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**OPTOELECTRONIC PROPERTIES OF DYE SENSITIZED
CONDUCTING POLYPYRROLE FILMS**

**A THESIS SUBMITTED TO
UNIVERSITY OF PUNE
PUNE - 411 007**

**FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY (Ph.D)
(IN PHYSICS)**

BY

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CERTIFICATE

CERTIFIED that the work incorporated in the thesis "OPTOELECTRONIC PROPERTIES OF DYE SENSITIZED CONDUCTING POLYPYRROLE FILMS" submitted by Shri. Prakash Ravindra Somani was carried out by him under my supervision / guidance. Such material as has been obtained from other sources has been duly acknowledged in the thesis.



DR. S. RADHAKRISHNAN

(Supervisor / Research Guide)

Date : 26 / 11 / 01

Place : Pune

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Sonani P. V.

Prakash R. Somani

Date :

Place :

DEDICATED

TO

MY PARENTS

AND

IN THE NAME OF GOD

THAT WE ALL LOVE

CONTENTS

	Page No.
1. INTRODUCTION	
1.1 Introduction : Polymers for Optoelectronics	1
1.2 Photoconductivity in Polymers	4
1.2.1 Photoconductivity	4
1.2.2 Photoconductivity in Polymers	5
1.2.3 Sensitization of Photoconductivity	6
1.3 Conducting Polymers : An Introduction	8
1.4 Classification of Conducting Polymers	10
1.5 Doping of Conducting Polymers	12
1.5.1 Doping Techniques	12
1. Chemical Doping	12
2. Electrochemical Doping	13
3. Ion Implantation	13
4. Photochemical Doping	13
1.5.2 Types of Doping	13
1.6 Charge Transport in Inherently Electronically Conducting Polymers	14
1.6.1 Introduction	14
1.6.2 Nature of Charge Carriers	15
1.6.3 Conduction Mechanism in Thin and Thick Films	18
(A) Types of Contacts	18
a. Ohmic Contact	20
b. Neutral Contact	20
c. Blocking Contact	20
(B) Tunneling Effect	21
(C) Schottky and Poole-Frenkel Effect	23
(D) Space Charge Limited Conduction	23

1.7 Polypyrrole	27
1.7.1 Introduction	27
1.7.2 Electrochemical Synthesis of Conducting Polypyrrole	28
1.7.3 Applications of Conducting Polypyrrole	30
1.8 Electrochromism	31
1.8.1 Introduction	31
1.8.2 Electrochromism in Conducting Polymers	32
1.8.3 Electrochromism in Conducting Polypyrrole	35
1.9 Dyes and Pigments	35
1.9.1 An Introduction	35
1.9.2 Dyes for Sensitization of Photoconductivity	36
1.9.3 Dyes used as Photosensitizers for Polymers	38
1.9.4 Models Proposed for Dye Sensitization	38
1.10 Dyes used in Present Study	40
1.10.1 Prussian blue	40
1.10.2 Methylene blue	43
1.10.3 Crystal violet	45
1.10.4 Rhodamine B and rhodamine 6G	46
1.11 Aim and Scope of the Present Work	47
2. EXPERIMENTAL	
2.1 Introduction	49
2.2 Materials used	49
2.3 Sample Preparation	50
2.3.1 Preparation of Gold Electrodes	50
2.3.2 Electrochemical Deposition of Conducting Polypyrrole and Polyaniline Films on Gold Electrodes	52
2.3.3 Electro-deposition of Prussian blue films	52
2.3.4 Deposition of Dye Incorporated SPE Films on Conducting Polypyrrole and Polyaniline Films	53

2.4 Study of Electrical Properties	54
2.4.1 Current-Voltage Characteristics in Dark and Light	54
2.4.2 Cyclic Voltammetry	55
2.5 Other Characterization Methods Used	57
2.5.1 UV-VIS Spectroscopy	57
2.5.2 FT-Infrared Spectroscopy	57
2.5.3 Optical Polarizing Microscopy	58
2.5.4 Scanning Electron Microscopy	58
2.5.5 X-ray Diffraction	59
2.5.6 Thermal Studies (TG/DTA/DTG and DSC)	59
2.5.7 X-ray Photoelectron Spectroscopy	60

3. OPTOELECTRONIC PROPERTIES OF CONDUCTING POLYPYRROLE SENSITIZED WITH PRUSSIAN BLUE

3.1 Introduction	61
3.2 Experimental	63
3.3 Results and Discussion	66
3.3.1 Electrochromic Properties of Conducting Polypyrrole / PB Composite Films	66
3.3.1.1 Study of Ppy, PB and Ppy/PB Films by Cyclic Voltammetry	66
3.3.1.2 Effect of PB Film Thickness on the Electrochromic Contrast of Ppy/PB Films	71
3.3.1.3 Effect of Various Anions on the Electrochromic Contrast of Ppy/PB Films	74
3.3.1.4 XPS/ESCA Studies on the PB Films in the Oxidized and Reduced States	80
3.3.1.5 Morphological Study of the Ppy, PB and Ppy/PB Films in the Oxidized and Reduced States	82
3.3.2 Photosensitivity of Conducting Ppy/PB Bilayer Films	90

3.3.3	Photosensitivity of Conducting Ppy Sensitized with PB dispersed in Solid Polymer Electrolyte (Dry State)	100
3.3.3.1	PB Dye Aggregation	100
3.3.3.2	Effect of PB Aggregation on Photosensitization	105
3.3.4	Photosensitivity of Conducting Ppy/PB Bilayer Composite Films in PEC Mode	116
3.3.5	Photosensitivity of Conducting Ppy Sensitized with PB Dispersed in Solid Polymer Electrolyte (Wet State)	124
3.3.6	Summary and Conclusions	132

4 SENSITIZATION EFFECT IN CONDUCTING POLYPYRROLE AND POLYANILINE BY METHYLENE BLUE

4.1	Introduction	135
4.2	Experimental	136
4.3	Results and Discussion	138
4.3.1	Sensitization Effect in Ppy by MB incorporated in PVA+H ₃ PO ₄	138
4.3.1.1	Physico-Chemical Characterization of SPE+MB	138
4.3.1.1.1	UV-VIS Study	138
4.3.1.1.2	X-ray Diffraction Studies	142
4.3.1.1.3	FT-IR Studies	143
4.3.1.1.4	Thermal Studies	149
4.3.1.2	Sensitization of Photocurrents	155
4.3.2	Sensitization Effect in Undoped Ppy by MB incorporated in PVA+H ₃ PO ₄	165
4.3.3	Sensitization Effect in Ppy by MB incorporated in PVP+H ₃ PO ₄	173
4.3.4	Sensitization Effect in PANI by MB incorporated in PVA+H ₃ PO ₄	179
4.4	Summary and Conclusions	187

5.1 Introduction

5.2 Experimental

5.3 Results and Discussion

5.3.1 Sensitization Effect in Ppy by CRV incorporated in SPE

5.3.2 Sensitization Effect in Ppy by RB incorporated in SPE

5.3.3 Sensitization Effect in PANI by R6G incorporated in SPE

5.4 Summary and Conclusions

6 SUMMARY AND CONCLUSIONS

* REFERENCES

* PUBLICATIONS

MB

MIM

MO

OD

PA

PANI

Ppy

PD

PVA

PVB

PVP

PTC

Py

RD

191

192

194

194

209

223

240

List of acronyms

A	acceptor
B.E	binding energy
CPC	conducting polymer composite
CRV	crystal violet
D	donor
EM	electromagnetic
ESCA	electron spectroscopy for chemical analysis
FWHM	full width at half maximum
HOMO	highest occupied molecular orbital
ICP	intrinsically conducting polymer
IR	infra red
ITO	indium-tin-oxide
I-V	current vs. voltage
J-V	current density vs. voltage
LED	light emitting diode
Lof I - $\sqrt{V}$	lof current vs. square root voltage
MB	methylene blue
M-I-M	metal-insulator-metal
MO	molecular orbital
O.D	optical density
PA	polyacetylene
PANI	polyaniline
Ppy	polypyrrole
PB	Prussian blue
PVA	poly vinyl alcohol
PVB	poly vinyl butral
PVP	poly vinyl pyrrolodone
PTC	positive temperature co-efficient
Py	pyrrole
RB	rhodamine B

R6G	rhodamine 6G
SCLC	space charge limited currents / conduction
SE	Schottky emission
SEM	scanning electron microscopy
SCE	saturated calomel reference electrode
UV	ultraviolet
UV-VIS	ultraviolet - visible
VRH	variable range hopping
WAXD	wide angle X-ray diffraction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

List of Symbols

A_b	Absorbancy
C	Concentration
d	inter particulate Distance/Film thickness
E_f	Fermi Level
E_d	Energy level for donors
E_t	Energy level for trapping centers
ΔE_v	Difference between the valance states of the polymer and the dye
ΔE_c	Difference between the conduction states of the polymer and the dye
e	Electronic Charge
F	Electric field i.e. V/d
g	Gravitational acceleration
I	Current
k	Boltzman's constant
N	Density of states
N_d	Density of donor states
N_t	Density of trapping states
R	Resistance
T	Temperature
T_g	Glass transition temperature
V	applied voltage
α	absorption co-efficient
β	Poole-Frenkel parameter
β_{PF}	Poole-Frenkel parameter
β_{sc}	Schottky parameter
ϵ	dielectric constant of the material
ϕ_m	Work function of the metal
ϕ_i	Work function of the insulator

CHAPTER 1

CHAPTER – 1

INTRODUCTION

1.1 INTRODUCTION : POLYMERS FOR OPTOELECTRONICS :

Polymers are of great interest to the electrical and electronics industry because of their low cost, high processability, unusual properties such as high insulation, high dielectric strength, flexibility etc. Today, polymeric materials are widely used in all areas of electrical and electronic devices, circuit boards etc. for wide range of applications. They are used as packaging materials for individual microcircuits, protective coatings, wire and cable insulators, printed circuit boards, thick film circuits, equipment casings and housing which include electrical and mechanical parts.

The study of polymeric materials for use in optoelectronics is not only interesting from the academic point of view but has many industrial applications which have already acquired a large market potentials. Photochromic polymers (polymeric materials that reversibly transforms between two forms having different absorption spectra by photoirradiation) are one of the most promising candidates for use as optical data storage media. The photochemical stability of such materials needs to be improved so as to improve their durability [1, 2]. The photochromic biopolymers, particularly, Bacteriorhodopsins (BR) – a protein related to human vision - are also interesting and promising for use in optical information processing. Attempts were also made to use the proton pumping and photoelectric properties of BR for the desalination of sea water, for the conversion of sunlight into electricity and for the development of “biochips” with BR

as a molecular switch [3]. Several ferroelectric polymers like poly (vinylidene fluoride) (PVDF) have been studied for use in ferroelectric optical memory [4].

The study and the use of polymers in non-linear optics has progressed considerably in the recent years because of need for relatively inexpensive materials technology for active optical and integrated optical devices. Polymeric materials composed of chromophores (such as aromatic sulfones) with large molecular hyperpolarizability that are aligned in a polar fashion exhibits large, useful nonlinear optical coefficients [$\chi^{(2)}$ and $\chi^{(3)}$]. Due to the flexibility of polymer design and synthesis many of the solid state properties required for fabricating thin films for nonlinear optics can be optimized simultaneously [5, 6]. Many polymer/CT salt composites have been prepared and studied which shows nonlinear optical properties [7]. Many conjugated polymers like polydiacetylene, polythiophene, poly(paraphenylene-ethynylene) possesses third order nonlinear optical properties [8-13]. Several ferroelectric polymers like PVDF and its copolymers, blends and composites are shown to possess interesting nonlinear properties [14].

Recently, it has been shown that if mesogenic species are attached to a polymeric backbone through sufficiently long and flexible spacer groups, such a medium is expected to exhibit liquid crystalline behavior [15]. Several polymers have been prepared and their liquid crystalline behavior has been studied and the display devices were made [16]. Ferroelectric liquid crystalline polymer based electro-optic displays have been produced and studied [17].

Recently, conducting polymers have been extensively studied for use in electro-optic devices such as light emitting diode (LED), light emitting electrochemical cells, electrochromic displays etc. The LED's based on the poly(phenylene vinylene) (PPV) and MEHPPV have been successfully made and commercialized. Smart windows, electrochromic displays (ECD), laminated electrochromic displays have also been made using conducting polymers [18-43]. Conducting polymers are also promising candidates for solid state microlasers. Since the demonstration of optical gain in π -conjugated polymers, many optically pumped lasers using these as active materials have been reported. The viability of plastic lasers for application depends on achieving low values for the laser emission threshold. There are many challenges and scope for work in this new fascinating and technologically important area [44-49].

Polymeric photoconductors have undergone intense investigations because of growing need in new and novel materials for electrophotography, photothermoplastic recording, optoelectronics, holography, lasers and integral optics. As a result of which polymers with saturated bonds, heteroatoms, heterostructures and polyconjugated ones are now available as photosensitive materials. The typical examples of polymeric photoconductors are poly(N-vinyl carbazole) (PVK) and poly(epoxypropyl carbazole) (PEPCz) [50-54].

Thus, it can be concluded that polymers have been widely used for optoelectronic applications. Further, there is a huge interest and scope of research in the study of optoelectronic properties and applications of recently discovered and developed field of conducting polymers. The present work undertaken deals with the study of optoelectronic

properties (i.e. photosensitivity and electrochromism) of conducting polypyrrole (Ppy) sensitized with organic dyes and pigments.

1.2 PHOTOCONDUCTIVITY IN POLYMERS :

1.2.1 PHOTOCONDUCTIVITY :

The material of which electrical conductivity changes upon its exposure to light can be termed as a photoconducting material and the phenomenon can be termed as photoconductivity. The photoconductivity can be either positive or negative (i.e. the electrical conductivity of the material can increase or decrease upon exposure to light). The phenomenon of negative photoconductivity has also been observed, but very rare in the organic solids. The phenomenon is particularly pronounced in p-type dyes, but it has also been observed in germanium and other inorganic semiconductors. The typical example of negative photoconducting material is phloxin or pinachrome. The negative photoconductivity observed in organic solids is thought to be associated with the presence of centers capable of existing in two different valance states. An interesting example is that of chlorpromazine, for which it has been suggested that the center capable of existing in two different valance states is associated with the two free radicals which are known to result from the donation of one or two electrons from the two N atoms in the molecule.

In majority of the materials, positive photoconductivity has been observed. Unless otherwise stated, henceforward, photoconductivity means positive photoconductivity [55].

1.2.2 PHOTOCONDUCTIVITY IN POLYMERS :

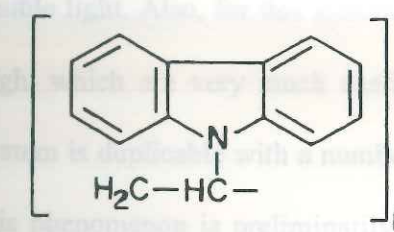
Photoconductive materials are characterized by an increase in the conductivity upon irradiation. They act as insulators in the dark and become semiconductors/conductors if illuminated. Photoconductors have very little free carrier density under ambient conditions. The carriers are mainly generated by the action of the light. Polymers capable of both producing charge carriers upon exposure to light and transporting them through the bulk are true photoconducting polymers. Polymers which do not absorb the incident radiation by themselves but accept the charges generated in an adjacent material are of merely charge transporting type e.g. hole transporting layers, ionically conducting solid electrolytes etc.

One of the most interesting and recent application of the polymeric photoconducting materials is in Xerography. This resulted from the discovery that charged polymers, when exposed to light, conducted away / neutralized the charged species which resulted in an image which could be developed electrostatically. In the absence of light most of the polymers, with the exception of those containing long sequences of double bonds, are fairly good insulators and conduct charge with difficulty. However, a surprising number of common vinyl and condensation polymers show a substantial increase in conductivity when exposed to light. These include poly(vinylfluoride), poly(vinylacetate) (PVAc), poly(N-vinyl carbazole) (PVC) etc. Most of these polymers absorb light in the UV region of the spectrum only. By doping such polymers with organic dyes, particularly with compounds which form charge-transfer complexes (CTC), the photosensitivity can be increased and can be extended into the visible region of the spectrum. The main areas of

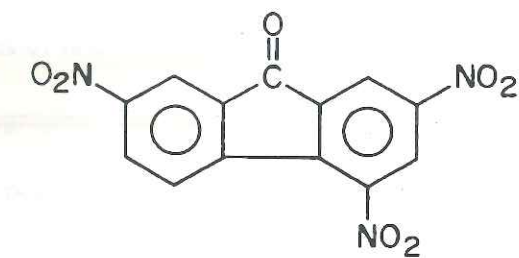
applications of polymeric photoconductors are – photocopiers, photothermoplastic recording, optoelectronics, holography, lasers and integral optics, printers, electrophotographic printing plates, electrophotographic microfilming [50-57].

1.2.3 SENSITIZATION OF PHOTOCONDUCTIVITY :

A material which when used along with the host material improves / increases the photosensitivity of the host material is known as a sensitizer (in particular a photosensitizer) and the phenomenon is called as photosensitization. The practical application of the PVK to Xerography resulted from the discovery that the photosensitivity could be extended in to the visible region by the addition of the dyes or other compounds capable of inducing charge-transfer complexes with PVK. A PVK film doped with 1.6 mol % of 2,4,7-trinitro-9-fluorenone (TNF) was first described by Lardon et. al. in 1967. Chemical structures of PVK and TNF are as shown in Figure (1.1).



(A)



(B)

Figure (1.1) : Chemical structure of PVK (A) and TNF (B)

Later it was reported by Shattuck and Vahtra in 1969 that increasing the TNF content increases the sensitization and that PVK film containing 1 : 1 molar ratio of PVK to TNF monomer unit display the maximum sensitization effect. PVK-TNF system have shown such an effect that it has gained practical importance as a photoreceptor in electrophotographic copiers.

Zinc oxide (ZnO) or cadmium sulfide (CdS) dispersed in binder resin have been reported to have good electrophotographic property. It has been shown that the Xerographic performance of the dye sensitized polymers can be as good as that of a - Se. Manufacturing the photoreceptors on a large scale along with the availability of the raw material and cost-economics makes the photoconducting polymers / dye-sensitized photoconducting polymers acceptable.

The PVK-TNF system is of particular interest because of its high photosensitivity to visible light. Also, for this system, the values of latent image γ and contrast potential are high, which are very much useful in Xerography. The behavior shown by PVK-TNF system is duplicable with a number of other polymers. Although the major application of this phenomenon is preliminarily in the field of Xerography, it seems likely that other applications are developing fast such as in switching and microcircuitary, for photographic processes etc. [50-57].

1.3 CONDUCTING POLYMERS : AN INTRODUCTION

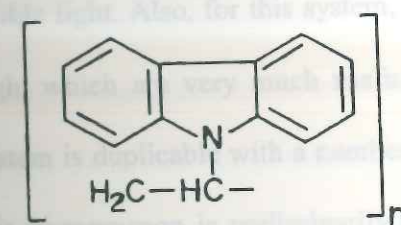
One of the most important property of the synthetic / conventional polymers is their ability to act as excellent electrical insulators, both at high frequencies and at high voltages. Their conductivity ranges in 10^{-18} to $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$. The typical examples are polyethylene, polytetrafluoroethylene (PTFE) etc. On the other hand, in recent years the polymers that can conduct electricity have been of great interest.

In practice, the term "conducting polymers" includes a range of materials which display a wide variety of properties and consequently fit many diverse areas of established or potential applications. The range of conductivity of interest is enclosed at one end of the scale by values associated with a typical good insulator, such as polyethylene, c. $10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$, and at the other end by those associated with a typical metallic conductor such as copper, c. $10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$. Conductivity may be an intrinsic property of the material, for example, poly(sulphurnitride)(SN)_x, the first "non-metallic metal" has a room temperature conductivity of c. $10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$; alternatively it may result from adding a conductive filler to an insulating polymer matrix. This additive approach has proved successful in producing practically useful materials, for example, conductive elastomers, fibres, plastics and paints are all produced by these techniques. The added conductive particle is often a 'carbon black', chopped carbon fibre, but may also be metal particle, fibre or flake; such materials find very widespread use in protection against build-up of static electricity and in shielding electronic devices against electromagnetic interference. The conductivities required are modest, typically between 10^{-7} to $1 \text{ ohm}^{-1} \text{ cm}^{-1}$. The systems mentioned so far are all electronic conductors, but the addition of the

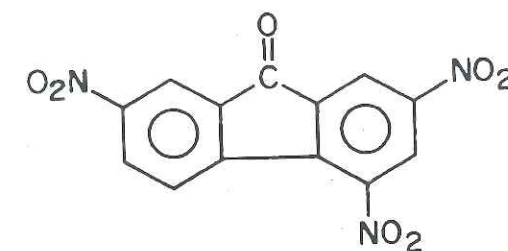
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These new materials are generally insulating.

In practice, the term "conducting polymers" includes a range of materials which display a wide variety of properties and consequently fit many diverse areas of established or potential applications. The range of conductivity of interest is enclosed at one end of the scale by values associated with a typical good insulator, such as polyethylene, c. $10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$, and at the other end by those associated with a typical metallic conductor such as copper, c. $10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$. Conductivity may be an intrinsic property of the material, for example, poly(sulphurnitride)(SN)_x, the first "non-metallic metal" has a room temperature conductivity of c. $10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$; alternatively it may result from adding a conductive filler to an insulating polymer matrix. This additive approach has proved successful in producing practically useful materials, for example, conductive elastomers, fibres, plastics and paints are all produced by these techniques. The added conductive particle is often a 'carbon black', chopped carbon fibre, but may also be metal particle, fibre or flake; such materials find very widespread use in protection against build-up of static electricity and in shielding electronic devices against electromagnetic interference. The conductivities required are modest, typically between 10^{-7} to $1 \text{ ohm}^{-1} \text{ cm}^{-1}$. The systems mentioned so far are all electronic conductors, but the addition of the

ionic species to an appropriate polymer can give ionically conducting materials; at present these are receiving a lot of attraction as, interalia, electrolytes for solid state batteries, electrochromic display devices (ECD's) etc.

