Chapter-3

Experimental
3.1. Materials

Aniline: Ranbaxy Chemicals (distilled under reduced pressure)

o-Methylaniline (o-toluidine): SD Fine Chemicals (distilled under reduced pressure)

p-Methylaniline (p-toluidine) (99%): Sisco Chemicals (recrystallized from alcohol and then from acetone)

p-Methoxyaniline (p-anisidine) (98%): CDH Chemicals (recrystallized from alcohol and then from acetone)

o-Nitroaniline (98%): Sisco Chemicals (recrystallized from alcohol and then from acetone)

o-Nitroaniline (98-99%): (recrystallized from alcohol and then from acetone)

p-Nitroaniline (99%): Sisco Chemicals (recrystallized from alcohol and then from acetone)

Potassium persulphate (99%): CDH Chemicals, AR grade (used as received)

Hydrochloric acid: Ranbaxy Chemicals, AR grade (used as received)

Ammonia: CDH, AR grade (used as received)

Dimethylsulfoxide (DMSO) (99%): Merck India (used as received)

Dimethylsulfoxide (DMSO): spectral grade (to record UV-VIS spectrum)

Dimethylformamide (DMF) (99%): Fluka (used as received)

Acetone (99%): Merck India, AR grade (used as received)

Methanol (99%): Merck India (used as received)
3.2. Polymer Preparation

Several aniline based polymers and copolymers were synthesized by well-known chemical methods [1-4] using ammonium persulphate as an oxidant under acidic conditions.

Desired quantities of aniline and substituted aniline monomers were dissolved in 1M HCl. Solution of potassium persulphate (K₂S₂O₈) in 1M HCl was slowly added to it from a burette with constant stirring for 5 hours. The dark colored viscous reaction mixture was filtered. The product was washed with triply distilled water several times to remove the excess of oxidant and HCl present until the filtrate became colorless and acid free. Before experimental use, the product was again treated with 0.1 M HCl solution and washed with distilled water thoroughly followed by methanol to remove low molecular weight oligomers and any HCl present in the polymer. Finally, the product was washed with acetone, vacuum dried and kept at 50°C in an air oven for 3 days. The finely ground product was stored in a vacuum desiccator for experimentation. A portion of as-prepared products was treated with 0.25 M NH₄OH solution for 2 hours under constant stirring to prepare the corresponding base from of the polymers as well as of copolymers. Dedoped product was filtered, washed with distilled water several times followed by acetone. vacuum dried and stored in a desiccator under vacuum.

The copolymers of aniline with m- and p-nitroaniline were synthesized for different molar ratios of the respective monomers in presence of potassium persulphate under acidic medium. However, the copolymer of aniline with o-nitroaniline was synthesized from a mixture of acetonitrile, water and HCl.
Aniline and substituted aniline in HCl

K₂S₂O₈ in HCl

Mixing with constant stirring for 5 hours

Washed with distilled water, methanol and then with acetone

Kept in air oven at 50°C for 3 days

Treated with 0.25 M NH₄OH for 2 hrs

Dried under vacuum, kept in air oven at 50° for two days

As-prepared conducting Emeraldine salt

Non conducting base form

Figure-3.1. Flow chart showing the steps involved in the preparation of polymers and copolymers
A flow chart for the synthesis of polymers and copolymers is presented in figure-3.1 and the details of individual preparations are given as under-

3.2.1. Copolymer of aniline with \( \sigma \)-toluidine, \( P(\text{AcoOT})1:1 \)

Aniline and \( \sigma \)-toluidine (0.01 mol each) dissolved in 150 ml of 1M HCl were reacted with potassium persulphate (0.025 mol) dissolved in 150 ml of 1M HCl at 26±2°C to obtain \( P(\text{AcoOT}) \).

