CHAPTER 2

MATERIALS AND METHODS

This chapter contains details of chemical and electrochemical synthetic methods, and the analytical techniques employed for the research study.

2.1 Monomers

Aniline, benzene and thiophene obtained from Sigma chemicals were purified by conventional vacuum distillation methods before using them for polymerization reactions.

2.2 Oxidants / Electrolytes

Potassium or ammonium peroxydisulfate for PANI and ferric chloride in case of Pth synthesis were used for chemical oxidation of the respective aniline and thiophene monomers. However 18M H2SO4 in microemulsion media consisting hydrocarbon monomer and surfactant was used as electrolyte for electrochemical oxidation of benzene and thiophene monomers during the electrosynthesis of PPP and PTh. The chemical oxidants were of analytical grade and used as-received.

2.3 Surfactants

The chemical details of surfactants that have been employed for the synthesis in these investigations are summarized in Table 2.1 [135]. General information on surfactant characteristics are given in chapter 1 (section 1.3). Concentrations of the surfactants close to or slightly above \textit{cmc} (0.5, 9.0, or 14.8 mM concentration) for electrochemical and higher
Table 2.1: A summary of chemical details of some surfactants [135].

<table>
<thead>
<tr>
<th></th>
<th>Surfactant</th>
<th>cmc$^{a}$</th>
<th>Formula weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sodium dodecyl sulfate (SDS), anionic</td>
<td>$8.1 \times 10^{-4}$ M</td>
<td>288.4</td>
</tr>
<tr>
<td></td>
<td>CH$_3$(CH$<em>2$)$</em>{10}$ CH$_2$SO$_4^-$ Na$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Polyoxyethylene(9,5) octylphenol (TritonX-100), nonionic</td>
<td>$3.0 \times 10^{-4}$ M</td>
<td>624.9</td>
</tr>
<tr>
<td></td>
<td>[CH$_3$(CH$_2$)$_3$ CHCH$_2$OOC]$_2$ CHSO$_3^-$ Na$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$CH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Sodium bis(2-ethylhexyl) sulfo succinate, Aerosol OT or (AOT), anionic</td>
<td>~$6.0 \times 10^{-4}$ M</td>
<td>444.6</td>
</tr>
<tr>
<td></td>
<td>[CH$_3$(CH$_2$)$_3$ CHCH$_2$OOC]$_2$ CHSO$_3^-$ Na$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$CH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Hexadecyltrimethyl ammonium bromide (CTAB), cationic</td>
<td>$9.2 \times 10^{-4}$ M</td>
<td>364.5</td>
</tr>
<tr>
<td></td>
<td>CH$_3$(CH$<em>2$)$</em>{15}$ N(CH$<em>3$)$</em>{15}^+$ Br$^-$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$ The concentration at which a surfactant forms a micelle is known as critical micellar concentration or cmc, the micelle is the solubilization of a surfactant in aqueous media wherein the headgroup (hydrophilic end) of the surfactant molecule is attached to the water molecule. That is, over a narrow range of cmc, there is a sudden transition in the structural properties of aqueous surfactants, this transition corresponds to the formation of aggregates and is used to define the cmc [135].
(upto 38.5 mM concentration) than \(\text{cmc}\) in case of chemical synthesis have been employed.

2.4 Experimental Techniques

2.4.1 Synthetic Methods

Chemical and electrochemical polymerization in microemulsion media have been employed in this study.

a) Chemical synthesis

PANI and Pth powders were obtained by chemical synthesis. For the synthesis of PANI, AOT or SDS was chosen as surfactant and \(n\)-butanol as co-surfactant to solubilize the aniline/anilinium hydrochloride (aqueous) monomer in excess of cyclohexane (oil) to make water-in-oil (w/o) microemulsions. The chemical oxidation was carried out using potassium or ammonium peroxydisulfate (\(K_2S_2O_8\) or \((\text{NH}_4)_2\text{S}_2\text{O}_8\)) as an oxidant.

In case of Pth, oil-in-water (o/w) microemulsions were prepared using thiophene monomer (oil) in excess of water having SDS or Triton X-100 as surfactant. The polymerization was carried out by chemical oxidation, the oxidant being ferric chloride.

In the chemical polymerization method, aqueous monomer (AM) and aqueous oxidant (AO) were made up separately. Then AO was slowly added to the AM with stirring. The solution was stirred thoroughly to enable homogeneous reaction. Then the solution was allowed to stand, filtered, and the filtrate was washed and dried to obtain the polymer powder.
b) Electrochemical synthesis

PPP and PTh films were prepared by electrochemical synthesis. Electrochemical Analyzer (BAS - 100 A model, USA) was used to carry out the electrochemical experiments using a three-electrode system. Transparent (indium doped tin oxide) indium-tin-oxide or ITO (Donnelly Corp, Michigan, USA) was used as working electrode while platinum and Hg / Hg₂SO₄ (MSE) were used as counter and reference electrodes respectively. A potential scan rate of \( v = 100 \text{ mV s}^{-1} \) was chosen for all the experiments.