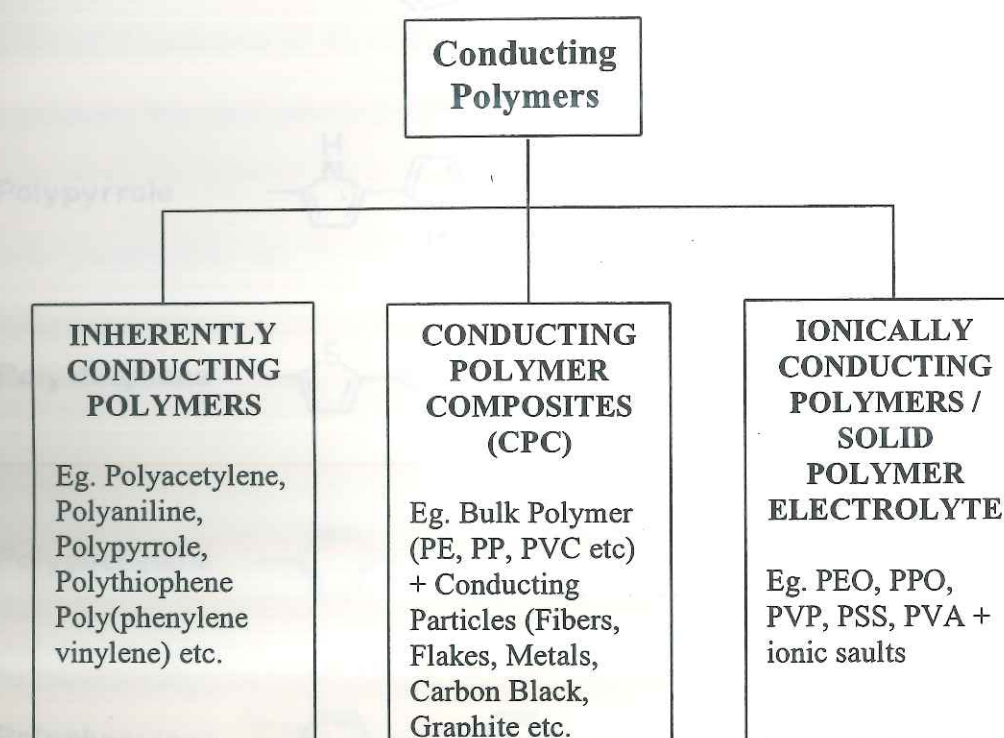
A type of conductive polymer which has generated much research activity in the last fifteen to twenty years fits neither the intrinsic nor the additive conductor classification. These new materials are generally insulators / poor conductors in their pristine state, but display marked increase in their conductivity on exposure to oxidizing or reducing agents. Thus, one may start with an insulating material and progressively oxidize or reduce it through the conductivity range of a semiconductor (p or n-type respectively), in to metallic regime. The residue from the oxidizing or reducing agent becomes part of the new material, which consequently has a structure and properties which are different from those of the starting material. The overall process which is often refereed to as 'doping', (a more appropriate word is an 'intercalation') represents a large scale modification of the starting material and should not be confused with the substitutive doping used in conventional silicon technology. The research in this field is boosted when Shirakawa was successful in making the free standing semiconducting film of polyacetylene (PA) having a band gap of about 1.4 eV in 1974. Later Ciang et. al. (in 1977) found that chemical oxidation of such films with arsenic pentafluoride and iodine increases the conductivity of the film by about eleven orders of magnitude. Leading on from this breakthrough, many other conjugated semiconducting/conducting polymers were successfully made. For the contributions made in this field by Sir Shirakawa, MacDermide, Alan J. Heeger – have been awarded the Nobel price in 2000. Also other

contributors like A. J. Epstein, R. H. Friend, D. C. Bradely, C. Talini, S. R. Forrest, J. L.

Bredas are worth to be mentioned [58-68].

1.4 CLASSIFICATION OF CONDUCTING POLYMERS :

In general, conducting polymers can be classified in to three types –



Some of the general important features of the inherently conducting pol ymers are –

- Have high degree of electrical conductivity (from 10^{-7} to $10^2 \text{ ohm}^{-1} \text{cm}^{-1}$).
- Have π conjugated double bond.
- Contains delocalized π - electrons which yields high carrier concentrations and hence have high conductivity.
- Energy band gap is much lower than that of the conventional polymers (Eg ~ 1.1 to 2.7 eV).



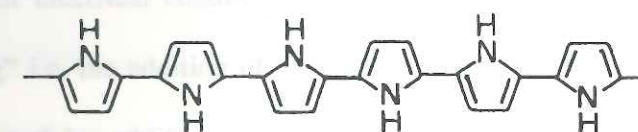
trans-Polyacetylene



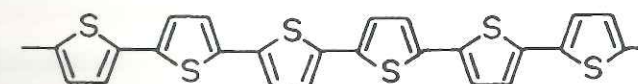
cis-Polyacetylene



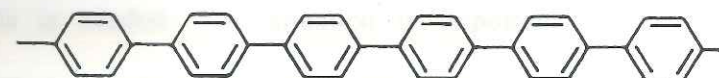
⇒ Polydiacetylene



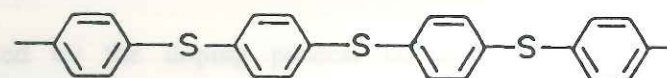
Polypyrrole



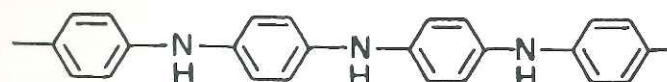
Poly thiophene



Polyphenylene



Polyphenylene
sulphide



Polyaniline



Polycarbene

Figure (1.2) : Some of the most studied conducting polymers.

Some of the most studied conducting polymers are polyacetylene, polyaniline, polypyrrole, polythiophene, poly(p-phenylene vinylene) etc. The structures of these polymers are as shown in Figure (1.2) [69].

1.5 DOPING OF CONDUCTING POLYMERS :

The potential usefulness of the conductive polymers has been increased dramatically by the discovery that their electrical conductivity could be increased by several orders of magnitude by "doping" i.e. the addition of electron acceptors (p-type) such as iodine or arsenic pentafluoride and by addition of electron donors (n-type) such as sodium or sodium naphthalide.

For a polymer to be electrically conducting, a network of overlapping intra or intermolecular orbitals is needed. This situation is important for the creation of significant electron (or hole mobility). Because electron mobility is almost nonexistent in most organic polymers, a mechanism for the creation of that nobility is needed and is generally accomplished by the doping process (a more appropriate word is the 'intercalation', oxidizing or reducing). Therefore, polymers that are easily oxidized or reduced are desirable.

1.5.1 DOPING TECHNIQUES :

There are various doping techniques used, as discussed in detail below -

1. **Chemical Doping** : The doping process is accomplished in the vapor phase by exposing the polymer to the vapor of the dopant or in liquid phase, by immersing the

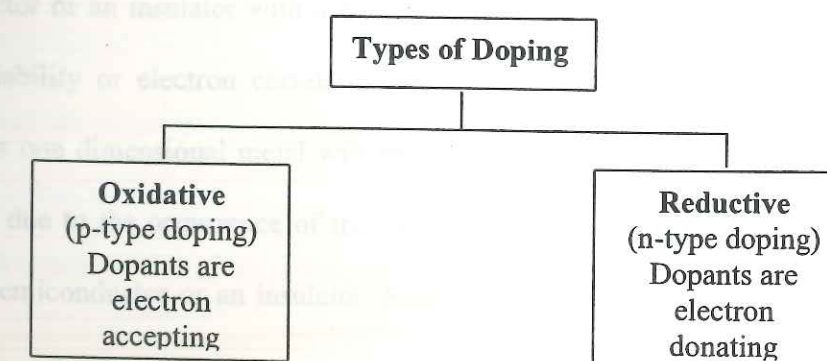
polymer film in the dopant solution. The amount of the dopant incorporated in the material (doping level) depends upon the vapor pressure of the dopant or its concentration, the doping time, and the temperature of the doping source and of the polymer.

2. **Electrochemical Doping** : Conjugated polymers can be doped and undoped / dedoped by immersing the material as an electrode in an organic electrolyte solution or in aqueous electrolytes and by applying the appropriate potentials
3. **Ion implantation** : When the proper ion beams are used, conjugated polymers can become conducting by implanting ions in the polymer's lattice, forming covalent bonds with the material. The doping level depends upon the energy of the ion beam to which the material is exposed.
4. **Photochemical Doping** : This is accomplished by treating the polymer with the dopant species, which are initially inert towards the material but becomes active upon ultraviolet irradiation.

The most common are the electrochemical and the chemical technique [69].

1.5.2 TYPES OF DOPING :

The polymers can be doped with either the electron donating or electron accepting molecules/groups to make them either n or p-type respectively [69].



1.6 CHARGE TRANSPORT IN INHERENTLY ELECTRONICALLY CONDUCTING POLYMERS :

1.6.1 INTRODUCTION :

The quasi one dimensional

electron interaction, leading to

Polarons and Bipolarons

important role in

1.6.2 NATURE OF THE CHARGE

Conducting polymers

that the charge carriers in

bipolarons, i.e. of

which is shown in Figure 1.3

in the presence of a weak

midway up the gap. The

occupied and then free, the

workers [71-73] have noted from the theory

over some 15 carbon atoms. It is the only

[70], such a system can not exist as a one dimensional metal but rather acts as a

semiconductor or an insulator with a band gap forming at the fermi level, either due to

Peierls instability or electron correlation, or a combination of both. [Peierls theorem

states that a one dimensional metal will be unstable and an energy gap will form at the

fermi level due to the occurrence of the lattice distortion so that the materials becomes

a negatively charged. This gives rise to the

either the semiconductor or an insulator. Elastic energy is used during lattice distortion,

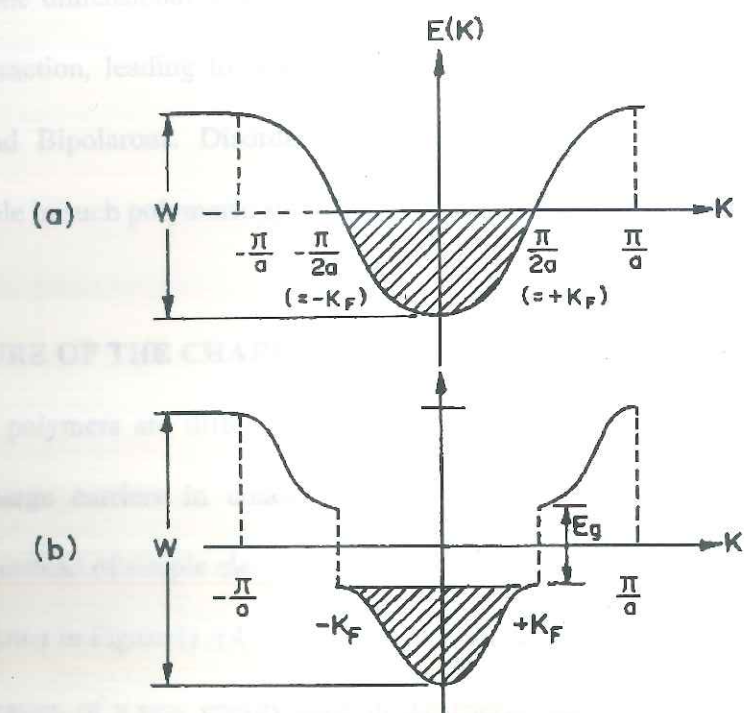


Figure (1.3) : Peierls Instability

Polymers and other materials with a π -conjugation are usually electrically conducting which may be considered as one dimensional metal. According to Rehwal and Keiss [70], such a system can not exist as a one dimensional metal but rather acts as a semiconductor or an insulator with a band gap forming at the fermi level, either due to Peierls instability or electron correlation, or a combination of both. [Peierls theorem states that a one dimensional metal will be unstable and an energy gap will form at the fermi level due to the occurrence of the lattice distortion so that the materials becomes a negatively charged. This gives rise to the either the semiconductor or an insulator. Elastic energy is used during lattice distortion,

which is compensated for by a lowering in the electronic energy of the occupied states and the generation of the band gap as represented in Figure (1.3)]. With the energy gap of the order of 1 to 2 eV, polymers seem to resemble inorganic crystalline semiconductors. The quasi one dimensional structure of these materials gives rise to a strong electron - phonon interaction, leading to new quasi - particles upon doping : these are Solitons, Polarons and Bipolarons. Disorder within the chain and its environment plays an important role in such polymeric systems.

1.6.2 NATURE OF THE CHARGE CARRIERS :

Conducting polymers are different from the conventional semiconductors in the sense that the charge carriers in conducting polymers are mainly solitons, polarons and bipolarons, instead of simple electrons and holes. Solitons can be due to the conjugational defect as shown in Figure (1.4A) for the polyacetylene. The presence of this defect results in the generation of a new energy state in the energy gap. This energy level is located midway up the gap. The neutral defect is termed as a soliton. The energy level is singly occupied and therefore, the defect state has an associated spin value of $\frac{1}{2}$. Bredas and co-workers [71-73] have noted from the theoretical calculations that the defect is delocalized over some 15 carbon atoms. It is the presence of these neutral solitons that gives trans polyacetylene the electrical characteristics of a semiconductor with an intrinsic conductivity of about 10^{-7} to 10^{-8} S cm⁻¹. The neutral soliton is paramagnetic. The conductivity of the polymer can be considerably enhanced by doping. The soliton energy level can accommodate zero, one or two electrons and so soliton may also be positively or negatively charged. This gives rise to the interesting observation that the

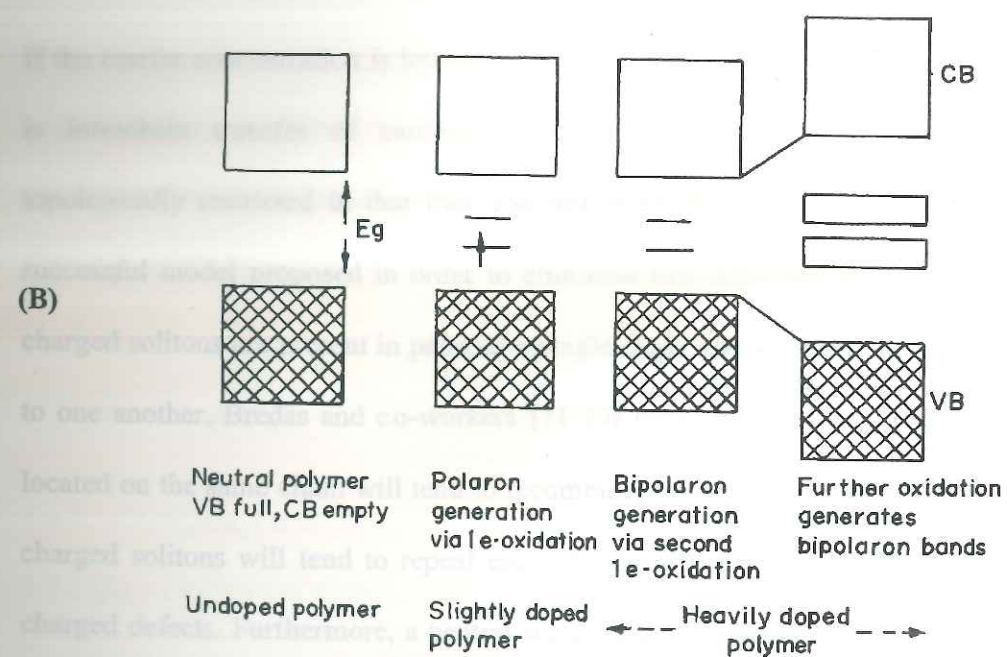
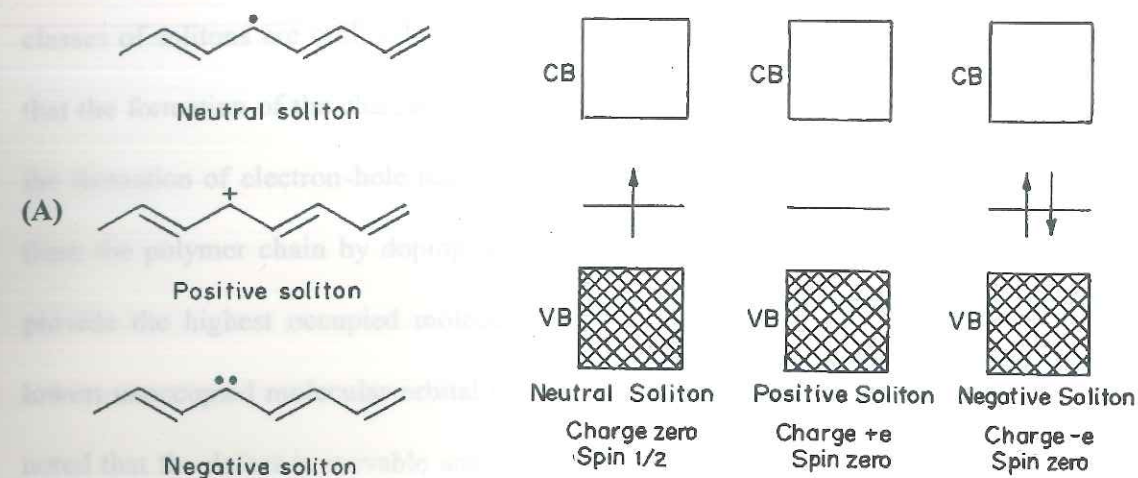


Figure (1.4) : Solitons, polarons and bipolarons

charged solitons have no spin, whereas neutral soliton have spin but no charge. The three classes of solitons are outlined in Figure (1.4B). Theoretical calculations have indicated that the formation of the charged solitons on doping is more energetically favorable than the formation of electron-hole pair. Moreover, when the charge is added to or removed from the polymer chain by doping, it will be located in the midgap states as the latter provide the highest occupied molecular orbital (HUMO) for charge removal and the lowest unoccupied molecular orbital (LUMO) for the charge injection. It should also be noted that the defect is movable and can move quite readily along the chain. Hence, the intrinsic conductivity of the polymer can be modeled in terms of the movement of the defects along the chain.

If the carrier concentration is low, then it has been established that the rate-limiting step is interchain transfer of carriers. However, this rises a difficulty. Solitons are topologically restricted in that they can not move from one chain to other. The most successful model proposed in order to eliminate this difficulty is the one in which the charged solitons are present in pairs on a single chain and are constrained to remain close to one another. Bredas and co-workers [71-73] have noted that the two neutral solitons located on the same chain will tend to recombine, leaving no deformation. However, two charged solitons will tend to repeal each other and therefore gives rise to two isolated charged defects. Furthermore, a neutral soliton and a charge one can achieve a minimum energy configuration by pairing. This will occur when they are both located on the same chain. This pairing gives rise to a polaron, which is a radical cation. The generation of the polaron gives rise to two energy states in the band gap that is symmetrically placed about

the midgap energy [74, 75]. This doubly charged excitation is termed as bipolaron, which in chemical terms is a dication. The process of interchain transport is then controlled by the rate at which these bipolarons can hop or possibly tunnel between the chains. The bipolaron model is now thought to have the most general validity and can be used to rationalize the electrical conductivity of the conjugated polymers whether or not they exhibit a degenerate ground state. Chance et. al. [76] have noted that like charged soliton pairs are analogous to bipolarons and they are not topologically restrained to interchain hopping. At high doping levels, the bipolarons interact to form bipolaron bands within the energy gap.

Hence, a general picture for polymers with a non-degenerate ground state is as follows. The neutral polymer has a full valence and empty conduction band separated by a band gap. Electrochemical doping removes one electron and results in the generation of a polaron level located at midgap. Further oxidation results in the removal of a second electron to generate a bipolaron. Still further oxidation results in the generation of bipolaron energy bands in the band gap. Electronic conductivity is rationalized in terms of bipolaron hopping.

1.6.3 CONDUCTION MECHANISMS IN THIN AND THICK FILMS :

1.6.3 (A) : TYPES OF CONTACTS :

The type of contacts that can exist at a metal-insulator interface falls in three categories :

(a) ohmic contact (b) neutral contact and (c) blocking contact, depending upon the placement of the work function of the metal (ϕ_m) with respect to the work function of the insulator (ϕ_i).

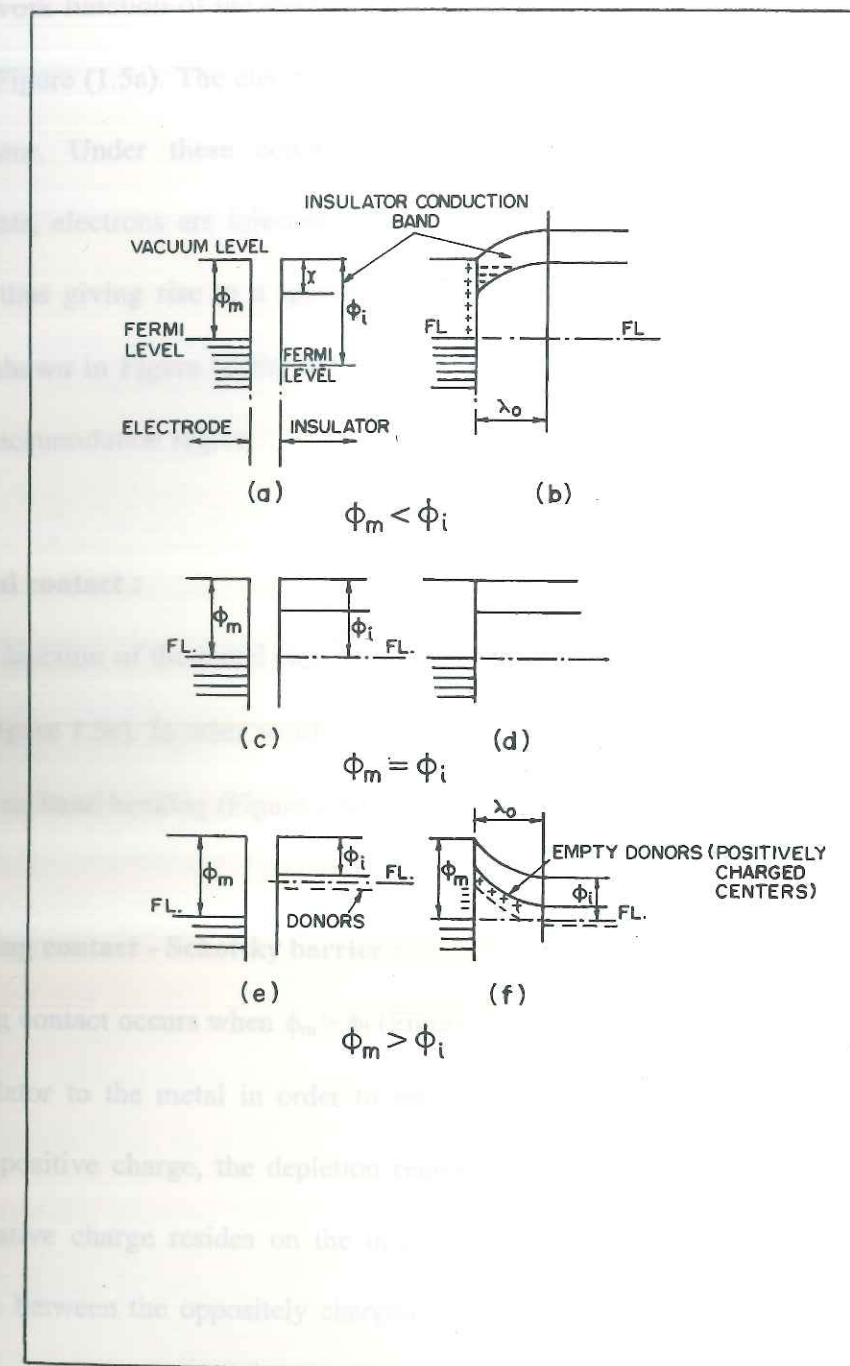


Figure (1.5) : Energy diagrams presenting various types of contacts at the metal-insulator interface ; (a, b) ohmic contacts, (c, d) neutral contact and (e, f) blocking contact.

