procedure [3]. In a typical experiment, the volume ratio of organic phase to aqueous was maintained at 1:1; the aniline/chloroform solution formed the lower organic phase and the APS solution formed the upper aqueous phase. Aniline (0.1 M) was dissolved in chloroform (total volume 100 ml) and was taken in 250 ml separatory funnel. To this was added, gently and with minimum agitation along the sides of the funnel, an aqueous solution (100 ml) of APS (0.1 M). The resulting two-phase system was closed to minimize solvent evaporation and left undisturbed for 48 h. The polymerization was carried out without stirring at room temperature (~300 K). The aqueous mixture containing the polymer sample was then collected, suction-filtered and washed with DDW, acetone and 0.1 M H$_2$SO$_4$ to remove the unreacted chemicals and aniline oligomers. The obtained polymer sample was dried in air oven at 120 °C for 5 h and ground into fine powder and stored.

PANI-PVP and/or SDBS blend materials

The same interfacial polymerization described above was adopted for the synthesis of PANI-PVP and PANI-SDBS blend materials. An aqueous APS solution (100 ml) with appropriate quantities of PVP and SDBS corresponding to the concentrations of 10 mM and 2 mM respectively was added to the organic aniline/chloroform phase. In the case of PANI-PVP-SDBS material preparation, aniline,
PVP and SDBS were maintained in the same molar ratio. In all the cases, the reaction temperature was ambient (~300 K). The materials were subjected to washing and drying as described earlier.

3.3.3. Electrochemical synthesis

PANI

PANI was synthesized separately by electrochemical oxidative polymerization under air atmosphere by adopting the literature procedure [2]. It was carried out in one compartment cell containing two stainless steel electrodes (7.0 cm$^2$) under constant potential of 1.5 V from a DC power supply unit (Testronix 30B DC power supply) without stirring. The polymerization was terminated after 1 h. The anode plate was removed and air-dried at room temperature for 24 h and the sample was scrapped and stored in an air-tight plastic packet.

PANI-PVP and/or HBA blend materials

PANI-PVP, PANI-HBA and PANI-PVP+HBA blend materials were synthesized electrochemically as described above using the same molar stoichiometric ratio as mentioned in chemical synthesis. Ultrasonic action was adopted to get homogeneous solution.

PANI-TSA/TSA+SDS composite materials

Four different composite materials were synthesized separately by in situ electrochemical oxidative polymerization maintaining the conditions of chemical synthesis.

PANI-CD and/or HBA composite materials

PANI-CD, PANI-HBA and PANI-CD+HBA blend materials were also synthesized electrochemically maintaining the conditions of chemical synthesis.
3.4. Methods of characterization

3.4.1 Chemical analysis

Estimation of water content

The estimation of water content was necessary to fix the composition of chemically synthesized PANI materials. Water content was computed from the weight changes on drying of a known quantity of sample in a vacuum oven at 120 °C for about 2 h. The weight measurements were made repeatedly until constant weight was reached. (Four decimal balance with 0.1 mg accuracy–Shimadzu).

3.4.2 Instrumental characterization

FTIR spectroscopy

The FTIR spectra of polymer materials in KBr pellets were recorded with JASCO FTIR-410 spectrophotometer provided with computer software. The recording was performed in the wavenumber range 4000-400 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\).

UV-visible spectroscopy

The UV-visible electronic absorption spectra of polymer materials in the solvents, NMP, DMSO, methanol, ethanol and 1.0 M H\(_2\)SO\(_4\) were recorded with Techcomp UV2301 spectrophotometer and Perkin-Elmer UV-vis spectrophotometer–Lambda 25 Model by scanning the wavelength in the range 330-1100 nm at a scan speed of 240 nm/min in matched 1 cm quartz cuvettes. The corresponding solvents were used as blank.

Optical band gap determination

The optical absorption coefficient was calculated using the relation

\[
\alpha = \frac{[A(h\nu-E_g)^m]}{h\nu} \quad -- 3.1
\]

where \(E_g\), \(h\), \(\nu\) and \(A\) were the band-gap, Planck’s constant, frequency and constant respectively \([4]\). The exponent, \(m\), represents the nature of transition and can take values
1/2, 3/2, 2 or 3 for allowed direct, allowed indirect, forbidden direct or forbidden indirect transitions respectively [5]. In our case, $m = 1/2$ offered the best fit value for the optical absorption data and supported the allowed direct band transition of PANI materials. Tauc plot of $(\alpha h\nu)^2$ vs $h\nu$ was made and the band-gap values were obtained by extrapolating the linear portion of the plot on $h\nu$ axis (i.e., x-axis) at $\alpha = 0$.

