

## CHAPTER - II

### EXPERIMENTAL TECHNIQUE

#### 2.1 Introduction

This chapter deals with the synthesis of polymers and preparation of polymer thin films. Polyaniline-EB was synthesised chemically and doping was done using methylsulfonic acid (MSA). Polypyrrole was also prepared chemically. Thin films of the polymers were deposited using solution casting technique. Structure of the film samples was checked using X-ray diffractogram. Elemental analysis was done chemically. Fourier Transform Infrared (FTIR) method was employed for the identification of the polymers. The details of the various procedures are described in the following sections.

#### 2.2 Synthesis of Polyaniline

Salt form of polyaniline (Pani-ES) can be synthesized chemically [1] or electrochemically [2] and this can be converted into Pani-EB (polyaniline emeraldine based). Chemical synthesis method was employed in the present study for the polyaniline preparation. The various steps involved are given below. **The synthesis was carried out at the special polymer division, Vikram Sarabhai Space Center, Trivandrum, India.**

### 2.2.1 Chemical Polymerization

The chemical oxidative polymerization was performed by adding drop by drop of 1 M aqueous ammonium persulphate solution to 0.1 M aniline in 1 M  $\text{H}_2\text{SO}_4$  in a beaker kept at  $0^\circ\text{C}$  (Fig.2.1). The reaction mixture was continuously stirred for 2 hours. It was then vacuum filtered and then washed repeatedly with distilled water, methyl alcohol, acetone and finally with 1 M aqueous solution of  $\text{H}_2\text{SO}_4$ . The polymer so obtained was the emeraldine salt (Pani-ES).

### 2.2.2 Conversion of Pani-ES to Pani-EB

Pani-ES chemically obtained was treated with excess of ammonia and kept for 24 hours. The mixture was then filtered and dried under dynamic vacuum at  $100^\circ\text{C}$ . The product so obtained was the Pani-EB (chemical) which was characterised and used for protonation.

### 2.2.3 Doping of Pani-EB using organic acid

The structure of Pani-EB is shown below (Fig.2.2a). The molecular weight of Pani-EB for 2 rings is 191. Pani-EB was doped with organic acid- $\text{CH}_3\text{SO}_3\text{H}$ - the methylsulfonic acid (MSA).

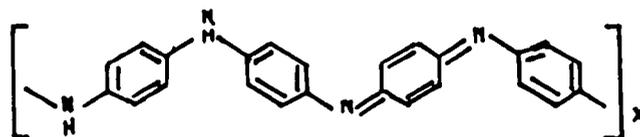


Fig 2.2a Structure of Polyaniline-EB

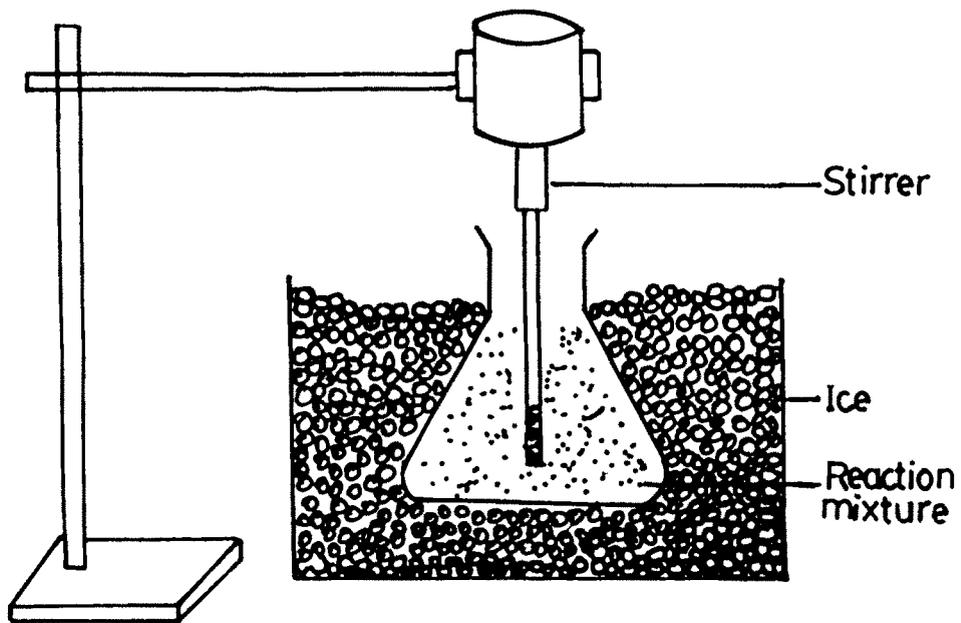


Fig. 2.1 Experimental set-up for chemical polymerization

The dopant MSA was recrystallized in dark, and their sample purity was examined by FTIR spectrum. Doped samples were obtained by keeping the known amount of Pani-EB in a known quantity of aqueous acid of required concentration in a Gooch type crucible with sintered disc (G4) funnel. The mixture was kept for 24 hours and then vacuum filtered, washed with distilled water and dried under dynamic vacuum at 50° C. The product obtained was referred as acid doped polymer.

In the present study acid doped polyaniline [Pani EB-(MSA)<sub>x</sub>] was obtained with two different doping levels, i.e., with doping concentration  $x = 0.18$  ( used for dielectric and electrical breakdown studies) and  $x = 0.5$  (used for other studies).

The doping level was determined by potentiometric titrations which were cross checked by determining the actual weight gain of EB upon doping. The weight was recorded after drying the samples at 50° C under dynamic vacuum till a constant weight was obtained. The structure of doped polyaniline is shown below

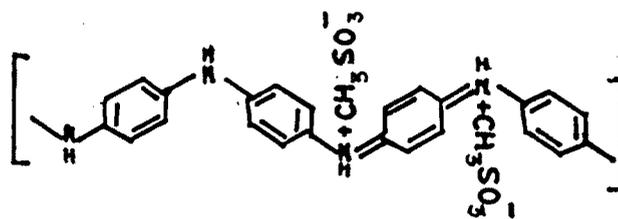


Fig.2.2b Structure of Acid doped Polyaniline

## 2.3 Polypyrrole Synthesis

Acetonitrile was added to anhydrous  $\text{FeCl}_3$  contained in a 500 ml round bottom flask containing a magnetic stirrer bar and fitted with a reflux condenser. Freshly distilled pyrrole was then added in a single portion to the above solution, a reaction exotherm was noted (temperature increased to  $35^\circ\text{C}$ ) and the solution instantly acquired a black color as the precipitate of PPY formed. The doping level of the pyrrole was varied by changing the  $\text{Fe}^{3+}$ /pyrrole ratio [3]

After a reaction time of 1 hour at  $22^\circ\text{C}$ , the mixture was filtered and the precipitate was washed with copious amounts of distilled water, followed by a wash with 50 ml of 10 % HCl. The product was then rinsed with water until the washings tested neutral with pH paper. After a final rinse with ethanol and then diethyl ether, the black powder was dried in vacua ( $65^\circ\text{C}$ , 4 hours) to yield the required polymer. The sample purity was examined by FTIR spectrum (Fig 2.3 a to c).