(a) Ohmic contact - Mott-Gurney contact :

here, the work function of the electrode (ϕ_m) is smaller than that of the insulator (ϕ_i), as shown in Figure (1.5a). The electrode can rapidly supply / inject the charge carriers in to the insulator. Under these conditions, in order to satisfy thermal - equilibrium requirements, electrons are injected from the electrode into the conduction band of the insulator, thus giving rise to a space charge region in the insulator. This space charge region is shown in Figure (1.5b) and this extends a distance λ_o into the insulator and is known as accumulation region.

(b) Neutral contact :

The work function of the metal (ϕ_m) is equal to the work function of the insulator (ϕ_i) i.e. $\phi_m = \phi_i$ (Figure 1.5c). In other words, the conduction band is flat right up to the interface and hence no band bending (Figure 1.5d).

(c) Blocking contact - Schottky barrier :

A blocking contact occurs when $\phi_m > \phi_i$ (Figure 1.5e) and in such case, the electrons flow from insulator to the metal in order to establish thermal equilibrium. A space charge region of positive charge, the depletion region, is thus created in the insulator and an equal negative charge resides on the metal electrode. As a result of the electrostatic interaction between the oppositely charged regions, a local field exists at the surface of the insulator. This causes the bottom of the conduction band to bend downwards until the fermi level within the bulk of the insulator lies below the vacuum level (Figure 1.5f).

Various workers in this field have suggested different conduction processes such as tunneling, space charge limited conduction, Poole-Frenkel effect, Schottky emission etc. A detailed review of these physical processes is given below.

1.6.3 (B) TUNNELING EFFECT :

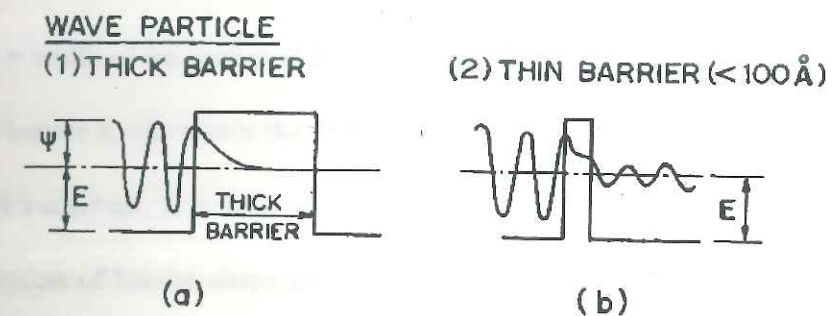


Figure (1.6) : Quantum mechanical tunneling of an electron at metal-insulator-metal junction (a) at a thick barrier and (b) at a thin barrier.

The tunneling of an electron occurs in the metal-insulator-metal (M-I-M) structure when the energy of the incident electron is less than the potential barrier. Classically, such an electron will not be able to move and reach the second electrode. But quantum mechanically, such an electron will tunnel through the potential barrier and will reach the second electrode. Thus, the probability of finding the electron at the second electrode will be non-zero and is given by $\Psi\Psi^*$ where Ψ is the quantum mechanical wavefunction of the electron. Such type of tunneling of charge carriers will occur when the barrier is very thin (usually in thin films of thickness less than 100 Å). Figure (1.6) represents schematic of the tunneling of an electron at a thin barrier in metal-insulator-metal junction. The

generalized formula gives the relationship connecting the tunnel current density with the applied voltage for a barrier of arbitrary shape as -

$$I = I_0 \{ \phi \exp(-A \phi^{1/2}) - (\phi + eV) \exp[-A(\phi + eV)^{1/2}] \} \quad \text{----- (1.1)}$$

$$\text{where } I_0 = e / [2\pi h (\beta \Delta s)^2] \text{ and } A = [4\pi \beta \Delta s (2m)^{1/2}] / h \quad \text{----- (1.2)}$$

where Δs = width of the barrier at the fermi level of the negatively biased electrode.

ϕ = mean barrier height above the fermi level of the negatively biased electrode

h = Planck's constant, m = mass of the electron, e = unit of electronic charge and

β = a function of barrier shape and is usually approximately equal to unity, a condition we will assume throughout.

Expressed in conventional units, except for Δs , which is expressed in angstroms, equation (1.1) becomes -

$$I = [6.2 \times 10^{10} / (\Delta s)^2] \{ \phi' \exp(-1.025 \Delta s \phi'^{1/2}) - (\phi' + V) \exp[-1.025 \Delta s (\phi' + V)^{1/2}] \} \quad \text{----- (1.3)}$$

The tunneling process is independent of the temperature. Charge carrier tunneling predominates at low temperatures and at low voltages, whereas Schottky barrier lowering was observed in most of the organic semiconductors at high temperatures and at high voltages. Tunneling of charge carriers occurs in relatively thin films (below 100 °Å). For

500 - 1200 °A thin films, Schottky emission generally dominates or the observed conduction can be thought of a combination of Schottky effect and tunneling [77-78].

1.6.3 (C) SCHOTTKY AND POOLE FRENKEL EFFECT :

It can be defined as the field dependent lowering of the potential barrier for injection of the charge carriers. The relationship between resistivity and the sample thickness for different values of voltage (V) is given by -

$$I = A T^2 \exp(-\phi / kT) \exp[(q^{3/2} V^{1/2}) / (\epsilon^{1/2} d^{1/2} k T)] \quad \text{-----(1.4)}$$

where V is the voltage across the film of thickness d. ϵ is the permittivity and ϕ is the potential barrier at the electrode / polymer interface.

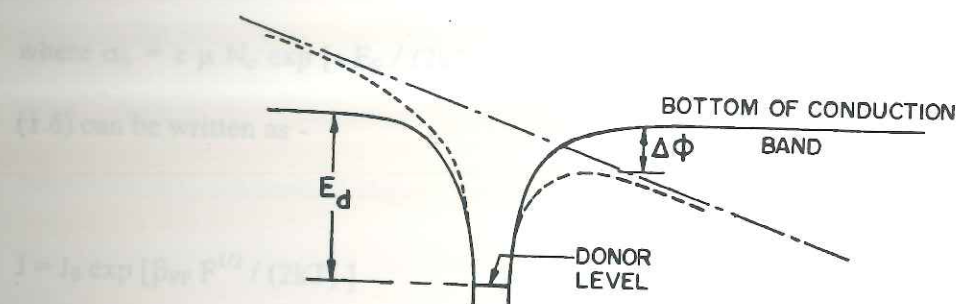


Figure (1.7) : Lowering of Coulombic potential barrier in Poole-Frenkel effect.

The Poole-Frenkel effect (field assisted thermal ionization) is lowering of the Coulombic potential barrier by the application of an electric field [as represented in Figure (1.7)]. This process is the bulk analog of the Schottky effect at an interfacial barrier. Since the

potential energy of an electron in a Coulombic field $[-e^2 / (4 \pi \epsilon_0 Kx)]$ is four times that due to image - force effects, the Poole-Frenkel attenuation of a Coulombic barrier $\Delta\phi_{PF}$ in a uniform electric field is twice that due to the Schottky effect at a neutral barrier :

$$\Delta\phi_{PF} = [e^3 / (\pi \epsilon_0 K^*)]^{1/2} F^{1/2} = (\beta_{PF}) F^{1/2} \quad \text{-----(1.5)}$$

This result was first applied by Frenkel [79] to the hot atoms in the bulk semiconductors and insulators. He argued that the ionization potential E_0 of the atoms in a solid are lowered by an amount given by above equation in the presence of a uniform field. The conductivity is given by -

$$\sigma = \sigma_0 \exp [\beta_{PF} F^{1/2} / (2kT)] \quad \text{-----(1.6)}$$

where $\sigma_0 = e \mu N_c \exp [-E_0 / (2kT)]$ is the low field conductivity. The above equation (1.6) can be written as -

$$J = J_0 \exp [\beta_{PF} F^{1/2} / (2kT)] \quad \text{-----(1.7)}$$

where $J_0 (= \sigma_0 F)$ is the low field current density.

It is interesting to note that although $\Delta\phi_{PF} = 2 \Delta\phi_s$, the coefficient of $F^{1/2}$ in the exponential is the same for both the Richardson -Schottky and Poole-Frenkel J-F characteristics (i.e. $\beta_{PF} / 2 = \beta_s$). Mead [80] has suggested, however, that since traps

around in an insulator and that a trap having a coulombic -type barrier would experience the Poole-Frenkel effect at high fields, thereby increasing the probability of escape of an electron immobilized therein, the current density in the thin film insulators containing shallow traps is given by -

$$J = J_0 \exp [\beta_{PF} F^{1/2} / (kT)] \quad \text{-----}(1.8)$$

Note in this case that the coefficient of $F^{1/2}$ is twice that in above equation and for this reason, this equation is usually the form of Poole-Frenkel equation associated with thin film insulators rather than the above equation.

Thus, it should be possible to differentiate between the Schottky and Poole-Frenkel effects in thin film insulators from their different rates of conductivity with field strength ; vis. a plot of $(\ln J)$ vs. $(F^{1/2}/kT)$ results in a straight line of slope β_s or β_{PF} , depending upon whether the conduction process is Schottky or Poole-Frenkel type. These experimentally determined slopes can be compared with the theoretical β_s or β_{PF} , which can agree quite accurately provided the high frequency dielectric constant K^* should satisfy the equation $K^* = n^2$, where n is the refractive index for the material.

1.6.3 (D) SPACE CHARGE LIMITED CONDUCTION :

An insulator which does not contains donors and which is sufficiently thick to inhibit tunneling will not normally conduct significant current. However, if an ohmic contact is made to the insulator, the charges are injected in to the conduction band of the insulator.

Charges injected in this way may get trapped in defect states. The spatial distribution of such a charge in an insulator is known as a space charge and the conduction observed is termed as space charge limited conduction. The space charge limited conduction arises due to following reasons -

- (i) injected charges accumulate within the solid and thus alters the internal field.
- (ii) At sufficiently high field, solid is unable to transport all the injected charge and thus a built-up of charge begins within the solid.
- (iii) Existence of traps within the solids. Trap may be a localized state within the energy gap associated with impurities, disorder or the molecular nature of the polymer.
- (iv) Partially blocking electrodes
- (v) One type of charge carrier is much more mobile than the other

Mott and Gurney have derived an equation describing the space charge limited currents on the following assumptions -

- (i) the electrode can supply all the charge carriers which the solid can transport and there is no potential barrier at the electrode / insulator interface.
- (ii) The current flowing through the sample is independent of the position in the sample.
- (iii) Poisson's equation is obeyed.
- (iv) The integral of the field strength across the sample is the applied voltage (V).

The current - voltage (I-V) relation given by Mott and Gurney is [78] -

$$I = 9 \epsilon \mu V^2 / (8 d^3) \quad \text{-----}(1.9)$$

The equation (1.9) is known as "Child's law" for the trap free insulator. The Child's law for an insulator with shallow traps is given by -

$$I = 9 n_{\text{eff}} \exp -[E_T / kT] \epsilon \mu V^2 / (8 d^3 N) \quad \text{-----}(1.10)$$

The generalized equation is -

$$I = (9/8) \epsilon \mu \theta V^{(n+1)} / d^{(2n+1)} \quad \text{-----}(1.11)$$

where $\theta = \{ n_{\text{eff}} \exp - [E_T / kT] \} / N$

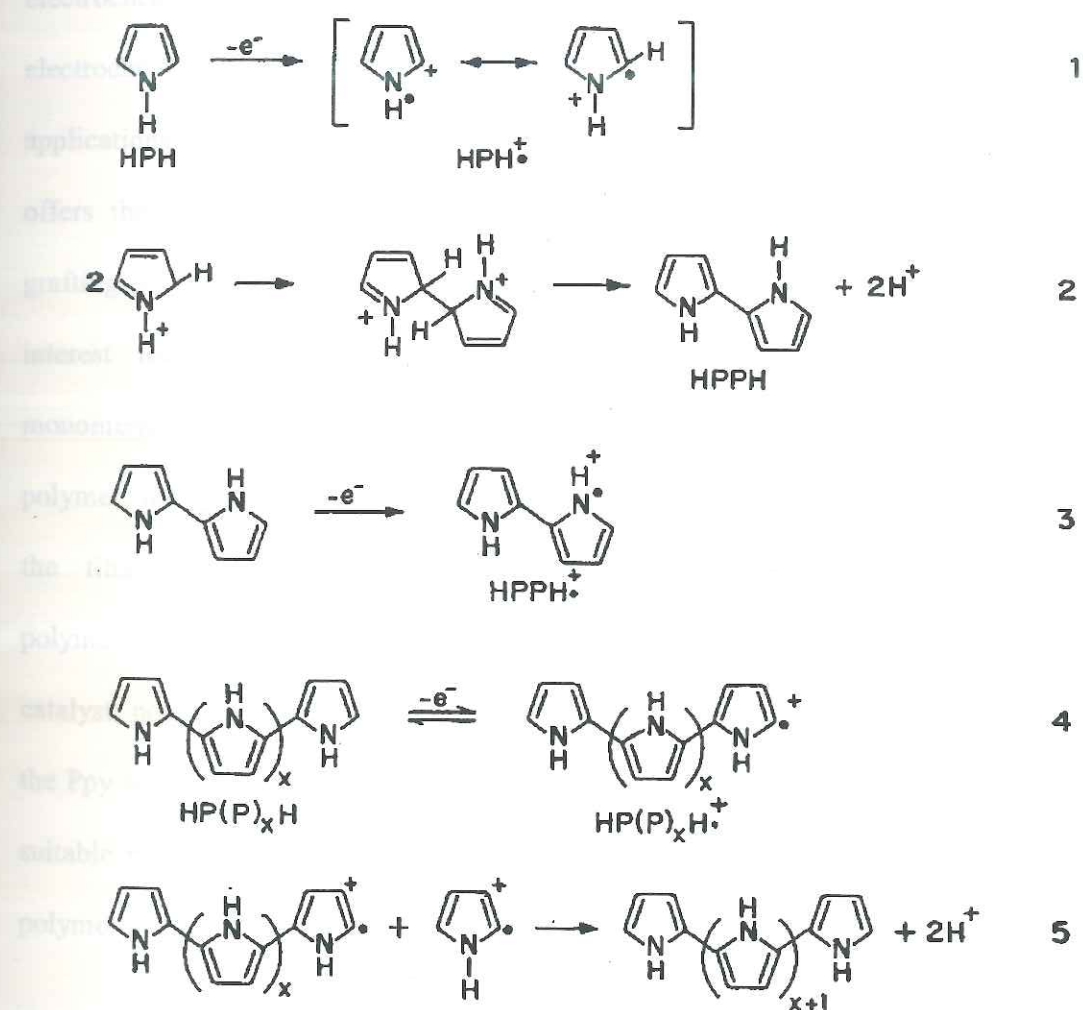
1.7 POLYPYRROLE :

1.7.1 INTRODUCTION

Polypyrrole (Ppy) is one of the most important conducting polymer and have been extensively studied because of its good environmental and thermal stability, ease of synthesis and can be easily doped with various oxidants, long term stability of its conductivity, and the possibility of forming homopolymers or composites with optimal mechanical properties. Ppy was first polymerized in 1916 by the oxidation of pyrrole with H_2O_2 to yield an amorphous powdery product known as pyrrole black. The electrochemical synthesis of Ppy dates to the early work of Dall'Olio [81], who also obtained pyrrole black by electrochemical oxidation of pyrrole in aqueous sulfuric acid

on a platinum electrode. In the years later, chemical and electrochemical methods of its synthesis have been improved in order to optimize the physical and chemical properties [82].

1.7.2 ELECTROCHEMICAL SYNTHESIS OF CONDUCTING POLYPYRROLE :



Scheme. 1

Scheme 1 : Proposed mechanism for the electrochemical polymerization of the pyrrole.

Conducting Ppy has been prepared by various methods such as chemical, electrochemical, vapor phase deposition etc. Among these the chemical and electrochemical polymerization are widely used. The principal advantage of chemical methods is related to the possibility of its mass production at a low cost, which is often difficult to achieve with electrochemical methods, although the continuous synthesis of electrochemically polymerized pyrrole has also been developed. On the other hand, the electrochemical methods offer materials with better conducting properties and for some applications like the construction of electronic devices, electrochemical polymerization offers the possibility of *in-situ* formation. Electrochemical synthesis permits direct grafting of the conducting polymer on to the electrode surface, which can be of special interest for electrochemical applications. As the electrical potential needed for monomeric oxidation is significantly higher than the charging (or doping) of the formed polymer, the polymer is directly obtained in its conducting state. Also, the thickness of the film can be easily controlled by the electrical charge employed during polymerization. Electrochemical polymerization is the fast, easy and clean (absence of catalyst, possibility to use water as a solvent etc) and the most useful method to obtain the Ppy with high conductivities. The only drawback associated with it is that it is not a suitable method for large scale production and the difficulties found in correlating the polymer properties with the conditions of synthesis [82].

In general, electrochemical polymerization of the pyrrole is carried out in a single compartment electrolytic cell having saturated calomel electrode (SCE) as a reference electrode, platinum counter electrode, and a working electrode (like gold films deposited

on glass, ITO coated glass, stainless-steel, graphite etc.) containing pyrrole monomer and a suitable electrolyte, either in aqueous, non-aqueous or a mixed medium [83-87]. The procedure used by us have been described in the chapter 2. The proposed mechanism for the electrochemical polymerization is represented in Scheme 1. The steps involve oxidation and dimerization of pyrrole followed by aromatization and oxidation of the dimer. The last step is included because the aromatic dimer and the higher molecular weight oligomers are known to oxidize more easily than the monomer. By extension of these reactions, the steps for the polymerization process can be described as in equation 4 and 5 in Scheme 1. The polymerization reaction has been shown to involve two electrons / molecule of pyrrole reacted and the resulting polymer is produced in the oxidized state with 0.25 to 0.33 cation centers per pyrrole unit depending upon the electrolyte anion used [88].

1.7.3 APPLICATIONS OF CONDUCTING POLYPYRROLE :

Conducting polypyrrole has been used in antistatics [89-90], electromagnetic shielding [91], conductive textiles and fabrics [92], sensors and actuators [93-98], capacitors [99], polymer batteries [100-101], electroplating [102-104], as a catalyst [105-108], membranes [109-111], electrochromic display devices (ECD) [112-116] etc.

1.8 ELECTROCHROMSIM :

1.8.1 AN INTRODUCTION :

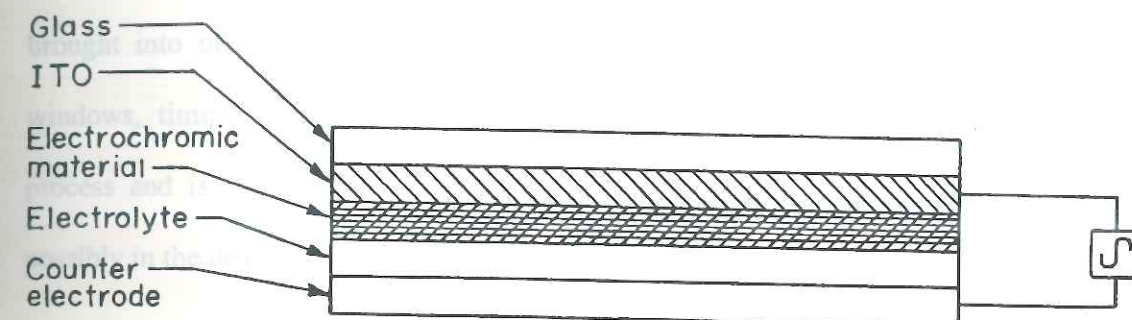


Figure (1.8) : Schematic of the Electrochromic Display Device (ECD).

An electrochromic material is the one that changes color in a persistent but reversible manner by an electrochemical reaction and the phenomenon is called as electrochromism. Electrochromism is the reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation-reduction reaction. It results from the generation of different visible region electronic absorption bands on switching between redox states. The color change is commonly between a transparent ('bleached') state and a colored state, or between two colored states. In case more than two redox states are electrochemically available, the electrochromic material may exhibit several colors and may be termed as polyelectrochromic or can be said to possess multicolor-electrochromism. This optical change is effected by a small electric current at low d-c potentials. The potential is of the order of few volts. Figure (1.8) illustrates an electrochromic device configuration. Several electrochromic materials have been discovered and studied for their possible application in electrochromic display devices

(ECD's) like conducting polymers such as polypyrrole, polyaniline, polythiophene etc., polymeric gels, prussian blues, phthalocyanines, several transition metal oxides. Several prototype and commercial electrochromic display devices (ECD) have been made and brought into market by many US companies. Also, study of EC materials for smart windows, time-temperature integration, for moving electrochromic images is still in process and is very much interesting not only from the academic point of view but possibly in the near future can find a huge market [116].

1.8.2 ELECTROCHROMISM IN CONDUCTING POLYMERS :

In their oxidized form, conducting polymers (CPs) are "doped" with counter anions (p-doping) and possess a delocalized π -electron band structure. The energy gap (E_g) between the highest occupied π -electron band (valance band) and the lowest unoccupied band (conduction band) determines the intrinsic optical (and of course electrical) properties of these materials. It is well known that we can tune the optical properties of these materials by controlled doping (and/or dedoping). The doping process (oxidation) introduces polarons, which are the major charge carriers. Other charge carriers such as solitons, bipolarons etc. are also very important in such systems. The introduction of new states in the band gap (or forbidden gap) with doping process is the main reason for the changes in the optical properties of CPs and is the main cause for the electrochromism of such materials as represented in Figure (1.9). Reduction of CPs with concurrent counter anion exit-removes the electronic conjugation, to give the "undoped" (neutral) electrically insulating form. Conducting polymers can also undergo cathodic doping with

cation insertion (n-doping). However, n-doped forms are less stable than p-doped forms.

There are few reports on the electrochromism of the n-doped conducting polymers.

