CHAPTER IV

STRUCTURAL STUDIES

4.1 X-ray Diffraction Studies

4.1.1 Introduction

As thin films, materials exist effectively in amorphous, polycrystalline or single crystal forms. Adatom mobility during deposition defines the structural order of atomistically deposited films and can vary from highly disordered to an ordered state [1]. The nucleation and growth phenomena in thin films have been studied in detail by earlier investigators [2-4]. The condensation (subsequent to the initial few atom layers) and the formation of final structure are determined primarily by the state of the deposit itself [5]. It is worthwhile to note the wide range of possible thin film structures as the conditions of film formation have a greater variety in comparison to the conditions of formation of a bulk solid [6]. In general one could expect only a limited number of crystal structures in a thin film and these may be anticipated from the chemical composition and from the preparation conditions.

Probably the most important methods for studying the microstructure of thin films involve high energy electron and X-ray diffraction together with their microscopy counter-parts TEM and X-ray topography. XRD is the most precise system for studying the crystal structure of the solids. This is essentially non-destructive while requiring no elaborate sample preparation. In the case of electron diffraction, sample preparation becomes quite tricky in the sense that the sample has to be transferred from the substrate to the electron microscope specimen grid. The relative ease and convenience, large diffraction angles representation
of the average crystalline lattice throughout the film and simultaneous display of diffraction patterns from the film, make the XRD method a successful analytical technique for the study of the structure of films.

XRD technique for analysis of structure of organic thin films has been widely employed by earlier investigators [7-11]. In the present investigation, XRD method has been adopted for the studies of the structural aspects of perylene and p-terphenyl films formed by vacuum deposition and ion plating techniques.

4.1.2 Experimental

The method of XRD analysis employed for the determination of film structure comprises of three parts, a basic diffraction unit, a counter goniometer and an electronic circuit panel with an automatic recorder. The diffraction angles and intensity of the lines are recorded on the '2θ-Intensity' curves.

A schematic diagram of focusing arrangement for formation of X-ray diffraction pattern is illustrated in Figure 4.1. A diverged X-ray beam falls on the specimen which rotates about the goniometer axis. The diffracted rays are received by a counter. The counter tube is moved along the goniometer circle. The focusing arrangement, which requires that the sample surface bisects the diffraction angle and thereby remains tangential to the focusing circle, is maintained by rotating the counter about the same axis as the specimen but at twice the angular speed. The counter detects the diffracted beam. The rate at which the pulses are emitted by detector, after passage through the pulse height analyser is resolved in a scaling circuit and then fed into a ratemeter which gives the final output by actuating a pen on a strip-chart pen recorder, as a permanent graphical record of the diffrac-
FIG. 4.1 SCHEMATIC DIAGRAM GIVING DETAILS REGARDING FORMATION OF X-RAY DIFFRACTION PATTERN AND FOCUSING METHOD
tion pattern. The scanning motion of the detector is synchronised with the rotation of the chart, and consequently the position of the peak is readily interpreted in terms of 2\( \theta \) (diffraction angle). The experimental arrangement of X-ray diffraction system is exhibited in Figure 4.2. The equipment used in the study consists of a Philips X-ray generator PW 1010, diffractometer PW1051, proportional counter and single channel pulse-height analyser. The X-ray diffractogram of the film is obtained by mounting the specimen in the centre of the diffractometer and rotated by an angle \( \theta \) about an axis while the counter rotates to an angle 2\( \theta \) around the same axis. It can be observed that the diameter of the focusing circle continuously shrinks with increasing diffraction angle. Only (hkl) planes parallel to the film plane contribute to the diffracted intensity. The effective thickness \( t/\sin \theta \) which a film of thickness \( t \) exposed to the incident beam also decreases with increasing diffraction angle. Thus the effective thickness of a film in the range of 1000 Å is sufficient to excite measurable diffracted radiation at small angle but the intensity falls off rapidly for higher index reflections.