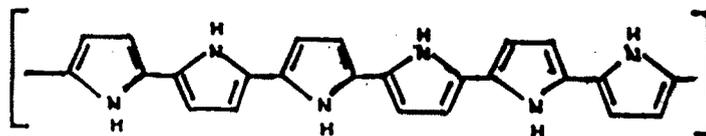


Fig 2.2c Structure of polypyrrole

## 2.4 PPY/Pani-EB blend preparation

Interest in conducting polymers has grown tremendously in the past several

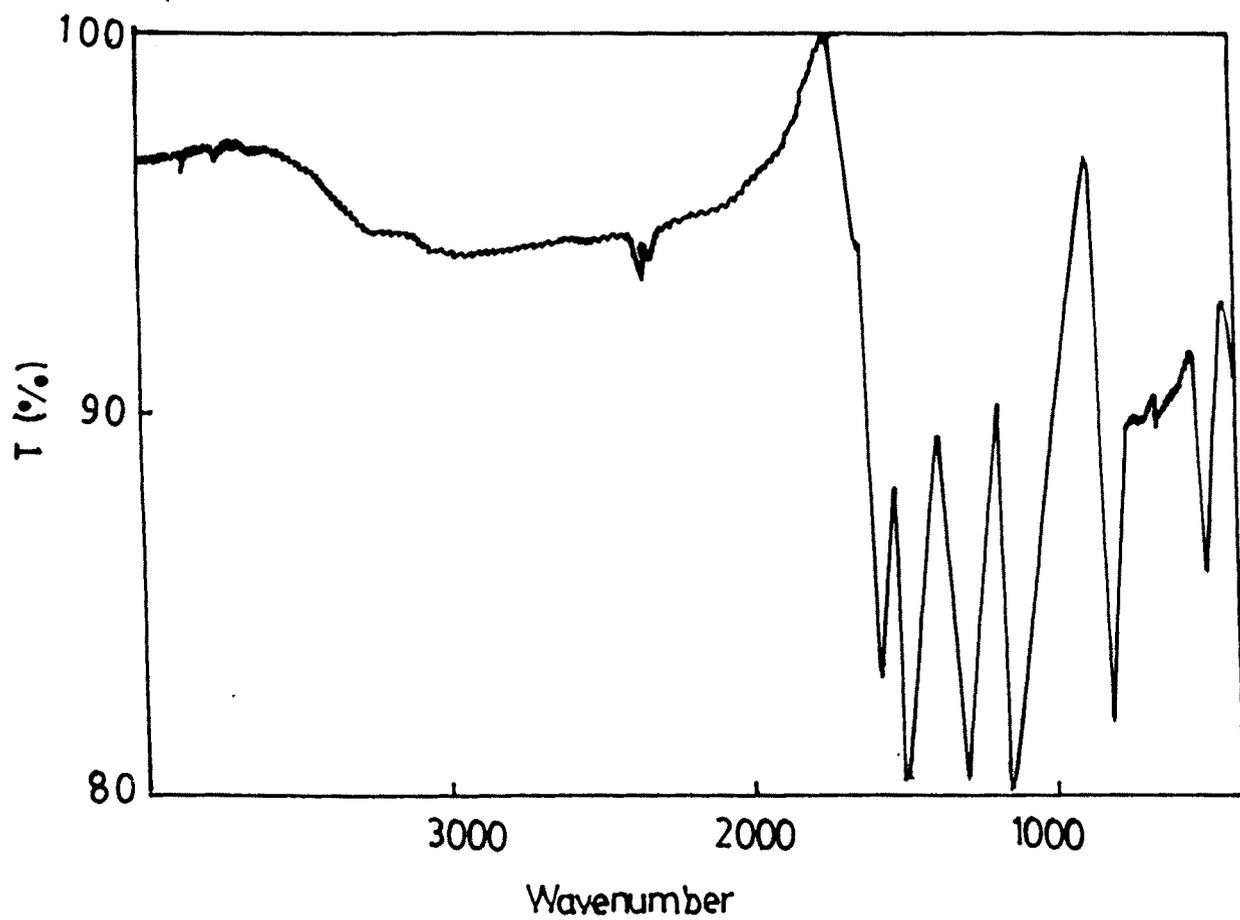


Fig. 2.3(a) FTIR spectrum of Pani-EB film

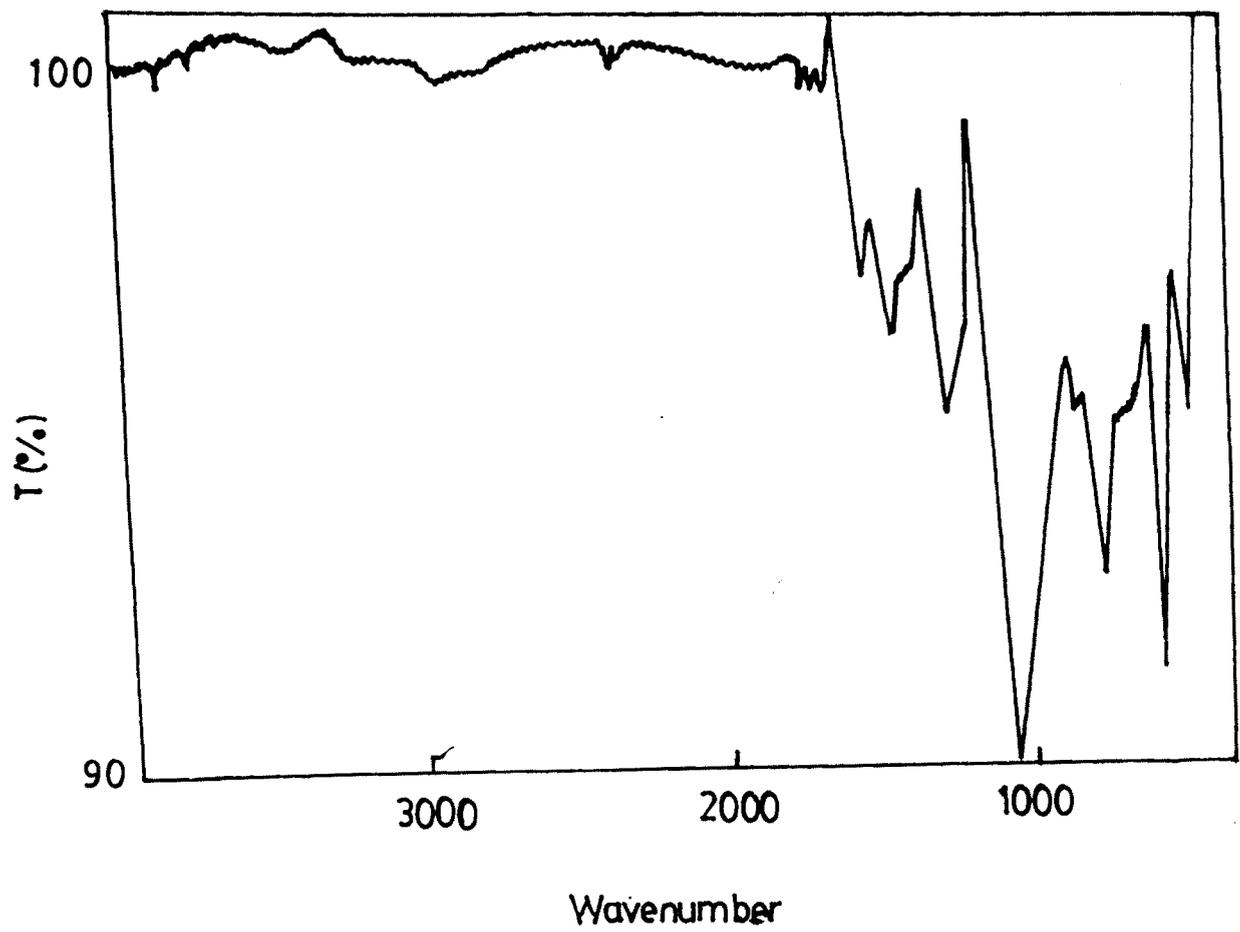


Fig. 2.3(b) FTIR spectrum of Acid doped Pani film

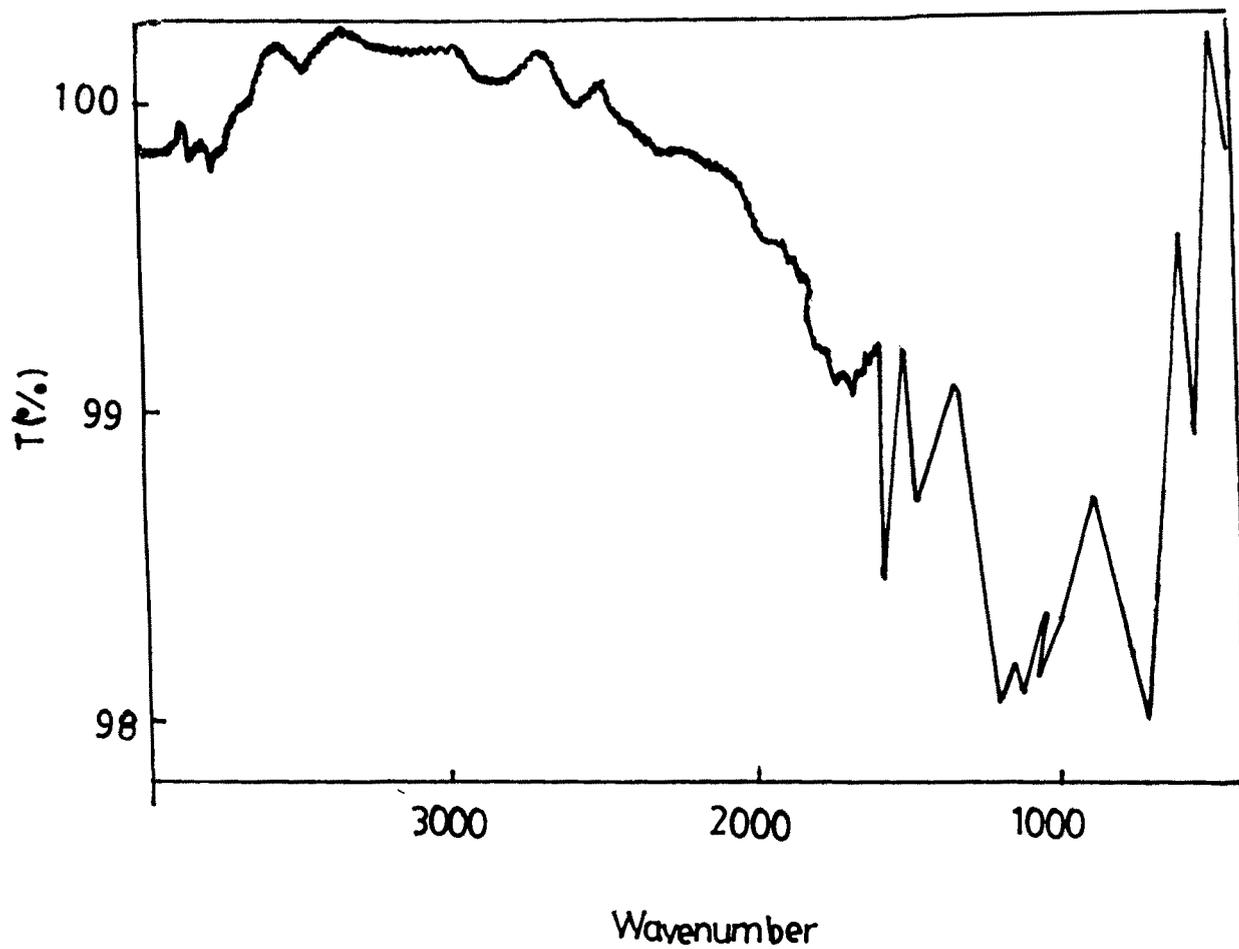


Fig. 2.3(c) FTIR spectrum of PPY film

years. Especially, heterocyclic polymers such as polythiophene and polypyrrole have received a great deal of attention due to their good environmental stability and high electrical conductivity [4,5]. However, they lack mechanical properties and processability. These are the major obstacles for practical usage. In recent years, several attempts have been made [6,7]. The mechanical blending in melt state is undesirable because the conducting property of the polymer decreases due to thermal effect during processing. The polymer combination exhibit many interesting properties such as energy transport, energy conversion and energy saving memory storage. Therefore effort should be undertaken to realize more of these systems for practical applications.

Blending of polymers is a versatile method for obtaining new materials with improved properties. Thus the purpose of blending polymers is either to improve processability or more often to obtain materials suitable for specific needs by tailoring one or more properties with minimum sacrifices in other properties. The two important blending techniques are (a) solid state blending and (b) solution blending. In the present study solution blending was used. Solution blending was carried out by dissolving the materials separately in the solvent. The two solutions were mixed well and was stirred for one hour and then the films were formed.