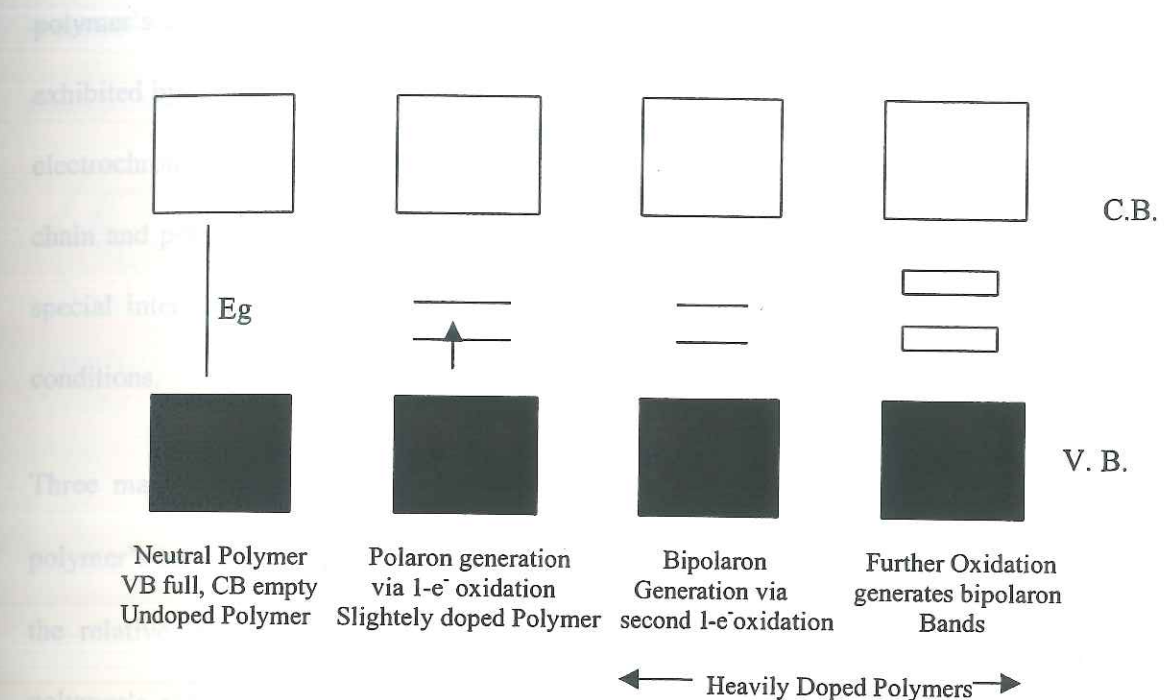


Figure (1.9) : polaron, bipolaron and doping in conducting polymers

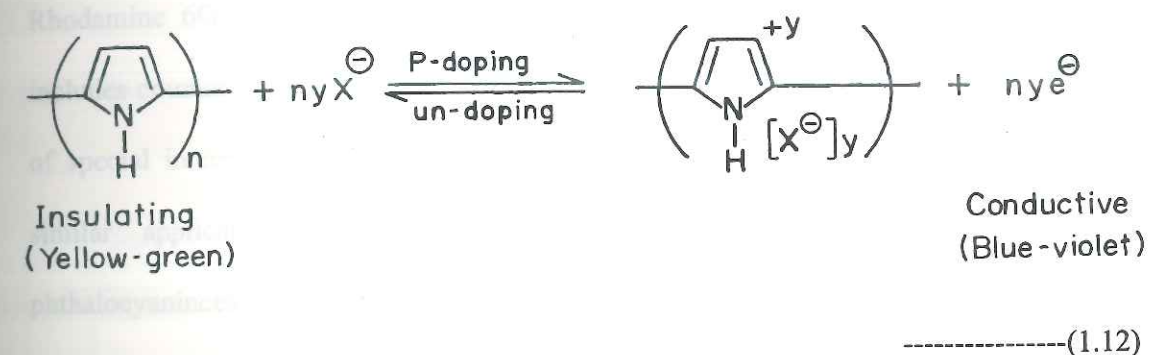
In the recent years, conducting polymers have gained a lot of attention for ECD's. This is due to the fact that all electroactive and conducting polymers are potentially electrochromic materials, and are more processable than inorganic electrochromic materials and offer the advantage of a high degree of color tailorability. This tailorability has been achieved through the modification of various polymer systems via monomer functionalization and copolymerization as well as with the use of blends, laminates and composites. Complex colors are achieved by mixing two existing colors in a dual polymer device.

In conducting polymers, electrochromic changes are induced by redox processes which are accompanied by ion insertion / expulsion and results in a modification of the polymer's electronic properties giving rise to changes in color of the material. The color exhibited by the polymer is closely related to the band gap. A major focus in the study of electrochromic polymeric materials has been that of controlling their colors by main-chain and pendant group structural modification. Polyheterocycles have proven to be of special interest for this due to their environmental stability under ambient and in use conditions.

Three major strategies of color control are used with electrochromic properties. The polymer's band gap (defined as the onset of the π to π^* transition) is directly related to the relative energies of the HOMO and the LUMO. By judiciously substituting the polymer's repeat unit, the electrochromic properties can be controlled by the induced steric and electronic effects. These substituents determine the effective conjugation length and the electron density of the polymer backbone. Copolymers offer a second means of controlling the electrochromic properties of the conducting polymers. Copolymerization of distinct monomers or homopolymerization of hybrid monomers containing several distinct units, can lead to an interesting combination of the properties observed in the corresponding homopolymers. Indeed, it has been observed that the color of copolymers based on carbazole, thiophene and pyrrole derivatives can be controlled by altering the ratio of the respective monomers. Blends, laminates and composites offer a third method, similar to copolymers, for combining the electrochromic properties of several systems. The use of two polymers covering different color regions is a simplest way to achieve multicolor electrochromism [116].

1.8.3 ELECTROCHROMISM IN CONDUCTING POLYPYRROLE :

Doped (oxidized) polypyrrole film is blue-violet ($\lambda_{\text{max}} = 670 \text{ nm}$). Electrochemical reduction yields the yellow-green ($\lambda_{\text{max}} = 420 \text{ nm}$) "undoped" form. The schematic of the doping/dedoping process can be given as :



Removal of all dopant anions from polypyrrole yields a pale-yellow film. However, complete dedoping is only achieved if the Ppy films are extremely thin. This means that Ppy of thickness commensurate with device construction ($> 1 \mu\text{m}$) has a low contrast ratio. There are many reports on the study of the electrochromic properties of conducting polypyrrole either as it is or when combined with the other complementary electrochromic materials [116].

1.9 DYES AND PIGMENTS :

1.9.1 AN INTRODUCTION :

Dyes may be classified according to either their chemical structure or method of applications. The dyes have been classified according to their chemical structure in to following types – Azo Dyes, Cationic Dyes, Anthraquinone Dyes, Vat Dyes, Sulphur Dyes, Reactive Dyes, Solvent Dyes and Miscellaneous Dyes [117-119]. Pigments can be classified as organic and inorganic, both having white and colored as subtypes.

The use of dyes for light amplification and stimulated emission of radiation (LASER) is the most important application of the organic dyes, making use of the fluorescence of the dyes. The first organic dye reported to lase is chloro-aluminium phthalocyanine, utilized by Sorokin and Lankard (1966) in their transverse ruby-laser-pumped dye lasers. Rhodamine 6G is the most successful and widely used dye. Other important dyes include coumarines, pyridinium oxazoles etc [120]. The chromic property of the dyes is of special interest. Many photochromic dyes have been used in sunglasses and other similar applications [121-122]. Electrochromic dyes such as prussian blues, phthalocyanines etc. have been used in electrochromic display devices (ECD) [123-127]. Dyes like 2,6-diphenyl-4-(2,4,6-triphenylpyridinio) phenolate (DTPP) and cresol red which displays thermochromic behavior can be used as a visual indication of the temperature [128]. Dyes like near-infrared dyes (NIR), phthalocyanines, prussian blues have been studied for their sensing behavior/characteristics towards various gases and chemical vapors like ammonia, nitrogen-di-oxide (NO_2), alcoholic vapors etc. [129-140].

1.9.2 DYES FOR SENSITIZATION OF PHOTOCONDUCTIVITY :

Dyes and pigments have been widely used as photosensitizers. Photosensitization is the process which increases the light sensitivity of a photosensitive system or in some cases renders light sensitive an insensitive one. Dyes have been used as photosensitizers in many physical effects like photogeneration of charge carrier production and photosensitization of luminescence as well as in many chemical effects like photosensitization of oxidation (i.e. oxygen transfer or hydrogen abstraction), photosensitization of polymerization or for polymer cross-linking. Adsorption of the

molecular dye to the surface of wide band gap semiconductors can result in the sensitization of the semiconductors to visible light. Such sensitization processes are the basis and used in color photography. Dyes and pigments have also been used as sensitizers in many photosensitized reactions of biological importance [141].

Sr. No	Dye	Polymer	Ref. No.
1.	Squaraines	Poly methyl methacrylate, Poly styrene	142
2.	Malachite Green	Poly methyl methacrylate (PMMA)	143
3.	Chlorophyll	Poly copper phenyl acetylenide	144
4.	Pynacyanol	Poly N-vinyl carbozole (PVK)	144
5.	Methylene Blue	Poly copper organo acetylenides e.g. Poly copper phenyl acetylenide Poly N-vinyl carbozole (PVK), Poly methyl methacrylate (PMMA), Poly styrene, PVDF etc.	144
7.	Rhodamine B		
8.	Carbo and Pentacyanines		
9.	Erythrosin		
10.	Rose Bengal		
11.	Chlorophyll		
12.	Phthalocyanines		
13.	Hematin		

Table 1.1 : Different dyes used as photosensitizers for polymers.

1.9.3 DYES USED AS PHOTSENSITIZERS FOR POLYMERS :

Dyes have also been used as photosensitizers for polymers, particularly insulating polymers. Different types of dyes such as cationic, anionic, neutral were employed as photosensitizers for different polymers. Some of them have been listed in Table (1.1). One of the most important applications of such dye sensitized photoconducting polymers is in Xerography. Poly vinyl carbazole (PVK-TNF system in particular) have attracted much attention and is one of the thoroughly studied materials [142-144].

1.9.4 MODELS PROPOSED FOR DYE SENSITIZATION :

The following important observations were made in the earlier studies and models proposed on dye sensitization in semiconductors such as TiO_2 , ZnO , CdS etc. and insulating polymers like PMMA, PVK, PVDF etc. [145-148] -

- The material which is to be used as a sensitizer (i.e. dye) should absorb in the spectral region different from that of the material to be sensitized.
- Trapping of the minority carriers from the material to be sensitized is very important which in turn increases the free majority carrier concentration [145].
- No marked difference is observed between dyes of different types (i.e. oxidants and reductants) [146].
- The sensitization efficiency does not depend upon the presence of the photoconductivity in the solid sensitizer itself, nor on the sign of the photocarriers [146].
- The optimum photosensitization is observed at a cover age less than monomolecular of the semiconductor surface [146].

- The aggregation of dyes on the semiconductor surface is observed to play an important role in the dye sensitization processes. Some dyes show supersensitizing character in the presence of J-aggregation on the semiconductor surface [147].
- Local electronic levels of a semiconductor play an important role in the sensitization processes [148].
- The adsorption of different dyes on the semiconductor surface either enhances or quenches the photosensitivity depending upon the type of the dye and the semiconductor surface [148].

It can be observed that most of the dye sensitization work in polymers earlier is on the insulating polymers. Many of them do not absorb in the visible region and possess low number of free charge carriers. Also, the mobility of the charge carriers is low. Dye sensitization effects in case of conducting polymers is not yet fully disclosed and such study is quite interesting as most of the conducting polymers absorb in the visible region. Also, the free charge carriers and their mobility are quite high as compared to the insulating polymers. Hence, in order to know the photosensitization effect in conducting polymers such as polypyrrole (Ppy) and polyaniline (PANI), the present work has been undertaken in which different types of dyes such as Prussian blue (PB), methylene blue (MB), crystal violet (CRV), rhodamine B (RB), rhodamine 6G (R6G), possessing different optical properties and hence electronic structure, different optical absorption coefficients, different types (n- and p-type) were used. Their effect on the doped and undoped state of the conducting polymers has also been proposed to investigate. Also, the

study is aimed to investigate the important factors that govern the sensitization effect in conducting polymers and to propose a model for the same.

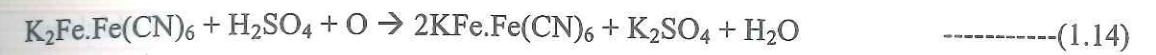
1.10 DYES USED IN PRESENT STUDY :

As, mentioned earlier, Prussian blue (PB), methylene blue (MB), crystal violet (CRV), rhodamine B (RB), rhodamine 6G (R6G) dyes have been used as photosensitizers for conducting polypyrrole (Ppy) and polyaniline (PANI). This section gives a brief introduction to each dye used in present study and its important known physico-chemical properties.

1.10.1 PRUSSIAN BLUE (PB) :

The Prussian Blue (PB) series of pigments, of which the first example was made by Diesbach in 1704, are still of importance. Much experimental work has been carried out to determine their structure, and they are now usually represented by the formula $MFe.Fe(CN)_6.xH_2O$, where M is the ion of an alkali metal or ammonium. They may be regarded equally correctly as alkali metal ferric ferrocyanides or ferro-ferricyanides. The potassium compounds are generally preferred, but sodium ammonium blues are often used because of their low cost. Although they contain carbon, these pigments are usually classified as inorganic. PB do not dissolve in water and weak acids.

Prussian Blues are manufactured by reaction of ferrous sulphate with potassium ferrocyanide to give a 'white paste', and this is then oxidized by acid potassium dichromate to give the blue pigment :



There are many commercial brands (CI Pigment Blue 27; CI 77510, CI 77520), giving clear blue shades with a bronze effect in full shades. They have excellent fastness to light, and withstand temperatures up to 120 °C, but are sensitive to alkali. It is not attacked by acids but decomposed by alkalis in to brown oxide of iron [149].

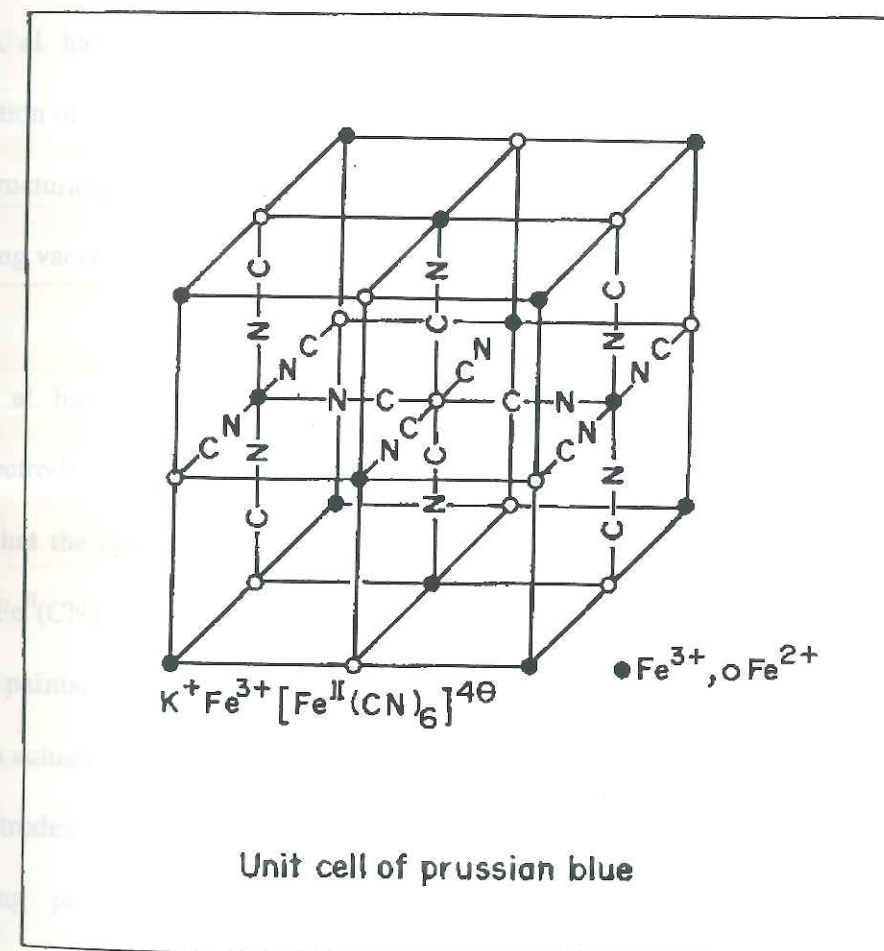


Figure (1.10) : crystal structure of PB

As is well known, there are two proposed formulas of PB, which have been called "water insoluble PB" ($\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$) and "water soluble PB" ($\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$). This pigment is an iron (III) hexacyanoferrate (II). The crystal structure of PB originally proposed by Keggin and Miles is the cubic face-centered type, with a lattice constant of about 10°A , indicating a very roomy crystal structure. PB has been known as a zeolite with channel diameters of about 3.2°A . Figure (1.10) represents the crystal structure of PB. In the case of "water insoluble PB" ($\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$), the model proposed that the two fourfold positions, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ were occupied by the required number, $4/3$, of Fe^{III} . Ludi et. al. have proposed a new modified structure of PB analogues that discards the assumption of the existence of interstitial Fe^{III} . A recent paper has proved the existence of two structurally distinguishable water molecules by a neutron diffraction study, indicating vacancies of $\text{Fe}^{\text{II}}(\text{CN})_6$ [150-153].

Neff et. al. has presented a method of preparation of thin films of PB on platinum and gold electrodes and demonstrated the redox behavior of PB [154-155]. It has been also shown that the chemical reduction and the oxidation of PB can lead to Prussian white ($\text{K}_2\text{Fe}^{\text{II}}.\text{Fe}^{\text{II}}(\text{CN})_6$) and Prussian Green / Berlin Green ($\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$). Prussian blues are used in paints, printing inks, lacquers, linoleum and leather cloth; a 'soluble' version which is actually a fine dispersion is used for coloring the paper. It has been shown that the electrodes modified with PB and other cyanometalate compounds exhibits many interesting properties that make them potentially applicable in areas such as electrochromism, catalysis, photosensing devices, energy storage and ion-selecting sensors [149-155].

1.10.2 METHYLENE BLUE (MB) :

Methylene blue, a redox dye, (MB, CI Basic Blue 9, CI Solvent Blue 8 ; CI 52015) is one of the most important cationic (thiazine) dye. It is discovered by Caro in 1876 and has the structure as shown in Figure (1.11). It was originally obtained by ferric chloride oxidation of N,N-dimethyl-p-phenylenediamine in presence of hydrogen sulphide, but the commercial process developed later by Bernthsen consists in oxidation of the same intermediate by means of acid dichromate in presence of sodium thiosulphate, condensing the resulting 4-(dimethylamino)aniline-2-thiosulphonic acid with dimethylaniline to form an indamine, and oxidizing by dichromate and copper sulphate to yield Methylene Blue [156].

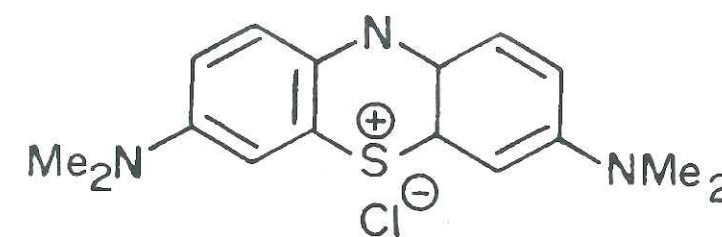


Figure (1.11) : Chemical structure of methylene blue

Methylene blue (MB) shows an interesting photochromism. It exists in two stable forms : a colorless (leuco) reduced form and colored oxidized form of the dye itself which are interconvertible by a photochemically induced two-electron redox reaction as shown in Figure (1.12).

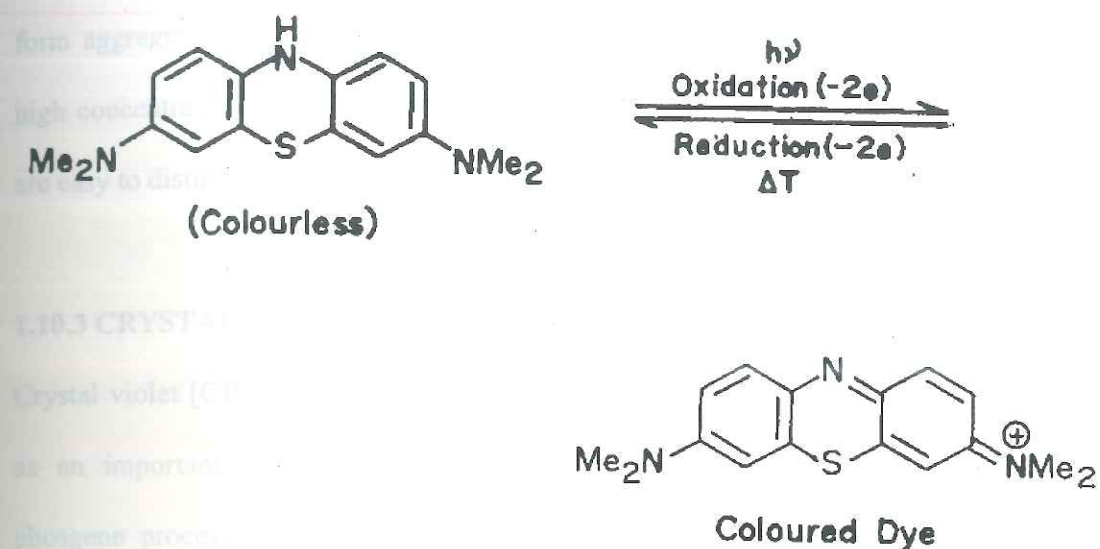


Figure (1.12) : Photochromism in methylene blue

The forward reaction involves absorption of a photon by the colorless form, which in its excited state can be oxidized to the normal or colored form of the dye. The reverse or thermal process, in the absence of radiation, involves the reduction back to the colorless form. An advantage of this system is that the dye has a high extinction coefficient and a small amount of photo-oxidation results in a large change in optical density. The rates of forward and backward reactions and the intensity of the colored produced depend upon the temperature, pH, concentration of the dye, reducing and oxidizing agent and the matrix or solvent used for the system. It is frequently used as a photosensitizer in free radical polymerizations. Also, the use of MB as a polymerization inhibitor of several vinyl monomers has been reported in several patents and research papers. A short review on the use of MB as a redox stabilizer has been published recently. Haines and Waters

observed that MB is reversibly decolorized by α -cyano alkyl radicals. MB is reported to form aggregates. The dimerization of the MB in aqueous solutions occurs at relatively high concentrations (dimerization constant : $4.71 \times 10^3 \text{ M}^{-1}$). Monomers and dimers are easy to distinguish by UV-VIS spectroscopy [157–161].