4.2 IR Spectral Analysis

4.2.1 Introduction

The infrared spectrum provides a rich array of absorption bands. The absorption bands assigned accurately provide a wealth of structural information about a molecule [12]. As IR radiation is passed through a sample of material to be studied, at resonance, the molecule of the material would be vibrationally excited. Consequently this results in loss of energy from the radiation and gives rise to an absorption band. The frequency at which a group absorbs is given by the masses of the vibrating atoms, the force constant of the band and the molecular environ-
FIG. 4.2  (a) COUNTER GONIOMETER  
(b) X-RAY DIFFRACTION UNIT
FIG. 4-5  KBr DISCS WITH THE THIN LAYER OF
(a) VACUUM DEPOSITED PERYLENE (t = 2950 Å)
(b) ION PLATED PERYLENE (t = 810 Å)
(c) VACUUM DEPOSITED p-TERPHENYL (t = 2350 Å)
(d) ION PLATED p-TERPHENYL (t = 850 Å)
ment of the group. The spectrum of a molecule generally consists of several such bands arising from different vibrational motions of the molecule.

The most powerful function of infrared spectroscopy is to establish conclusively the identity of two samples that have identical spectra when determined in the same medium. This proof of identity is far more characteristic than the comparison of any other physical property. For two spectra to be really identical would involve recording of the spectra on the same machine under identical conditions of sampling, scan speed, slit widths etc. The region 7-11 μ (1430-910 cm\(^{-1}\)) contains many absorptions caused by bonding vibrations as well as absorptions caused by C-C, C-O and C-N stretching vibrations. As there are many more bonding vibrations in a molecule than stretching vibrations, this region of the spectrum is particularly rich in absorption bands and shoulders. For this reason, it is frequently called the fingerprint region. There will nearly always be discernable differences in the fingerprint region [14].

4.2.2 Sampling technique

Infrared absorption spectra are usually obtained by placing the sample in one of the beams of a double beam IR spectrophotometer and measuring the relative intensity of transmitted light energy versus wavelength (or wave number). The spectrum of a solid sample can be obtained for a thin film of the substance by depositing the same on an alkali halide (KBr) disc. Since potassium bromide does not absorb infrared light in the region 2.5-15 μ, a complete spectrum of the sample can be obtained [15].

KBr powder was dried well at 383 K and used for the preparation of the discs. To form a cohesive disc of the dried KBr, a special die [16] was used from
which air can be evacuated before hydraulic compression to about 10 tons of load. Discs produced in this way are fairly easy to handle and measure commonly 13 mm in diameter and 0.3 mm in thickness. The KBr disc formed was transformed to vacuum chamber. After depositing the film on the disc it was immediately mounted in the sample holder of IR spectrophotometer. KBr discs coated with thin layers of different samples are shown in Figure 4.5. Due care should be taken to avoid the condensation of atmospheric moisture, which gives rise to broad absorption at 3500 cm\(^{-1}\). This can be alleviated by having a blank disc in the reference beam but the best remedy is prevention.

4.2.3 Experimental

The film samples on KBr discs were analysed using a Perkin-Elmer Model-597 IR spectrophotometer of resolution 3 cm\(^{-1}\) at 1100 cm\(^{-1}\). The IR transmittance curves were recorded on Perkin-Elmer charts.

4.3 Thin Layer Chromatography

4.3.1 Introduction

Application of qualitative thin layer chromatography often provides tentative identification of the substance with the authentic substance due to the same R\(_F\) values. A match in R\(_F\) values between the unknown and a standard (authentic) provides strong evidence as to the chemical identity of them [17]. Chromatography is a separation and identification technique which depends on the differential distributions of the compounds of a mixture between a mobile bulk phase and an essentially thin film stationary phase.
4.3.2 Theory

In thin layer chromatography (TLC) the stationary phase will be in the form of a thin layer adhering to a suitable form of supporting (or backing) material over which the mobile phase is allowed to ascend by capillary action [18]. In TLC technique, the steps involved include preparation of thin layer plates, application of sample onto the plates, development of chromatograms and the location of the separated species. It is usual to employ glass plates coated with layers of the solid stationary phase which adhere to the plates. Commonly used stationary phases for TLC include silica gel, alumina, cellulose powder etc. Sample as a 0.01 to 1% solution, is applied as a spot. Manual application of samples is performed by means of capillary tube or by use of a hypodermic syringe. Care is taken that the sample applied at a sufficient distance from the edge of the plate never immerses in the developer. Development of chromatogram takes place in the closed chamber as in Figure 4.8 (a). Even though there are several methods available for location or visualization on thin layer plate, in chemical methods, common detecting agent for organic compounds is iodine vapour. The dried plate is allowed to stand in a closed chamber containing a good amount of iodine crystals scattered over the bottom of the chamber. The spots are revealed as brown spots or stains. Their positions should be marked as soon as the plate has been removed from the chamber.