## **2.5 Polymer film Preparation**

The various physical properties of thin films are strongly sensitive to the

mode of preparation. In general, the deposition techniques can be broadly classified into two groups namely physical and chemical methods.

The physical vapour deposition is subdivided into many groups like vacuum evaporation, sputtering, etc. Vacuum evaporation technique was used for electrode deposition. The chemical method includes the chemical vapour deposition, dip/solution growth technique, syringe coating, film brush coating/casting technique, etc. Film casting technique was employed in the present study for the polymer film preparation.

#### **2.5.1 Selection and cleaning of substrates**

The casting of the films has to be carried out onto a base, namely the substrate. A number of materials like glasses, ceramics silicon wafers and quartz are available for use as substrates. In the present investigation, glass substrates have been mostly used for the film formation. Glass substrate has got maximum surface smoothness, optically plane surface and is very economic [8,9]. It is required that the glass substrates should be properly cleaned to get a high quality of films with durable and reproducible properties. The cleaning process results in the breaking of the bonds between the contaminant molecules and the substrates as well as between the contaminant molecules themselves. There are a variety of procedures available for the removal of contaminants without causing damage to the substrate. The final choice of cleaning technique depends on the nature of

the substrate and the type of impurities present on the substrate.

The cleaning technique adopted in the present study is as follows:

The glass slides are kept in a glass container containing dilute NaOH solution for half an hour to dissolve fatty materials by saponification. Then they are cleaned with detergent solution followed by distilled water washing. The substrates are then placed in an ultrasonic bath for about thirty minutes in the detergent solution and in distilled water. The shock waves created in the solvent render the possible removal of residues from the substrates. Then the substrates are subjected to vapour degreasing with isopropyl alcohol to increase the rate of surface contaminant removal. Finally the substrates were kept in an oven for a few hours for drying.

Masks prepared by photolithographic method [10] have been employed to form the desired patterns of the thin film samples. Brass masks were employed for electrode deposition. The masks should be cleaned prior to evaporation to remove surface contaminants that might become volatile when heated. These contaminants might be absorbed by the substrates and cause a weak spot in the film coated on it. The masks were initially cleaned with acetone and then heated for about half an hour at 150 °C. They were then ultrasonically agitated and finally dried in an oven. The sizes of the substrates used for different studies of the present investigation are given in Table 2.1.

### 2.5.2 Solution casting of polymer films

Finely-ground synthesized polymer powder was added to the solvents of N-methyl pyrrolidone(NMP) and Dimethylformamide (DMF) to produce the solution. This solution was stirred at room temperature for 60 minutes in order to dissolve it completely. The insoluble material was removed by filtering through a filter paper. A very thin film of base form of polymer on slide glass was made by a casting technique at an elevated temperature (60 °C).

In the solution casting method the solution was dropped from a syringe onto a substrate to form a film.

The substrate was rotated at a controlled and slow rate, so that the film formation is uniform. The thickness of the film can be controlled by the concentration of polymer in the solvent and the quantity of the solution dropped on the slide glass. In the present study, polyaniline emeraldine base (Pani-EB), acid doped polyaniline (acid Pani), polypyrrole (PPY) and polypyrrole/polyaniline emeraldine base (PPY/Pani-EB) blend films formed on pre-cleaned glass substrates using the solution casting technique.

To make a capacitor configuration for dielectric and conduction studies, pure aluminium (Al) or gold (Au) was evaporated in a vacuum of  $2.5 \times 10^{-3}$  Pa from a tungsten filament onto glass substrates to form the

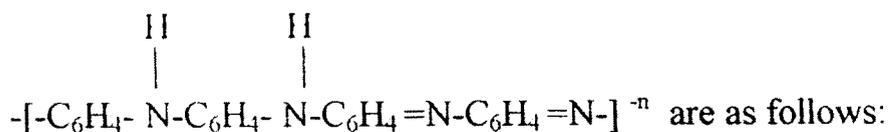
bottom electrode. The polymer film was deposited over the bottom electrode using drop/syringe coating technique from the solution of polymer material dissolved in DMF or NMP solvent. Finally Al/Au was evaporated over the polymer layer to complete the Metal-Polymer-Metal sandwich structure. Fig 2.4 shows the schematic diagram of thin film coating unit.

## 2.6 Characterisation

### 2.6.1 Elemental analysis

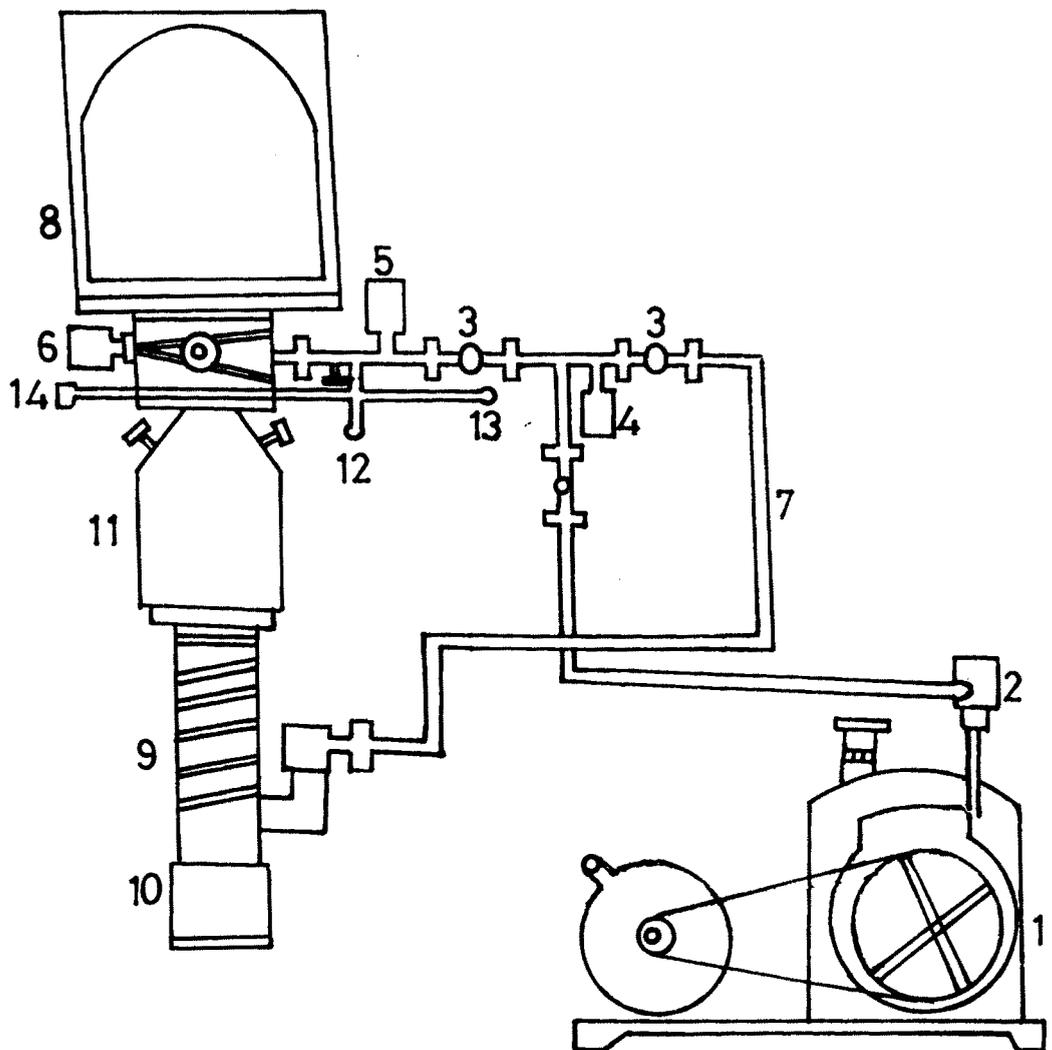
The elemental analysis of emeraldine base Pani -EB (C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>) was done and the results are as given below,

The molecular structure :



	C(%)	H(%)	N(%)
Calculated	79.5	4.7	15.6
Found	80.2	4.7	15.1

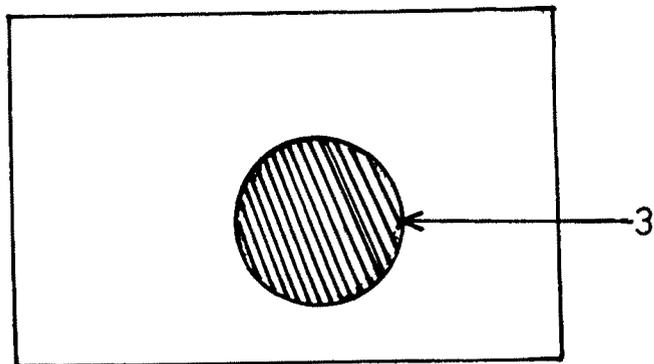
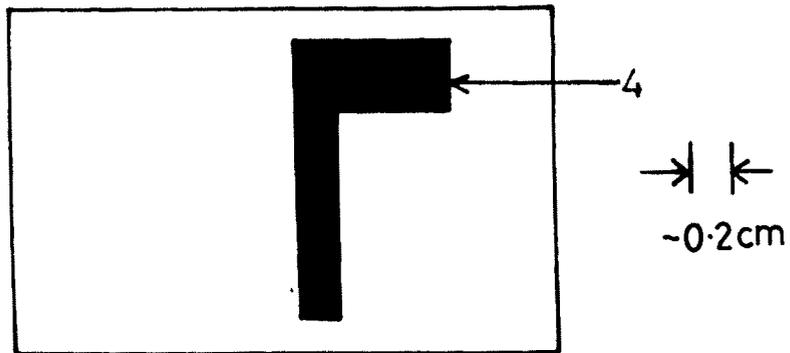
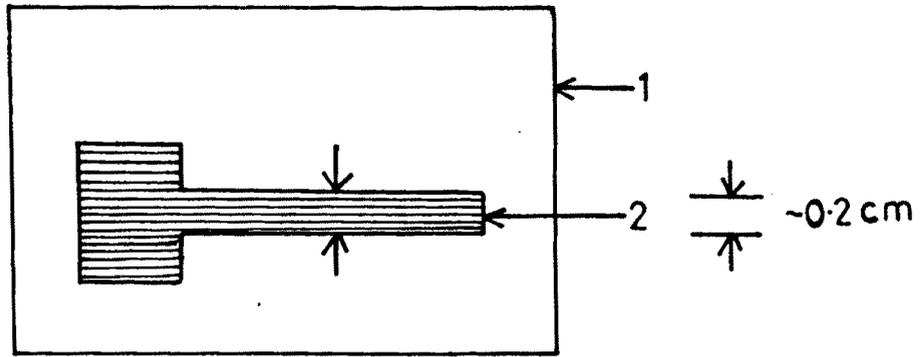
Chemical elemental analysis was also done for [Pani EB-(MSA)<sub>x</sub>] with x = 0.18 and 0.50. The percentage of C,H and N obtained are given in Table 2.2. The percentage of S and O estimated from C, H, and N