1.10.3 CRYSTAL VIOLET (CV) :

Crystal violet [CRV, chemical structure shown in Figure (1.13)] has been manufactured as an important cationic dye by phosgene, carbinol and aldehyde processes. The phosgene process is as follows – reaction of N,N-dimethylaniline with phosgene in presence of zinc chloride yields 4,4-bis(dimethylamino)-benzophenone (Michler's ketone), and this may be condensed with a further molecule of dimethylaniline (or another base) to yield a rosaniline base [162].

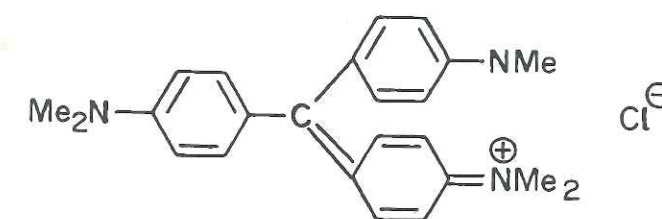


Figure (1.13) : Chemical structure of crystal violet.

Crystal violet is used for trace elemental detection and has been incorporated in polymers such as Nafion for optical humidity detection. CRV is known to be a n-type dye. [163 168].

1.10.4 RHODAMINE B (RB) AND RHODAMINE 6G (R6G) :

Rhodamine dyes have been classified under xanthene dyes. The first and the most important member of this class is the rhodamine B (RB, CI Basic Violet 10; CI 45170). Figure (1.14) represents the chemical structure of rhodamine B. It is obtained by condensing phthalic anhydride with m-diethylaminophenol. Rhodamine dyes can be applied to mordanted cotton as well as to silk. The shades on silk are bright, bluish red, with a strong fluorescence. These dyes have a good fastness to light. Rhodamine dyes are distinguished by a high quantum yield of fluorescence and high photostability. Owing to these characteristics, these dyes are often used for widespread applications, e.g. single molecule detection, fluorescence labeling, dye lasers etc. Rhodamine B (RB) shows great sensitivity to the solvent environment (varied pH) because of the number of possible molecular forms, such as zwitterionic, cationic, and lactone. The photophysical properties of RB depend not only on the solvent polarity but also on the solvent viscosity [169-172]. Rhodamine 6G is an analog of rhodamine B. RB and R6G, both are known to be n-type dyes.

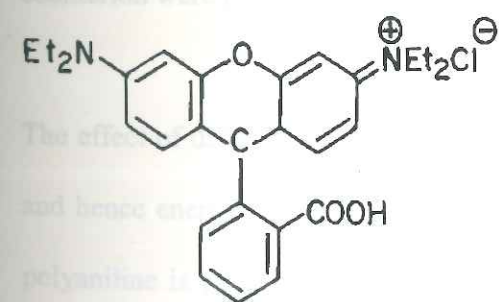
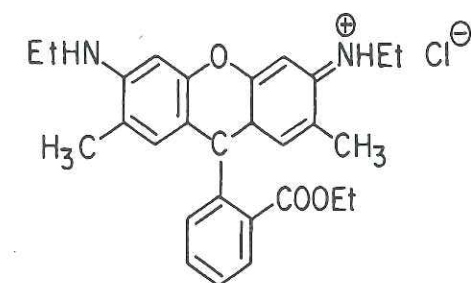


Figure (1.14) : Chemical Strycture of RB



Structure of Rhodamine 6G. (Et $\equiv$ C₂H₅)

Figure (1.15) : Chemical Structure of R6G

1.11 AIM AND SCOPE OF THE PRESENT WORK

As discussed earlier in this chapter, dyes and pigments have been used as sensitizers for improvement of various properties such as photoconductivity, electrochromism, photoelectrochemical response, photovoltaic effect etc. of inorganic semiconductors as well as for insulating polymers. But their response with conducting polymers is not yet fully known. Hence, it is very interesting to carry out studies on the dye sensitization effects in conducting polymers. The aim of the present work undertaken is to investigate the optoelectronic properties particularly electrochromism and the photosensitivity (to visible light) of the conducting polypyrrole and polyaniline sensitized with organic dyes and pigments. This will lead to better understanding of the important parameters which govern the dye sensitization process in conducting polymers. The aim of the present work undertaken is to propose a model for dye sensitization in conducting polymers.

In the study of electrochromic properties of dye sensitized conducting polymers, study of contrast in different electrolytes, with different film thickness and the effect of size of the counterion were planned to investigate.

The effect of different types of dyes (i.e. p- or n-type, having different optical properties and hence energy band diagrams) on the photosensitivity of conducting polypyrrole and polyaniline is planned to study by preparing the sandwich type photocells between the gold and ITO electrodes and using conducting polymer and the dye incorporated in solid polymer electrolyte (SPE) and studying its photoresponse in dark and under white light illumination. The dyes used in present study were carefully chosen so that their

combination with conducting polymers can represent the behavior of similar dyes and pigments and overall conclusions about the dye sensitization in conducting polymers can be drawn. Studies were planned so as to know whether the sensitization effect depends upon the matrix in which the dye has been incorporated, the doped / undoped state of the conducting polymer and whether a dye sensitizes different conducting polymers to the same extent. It is also proposed to study the charge transport mechanism in such dye sensitized conducting polymer films, since it can be the rate determining factor for such processes along with study of all other physico-chemical characterization in order to understand the systems well. Studies were also planned to know whether the dye sensitizes conducting polymer when used in photoelectrochemical (PEC) cell configuration.

2.1 INTRODUCTION

The theoretical aspects

presented in this

polymerization of

as the process for

experimental procedure

fabrication of the

technique etc. The

study the prepared

XRD, TGA/DTA

measurement of

photoresponse in

chapter.

CHAPTER 2

2.2 MATERIALS

The following materials

Sr.	Name
No.	
1	Pyromellitic
2	Aniline

CHAPTER 2

EXPERIMENTAL

2.1 INTRODUCTION :

The theoretical aspects related to the present work and literature review have been presented in the previous chapter. On the basis of this, the electrochemical polymerization of polypyrrole (Ppy) on preconditioned substrates/electrodes was chosen as the process for depositing the conducting polypyrrole film. This chapter describes the experimental procedure and methodology employed such as the materials used, fabrication of the films, details of depositing dyes incorporated SPE films by dip-coating technique etc. The chapter also describes various characterization techniques used to study the prepared materials such as UV-VIS spectroscopy, FTIR, cyclic voltammetry, XRD, TG/DTA/DTG, DSC, SEM, optical polarizing microscopy, ESCA etc. The measurement of electrical properties, I-V characteristics in dark and light, study of photoresponse in photoelectrochemical (PEC) mode have also been discussed in this chapter.

2.2 MATERIALS USED :

The following table gives the list of the materials used in the present study.

Sr. No.	Name of the Chemical	Acronym	Source	Purity (%)
1	Pyrrole	-	Aldrich, USA	99
2	Aniline	-	Thomas Baker, India	99

3	Poly (vinyl alcohol)	PVA	Loba Chemie, India	97
4	Poly (vinyl pyrrolidone)	PVP	Loba Chemie, India	97
5	Poly (vinyl butral)	PVB	Loba Chemie, India	97
6	Prussian Blue	PB	Aldrich, USA	98
7	Methylene Blue	MB	Thomas Baker, India	97
8	Crystal Violet	CRV	Thomas Baker, India	90
9	Rhodamine B	RB	Loba Chemie, India	97
10	Rhodamine 6G	R6G	Loba Chemie, India	97
11	Phosphoric acid	H ₃ PO ₄	Qualigens, India	
12	Hydrochloric acid	HCl	Qualigens, India	36

2.3 SAMPLE PREPARATION :

2.3.1 PREPARATION OF GOLD ELECTRODES :

The glass substrates on which the gold electrodes were to be deposited cleaned properly using acetone. 0.5 gm of polyvinyl butral (PVB) is dissolved in 100 ml methanol and a film is coated on these glass substrates by simple dip-coating method. The film gets deposited on both the sides of the glass substrate. The film at the back is carefully removed. The film is first dried at room temperature and then heated at about 50 °C for about 10 min so that the film gets dried thoroughly. The film becomes transparent from milky white after heat treatment. These PVB coated glass substrates were used for deposition of gold films. The backing PVB layer improves the adhesion of the gold film on the substrate. Gold films were deposited on these substrates by using 0.22 gm of gold. The gold is resistively heated in the vacuum evaporation unit (Hind High Vacuum, Model

12A 4D) at 10^{-6} torr and hence gets first melted and then gets evaporated to form a highly conducting film on the substrates which were kept at a distance of about 10 cm from the evaporator. A copper wire is attached to these gold electrodes by using silver paint / paste and the substrates were used for electrochemical deposition of the conducting Ppy, PANI and PB films.

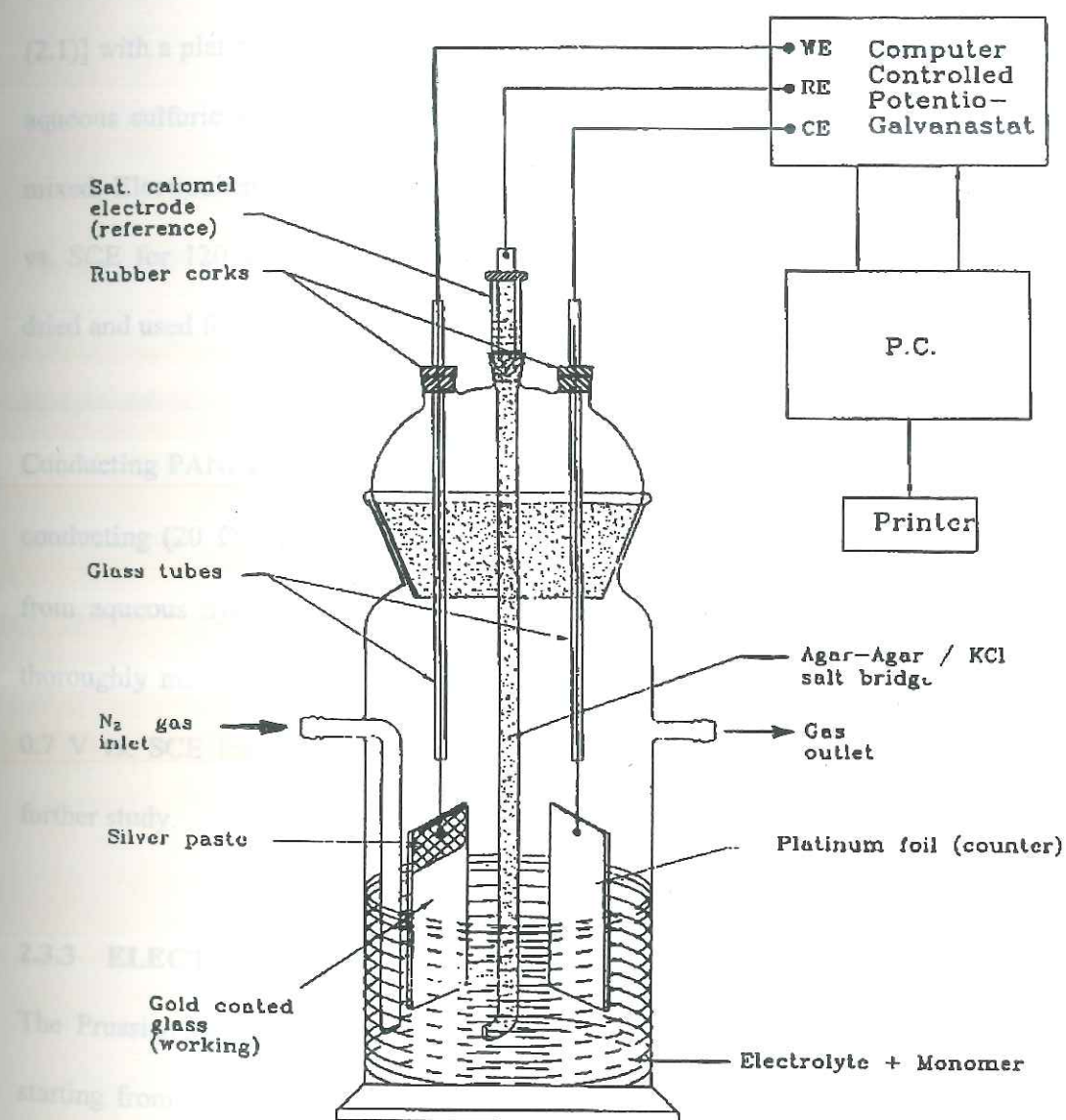


Figure (2.1) : Computer controlled electrochemical cell.

2.3.2 ELECTROCHEMICAL DEPOSITION OF POLYPYRROLE AND POLYANILINE FILMS ON GOLD ELECTRODES :

Conducting Ppy films were deposited on gold coated glass and also on the transparent conducting ($20 \Omega / \text{sq}$) indium-tin-oxide electrode (ITO) electrodes by conventional potentiostatic technique, using a single compartment electrolytic cell [as shown in Figure (2.1)] with a platinum counter electrode, saturated calomel reference electrode (SCE) and aqueous sulfuric acid (0.1 M) in which the pyrrole monomer (0.1 M) was thoroughly mixed. Electrochemical polymerization was carried out at a constant potential of 0.7 V vs. SCE for 120 s when greenish-blue Ppy films were obtained, which were washed, dried and used for further studies.

Conducting PANI films were deposited on gold coated glass and also on the transparent conducting ($20 \Omega/\text{sq}$) ITO electrodes in the same manner as that of Ppy films starting from aqueous hydrochloric acid (0.5 M) in which the aniline monomer (0.1 M) was thoroughly mixed. Electrochemical polymerization was carried out potentiostatically at 0.7 V vs. SCE for 150 s. The PANI films obtained were washed, dried and used for further study.

2.3.3 ELECTRO-DEPOSITION OF PRUSSIAN BLUE FILMS :

The Prussian blue (PB) films of different thickness were deposited electrochemically starting from 0.002 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ aqueous solutions, on the electrochemically deposited Ppy films, by applying a constant potential of 0.5 V vs. SCE. The PB films were also deposited under identical conditions on the transparent

conducting ($20 \Omega/\text{sq}$) ITO electrodes and the UV-VIS spectra of these films were recorded using Shimadzu UV-240 spectrophotometer. The PB film thickness were estimated from the value of the optical density (O.D) and using Beer-Lambert's relation and taking into account the standard reported value of the absorption coefficient (9800 cm^{-1}) for PB. It ranged from 200 to 800 nm depending upon the deposition time.

2.3.4 DEPOSITION OF DYE INCORPORATED SPE FILMS ON CONDUCTING POLYPYRROLE AND POLYANILINE FILMS :

The electrochemically deposited Ppy and/or PANI films on gold coated glass electrodes were subsequently dip-coated with poly vinyl alcohol (M.W. 10^4) or poly vinyl pyrrolidone (PVP, M.W. 10^4) films containing phosphoric acid (1:1) from aqueous solution (1 wt %) containing different dyes in the concentration range of 0 to 15 mM/monomer. These were then dried at room temperature and presses against a transparent conducting ($20 \Omega/\text{sq}$) ITO electrodes so as to form the sandwich cell configurations Au/Ppy (or PANI)/SPE+dye/ITO.

Figure (2.2) : Dye
the samples.

2.4 STUDY OF ELECTRICAL PROPERTIES :

2.4.1 CURRENT-VOLTAGE CHARACTERISTICS IN DARK AND LIGHT :

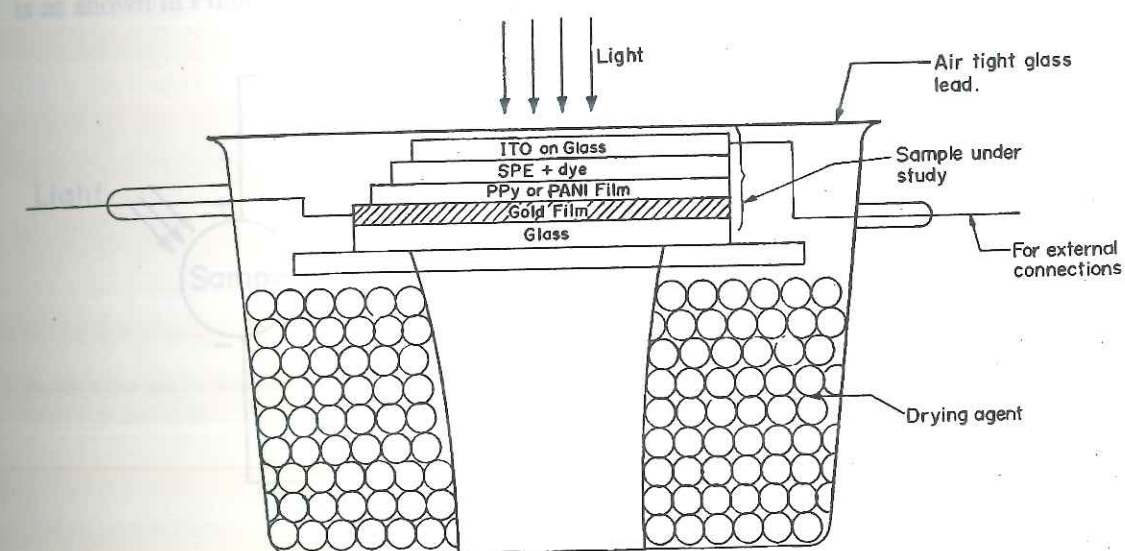
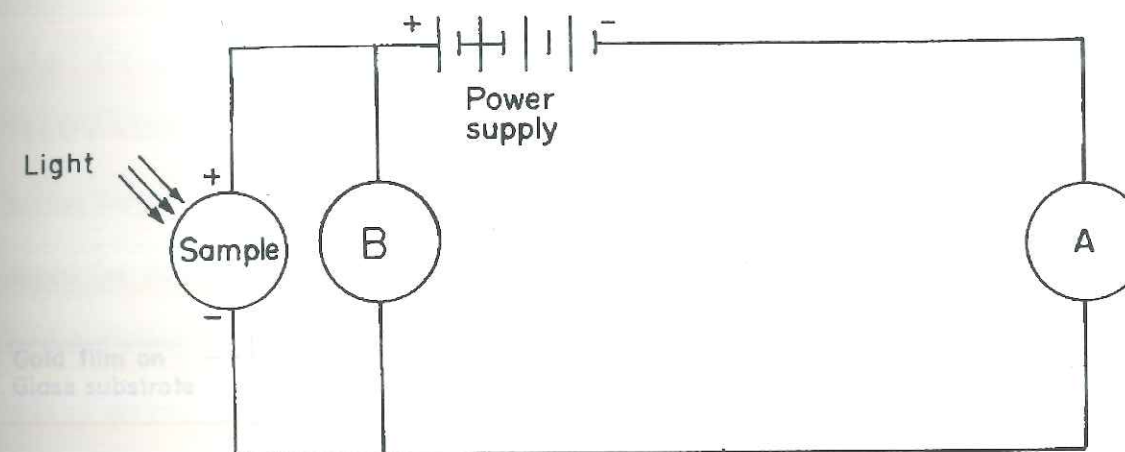


Figure (2.2) : Dry box employed for studying the current - voltage (I-V) characteristics of the samples.

The I-V characteristics of the photocells in sandwich cell configuration were carried out in dark and under white light illumination (5.0 mW/cm^2 , tungsten lamp source) in the dry cell / box prepared as shown in Figure (2.2). The current values were recorded instantaneously after applying the voltage. The reading were taken at room temperature. The circuit employed for measuring the I-V characteristics in dark and under illumination is as shown in Figure (2.3).



A: Keithley Electrometer, B : Digital Voltmeter

Figure (2.3) : Circuit diagram for studying the I-V characteristics of the various photocells prepared in dark and under illumination.

2.4.2 CYCLIC VOLTAMMETRY :

Cyclic voltammetry studies of the Ppy and PB films and the Ppy/PB composite films were carried out using different electrolytes such as KCl, LiClO_4 , KI/I_2 , K_2SO_4 , K_2CO_3 etc. at the scan rate of 50 mV/s . The electrochromic contrast of the Ppy and PB sensitized Ppy films were studied by depositing Ppy films and the Ppy/PB films of varying thickness of PB on the transparent ITO electrodes and recording the UV-VIS spectra in the oxidized and reduced states. The contrast was estimated by taking the

difference in the optical density (O.D) values in the two cases and plotting the same as a function of the wavelength. This was carried out for all the electrolytes mentioned above, taking care that the fresh samples were used in each case.

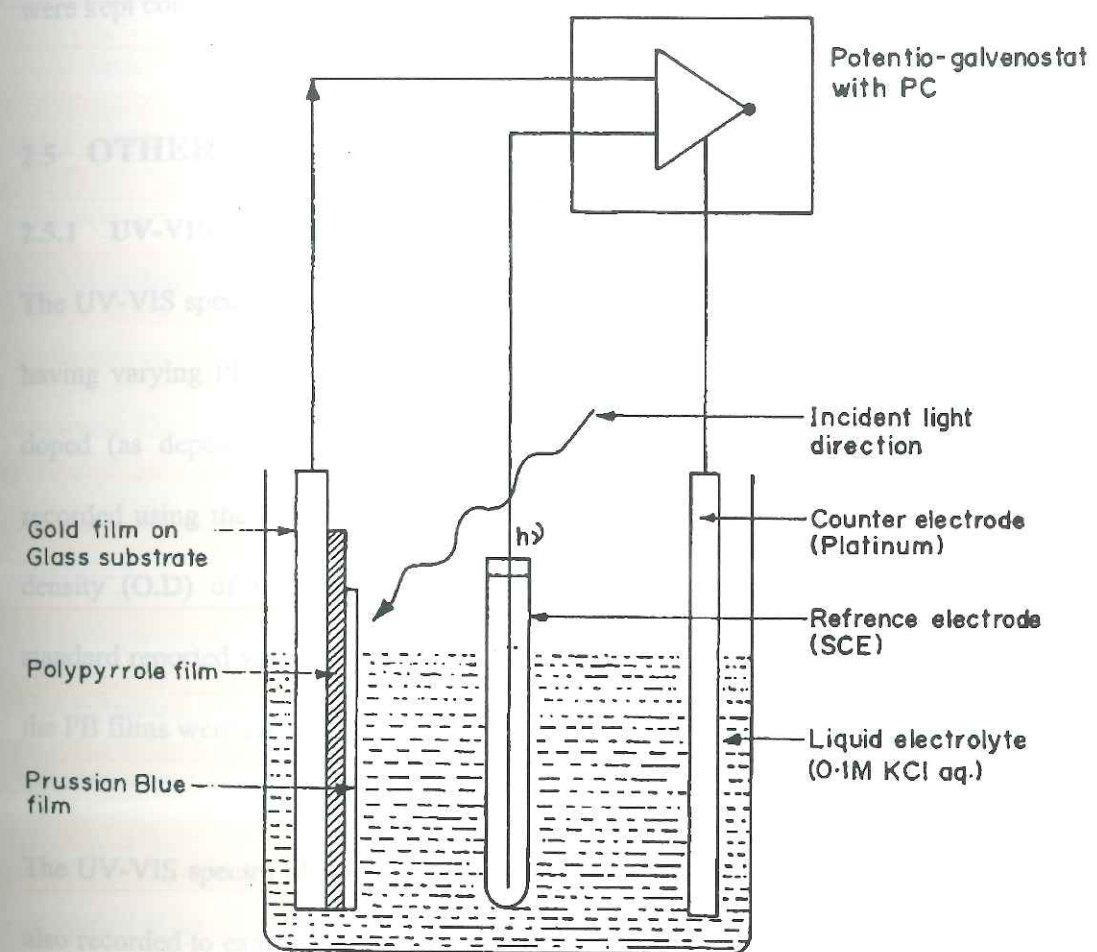


Figure (2.4) : Schematics of the photoelectrochemical (PEC) cell prepared using Ppy/PB composites films and aqueous liquid electrolyte.