For the electrochemical experiments, an oil-in-water (o/w) microemulsion was prepared using benzene or thiophene as monomer (oil) solubilized in H₂SO₄ by the addition of SDS or Triton X-100 surfactant. The microemulsion solutions were employed as both organized media and the electrolyte for electrochemical oxidation reaction. On oxidation, benzene or thiophene undergoes polymerization to form a film on the ITO glass-electrode. The films were washed in water and tetrahydrofuran (THF), and dried. The potential was scanned between + 0 91 and - 0 21 V vs MSE. The growth of the film was followed by continuously recording the cyclic voltammograms. The o/w microemulsions have been chosen here because of the fact that they are conductive in nature, suitable for electrochemical studies for electrodes of any size, as their conductivities approach those of homogeneous aqueous electrolyte solutions [93].

c) Polymerization reactions

Polymerization reaction schemes corresponding to PANI (Genies et al [156]), PPP (Phani et al [153]) and conjugated PTh polymers are given in Fig 2 4 1.

2.4.2 Analytical Methods

a) X-ray diffraction X-ray diffraction is a powerful technique for the structural characterization of crystalline solids. The basic concept is that when
(a) Aniline polymerization

(cation formation) \( \text{(1)} \)

(cannotical form) \( \text{(2)} \)

(polymerization by radical cation coupling; quinoid-type) \( \text{(3)} \)

(b) Benzene polymerization

\[
\begin{align*}
\text{benzene} & \quad \text{H}^+ \quad \rightarrow \quad \text{benzene}^+ \quad \rightarrow \quad \text{benzene}^+ \quad \rightarrow \quad \text{benzene}^+ \quad \rightarrow \quad \text{polymer} \quad \text{(PANI)} \\
\end{align*}
\]

(c) Thiophene polymerization [PTh]

(monomer oxidation) \( \text{(1)} \)

[2,5 or \( \alpha-\alpha' \) coupling reactions] \( \text{(3)} \)

Figure 2.4.1: Polymerization reaction Schemes for (a) aniline (Genies et al [156]), (b) benzene (Phani et al [153]) and (c) thiophene monomers.
a beam of monochromatic x-rays (of wavelength $\lambda$) is incident on a crystalline material (having parallel planes measured as $d$-spacings present in a three-dimensional crystal lattice), uniform (or coherent) scattering takes place such that $2d \sin \theta = \lambda$; where $\theta$ is the Bragg (incident) angle and $2\theta$ is the diffraction angle. Sharp x-ray diffraction peaks are observed corresponding to every diffraction (parallel) planes of the crystal lattice of the crystalline material. Thus a plot (x-ray diffraction pattern) is obtained as $2\theta$ on the x-axis and intensity on the y-axis, depicting diffraction peaks (also called lines or reflections) representing the diffraction planes of the crystal lattice.

A typical set of x-ray diffraction patterns of fully crystalline, completely amorphous and semicrystalline polymers are schematically shown in Fig.2.4.2; the corresponding polymer macromolecular arrangements are also given. The volume of crystalline contribution present in the semicrystalline polymer material is estimated as degree of crystallinity $X_{cr}$. It is conventionally measured as the percentage ratio of the (integrated) intensities corresponding to the crystalline volume ($I_c$) to that ($I_a$ and $I_c$) of the whole (amorphous and crystalline) matrix. That is,

$$\text{degree of crystallinity, } X_{cr} (\%) = \left[ \frac{I_c}{I_a + I_c} \right] \times 100$$

This equation is derived and simplified from the relevant conditions mentioned in the literature [136,137] for the x-ray powder diffraction for semicrystalline polymers. Since homogeneous coexistence of both amorphous and crystalline contributions can be treated as two-phase system [as shown in Fig.2.4.2(c)], the same basic concept of volume occupied by crystalline and amorphous phases in the surface region of semicrystalline polymer matrix is applicable to the x-ray powder diffractometer geometry. The volumes of these two phase regions are then conventionally estimated using integrated intensity or area covered by the x-ray diffraction peaks. However for
Figure 2.4.2 Typical x-ray diffraction patterns depicting the (a) crystalline, (b) amorphous and (c) semicrystalline polymers are shown corresponding to their molecular arrangements (on the right) C- crystalline, A- amorphous, I- intensity.
crystalline anisotropic polymer films, only the peak height (minus background) intensities (~10^4 counts per sec) are used here since the reflections are highly intense and extremely narrow [FWHM being almost close to the instrumental or standard broadening]. No softwares, theoretical, simulation or computational methods are employed here to estimate degree of crystallinity. All these measurements and others for the x-ray analysis were carried out only manually.