- 1- Rotary Pump
- 2- Magnetic Isolation Valve
- 3- Butterfly Valve
- 4- Pirani Gauge I
- 5- Pirani Gauge II
- 6- Penning Gauge
- 7- Backing Line

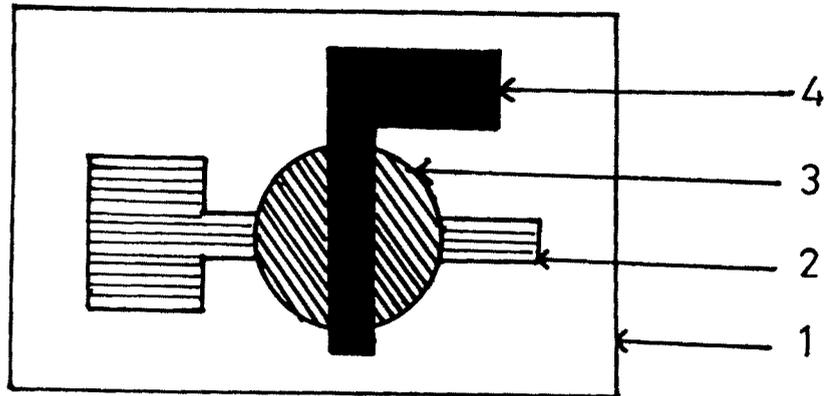
- 8- Glass or Metal Bell Jar
- 9- Diffusion Pump
- 10- Diffusion Pump Heater
- 11- Liquid Air Trap
- 12- Air Admittance Valve
- 13- Needle Valve
- 14- Baffle Valve

Figure 2. 4 Schematic diagram of thin film coating Unit



- |                |                    |
|----------------|--------------------|
| 1 Substrate    | 2 Bottom electrode |
| 3 Polymer film | 4 Top electrode    |

Masks used to form MPM structure

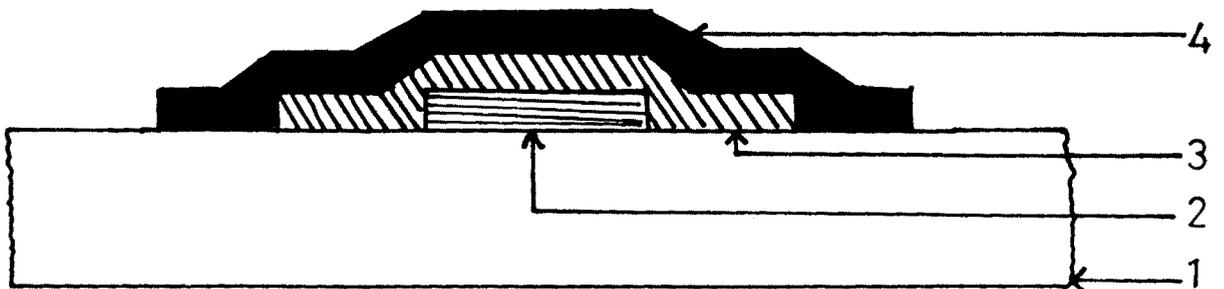


1 Substrate

2 Bottom electrode

3 Polymer film

4 Top electrode



**MPM sandwich structure and its vertical cross sectional view**

percentage are also given. Qualitatively it shows that the S and O content is higher for higher  $x = 0.5$  than for  $x = 0.18$ .

The elemental analysis of polypyrrole (PPY) is given below,

	C(%)	H(%)	N(%)	Fe(%)	Cl(%)	O(%)
Calculated	51.96	3.89	14.88	7.17	13.41	8.69
Found	50.96	4.89	15.88	6.27	13.21	8.99

### 2.6.2 X-ray Diffraction Technique

X-ray diffraction is a very powerful and suitable technique for characterizing the microstructure of thin films. It is nondestructive and it provides a variety of informations, such as presence of elements, film thickness, grain size and orientation, strain state, interfaces and solute concentration distribution between layers. This method has the advantage that it requires a small amount of the sample.

The structural analysis of thin films is often aided by the use of diffraction technique which can uniquely identify the crystalline nature. X-ray diffraction is commonly employed for these studies. With the progress made in the last few decades in computer control and high power X-ray sources, diffractometers equipped with counters to measure diffracted intensity have become very popular and are widely used.

The basis of X-ray diffraction is the Bragg equation which describes the condition for constructive interference for X-rays scattered from atomic planes of a crystal. The condition for constructive interference is  $2d \sin\theta = n\lambda$ , where  $\lambda$  is the wavelength of X-rays.

### 2.6.2.1 Experimental details

The diffractometer consists of three important parts, a diffraction unit, a counter goniometer and an electronic circuit panel with an automatic recorder. Fig. 2.5 illustrates the schematic diagram of XRD measurements. The sample is mounted in the sample holder and rotated by an angle  $\theta$  about an axis while the counter rotates through an angle  $2\theta$  around the same axis. The Bragg diffracted rays are received by the counter. Only the crystallites of the thin film that are oriented with a specific set of lattice planes parallel to the surface contribute to the diffracted intensity.

In the present work, conducting polymer film samples of polyaniline-EB, acid doped polyaniline, polypyrrole, polypyrrole/polyaniline-EB blend films prepared by film casting technique and analysed by a Philips X-ray diffractometer (Model PW 1050/70) with a Ni filtered  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) at 30 kV and 20 mA in the  $2\theta$  range 30 to 70° with a scan speed of  $2^\circ \text{ min}^{-1}$ . The X-ray diffractograms of conducting polymer films are recorded by a X-ray diffractometer with an Ni filtered  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) at 30 kV and 30 mA in the  $2\theta$  range of 30 to 80°.

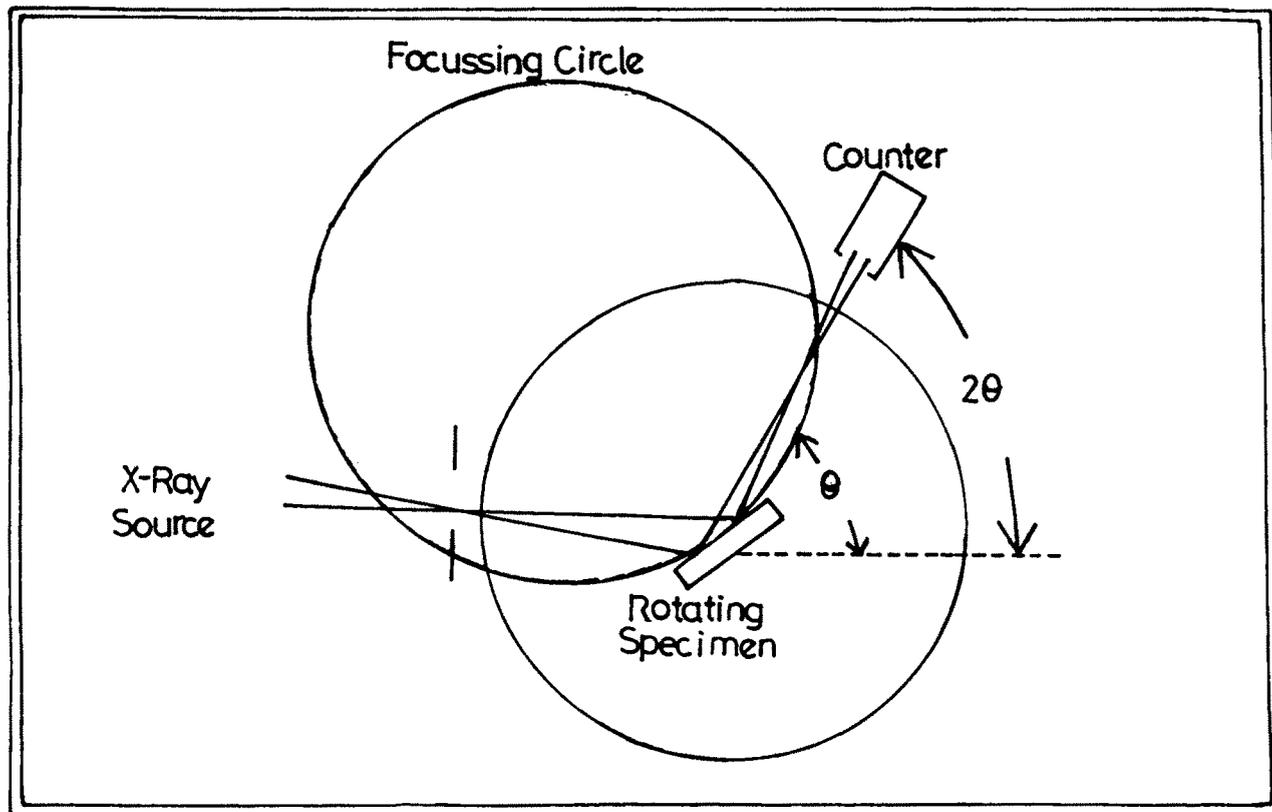


Fig. 2.5 Schematic diagram of X-Ray diffraction measurement

From the angular position  $\theta$  of the diffracted lines, lattice or d-spacings, characteristic of the symmetry and dimensions of the unit cell can be determined.