The photosensitivity of Ppy and Ppy/PB composite films were studied in photoelectrochemical (PEC) mode using different aqueous electrolytes such as KCl, LiClO_4 etc. using the single compartment electrochemical cell as shown in Figure (2.4).

The direction of the light incident is perpendicular to the sample surface. Cyclic voltammograms were recorded in dark and under white light illumination. The other parameters such as scan rate (50 mV/s), molar concentration of the liquid electrolyte etc. were kept constant throughout the experiment.

2.5 OTHER CHARACTERIZATION METHODS USED :

2.5.1 UV-VIS SPECTROSCOPY :

The UV-VIS spectra of the Ppy film, PB films of various thickness, Ppy/PB bilayer films having varying PB film thickness - deposited on ITO by electrochemical method in the doped (as deposited, oxidized state) and in the undoped state (reduced state) were recorded using the Shimadzu UV-240 spectrophotometer. From the value of the optical density (O.D) of the PB electrodeposited films of varying thickness and using the standard reported value of the optical absorption coefficient (9800 cm^{-1}), the thickness of the PB films were calculated by using the Beer-Lambert's relation.

The UV-VIS spectra of the dye doped SPE films deposited on glass by dip-coating were also recorded to examine whether the dye changes its optical properties in the SPE, forms an aggregates, forms a charge transfer complex, splitting of the ground state (i.e. singlet state into a triplet) due to the interaction with the matrix etc.

2.5.2 FOURIER TRANSFORMED INFRA-RED SPECTROSCOPY :

FTIR studies were carried out on the free standing film of PVA, MB in KBr and MB incorporated in PVA free standing film in order to confirm the formation of a complex

between the polymer matrix and the dye. The free standing films and the KBr pallet having dye were mounted on the IR cell in the conventional way to record the FTIR spectrum in using Perkin Elmer -model 1600. The characteristic absorption bands were tabulated and compared with known data.

2.5.3 OPTICAL POLARIZING MICROSCOPY :

The structural and morphological details of the samples prepared were observed using an optical polarizing microscope (12 POL, Leitz, Germany). The microscope also had photomicrograph attachment with the help of which micrographs of various films were obtained. The magnification of 40, 100, 200 and 320 objectives were employed and total magnification after enlargement was calculated using graticules and standard calibration procedure.

The formation of dye aggregation and increase in the aggregate/particulate size with the PB concentration was noticed using optical polarizing microscope. This technique was also used in order to prove that the other dyes (i.e. MB, CV, RB, R6G) when incorporated in SPE does not present in an aggregated form (at least in the region of concentrations of our interest).

2.5.4 SCANNING ELECTRON MICROSCOPY :

To understand the changes in the surface morphology of the electrochemically deposited polymer films when they are electrochemically switched from oxidized to reduced state, the samples were studied with the scanning electron microscopy (SEM) Leica Stereoscan

440 Model manufactured by M/s Leica Cambridge Ltd. UK. The samples were mounted on the standard specimen mounting stubs by using conducting silver paste. The samples were coated with a thin layer of gold in Polaron coating unit E5000 to prevent the charging of the sample. For comparative study, the electron beam parameters were kept constant while analyzing all the samples. The micrographs of the samples with 20 KV and 25 pA beam current were recorded by 35 mm camera attached on the high resolution recording unit. The details of the samples such as sample name, magnification etc. is also written on the respective SEM micrographs.

2.5.5 X-RAY DIFFRACTION STUDIES :

The XRD of various dyes were taken in order to know whether they have crystalline structure. The presence and / or absence of dye aggregation in SPE films were studied using wide angle x-ray diffractometer (Phillips PW 1730) having Cu K_α source and Ni filter.

2.5.6 TG/DTA/DTG AND DSC STUDIES :

Thermal analysis (i.e. TG/DTA/DTG and DSC) were carried out on the dye (particularly MB), PVA, PVA+H₃PO₄, PVA+dye, PVA+H₃PO₄+dye in order to know how the incorporation of the dye affects the thermal properties of the SPE. Information about the glass transition temperature (T_g) of the polymer and polymer / dye composites, thermal stability, degradation processes were obtained from these studies. The studies were made on a Mettler Toledo Star[®] system.

2.5.7 X-RAY PHOTOELECTRON SPECTROSCOPY OR ESCA STUDIES :

X-ray photoelectron spectroscopy (XPS) studies of the PB films before and after cycling in liquid electrolyte (i.e. on the as-deposited films and the reduced films) were carried out on a V. G. Scientific ESCA-3-MK-2 electron spectrometer with an Mg-K α X-ray source (non-monochromatic). For the present measurements, the anode was operated at 140 W (14 kW, 10 mA) and the analyzer was operated at a constant pass energy of 50 eV. All the spectra were recorded with similar spectroscopic parameters. The binding energy (B.E) scale was calibrated by determining the B.E of Au4f_{7/2} (84 eV), Ag3d_{3/2} (368.4 eV) and Cu2p_{3/2} (932.4 eV) levels using spectroscopically pure metals from Johnson-Matthey, London. The binding energy value (measured to an accuracy of 0.2 eV) are in good agreement with the literature values. The resolution in terms of the full width at half maximum (FWHM) of the Au4f_{7/2} level is 1.6 eV.

OPTO POLY

1.1 INTRODUCTION

Russian blue (PB1)

paints, lacquers, pigments

General formula: $\text{Fe}^{III}(\text{OH})_2$

They may be regarded

as ferricyanides. A hexacyano

ferrous ion to the hexacyano

ferrous ion to the hexacyano

ferrous ion to the hexacyano

ferrous ion to the hexacyano

CHAPTER 3

There are two well-known

soluble PB²⁺ (Fe^{II}_2)₃

an iron (III) hexacyano

ferrous ion to the hexacyano

ferrous ion to the hexacyano

ferrous ion to the hexacyano

ferrous ion to the hexacyano

ferrous ion to the hexacyano

ferrous ion to the hexacyano

CHAPTER 3

OPTOELECTRONIC PROPERTIES OF CONDUCTING POLYPYRROLE SENSITIZED WITH PRUSSIAN BLUE

3.1 INTRODUCTION :

Prussian blue (PB) has been manufactured as an important inorganic pigment for use in paints, lacquers, printing inks, and other color uses. They are usually represented by the general formula $MFe_3(CN)_6 \cdot xH_2O$, where M is ammonium or an alkali metal ion. They may be regarded equally correctly as alkali metal ferric ferrocyanides or ferrocyanides. A high spin ferric ion is coupled to a low spin ferrous ion by a cyanide bridge $Fe(III)-N \equiv C-Fe(II)$, i.e. the first ferric ion is coupled to the nitrogen and second ferrous ion to the carbon. The potassium compounds are generally preferred, but sodium ammonium blues are often used because of their low cost. Although, they contain carbon, these pigments are usually classified as inorganic [1] rather than organic.

There are two well characterized formulas of PB, which have been called "water insoluble PB" ($Fe^{III}_4[Fe^{II}(CN)_6]_3$) and "water soluble PB" ($KFe^{III}Fe^{II}(CN)_6$). This pigment is an iron (III) hexacyanoferrate (II). The crystal structure of PB originally proposed by Keggin and Miles [2] is the cubic face-centered type, with a lattice constant of about 10 °Å, indicating a very roomy crystal structure which is similar to a zeolite with a channel diameters of about 3.2 °Å. In case of "water insoluble PB" ($Fe^{III}_4[Fe^{II}(CN)_6]_3$), it is proposed that the two fourfold positions ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) and ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$) are occupied by the required number, 4/3, of Fe^{III} . Ludi et al [3] have proposed a new modified structure of PB analogues that discards the assumption of the existence of interstitial Fe^{III} . A more

recent paper has proved the existence of two structurally distinguishable water molecules by a neutron diffraction study, indicating vacancies of $\text{Fe}^{\text{II}}(\text{CN})_6$ [4].

The electrochemistry of PB was not fully investigated until Neff et al. [5, 6] presented for the first time a method of preparation of thin films of PB on platinum and gold electrodes and demonstrated the redox behavior of PB. It has also been shown that the chemical reduction and oxidation of PB can lead to Prussian white ($\text{K}_2\text{Fe}^{\text{II}}.\text{Fe}^{\text{II}}(\text{CN})_6$) and Prussian green / Berlin green (PG or BG, $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$). The electrodes modified with PB and other cyanometalate compounds exhibit many interesting properties that make them potentially applicable in areas such as electrochromism [7, 8], catalysis [9, 10], photosensing devices [11], energy storage [12, 13] and ion-selecting sensors [14].

Recently, Prussian blue has been combined with number of other interesting materials such as WO_3 , conducting polymers like polyaniline etc. which were studied for their photoresponse, electrochromic and catalytic properties etc. Ikeda et al [15] have deposited the polypyrrole (Ppy) films doped with PB and studied their electrochemical properties. Ppy and PB have been codeposited by Karyakin et al [16] and studied for their possible application in catalysis. Ppy is known to show electrochromic color change from brown (oxidized state) to yellow (reduced state). Also, PB changes its color from blue to colorless on electrochemical reduction. It is thus interesting to combine these two complementary electrochromic materials and study their electrochromic properties for their possible application in electrochromic devices. Both these materials can be deposited by simple electrochemical technique on conducting substrates. In the present

work undertaken, we have combined Ppy and PB and studied their electrochemical properties in order to explore their use in electrochromic devices. Since, PB absorbs in the visible region ($\lambda_{\text{max.}} \sim 685 \text{ nm}$) with a strong absorption co-efficient (9800 cm^{-1}), we have also used it as a photosensitizer in order to improve the photosensitivity of conducting polypyrrole. The interesting results are presented in this chapter.

3.2 EXPERIMENTAL :

The Ppy/PB bilayer composite films for study of their electrochromic properties in different electrolyte were prepared by the following method. Conducting polypyrrole films were first deposited on gold coated glass and also on transparent conducting ($20 \Omega/\text{sq}$) indium-tin-oxide (ITO) electrodes by conventional potentiostatic technique as described in the chapter 2. The PB films of varying thickness were deposited electrochemically starting from $0.002 \text{ M FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $0.002 \text{ M K}_3\text{Fe}(\text{CN})_6$ aqueous solution, on the electrochemically deposited Ppy films, by applying a potential of 0.5 V vs. SCE. It is worthwhile to mention here that the Ppy films were deposited by applying a potential of 0.7 V vs. SCE and hence not likely to get affected (dedoped or otherwise) during PB deposition. The PB films of different thickness were obtained by varying the deposition time during electrochemical deposition. The Ppy film thickness (600 nm) was kept constant in all the cases. The PB films were also deposited under identical conditions on the transparent conducting ITO electrodes and the UV-VIS spectra of these films were recorded using a Shimadzu UV-240 spectrophotometer. The PB film thickness for the PB deposits were estimated from the value of the optical density (OD) using Beer-Lambert's law and taking the standard reported value of the absorption coefficient (9800

cm^{-1}) for PB [17]. The film thickness ranged from 200 to 800 nm, depending upon the deposition time.

Cyclic voltammetry studies of the Ppy and PB films and the Ppy /PB composite films were carried out using different electrolytes such as KCl, LiClO_4 , KI/I_2 , K_2SO_4 , K_2CO_3 , KNO_3 etc., using a single compartment electrolytic cell and three electrode system as described in chapter 2. The cyclic voltammograms were recorded at a scan rate of 50 mV/s. The electrochromic contrast of Ppy and PB sensitized Ppy films was studied by depositing Ppy films and Ppy/PB films of varying thickness on the transparent ITO electrodes and recording the UV-VIS spectra in oxidized and reduced states. The contrast was estimated by taking the difference in the OD values in the two cases and plotting the same as a function of wavelength. This was carried out for all the electrolytes mentioned above, taking care that fresh samples were used in each case.

Ppy/PB bilayer films having different PB film thickness (ranging from 200 to 800 nm) were deposited electrochemically on gold coated glass in the same manner as described earlier. The Ppy film thickness (600 nm) was kept constant in all the cases. These Ppy/PB bilayer films were then pressed lightly (so as to get a good mechanical-contact) against a transparent conducting ($20 \Omega/\text{sq}$) ITO electrode so as to form a sandwich cell configuration (Au/Ppy/PB/ITO). The size of the test device was 2 X 2 cm. The I-V characteristics of these Ppy/PB bilayer films were studied in dark and under white light illumination in the same manner as described in chapter 2. The values of current were noted instantaneously after applying the voltage. The investigations were carried out

under dry conditions by doing the measurements in the dry box. The photosensitivity factor ($S=I_l/I_d$ where I_l is the current in presence of light and I_d is the dark current) is calculated for different PB film thickness. The Ppy/PB bilayer films with varying PB film thickness were also studied for their light sensitivity in PEC mode. The cyclic voltammograms of such films were recorded in dark and under white light illumination using aqueous KCl and LiClO_4 as electrolytes. The photosensitivity factor was calculated for different PB film thickness.

3.3.1 ELECTRO

In order to study the effect of PB at small concentrations (0 – 4 mM/monomer), PB was dispersed in SPE (i.e. $\text{PVA}+\text{H}_3\text{PO}_4$) and placed in contact with the electrochemically deposited Ppy films on gold coated glass prepared in the same manner as described earlier in the chapter 2. The PB dispersed SPE films were deposited on top of the Ppy films by the simple dip-coating method. The Ppy/SPE+PB films were thoroughly dried at room temperature and pressed lightly against a transparent conducting ($20 \Omega/\text{sq}$) ITO electrode so as to make a sandwich cell configuration Au/Ppy/SPE+PB/ITO. The I-V characteristics of these cells were studied in dark and under white light illumination in the same manner as described in the chapter 2. The studies were made under dry conditions (i.e. by using transparent dry box - as described in chapter 2). The variation of the photosensitivity factor, V_{TFL} etc. with the PB concentration was also studied. The PB dispersed SPE films were also deposited on pre-cleaned glass by simple dip-coating method and the films were studied using UV-VIS, XRD, optical microscopy for the formation of PB aggregates.

In order to study the effect of moisture, the Au/Ppy/PVA+H₃PO₄+PB/ITO system was investigated for photosensitivity. The I-V characteristics in dark and light were recorded for this photocell in "wet state". Here, the wet state means that the Ppy films after coating with PB dispersed SPE films, air dried and directly used for further study without full drying and the drying agent in the dry box.

3.3 RESULTS AND DISCUSSION :

3.3.1 ELECTROCHROMIC PROPERTIES OF CONDUCTING POLYPYRROLE / PRUSSIAN BLUE COMPOSITE FILMS :

3.3.1.1 Study of Ppy, PB and Ppy/PB film by cyclic voltammetry :

Figure (3.1) displays the cyclic voltammograms (CV) of the Ppy, PB and Ppy/PB composite films recorded in different electrolytes such as LiClO₄ (A), KCl (B), KNO₃ (C) and K₂SO₄ (D). In all the cases, cyclic voltammogram of the Ppy film is represented by (a), PB (b) and Ppy/PB films by (c) respectively. The scan rate (50 mV/s) and other parameters were kept constant for all the cases. Figure (3.1A) depicts the cyclic voltammograms (CV) of Ppy (a), Ppy/PB composite film (c) and of PB by itself (b) all in a aqueous 0.01 M LiClO₄ solution. It can be seen that Ppy film shows one oxidation and reduction peak at about + 0.1 V and 0 V vs. SCE. PB (b) film show one oxidation peak at around 0.5 V and two reduction peaks at around + 0.58 V and - 0.375 V vs. SCE. It is apparent that the cyclic voltammogram of the Ppy/PB composite film retain the features of both Ppy and PB observed individually and the waves in the figure can be attributed to the oxidation and reduction processes given in Equation (3.1) and (3.2) as follows –

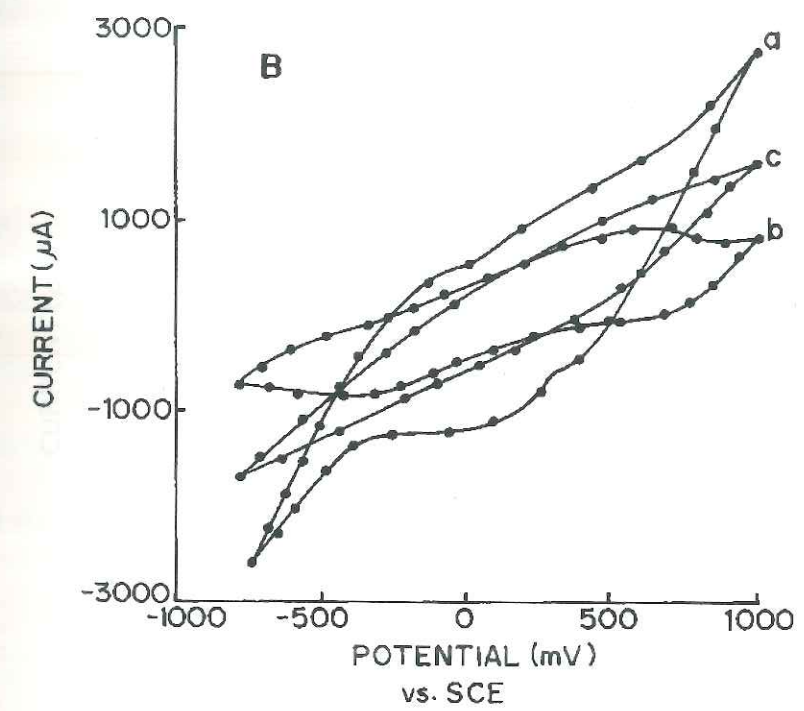
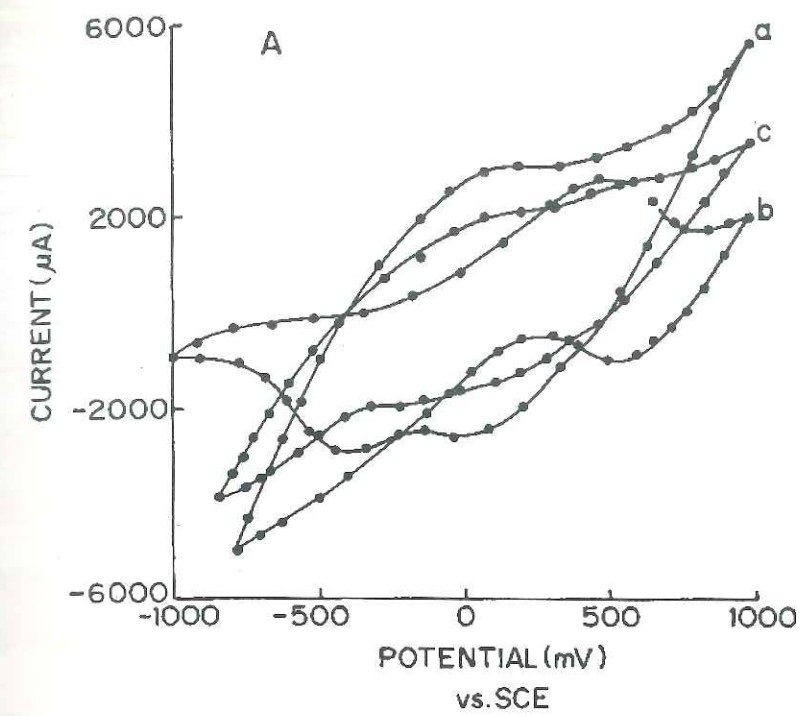


Figure (3.1) Cyclic voltammograms of different aqueous solutions are indicated as

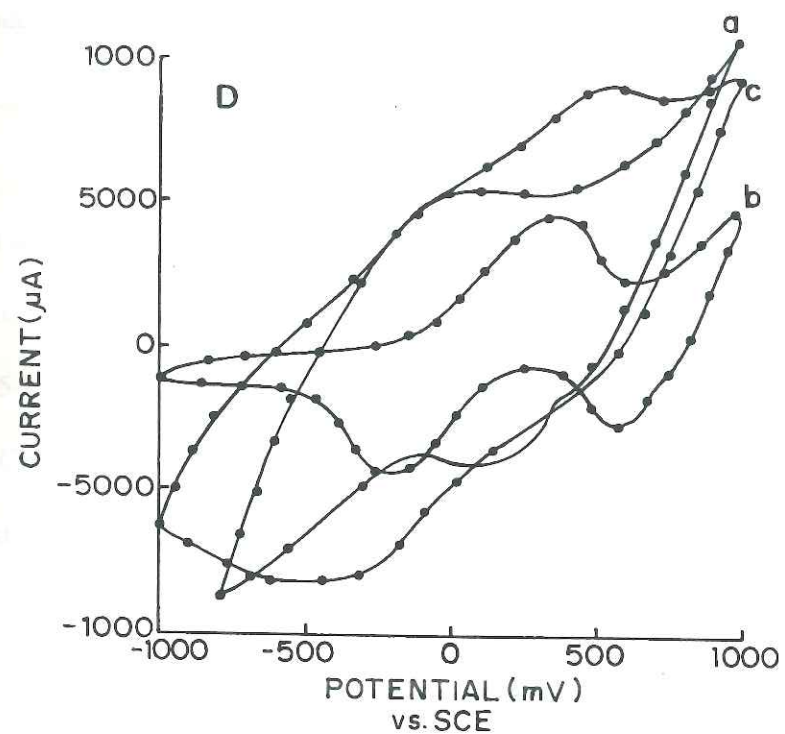
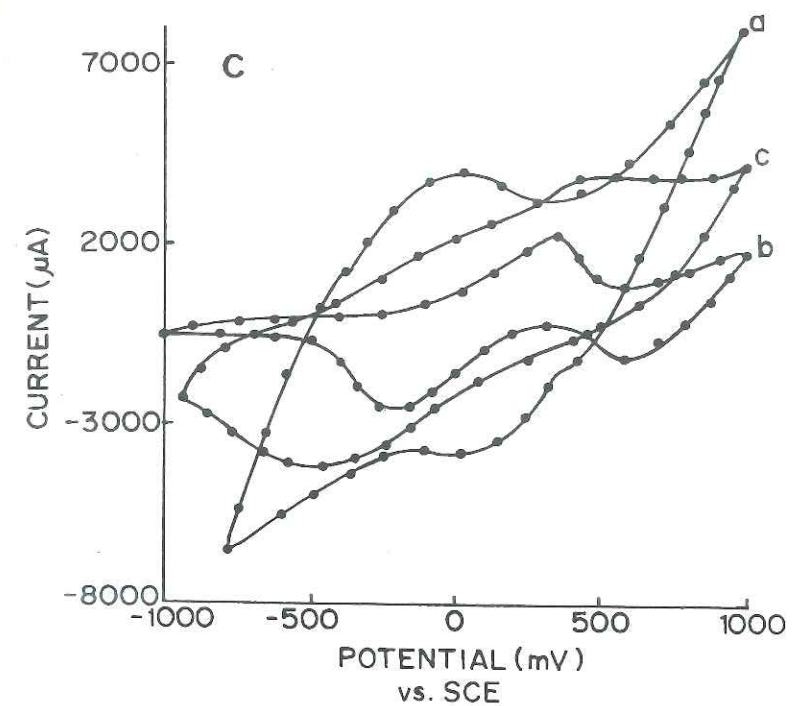
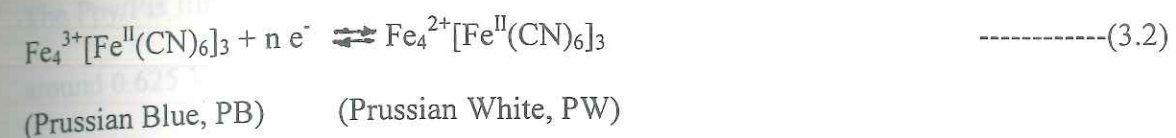


Figure (3.1) : Cyclic Voltammograms of (a) Ppy film (b) PB film and (c) PPy/PB film in different aqueous electrolytes (all 0.01 M) recorded at a scan rate of 50 mV/s. The parts are indicated as (A) LiClO₄ (B) KCl (C) KNO₃ and (D) K₂SO₄.