3.2.2. Copolymer of aniline with \( \rho \)-toluidine, \( P(\text{AcoPT}) \)

Aniline and \( \rho \)-toluidine (0.01 mol each) dissolved in 150 ml of 1M HCl were reacted with \( K_2S_2O_8 \) (025 mol) dissolved in 150 ml of 1M HCl at 26±2°C to obtain \( P(\text{AcoPT})1:1 \). Copolymers for 1:2 and 1:3 molar ratios of the monomers were also synthesized to obtain \( P(\text{AcoPT})1:2 \) and \( P(\text{AcoPT})1:3 \) respectively.

3.3.3 Copolymer of aniline with \( \rho \)-methoxyaniline, \( P(\text{AcoPMA}) \)

Aniline and \( \rho \)-methoxyaniline (0.01 mol each) dissolved in 150 ml 1M HCl were reacted with \( K_2S_2O_8 \) (0.025 mol) dissolved in 150 ml of 1M HCl at 26±2°C to obtain \( P(\text{AcoPMA}) \).

3.2.4 Copolymer of aniline with \( \sigma \)-nitroaniline, \( P(\text{AcoONA})-1:1 \)

Aniline and \( \sigma \)-nitroaniline (0.01 mol of each) dissolved in 200 ml of 9:1(v/v) mixture of 1M HCl and acetonitrile were reacted with \( K_2S_2O_8 \) (0.025 mol) dissolved in 150 ml of 1M HCl at 35±2°C to obtain \( P(\text{AcoONA})1:1 \).
3.2.5 Copolymer of aniline with o-nitroaniline, P(AcoONA)-1:3

o-Nitroaniline (0.015 mol) was dissolved in 200 ml of 9:1(v/v) mixture of 1M HCl and acetonitrile. Aniline (0.005 mol) was slowly added with constant stirring for 1 hour to get a homogeneous solution that was reacted with K₂S₂O₈ (0.025 mol) dissolved in 150 ml of 1M HCl at 35±2°C to obtain P(AcoONA)1:3.

3.2.6 Copolymer of aniline with m-nitroaniline, P(AcoMNA)

These copolymers were synthesized for 2:1, 1:1 and 1:2 molar ratios of aniline and m-nitroaniline. The monomers were dissolved in 150 ml of 1M HCl. K₂S₂O₈ (0.025 mol) dissolved in 150 ml of 1M HCl was used as oxidant. The reaction temperature was maintained at 30±2°C. The product were labeled as P(AcoMNA)2:1, P(AcoMNA)1:1, P(AcoMNA)2:1 respectively.

3.2.7 Copolymer of aniline with p-nitroaniline, P(AcoPNA)

These copolymers were synthesized for 2:1, 1:1 and 1:2 molar ratios of aniline and p-nitroanilines in a similar manner that adopted for the synthesis of copolymer of aniline with m-nitroaniline and labeled as P(AcoPNA)2:1, P(AcoPNA)1:1 and P(AcoPNA)1:2 respectively.

3.2.8 Copolymer of o-toluidine with p-methoxyaniline, P(OTcoPMA)

o-Toluidine and p-methoxyaniline (0.01 mol each) dissolved in 150 ml of 1M HCl were reacted with K₂S₂O₈ (0.025 mol) dissolved in 150 ml of 1M HCl at 26±2°C to obtain P(OTcoPMA).

All the above-mentioned copolymers were also prepared from 0.1M and 0.3 M HCl solutions following the same procedure to compare the electrical
conductivity of the polymers on the pH of the acid medium used for synthesis.

3.3. Solubility

Polyaniline and copolymers based on aniline both in their doped as well as in dedoped forms were studied for their solubility in several solvents such as water, conc. \( \text{H}_2\text{SO}_4 \), acetone, dimethylformamide (DMF), dimethylsulphoxide (DMSO), N-methyl pyrrolidone (NMP) etc.