X-ray diffractograms of the above said conducting polymer films are presented in Fig. 2.6 (a to d). It is found that acid Pani and polypyrrole (PPY) films show diffraction peaks whereas Pani-EB and PPY/Pani-EB blend films don't have any diffraction peaks, which indicate their amorphous structure. Four prominent peaks observed for acid Pani [Fig.2.6(a)] can be indexed to (212), (310), (024) and (115) planes.

The d-spacing are estimated from the angular position  $2\theta$  of the observed peaks, using the Bragg formula,

$$2d \sin \theta = n\lambda \quad \dots\dots\dots (2.1)$$

where  $n$  is the order of diffraction and  $\lambda = 0.1542$  nm. The d-spacing values are given in Table 2.3. The d - spacing values

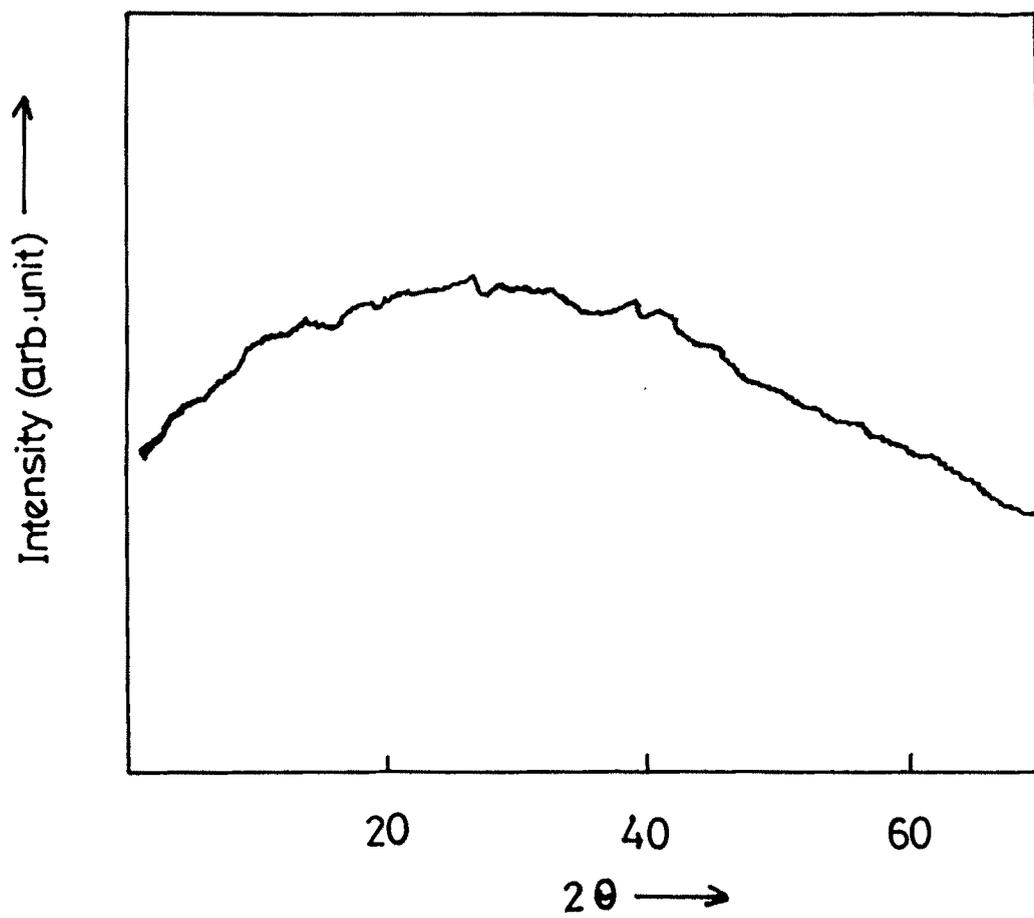


Fig. 2.6(a) X-ray diffractogram of Pani-EB film

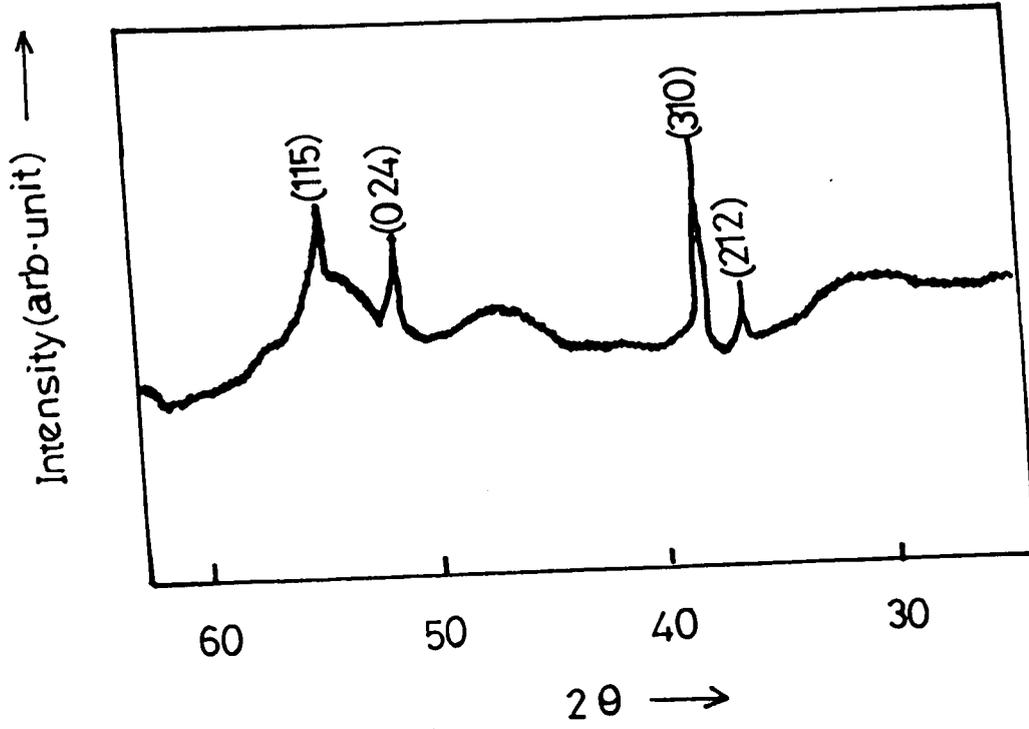


Fig. 2.6(b) X-ray diffractogram of acid doped Pani film

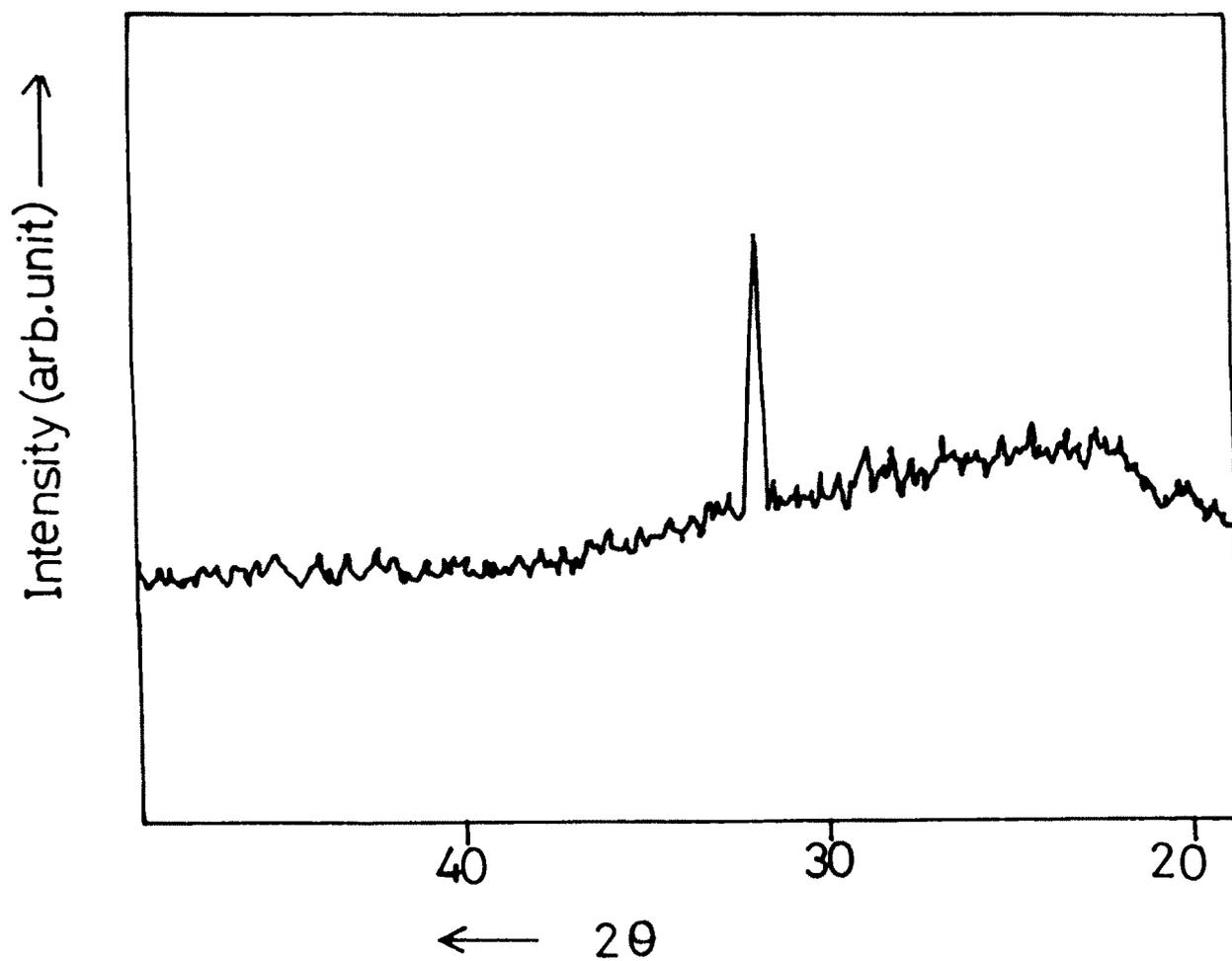


Fig. 2.6(c) X-ray diffractogram of PPY film

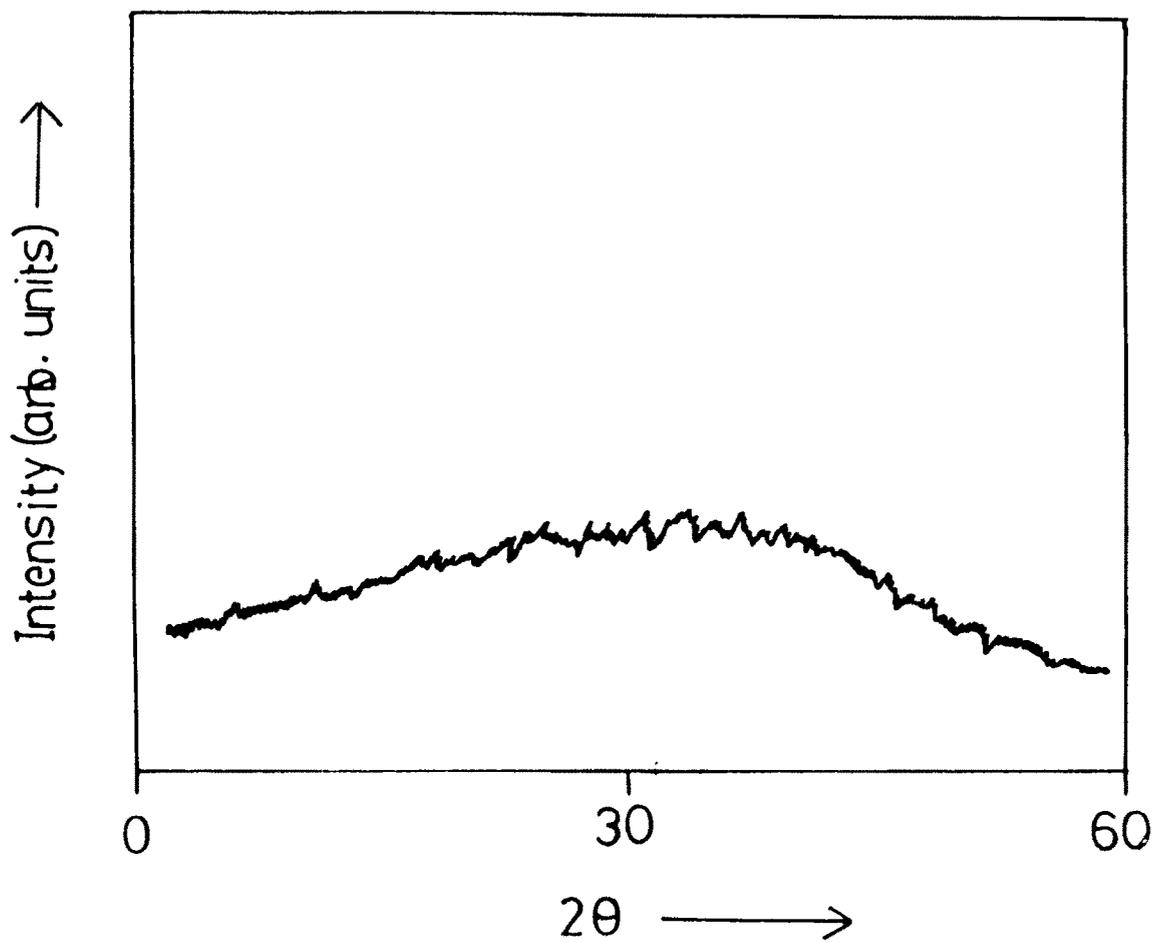


Fig. 2.6(d) X-ray diffractogram of PPY/Pani-EB film

obtained are in close agreement with the reported values of polyaniline-EB (bulk) THF/NMP- extracted powder [11]. The crystallite size (D) can be deduced from the value of  $\Delta(2\theta)$  [full width at half-maximum (FWHM)] using Scherrer formula [12,13],

$$D = \frac{0.94 \lambda}{\Delta(2\theta) \cos \theta} \dots\dots\dots (2.2)$$

From the calculated values of crystallite size, the dislocation densities ( $\delta_c$ ) are evaluated using the formula [14]

$$\delta = n/D^2 \dots\dots\dots (2.3)$$

where n is a factor which equals unity giving minimum dislocation density.

The lattice parameter **a** has been determined from the observed  $\sin \theta$  value in an indexed cubic pattern by employing the Bragg equation in the form,

$$\mathbf{a} = \frac{\lambda}{2} \frac{\sqrt{h^2+k^2+l^2}}{\sin \theta} \dots\dots\dots (2.4)$$

The values of the crystallite size, lattice parameter and dislocation densities are listed in Table 2.3.

## 2.6.3 FTIR Analysis

### 2.6.3.1 FTIR Characteristics of Pani-EB

Fig.2.3 (a) shows the FTIR spectrum of a Pani-EB film of thickness 20  $\mu\text{m}$ . The spectrum was recorded using a Nicolet FTIR spectrometer in the frequency range 4000 - 400  $\text{cm}^{-1}$ . The spectrum indicates the bands at 1568, 1487, 1294, 1230, 1132 and 794  $\text{cm}^{-1}$ . The band positions and corresponding modes are presented in Table 2.4