At the reproducible experimental conditions, the ratio of the distance to which any substance moved to that of the solvent front in a given chromatographic system is constant and characteristic of that substance. The constant is known as the \( R_F \) value or retention factor. It is defined as

\[
R_F = \frac{\text{Distance moved by the substance}}{\text{Distance moved by the solvent front}}
\]  

(4.1)
Figure 4.8 (b) indicates the method of measurement of $R_F$ values of each sample in a typical chromatogram. The coincidence of the $R_F$ values of the authentic substance and the substance after deposition is an evidence for their chemical identity.

### 4.3.3 Experimental

A thin layer of silica gel-G obtained from Merck Co., India, was spread on clean micro glass slides to a thickness of 100 to 200 $\mu$m (using a water-gel slurry and spreading with the help of a spreader). The thin layer was then dried and activated at 383 K in a hot air oven. The substances under analysis were dissolved in benzene separately and small amounts of them were spotted on silica gel coated surface. The solvent was allowed to evaporate.

The spots/substances were eluted with a suitable solvent system in a developing chamber [Figure 4.8 (a)]. As the solvent moved up due to capillary action, the adsorbed substances were also moved in the direction of the solvent. But the extent of movement of substance relative to the solvent front depends on its adsorptivity on the gel, its nature and polarity of the solvent system. When the solvent front reached almost the top of the chromatograph, the plate was taken out and the solvent front marked. After the solvent front dried up, the plate was kept in an iodine chamber to locate the positions of the substances after elution. The brown spots developed due to adsorption of iodine on the plate were marked and the $R_F$ values were estimated using the relation 4.1. Figure 4.9 shows a typical developed TLC plate.
FIG. 4.8 (a) DEVELOPING CHAMBER WITH ASCENDING FLOW

FIG. 4.8 (b) MEASUREMENT OF $R_F$ VALUES FROM CHROMATOGRAM
FIG. 4.9 DEVELOPED TLC PLATES
(a) AUTHENTIC SUBSTANCE
(b) SUBSTANCE FROM FILM
4.4 Measurements

4.4.1 X-ray diffractograms

The vacuum deposited and ion plated films of perylene and p-terphenyl on the thoroughly cleaned glass substrates of suitable dimensions, were used in XRD studies. X-ray diffractograms were obtained, in reflection mode, with filtered Cu Kα radiation (1.5418 Å), for the different film samples after annealing. The operating conditions of X-ray diffraction system (40 kV, 20 mA) for all the films were identical.

4.4.2 IR spectra

The IR transmittance characteristics for films of perylene and p-terphenyl prepared by vacuum evaporation and ion plating methods were recorded using the IR spectrophotometer with scan time 4 minutes and slit width 2 nm. For analysis, IR spectra of the specimens including fingerprint region were taken into account.

4.4.3 RF factor

From the chromatograms for each specimen the distances moved by the substance and the solvent front were measured accurately and the corresponding RF values were calculated. The RF values of the substances before and after deposition are given in Table 4.3.

4.5 Results and Discussion

The X-ray diffractograms of perylene and p-terphenyl films prepared by both the techniques (vacuum deposition and ion plating) are shown in Figure 4.3 and 4.4. From the positions of the various peaks observed in the '2θ - Intensity' curves is Figure 4.3 (a) and 4.4 (a) for vacuum deposited perylene and p-terphenyl films respectively, the values for d spacings have been calculated using Bragg's
FIG. 4.3 X-RAY DIFFRACTOGRAMS OF PERYLENE THIN FILMS: (a) VACUUM DEPOSITED FILM (t = 5750Å) (b) ION PLATED FILM (t = 2750 Å)
FIG. 4.4  X-RAY DIFFRACTOGRAMS OF p-TERPHENYL THIN FILMS: (a) VACUUM DEPOSITED FILM ($t = 5200 \text{ Å}$)
(b) ION PLATED FILM ($t = 2200 \text{ Å}$)
relation with the wave length of CuKₐ = 1.5418 Å. The d values determined for the peaks in the diffractograms agree fairly well with those of the bulk materials reported in ASTM cards (No. 4-0412 for perylene and No. 4-0293 for p-terphenyl). It shows that the vacuum deposited films possess the same crystalline structures as the bulk substances. The comparison of X-ray diffraction data of vacuum deposited films of perylene and p-terphenyl with their respective ASTM data has been made in Tables 4.1 and 4.2 respectively. The occurrence of peaks in the same positions as in the ASTM data and the absence of additional peaks indicate the non-decomposition nature of the vacuum deposited films.