3.4. UV-VIS Spectral Studies

Dilute solutions of base form of polyaniline and copolymers based on polyaniline were prepared by dissolving in spectral grade dimethylsulphoxide. The UV-VIS spectra were recorded at room temperature using a UV-VIS Spectrophotometer (Elico, SL 151). Spectra of doped polymers were also recorded if they were found soluble in dimethylsulphoxide. Solvatochromic effect was also studied by taking the spectra in spectral grade dimethylformamide.

3.5. FTIR spectral studies

Polymers and copolymers were thoroughly ground to fine powder with KBr and FTIR spectra were recorded in KBr pellets using a Schemadzu, 8101-A FTIR Spectrophotometer at room temperature.

3.6. Electrical Conductivity Studies

The polymers were finely powdered and made into pellets using a stainless steel die of 1.326 cm\(^2\) cross-sectional area and by applying a pressure of 3 tons using a hydraulic press (Spectra Lab. India). The pellets
were placed between two polished platinum electrodes which were mounted on a stainless steel sample holder assembly between copper leads. The copper leads were electrically insulated from the sample holder by teflon sheets. The electrical conductivity was measured by two probe method using a RLC Digibridge (Genrad 1659 RLC Digibridge, USA) at two different frequencies, viz. 100 Hz and 10 KHz. The temperature dependence of electrical conductivity was also studied from room temperature up to 180°C at 10 KHz by keeping the cell containing the pellets in an air oven and maintaining a heating rate of 1°C/min.

To study the basic nature of charge transport, the temperature dependence of conductivity data were fitted in to Variable Range Hopping Model [6,7) given by the equation -

\[
\sigma(T) = \sigma_o \cdot \exp\left(\frac{-T_o}{T}\right)^{1/(n+1)} \quad \text{---- (3.1)}
\]

and equation corresponding to band conduction or Arrhenius model

\[
\sigma(T) = \sigma_o \exp\left(-\frac{E_A}{kT}\right) \quad \text{.... (3.2)}
\]

where \(n\) is the diamensionality of charge transfer, \(T_o\) is the Mott’s characteristic temperature and \(\sigma_o\) is the conductivity at room temperature, \(E_A\) is the activation energy for transport and \(k\) is the Boltzman’s constant. The measured conductivity values were plotted logarithmically as a function of reciprocal of temperature.
3.7. Electron Spin Resonance Spectral Studies

ESR spectra were recorded on a GEOL ESR Spectrometer (JES-RE2X) at room temperature under the following settings: modulation frequency: 100 KHz, microwave frequency: 9.44 GHz, microwave power: 5 mV, scan range: 300 G, field modulation 10 G, time constant 0.035 and center field: 3350 G. The ‘g’ values, peak to peak line widths (ΔH_{pp}) and time asymmetry parameter (a/b ratios) were estimated from the ESR spectra.

3.8. Thermogravimetric Analysis

Thermo-oxidative degradation of the polymers were studied by keeping samples in a TGA analyzer (Model: Perkin Elmer) under dynamic air flow of 50 cc/min in the temperature range 70-700°C. The heating rate was maintained at 10°C/min.

Activation energies for the thermo-oxidative degradation of the polymers were calculated using integral method of Broido [8]. According to Broido equation,

\[ \ln (\ln 1/y) = \frac{-E_A}{RT} + C \] ---- (3.3)

where \( y \) is the fraction of the sample yet not decomposed and \( E_A \) is the activation energy.

\[ y = \frac{w_t - w_{\alpha}}{w_0 - w_{\alpha}} \] ---- (3.4)

where \( w_0 \) and \( w_{\alpha} \) are the initial and final weights respectively and \( w_t \) is the weight a given temperature. A plot of \( \ln (\ln 1/y) \) versus \( \frac{1000}{T} \) (K⁻¹) gives a straight line. Activation energies were calculated from the slope, \( \frac{-E_A}{R} \), of the plot of \( \ln (\ln 1/y) \) versus \( \frac{1000}{T} \) (K⁻¹).

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REFERENCES