### 2.6.3.2 FTIR Characteristic of PPY

FTIR spectrum of the prepared polypyrrol sample is shown in Fig. 2.3(c). The absorption bands are observed at 1541, 1462, 1320, 1178, 1047, 900 and 790  $\text{cm}^{-1}$ . The spectrum shows a series of sharp peaks at energies above 1600  $\text{cm}^{-1}$ , characteristic of the doped materials [4].

According to the literature [15,16], polypyrrole has three bands at around 1610, 1490, and 1410  $\text{cm}^{-1}$  caused by ring stretching, and has a band at around 1050  $\text{cm}^{-1}$  caused by N-H bending. In plan and out of plane bending of C-H are expected at 980 and 960  $\text{cm}^{-1}$  respectively. The perchlorate ion by itself has strong absorption bands between 600  $\text{cm}^{-1}$  and around 1115  $\text{cm}^{-1}$ .

## 2.7 Thickness Measurements

A variety of methods [17-19] are being used to measure the film thickness. These include electrical, mechanical, gravimetric and optical interference methods. In the present investigation, gravimetric, and capacitance methods have been used to determine the thickness of polymer films. Rutherford Backscattering Spectrometric (RBS) technique was used to confirm the measured thickness of the polymer films.

### 2.7.1 Capacitance method

The thickness of the conducting polymer films are measured by using capacitance method. By knowing the capacitance (C) value of the film and dielectric constant ( $\epsilon$ ) of the polymer materials, the thickness (t) of the film is calculated using the relation,

$$t = \frac{\epsilon \epsilon_0 A}{C} \dots\dots\dots (2.5)$$

where  $\epsilon_0 = 8.85 \times 10^{-12}$  F/m and A is the area of the film.

### 2.7.2 Gravimetric method

In this technique, weighing of the substrate and substrate + film before and after the film deposition respectively have been made in order to find the average film thickness, which is given by,

$$t = \frac{100 (W_1 - W_2)}{A \rho} \dots\dots\dots (2.6)$$

where  $t$  is the film thickness,  $W_1$  and  $W_2$  are the weight of the substrate and substrate + film respectively,  $A$  is the area of the sample and  $\rho$  is the density of the film.

### 2.7.3 Rutherford Backscattering Spectrometry (RBS)

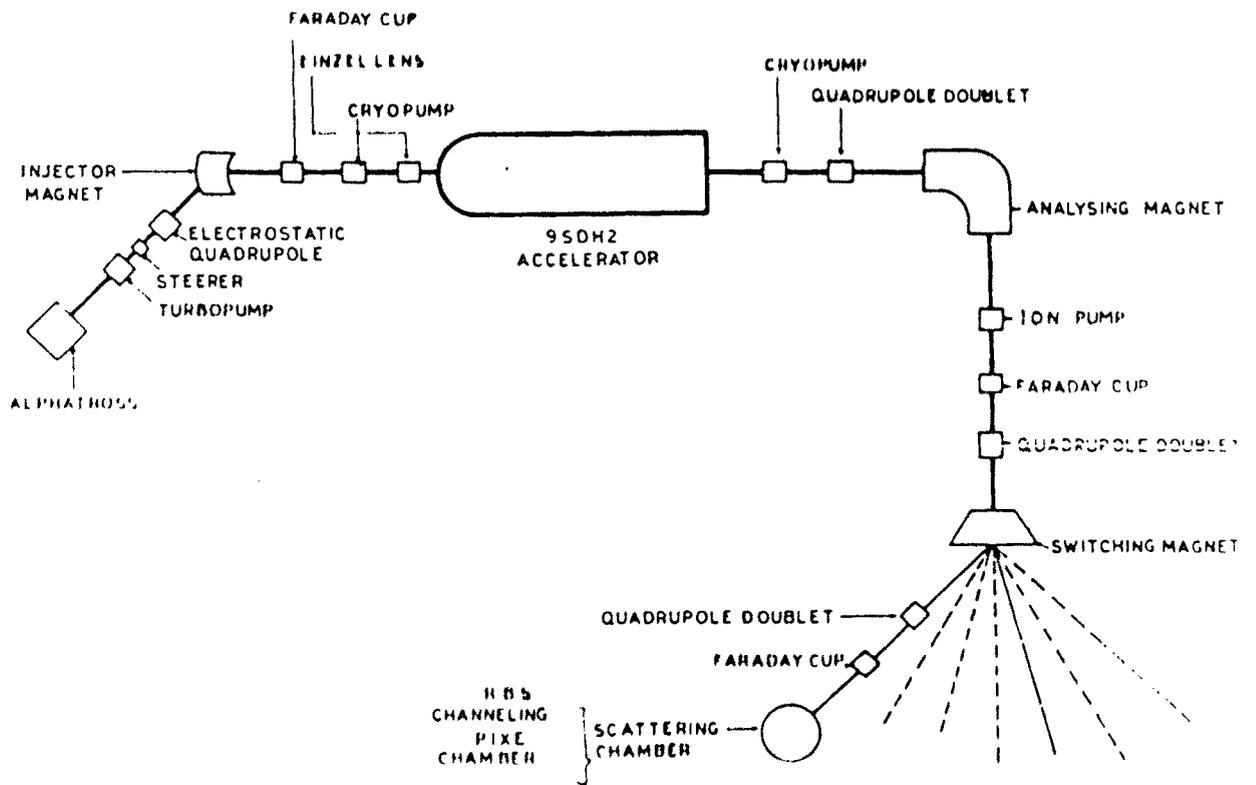
RBS is one of the most important techniques adopted for the analysis of thin film composition. Several books and review articles are available [20-23] on RBS technique for analysis of materials.