The crystalline peaks observed in the x-ray diffraction patterns are indexed (assigning Miller indices, namely, (hkl)) using standard analytical methods [138]. As the observed crystalline conjugated polymers seem to exhibit mostly orthorhombic or monoclinic crystal lattice; the corresponding lattice parameters and the unitcell volume (V_o) of the lattices have manually been computed using the following formulae:

(i) Orthorhombic

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]

\[ V_o = abc; \ (a \neq b \neq c ; \ \alpha = \beta = \gamma = 90^\circ). \]

(ii) Monoclinic

\[ \frac{1}{d^2} = \frac{h^2}{\sin^2 \beta} + \frac{k^2 \sin^2 \beta}{a^2} + \frac{l^2}{b^2} + \frac{2hk \cos \beta}{ac} \]

\[ V_o = abc \sin \beta; \ (a \neq b \neq c ; \ \alpha = \gamma = 90^\circ ; \ \beta \neq 90^\circ). \]

The crystallite size (L) of the conjugated polymer powder samples have been estimated using Scherrer formula:

\[ L = \frac{0.9 \lambda}{B_o \cos \theta}; \ B_r = B_o \times \frac{\pi}{180} \]
where $\lambda$ is the wavelength of the monochromatic x-radiation, $\theta$ is the Bragg angle, and $B_r$ and $B_0$ are the full-width half-maximum (FWHM) of the x-ray diffraction peak measured in degrees and radians respectively.

Texture or anisotropy of the polymer films are brought about by the observation of the intensities of individual diffraction planes or the crystallites of the samples. And the layered structure of the polymer film can be elucidated by the x-ray diffraction pattern, that is by the interplanar (d-) spacings of the axial reflections; for example, $d_{001} = 2d_{002} = 3d_{003} = 5d_{005} = 6d_{006}$, .... represent (00l)- texture. (Detailed pole-figure analysis normally used in metallurgy/mechanical engineering for metallic textures is not employed here).

All the x-ray diffraction patterns were recorded using a computer-controlled x-ray powder diffractometer system, JEOL (Japan) JDX-8030, at a rating of 40 kV, 20 mA. Ni-filtered CuK$\alpha$ radiation ($\lambda = 0.15418$ nm) was used. The $\theta$ - $2\theta$ mode of scan was used to record x-ray diffraction patterns of the polymer samples. The $2\theta$ -range is between $3^\circ$ and $65^\circ$ at a step scan of $0.1^\circ$ ($2\theta$) for a measuring time of 1s per step.

(b) Scanning Electron Microscopy (SEM)

The morphological details of the polymer samples were recorded using JEOL (Japan) JSM-35CF scanning electron microscope. Since most of the samples were conducting, they were directly mounted onto the sample holders with silver paste. However, a few non-conducting (non-crystalline) samples had to be gold-sputtered before taking it on to the specimen-stage of the SEM.
The polymer samples were generally scanned on different locations, and a uniform area was selected for microstructural features, and were recorded at an applied voltage of either 5kV or 15 kV (in case of higher magnifications) The samples were stable till the end of the scan and until the complete SEM observations.

(c) Other techniques

(i) The optical microscope REICHERT (Austria) Model 3001-362 (Universal type) was used for observations of the samples at lower magnifications before taking them to the SEM. The unique features of polarized facility were utilized to observe the *maltese cross* under crossed polarizers, exhibiting the anisotropic nature of the polymer film samples. This observation was clearly noticed by visual inspection. However, a direct observation of anisotropy of the *spherulite* morphology was recorded using SEM.

(ii) UV-Vis absorption spectra of the polymer samples were recorded using a computer-controlled HITACHI (Japan) U-3400 machine as digitized data to plot absorbance vs wavelength data of the polymer samples. Some of the polymer film samples were examined for their photoluminescence (PL) spectra using HITACHI (Japan) 650-105 fluorescence spectrophotometer. (iii) Differential thermal analysis of the polymer powder samples was carried out using a computer-controlled Standard Thermal Analyser STA 1500 (UK) system. A few milligrams of the sample were used for the analysis at a heating rate of 10°C.min⁻¹ in N₂ atmosphere. The DTA (or DSC) /TG (thermogravimetric) plots were recorded to support the results such as phase change and thermal stability of the polymers. (iv) In order to support the evidence for the presence of small amounts of surfactant in the polymer samples, and also to ascertain the polymer/oligomer nature of the samples, Fourier transform infrared (FTIR) spectrometer was employed.