**Structural characterization with XRD**

The XRD patterns of polymer materials were obtained using PANalytical X’PERT PRO MPD X-ray diffractometer operated at an accelerating potential of 40 kV and 30 mA filament current with CuKα radiation of wavelength 1.5406 Å available at Alagappa University, Karaikudi. The angle of diffraction ($2\theta$) was kept in the range 10 to 80°. The average crystallite size $D$ was calculated by applying the Scherrer formula given in equation 3.2.

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

--- 3.2

where $\lambda$ is the X-ray wavelength, $\theta$ is the diffraction angle and $\beta$ is full width at half maximum (FWHM) of the highest intensity X-ray reflection.

**SEM characterization**

SEM images of polymer materials were observed with JEOL JSM 5610LV microscope operating at 15/20 kV, after coating the samples with gold to a thickness of 100 Å using JEOL JFC 1600 auto fine coater applying sputtering technique available at Annamalai University, Chidambaram. Morphologies of a few powder polymer samples were examined with JEOL JSM-6390 microscope available at Karunya University, Coimbatore. SEM images of different magnifications were photographed and analyzed.
**Thermal characterization**

The thermal stabilities of different polymer materials were investigated from ambient (30 °C) to 850 °C using 'TA Instruments' Model Q500 High Resolution Thermogravimetric Analyzer (IITM, Chennai). The analyses were carried out with a heating rate of 10 °C/min under nitrogen atmosphere.

For some of the samples the thermal stabilities were examined using SIINT TG/DTA 6300-SII Nano-Japan Thermogravimetric Analyzer with a heating rate of 10 °C/min under air atmosphere available at Thiagarajar College of Engineering, Madurai.

**DC conductivity measurement**

DC electrical conductivity measurements of the pressed pellets were made by two methods:

1. Collinear four-probe method and
2. Two-probe method

**Collinear four-probe method**

DC electrical conductivities of freshly prepared polymer materials were measured by standard collinear four-probe method [6] at room temperature. The polymer samples were pressed into pellets of 13 mm diameter and about 1 mm thickness with the help of a hydraulic press (KIMAYA Engineers, India, Model WT-324) by applying three metric ton pressure. The current-voltage (I-V) values were recorded by making a gentle contact at different positions of the pellet with the collinear four-probe tips (inter-probe spacing = 2 mm) and by drawing current from a constant power supply unit (Scientific Equipment and Services, Roorkee, Model DFP02). From the slopes of I-V plots, the resistances were determined and the conductivities were calculated using the equation 3.3.

\[
\text{Conductivity} = \frac{1}{R^2\pi} \quad -- 3.3
\]
where $R$ is the resistance and $s$ is the distance between the two probes (2 mm). Measurements were made for a pair of pellets of the same polymer samples and average of the conductivities of the two pellets was computed for each sample.

Two-probe method

The bulk DC electrical conductivities of some of the polymer materials were measured by two-probe method using Keithley source meter (Model 2400) at room temperature for pressed pellets of the same dimension mentioned above. Specially designed copper electrodes were used to keep the pellet in between them and current-voltage measurements (I-V values) were made in this configuration. From the slopes of I-V plots that were linear, resistances were determined and converted into conductivity using dimensions of the pellet using equation 3.4.

$$\text{Conductivity} = \frac{t}{R \pi r^2} \quad --- \ 3.4$$

where $t = \text{thickness of the pellet}$, $r = \text{radius of the pellet}$ and $R = \text{resistance of the polymer material}$.

AC conductivity measurement

Investigation of AC electrical properties of PANI materials of high resistance was performed by complex impedance spectroscopy (CIS) in a two-electrode cell by means of Lock-in-Amplifier (Stanford Research System, Model SR830 DSP) that provided AC signal of 100 mV in the frequency range 5 Hz to 100 kHz. AC responses of the ground polymer samples were studied on cylindrical discs of diameter 13 mm and thickness of about 1 mm placed in between the two electrodes. Applying complex formalism the electrical properties of the materials were determined as described below.