Figures 4.3 (b) and 4.4 (b) represent the X-ray diffractograms of ion plated perylene and p-terphenyl films respectively. The absence of peaks in the diffractograms of the ion plated films reveals that the films seem to be amorphous in nature. Usually films deposited in a glow discharge are amorphous [19], because when the defects produced on ion bombardment are sufficiently immobile, the crystallography will be disrupted into an amorphous structure [20.21].

As IR spectroscopy has, for years, been the method of choice for qualitative analysis of organic materials [22], IR spectra of perylene and p-terphenyl films formed by both the techniques have been recorded and are depicted by Figures 4.6 and 4.7. The super-imposable spectra of vacuum deposited and ion plated films with respect to each substance prove their identity in chemical structure [13] and reveal that there is no possibility of decomposition. The observed frequency at 1620 cm⁻¹, indicates the C = C stretching of the aromatic compound [23].

In thin layer chromatography, as observed from Table 4.3, the authentic substance, the substance taken from vacuum deposited film and that from ion plated film for each material have shown the same R_F value [17] confirming the originality of the compound even in film forms.
### Table 4.1

XRD Data on bulk perylene given in ASTM card (No. 4-0412) and the experimental data on vacuum deposited perylene films.

<table>
<thead>
<tr>
<th>ASTM Data on bulk 2θ° (Cal)</th>
<th>d(Å)</th>
<th>Experimental data on films 2θ° (obs)</th>
<th>d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.71</td>
<td>10.15</td>
<td>8.75</td>
<td>10.11</td>
</tr>
<tr>
<td>11.34</td>
<td>7.80</td>
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<td>13.42</td>
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<td>17.99</td>
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<td>22.74</td>
<td>3.91</td>
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</tr>
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<td>26.45</td>
<td>3.37</td>
<td>26.55</td>
<td>3.36</td>
</tr>
<tr>
<td>36.53</td>
<td>2.46</td>
<td>36.30</td>
<td>2.48</td>
</tr>
</tbody>
</table>

### Table 4.2

XRD Data on bulk p-terphenyl given in ASTM card (No. 4-0293) and the experimental data on vacuum deposited p-terphenyl films.

<table>
<thead>
<tr>
<th>ASTM Data on bulk 2θ° (Cal)</th>
<th>d(Å)</th>
<th>Experimental data on films 2θ° (obs)</th>
<th>d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.34</td>
<td>13.95</td>
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<td>39.52</td>
<td>2.28</td>
<td>39.60</td>
<td>2.28</td>
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</table>
FIG. 4-6  IR SPECTRA OF PERYLNE FILMS
(a) ION PLATED FILM (t = 810 Å)
(b) VACUUM DEPOSITED FILM (t = 2950 Å)
FIG. 4.7  IR SPECTRA OF p-TERPHENYL FILMS
(a) ION PLATED FILM (t = 850 Å)
(b) VACUUM DEPOSITED FILM (t = 2350 Å)
Table 4.3

Estimated $R_F$ values for perylene and p-terphenyl before and after deposition by different techniques

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample taken from</th>
<th>Solvent system</th>
<th>$R_F$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perylene</td>
<td>Authentic substance</td>
<td>Petroleum ether</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>Vacuum deposited film</td>
<td>(BP = 60° - 80°C)</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>Ion plated film</td>
<td></td>
<td>0.84</td>
</tr>
<tr>
<td>p-terphenyl</td>
<td>Authentic substance</td>
<td>5:1 Petrol-Benzene mixture</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>Vacuum deposited film</td>
<td>mixture</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>Ion plated film</td>
<td></td>
<td>0.91</td>
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References