In Rutherford backscattering spectrometry, the presently employed technique for composition analysis of films, one is concerned with projectiles that move through a target, losing energy along their path, and are scattered by collision with a target atom. The four basic physical concepts such as scattering cross section, kinematic factor, stopping cross section and energy straggling form the basics of RBS.

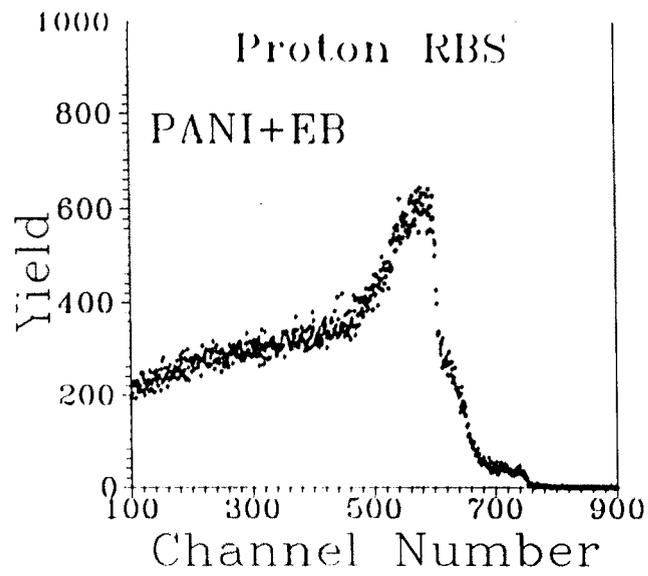
### 2.7.3.1 Experimental

Thickness measurement involves the RBS technique using the 1.415 and 3.045 MV tandem pelletron accelerator facility, which is available at the Institute of Physics, Bhubaneswar, India. Two types of ion sources are present. One (Alphatross) is for providing  $H^{++}$  and  $H^+$  ions and the other (SNICS) for almost all elements in the periodic table except inert gas ions. A multipurpose scattering chamber, designated to carry out RBS, channeling, NRA and PIXE studies is attached to the  $45^\circ$  beam line. A Si detector for X-ray detection, and a NaI detector for  $\gamma$ -ray detection are provided with the system. Two surface barrier detectors (SBD) can be placed inside the vacuum chamber. The chamber has two view ports and several other ports for various feedthroughs. The scattering chamber is provided with Balzers DIF-set pumping station with liquid nitrogen trap and a chilled water cooling facility. The vacuum attained by this pumping is of the order of  $1.3 \times 10^{-5}$  Pa. The scattered particles are detected by SBD. The detected signal is shaped, amplified and finally with a pulse height analysis the energy spectrum is stored and displayed in a Multichannel Analyser (MCA). The block diagram of the RBS experimental set-up is shown in Fig. 2.7.

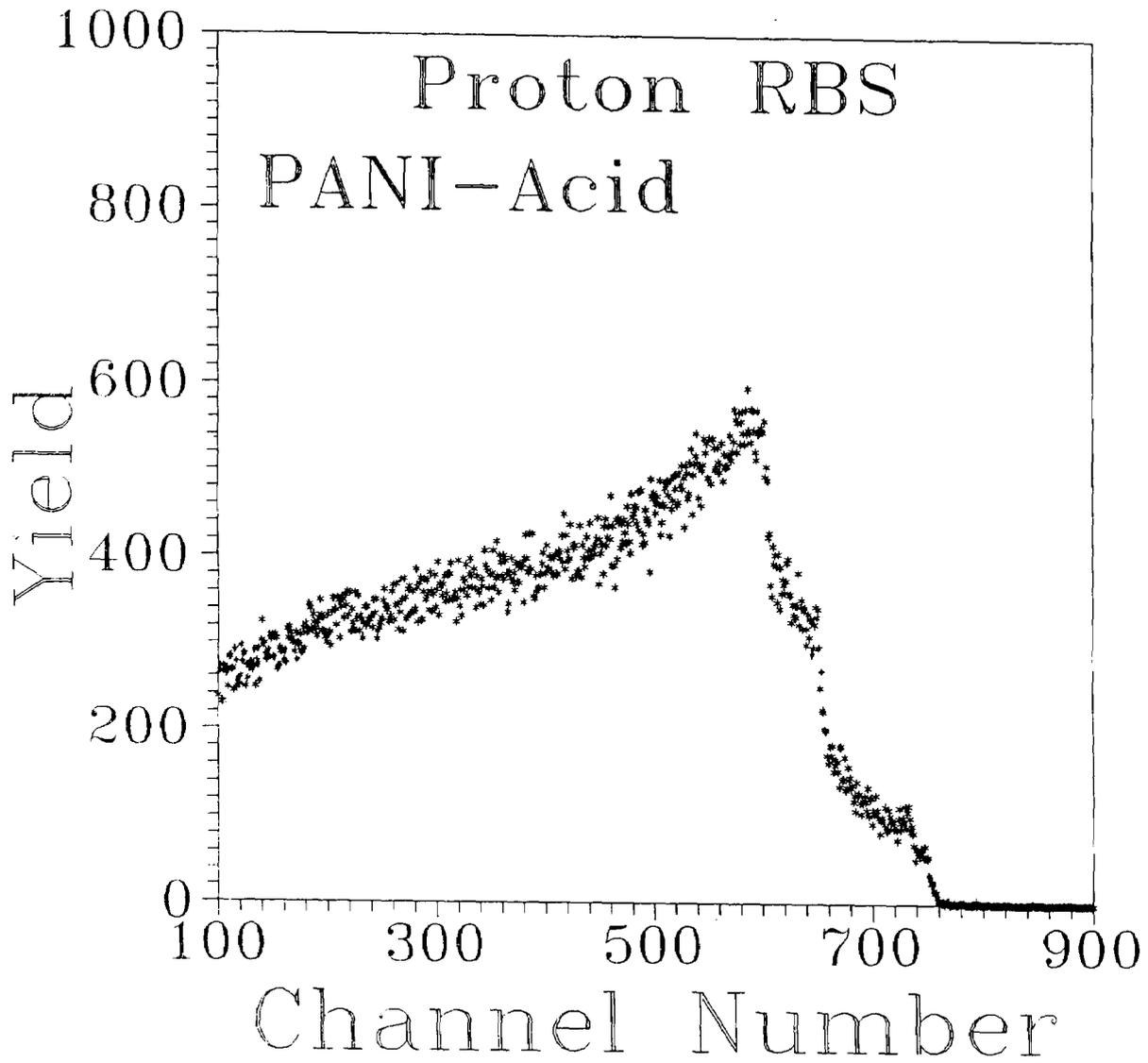
The RBS spectrum of Pani-EB, Acid doped Pani, PPY, PPY/Pani-EB films are shown Figs. 2.8 (a to d).