The ESCA studies have confirmed these processes which have been discussed later in this chapter.

It may be noted here that as compared to Ppy film, Ppy/PB composite film shows less current. The charge transfer process in PB is the homonuclear intervalence charge transfer process in which the atoms of the same element are present but on the different sites, which interacts as shown in equation (2). However, Ppy undergoes a doping and undoping process during the cyclic voltammetry which involves insertion and diffusion of ions [18].

Figure (3.1B) shows the cyclic voltammogram of the Ppy, PB and Ppy/PB films in 0.01 M aqueous KCl electrolyte. The Ppy film show one oxidation and one reduction peak at around -0.125 V and + 0.125 V vs. SCE. The PB film show one oxidation peak at around 0.657 V vs. SCE and two reduction peaks at around + 0.625 V and - 0.25 V vs. SCE. The Ppy/PB film show less current as compared to the Ppy film alone.

Figure (3.1C) shows the cyclic voltammogram of the Ppy, PB and Ppy /PB films in 0.01 M aqueous KNO₃ electrolyte. The Ppy film shows one oxidation peak at around 0.01 V and reduction peak at around + 0.7 V vs. SCE. The PB film show one oxidation peak at

around 0.375 V vs. SCE and two reduction peaks at around + 0.6 and - 0.25 V vs. SCE.

The Ppy/PB film shows one oxidation peak at around + 0.5 V and two reduction peaks at around 0.625 V and - 0.5 V vs. SCE.

Figure (3.1D) shows the cyclic voltammogram of the Ppy, PB and Ppy/PB films in 0.01 M aqueous K_2SO_4 electrolyte. Here, the Ppy film shows one oxidation peak at around - 0.1 V and one reduction peak at around + 0.25 V vs. SCE. The PB film shows one oxidation peak at around + 0.375 and two reduction peaks at around + 0.6 V and - 0.13 V vs. SCE. The Ppy/PB film shows one oxidation peak at around + 0.5 V and two reduction peaks at around + 0.5 V and - 0.25 V vs. SCE.

It can be seen that in all cases, the cyclic voltammogram (CV) of the Ppy/PB films is the result of the superimposition of the individual components and exhibit the oxidation and reduction waves arising from the individual components present but the peak height and the position depend on the actual anions present in the electrolyte. It was noted that during electrochromic cycling Ppy changed its color from dark greenish blue (in the oxidized state) to pale brown/yellow, and PB from blue to bleached transparent white state (when reduced). However, the Ppy/PB films changed its color from bluish green (in the oxidized state) to pale brown (in the reduced state).

3.3.1.2 Effect of PB film thickness on the electrochromic contrast of Ppy/PB films :

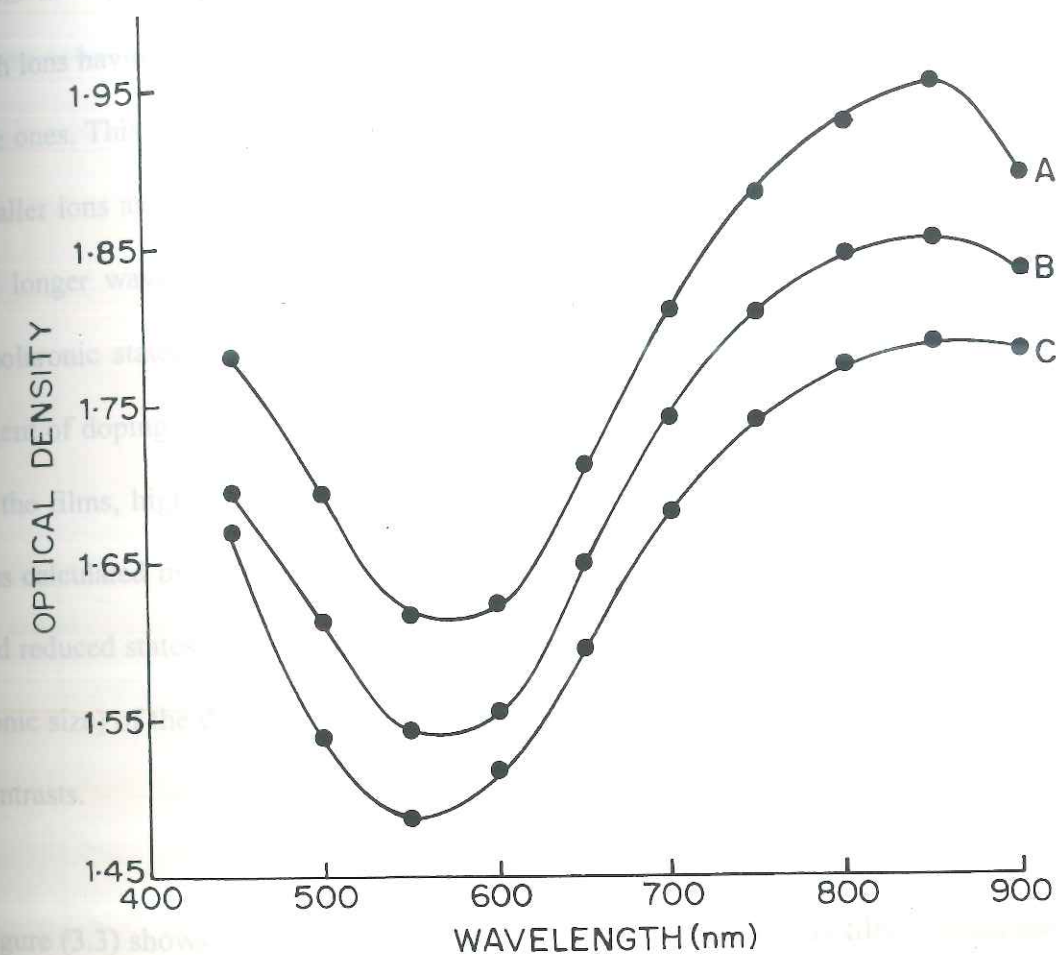


Figure (3.2) : Optical absorption spectra for Ppy/PB films in different electrolytes. Curves corresponds to (A) 0.01 M KCl (B) 0.01 M K₂SO₄ in the doped state and (C) in the undoped (dedoped) state.

In order to quantify the changes in the electrochromic contrast of Ppy/PB films, optical absorption spectra were recorded for these films in different electrolytes such as KCl, LiClO₄, K₂SO₄, K₂CO₃, KNO₃ etc.; the two cases of KCl and K₂SO₄ are shown in Figure (3.2) (all the spectra are not shown because of their representative nature). It can be seen that in the undoped state, the Ppy/PB film possess lowest optical density (OD). The

optical density is more than the undoped Ppy/PB film when cycled in K_2SO_4 and it is highest for films cycled in KCl. The ionic dimension of SO_4^{2-} is 0.4 nm and that of the Cl^- is 0.3 nm. Thus, under the identical experimental conditions, the Ppy/PB films doped with ions having smaller ionic dimensions will have more OD as compared to the bigger size ones. This is associated with ionic diffusion through the film which is facilitated for smaller ions as compared to ions of bigger sizes. The additional absorption observed in the longer wavelength region (800 - 900 nm) is due to the transition from / to the bipolaronic states arising from the doping of the Ppy films. It may be noted that the extent of doping controls the absorption in this region. Hence, more efficient the doping of the films, higher will be the OD in this spectral region. The electrochromic contrast was calculated by taking the difference in the optical density (OD) value in the oxidized and reduced states. Thus, it is clear that the OD of the Ppy/PB film depends on the nature (ionic size) of the dopants and thus are expected to show different electrochromic optical contrasts.

Figure (3.3) shows the contrast at various wavelengths for the Ppy films containing a PB top layer of increasing thickness and cycled in 0.01 M $LiClO_4$ aqueous electrolyte. Curves (a) to (g) corresponds to PB layer thickness of 0, 280, 315, 380, 430, 475 and 520 nm, respectively. It can be seen that the contrast is maximum (of the order of 0.3) at a certain wavelength of ~ 600 nm for the Ppy film alone. On the other hand, the Ppy/PB films not only show a higher contrast (> 0.6) than Ppy film alone at this wavelength but also at other wavelengths in the visible region, the maximum value being at longer wavelengths than the original Ppy. It is interesting to note that the wavelength of

maximum contrast ($L_{\max}$) shifts to red side with the increase of PB film thickness (see inset of Figure 3.3). It should be pointed out here that the figure depicts the difference in the OD and not the absorption spectrum itself. These findings suggest that both Ppy and PB are active in bringing about the electrochromic response of the composite film and it may be possible to tailor the $L_{\max}$ by the appropriate choice of PB content.

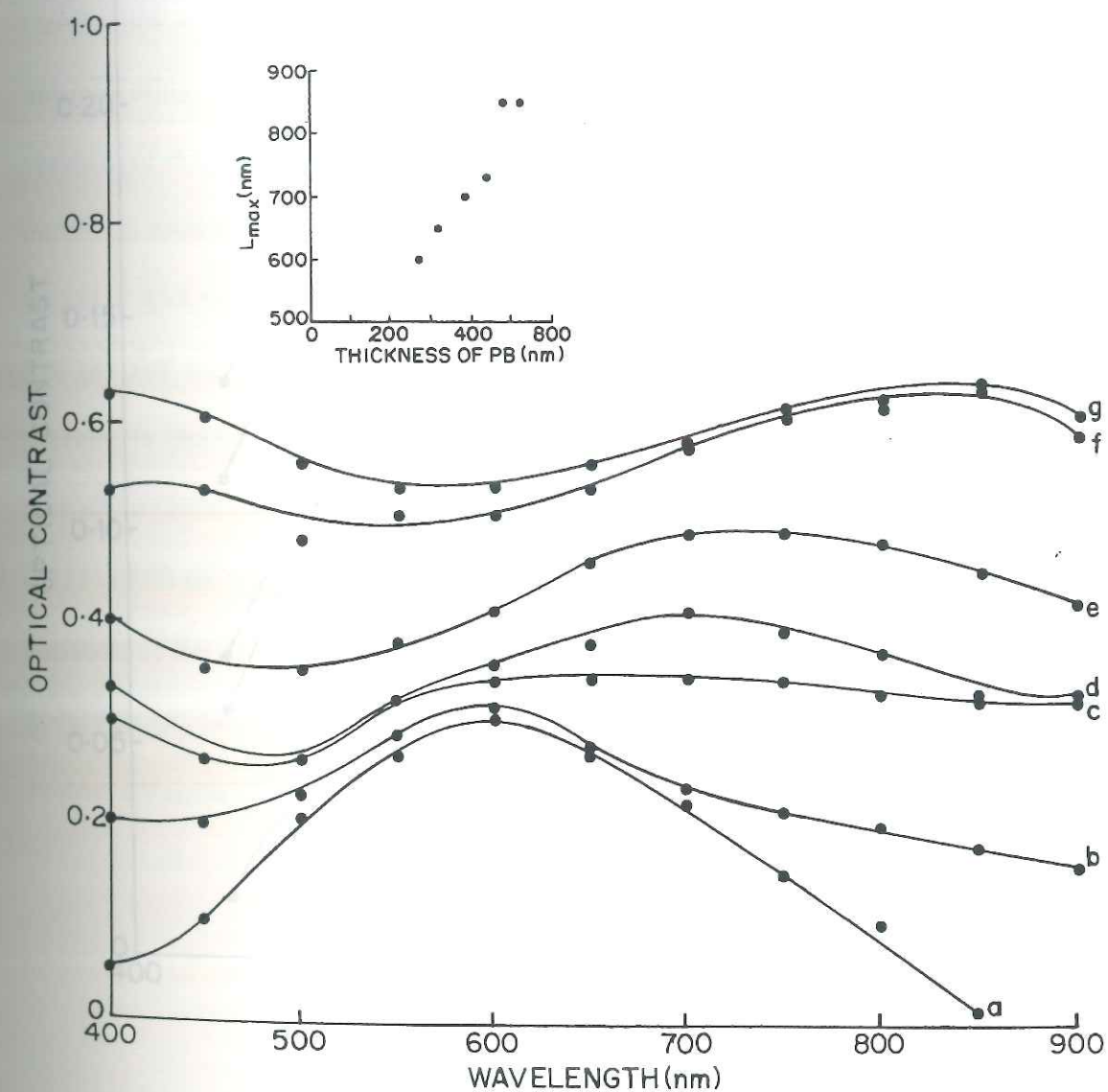


Figure (3.3) : Effect of Prussian Blue films on the electrochromic contrast of Polypyrrole films in 0.01 M aqueous LiClO_4 electrolyte. Curves (a) to (g) correspond to the PB film thickness of 0, 280, 315, 380, 435, 475, 520 nm respectively. The inset shows the shift in wavelength of maximum contrast $L_{\max}$ with the PB film layer thickness.

3.3.1.3 Effect of various anions on the electrochromic contrast of

Ppy/PB films :

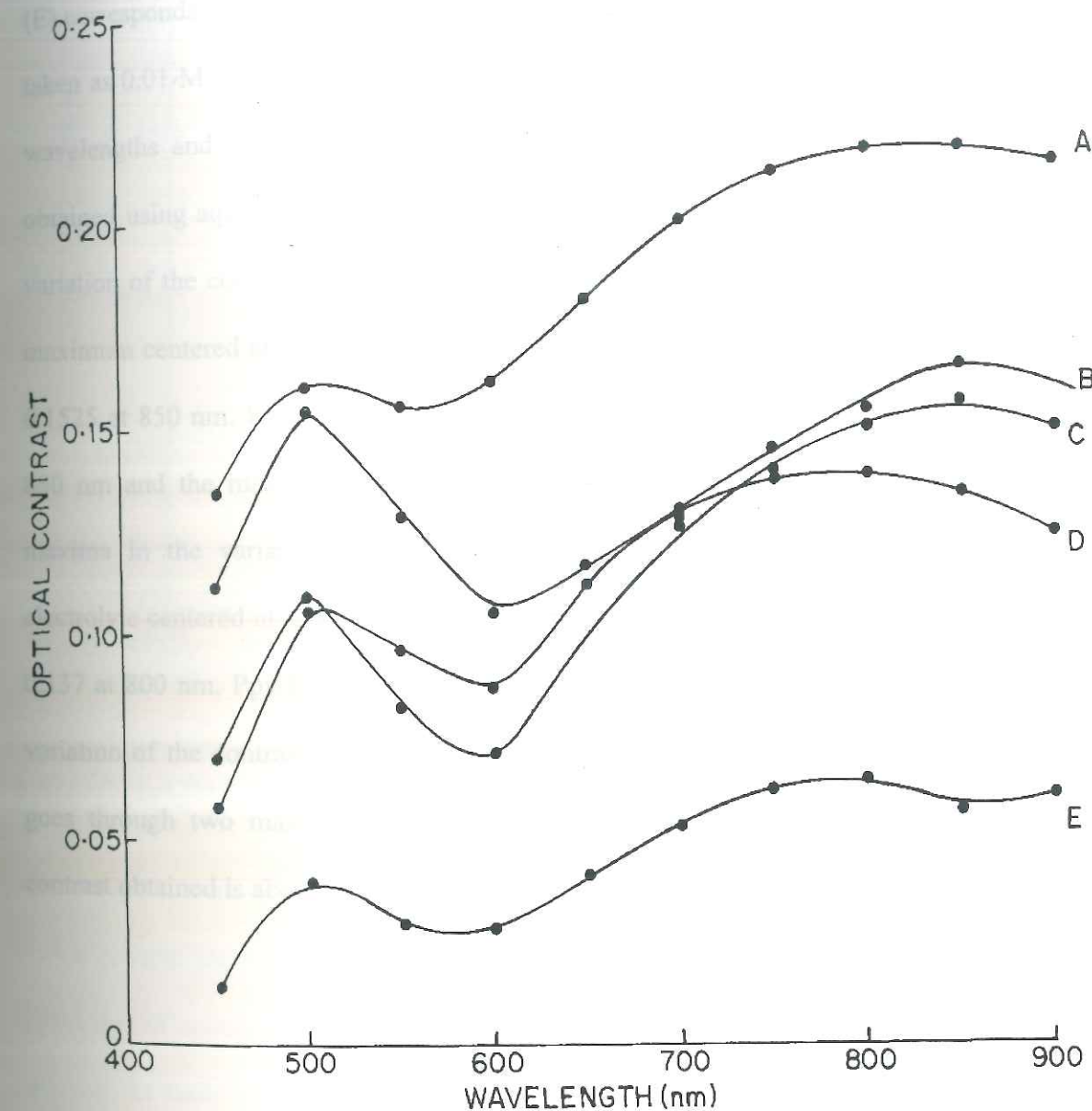


Figure (3.4) : Electrochromic Contrast of the Ppy/PB films in different electrolytes. Curves (A) to (D) corresponds to films cycled in KNO_3 , KCl , KI/I_2 , K_2SO_4 and K_2CO_3 (all aqueous 0.01 M) taken after application of -700 mV vs. SCE for 60 s. The PB films thickness was 476 nm in all the cases.

It has also been observed that the electrochromic response of the Ppy/PB bilayer films is dependent on the nature of the electrolyte. Figure (3.4) shows the electrochromic contrast at different wavelengths for Ppy/PB films cycled in various electrolytes. Curves (A) to (E) corresponds to the electrolytes KNO_3 , KCl , KI/I_2 , K_2SO_4 and K_2CO_3 , respectively, all taken as 0.01 M aqueous solutions. It is quite evident that the contrast is high for longer wavelengths and it is maximum for KNO_3 as the electrolyte. The maximum contrast obtained using aqueous KNO_3 as the electrolyte is of the order of 0.202 at 790 nm. The variation of the contrast with the wavelength using KCl as electrolyte goes through two maximum centered at around 500 nm and 850 nm and the maximum contrast obtained is 0.1525 at 850 nm. For KI/I_2 electrolyte, the observed two maximum are at 500 nm and 850 nm and the maximum contrast is 0.15 at 850 nm. The Ppy/PB films show two maxima in the variation of the contrast with the wavelength using K_2SO_4 as the electrolyte centered at around 500 nm and 800 nm and the maximum contrast obtained is 0.137 at 800 nm. Ppy/PB films are observed to possess lowest contrast for K_2CO_3 . The variation of the contrast with the wavelength for Ppy/PB films in K_2CO_3 as electrolyte goes through two maxima centered at around 500 nm and 790 nm. The maximum contrast obtained is about 0.05 for 790 nm.