Determination of AC electrical properties

The bulk electrical conductivity $\sigma_b$ was determined from the relation

$$\sigma_b = \frac{t}{(R_b a)} \quad --- \ 3.5$$
where \( t \) is the thickness, \( R_b \) is the bulk resistance and \( a \) is the area of cross-section of the pressed polymer sample in disc/pellet form. The critical frequency \( (f_c) \) of the material, independent of the geometrical parameters of the sample, was found from Bode plot, which fulfills the condition \( 2\pi f_c R_b C_b = 1 \). From this relation, the bulk capacitance \( C_b \) of the material, also called the geometrical capacitance, was calculated and the bulk dielectric constant \((\varepsilon_b)\) was determined using the equation 3.6.

\[
C_b = \frac{(\varepsilon_b \varepsilon_o a)}{t} \quad --- \text{3.6}
\]

where \( \varepsilon_o \) is the permittivity of free space [7,8]. The relaxation time \( \tau \) was obtained using the relation \( \tau = 1/(2\pi f_c) \).

**Analysis of conductivity data**

The bulk DC and AC conductivities as a function of temperature from ambient to 180 °C were measured in a similar way as described above using temperature-controlled chamber (Scientific Equipment Services, Roorkee, India) coupled with a variable voltage regulator (DIMVOLT, Bharat Electricals, Mumbai, India). The data obtained by two-probe method was subjected to graphical and mathematical analysis in order to deduce AC electrical properties and the activation energy of the polymeric materials.

**Determination of activation energy**

The activation process of polymer materials was studied by using Arrhenius relation 3.7 [9].

\[
\sigma(T) = \sigma_0 \exp \left(-\frac{E_a}{k_B T}\right) \quad --- \text{3.7}
\]

which was applied in the linear logarithmic form as in equation 3.8.

\[
\ln \sigma = \ln \sigma_0 - \frac{E_a}{k_B T} \quad --- \text{3.8}
\]

where \( \sigma_0 \) is the pre-exponential factor, \( E_a \) is the activation energy, \( k_B \) is the Boltzmann constant and \( T \) is the Kelvin temperature.
The parameter $E_a$ represents the activation energy of electron from $\pi$ to polaron band. $E_a$ was calculated from the slope of the linear plots of $\ln (\sigma_{dc})$ versus $1/T$ using equation 3.9.

$$E_a = \text{slope} \times 2.303 \times k \quad --- \ 3.9$$

**Sensor application**

In sensor experiment the interaction of volatile organic compound (VOC) vapors with PANI materials were investigated by the following two methods.

1. Static method and
2. Dynamic method

**Static Method**

The sensor experiment was performed by measuring the voltage change with four-probe set-up before and after exposure of the pellet to saturated vapors for about 30 min under static condition inside an air-removed and solvent-vapor-filled closed chamber. The technique of saturated vapor under static condition was adopted owing to weak solvent vapor-polymer interaction. A few minutes exposure to solvent vapor was found sufficient in altering the voltage but 30 min exposure was performed to ensure equilibrium. After equilibration, the voltage change was measured. On re-exposure to air, the vapor left the pellet by evaporation and the voltage returned to its initial value. The solvent vapor-induced voltage changes were measured two times in each case in order to ensure equilibrium in voltage value and to confirm the reversibility and regeneration of PANI materials on re-exposure to air.

**Dynamic method**

The sensor response in dynamic method was carried out by employing two-probe technique. In a typical experiment, two ohmic contacts were made at two opposite points on the same surface of the pellet using thin enameled copper wires and silver paste and
mounting the pellet on a printed circuit board (pcb). The pellet along with pcb was placed inside an air-removed and vapor-filled closed chamber. The electrical response of PANI materials was monitored by measuring dc resistance variation upon solvent-vapor exposure at room temperature with the convenient time scale. After attaining a steady resistance value, the pellet on pcb was exposed to air and the corresponding resistance changes were monitored. Solvent-exposure and air-exposure were made alternatively and the sensor response in resistance change was recorded for 4/5-cycles.

**FTIR spectroscopy characterization of sensor materials**

To understand and assess qualitatively the underlying interaction of each solvent-vapor with PANI materials, FTIR spectra of the materials after exposure to solvent-vapors were observed with KBr pellets using JASCO FTIR-410 spectrophotometer provided with computer software. The recording was performed in the wavelength range 4000-400 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\).
References