**Fig. 2.7 Experimental arrangements for RBS measurement**



**Fig. 2.8(a) RBS Spectrum of Pani-EB film**



**Fig. 2.8(b) RBS Spectrum of Acid doped Pani film**

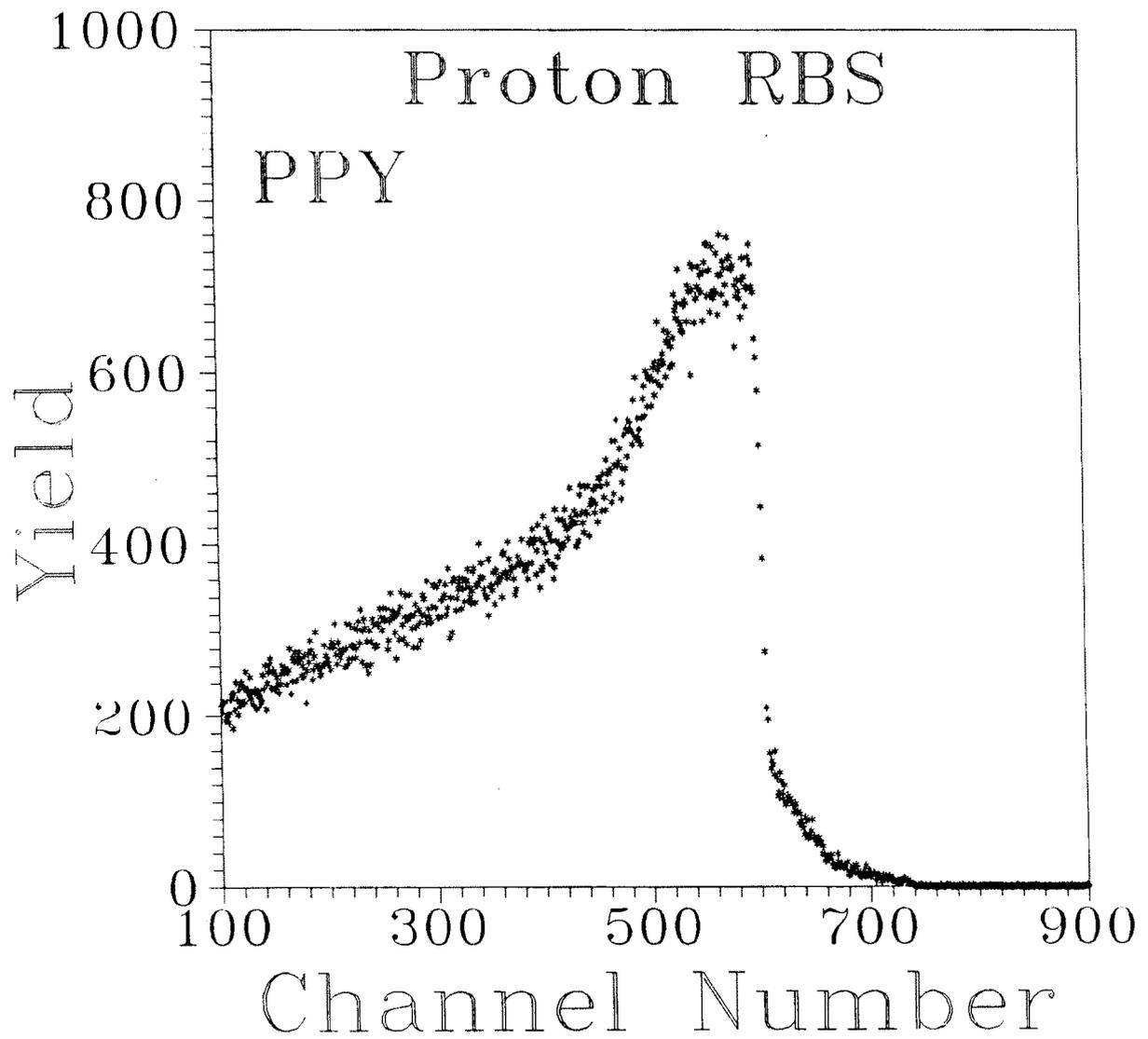


Fig. 2.8(c) RBS Spectrum of PPY film

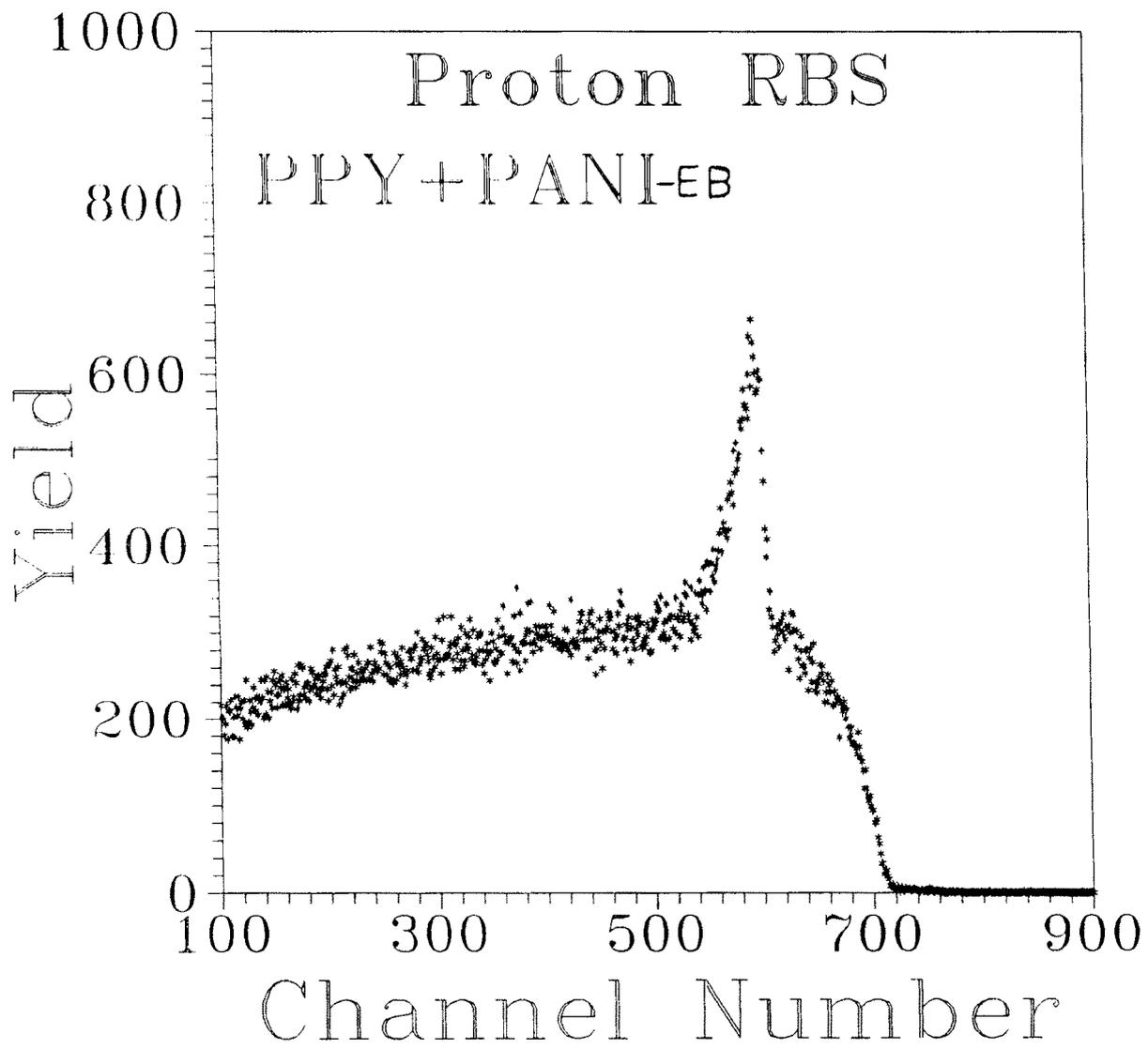


Fig. 2.8(d) RBS Spectrum of PPY/Pani-EB blend film

### 2.7.3.2 Thickness measurement

High energy ion scattering (HEIS) using proton beam with 1.415 MeV is employed to obtain RBS spectra of the Pani-EB films. In this technique, the ions can penetrate deeper into the sample, hence under the channeling condition the technique becomes very much surface sensitive. Fig. 2.8 (a) shows the RBS spectrum of a Pani-EB film. Thickness of the film corresponding to each channel  $\delta x$  in the spectrum has been calculated by using the formula,

$$\delta x = \frac{\delta E}{N_a \left[ \frac{\epsilon K(E_0)}{\cos \phi_1} + \frac{\epsilon (K E_0)}{\cos \phi_2} \right]} \dots\dots\dots (2.7)$$

where  $\delta E$  is energy per channel,  $k$  is kinematic factor,  $\epsilon$  is stopping cross section,  $E_0$  is incident energy,  $\phi_1 = 0$  for normal incidence,  $\phi_2 = \pi - \theta_s$  where  $\theta_s$  is the scattering angle and  $N_a$  is the number of atoms per  $\text{cm}^3$ . The whole thickness of the film can be calculated by using the following formula [24],

$$d = \text{number of channels} \times \text{thickness of each channel}$$

and the thickness of the film under consideration is determined as 6.4  $\mu\text{m}$ . This value is in accordance with the thickness value

determined from capacitance and weighing methods. The typical thicknesses (in micrometer) of the polymer films used in the present investigation are given below

Pani-EB	6.4
Acid Pani	3
PPY	5.5
PPY/Pani-EB	7

**Table 2.1** Sizes of the substrates used for different studies

Study	Size of the Substrate( $10^{-4} \text{ m}^2$ )
Structure	1 x 1
Dielectric	3.75 x 2.5
Conduction	3.75 x 2.5
TSDC	3.75 x 2.5
Breakdown	3.75 x 2.5
Hall	1 x 1
TEP	3.75 x 1.25
Resistivity	3.75 x 1.25
laser	7.25 x 2.5
damage	3.75 x 2.5
Applications	3.75 x 2.5

**Table 2.2** Percentage of C, H and N for acid doped pani

Sample	C %	H %	N%	S%+O%
Pani-MSA <sub>0.5</sub>	53.7	4.8	5.9	35.6
Pani-MSA <sub>0.18</sub>	69.3	5.0	10.2	15.5

**Table 2.3** Microstructural parameter comparison of the XRD studies for acid pani [d = 6.4  $\mu\text{m}$ ]

d - spacing		Lattice constant (a)		Crystallite size ( D ) 10 <sup>-10</sup> m	Dislocation density( $\delta_c$ ) 10 <sup>16</sup> lines/m <sup>2</sup>	hkl
Bulk 10 <sup>-10</sup>	Film m	Bulk 10 <sup>-10</sup>	Film m			
2.62	2.637	7.65	7.549	72	1.929	212
2.32	2.368	7.488		45	4.938	310
1.90	1.869	7.865		50	4.000	024
1.85	1.787	7.250		53	3.559	115

**Table 2.4** FTIR analysis of Pani-EB film

<b>Mode</b>	<b>Pani-EB cm<sup>-1</sup></b>	<b>MSA cm<sup>-1</sup></b>
N-Benzenoid- Quinoid	1595	1568
N-H Stretching	1504	1487 1296
C-C		-
C-N		1189
SO <sub>3</sub> (C-H) band		1147
SO <sub>3</sub> (C-H) out of plan band	808	1080 801

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