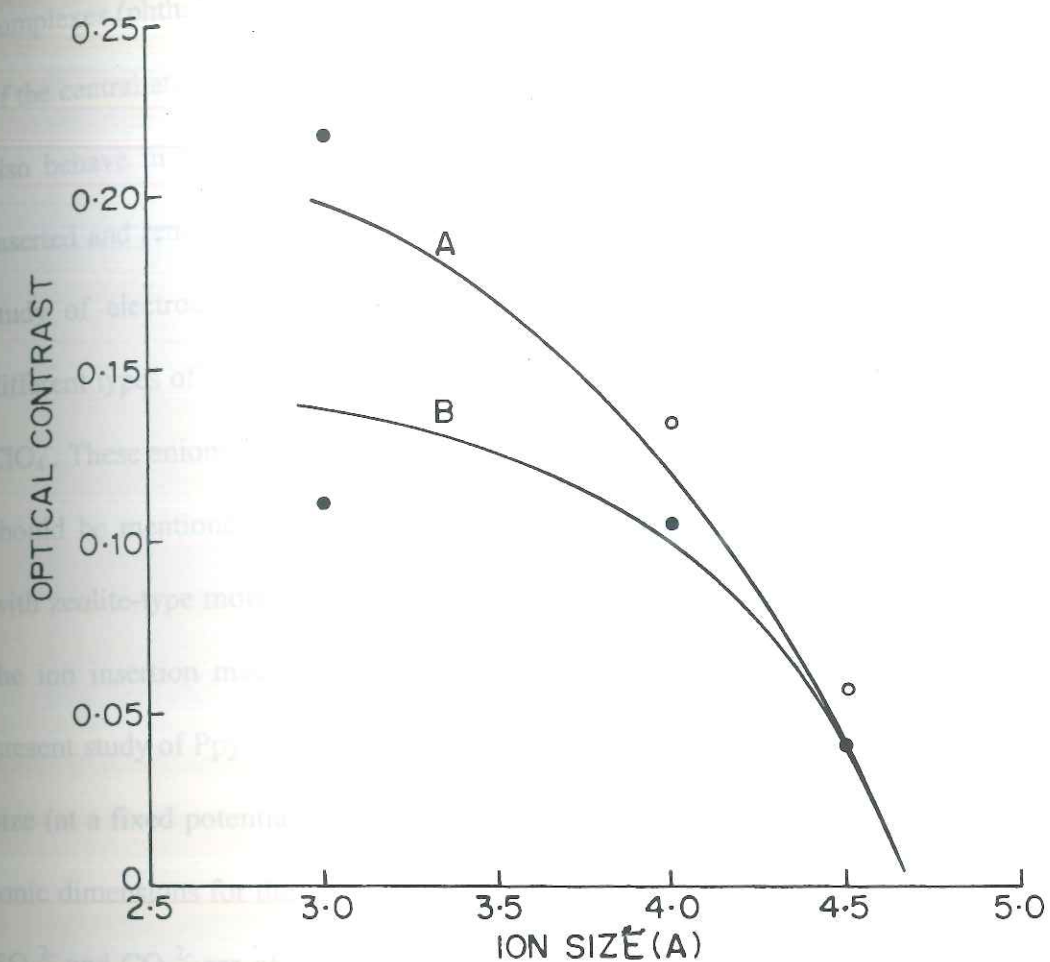
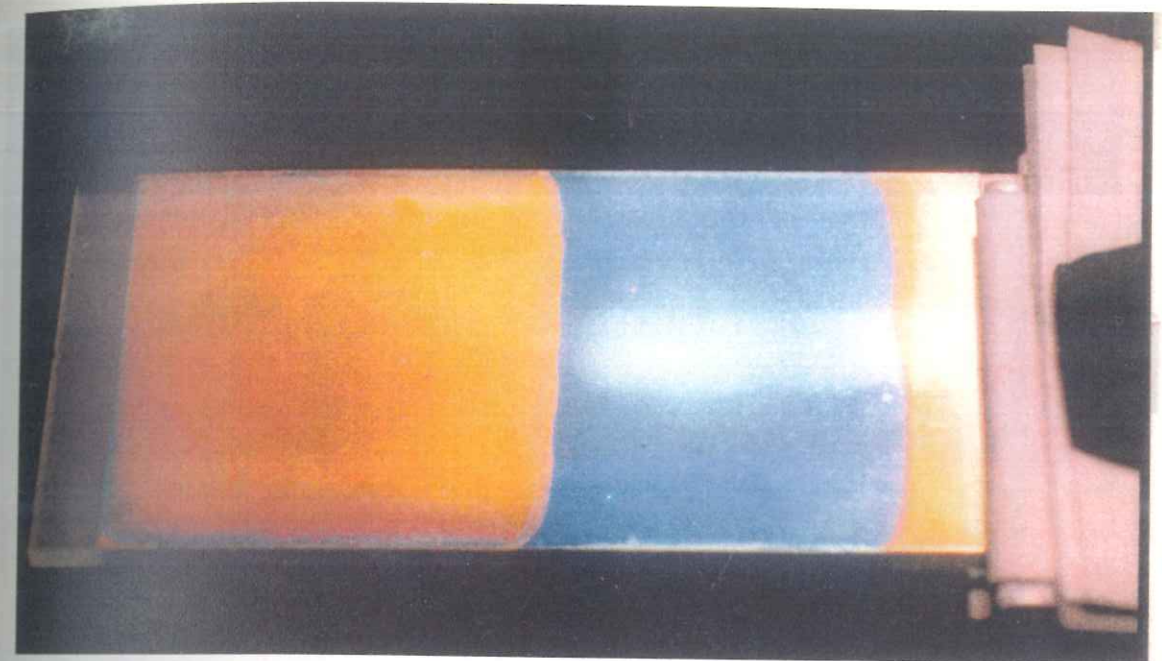


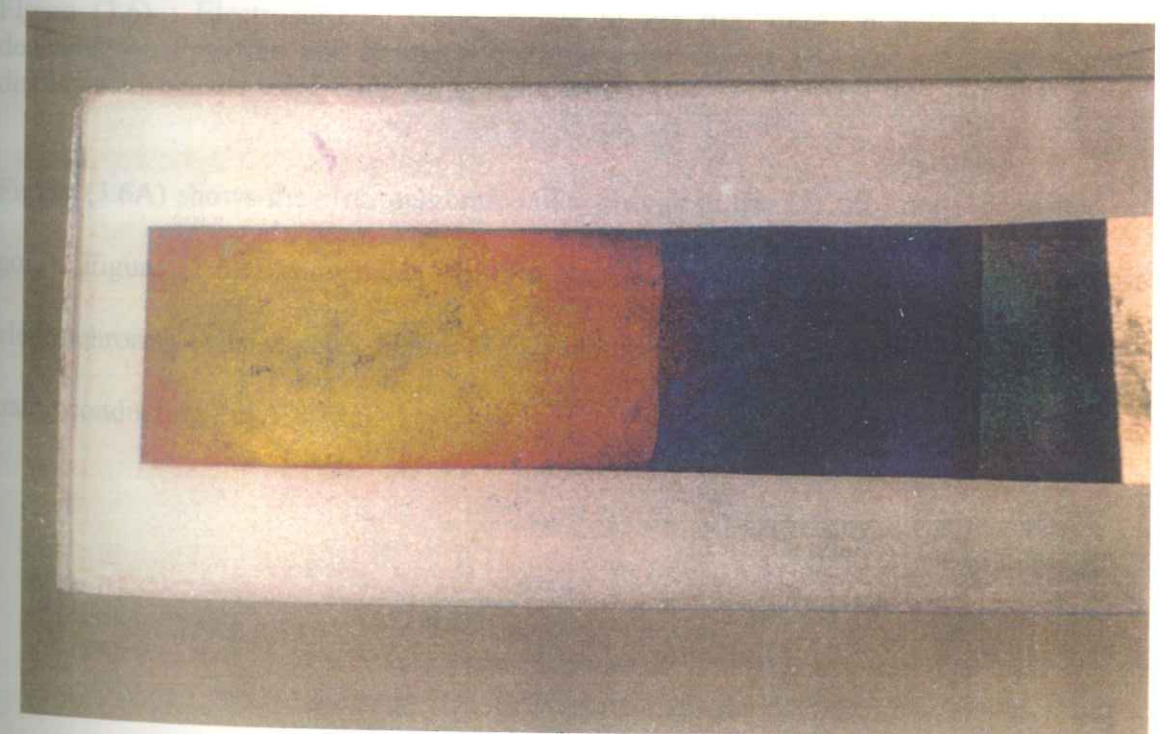
Figure (3.5) : Effect of dopant ion size on the electrochromic contrast in Ppy/PB films. Curve (A) at a wavelength of 850 nm and (B) at 500 nm.

The electrochromic effect in conducting polymers have been investigated in the past by several groups. Most of them have reported the change in the absorption spectra after the application of certain potential and attribute the changes to doping and undoping of the polymer. As such there are several types of electrochromic materials known for which different types of processes are responsible for the color change [19]. For example, tungsten trioxide (WO_3) or nickel oxide are ion insertion materials while viologens are chemical deposition materials [20]. On the other hand, there are some organo-metallic

complexes (phthalocyanines), which change color due to the change in the oxidation state of the central atom [21]. In case of conducting polymers, some authors contend that these also behave in a similar fashion to ion insertion materials, wherein the dopant ion is inserted and removed from the polymer film during the electrochemical cycling. For the study of electrochromic response of Ppy/PB composite films, we have investigated different types of electrolytes with various anions such as Cl^- , I^- , NO_3^- , SO_4^{2-} , CO_3^{2-} and ClO_4^- . These anions have different ionic sizes and activity in the aqueous medium [22]. It should be mentioned here that PB films are known to have an orthorhombic structure with zeolite-type morphology with pore dimensions of 0.32 nm [23]. Hence, considering the ion insertion mechanism to be appropriate for the electrochromic behavior in the present study of Ppy/PB composite films, the extent of doping would depend on the ionic size (at a fixed potential), since their penetration depth would be related to the size. The ionic dimensions for the halide and nitrate ions are of the order of 0.3 nm while those for SO_4^{2-} and CO_3^{2-} are of the order of 0.4 and 0.45 nm respectively [24]. Thus, one would expect that the halide and nitrate ions to move freely inside the Ppy as well as PB lattice but not in case of sulphate or carbonate ions. This could lead to the difference in the electrochromic contrast for these cases which indeed has been observed by us. Figure (3.5) shows the variation of contrast with respect to the ionic size for Ppy/PB films cycled under the same conditions of voltage and concentration but in different electrolytes. It is quite clear that much more contrast is obtained for ions with a smaller size than that for a larger size. It may also be noted that when the ionic dimension is the same, the electronegativity becomes important as can be noted in case for Cl^- and I^- since more charge would be transferred in the former case than in the latter.



(A)



(B)



(C)

Figure (3.6) : Electrochromic color change in PB film only on gold (A), PB film deposited on Ppy film and its electrochromic color change (B) and an electrochromic display device made using conducting Ppy/PB film (C).

Figure (3.6A) shows the electrochromic color change in the PB film only (deposited on gold). Figure (3.6B) shows the PB film deposited on top of the Ppy film and its electrochromic color change. Figure (3.6C) represents the electrochromic display device using conducting Ppy/PB film.

3.3.1.4 XPS (ESCA) studies on PB films in oxidized and reduced states :

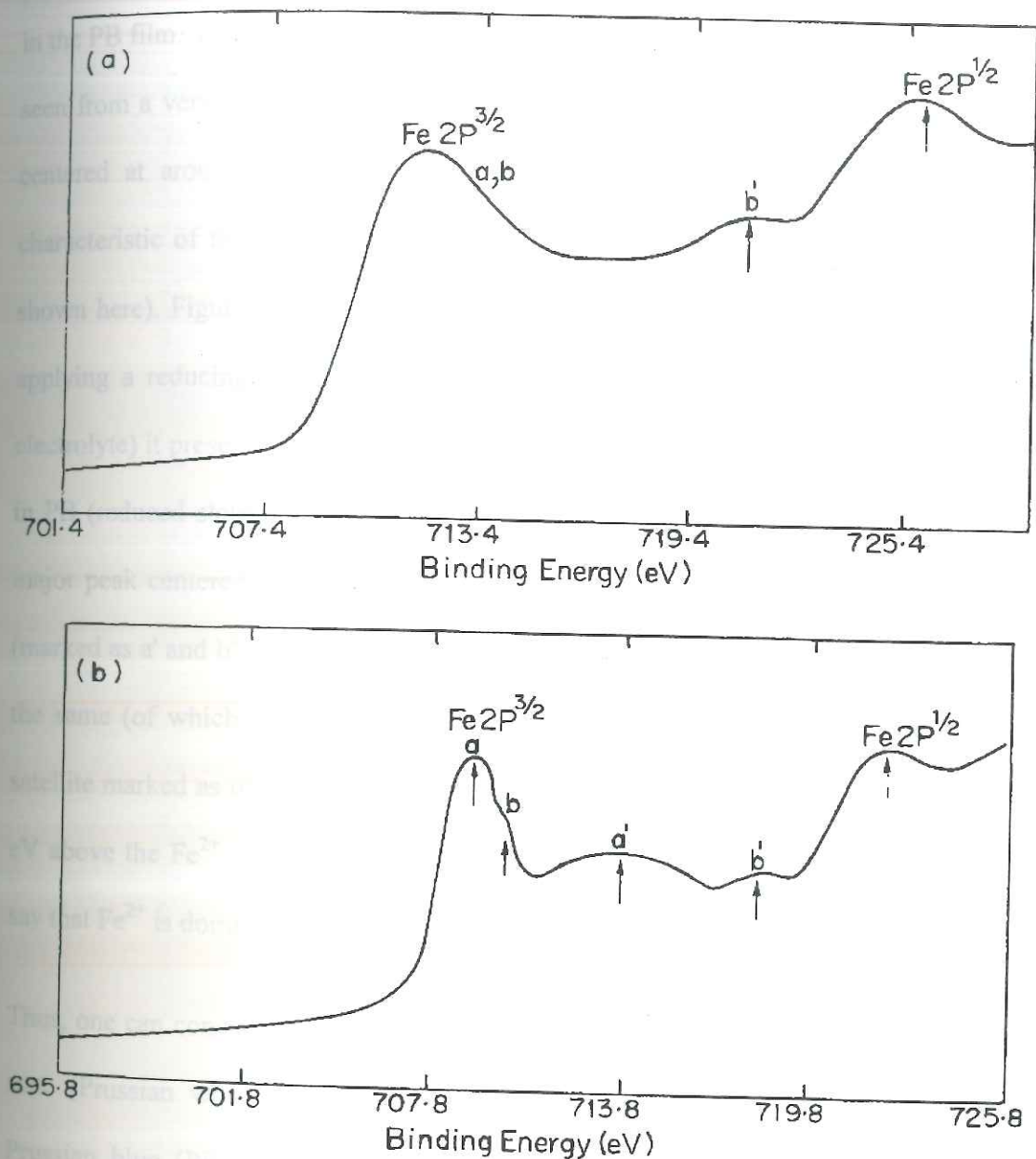


Figure (3.7) : XPS of the PB film – as deposited (a) and in the reduced state (b – obtained by applying a reducing potential of 0.7 V vs. SCE for 60 s in 0.01 M aqueous KCl electrolyte).

Figure (3.7a and b) show the XPS spectra of the PB films in the as deposited form and the reduced one (obtained by applying a reducing potential of 0.7 V vs. SCE for 60 s

through an aqueous liquid electrolyte of 0.01 M KCl), respectively. Figure (3.7a) presents the XPS spectra of the PB as deposited film. It represents the $2P_{3/2}$ and $2P_{1/2}$ levels of Fe in the PB film. The $2P_{3/2}$ level of Fe in PB is composed mainly of Fe^{3+} state which can be seen from a very broad peak centered at around 711.6 eV and a corresponding satellite centered at around 721.0 eV (9.4 eV above the Fe^{3+} $2P_{3/2}$ position – is the main characteristic of the Fe^{3+} species ; also confirmed from the broad auger parameter, not shown here). Figure (3.7b) shows the XPS spectra of the PB reduced film (obtained by applying a reducing potential of 0.7 V vs. SCE for 60 s in 0.01 M aqueous KCl as electrolyte) it presents the $2P_{3/2}$ and $2P_{1/2}$ levels of Fe in the PB film. The $2P_{3/2}$ level of Fe in PB (reduced state) is composed of two states – Fe^{2+} and Fe^{3+} as can be seen from a major peak centered at around 708.8 eV and a hump at around 710.0 eV in the spectra (marked as a' and b' in the spectra), respectively. The two satellites observed also indicate the same (of which the first satellite marked as a' corresponds to Fe^{2+} and the second satellite marked as b' corresponds to Fe^{3+}). The broad satellite at around 713.8 eV (5 to 6 eV above the Fe^{2+} species) is the main characteristic of the Fe^{2+} species. Here, one can say that Fe^{2+} is dominating over Fe^{3+} (as expected in Prussian White).

Thus, one can conclude that Fe^{3+} state (in Prussian blue) are getting converted in to Fe^{2+} state (Prussian white) by applying a reducing potential. Thus, we conclude that the Prussian blue (PB) is getting converted to Prussian white (PW) by application of a reducing potential. This confirms equation (2) and this change of oxidation state of Fe is the reason for showing the electrochromic color change in the PB films.

3.3.1.5 Morphological study of the Ppy, PB and Ppy/PB films in the oxidized and reduced states :

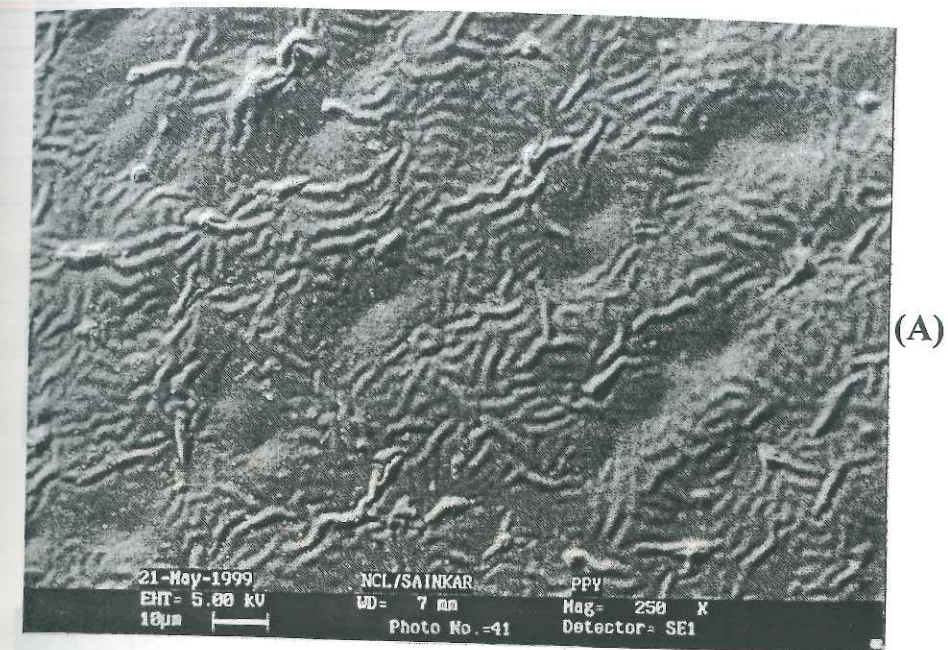
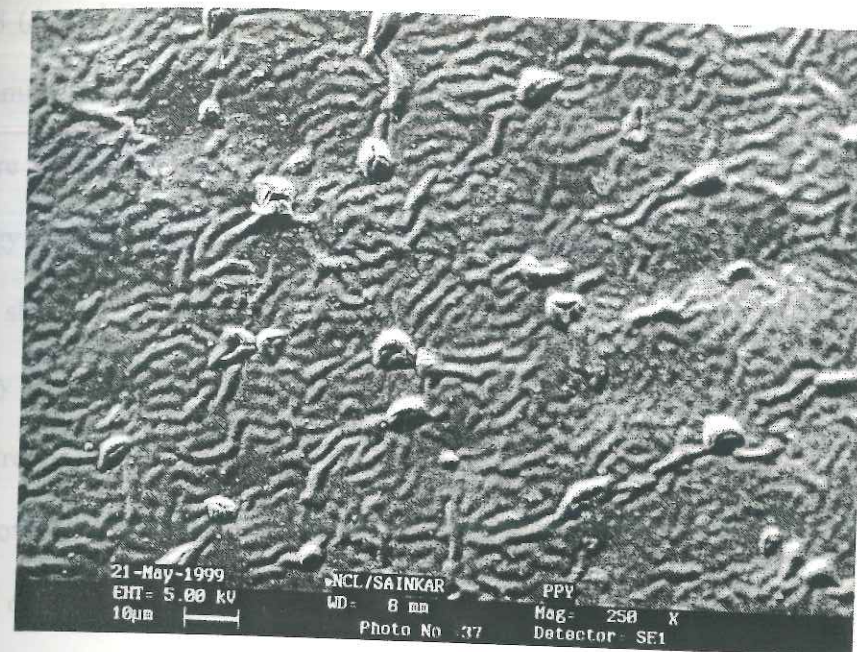


Figure (3.8) : SEM of the electrochemically as deposited Ppy film at 250x (A) and 1.25x (B) magnifications.



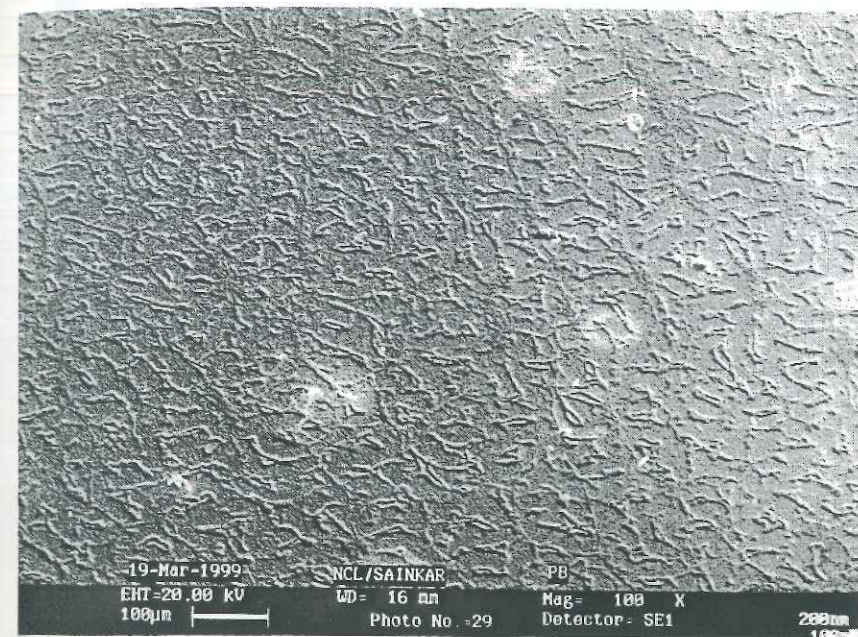
(A)



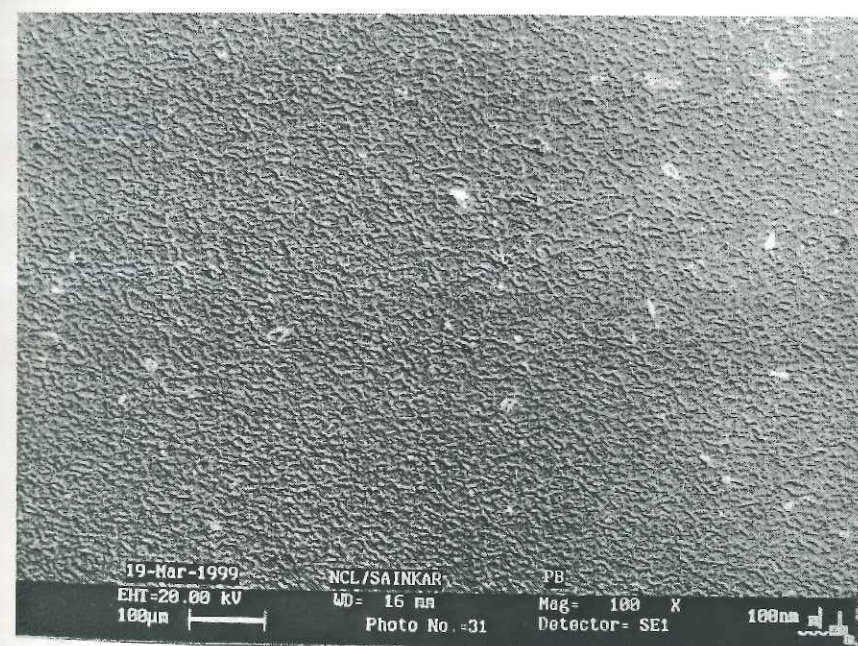
(B)

Figure (3.9) : SEM of the electrochemically deposited Ppy film (in the reduced state) at 250x (A) and 1.25x (B) magnifications.

Figure 3.8 (A and B) shows the scanning electron micrograph of the PPy film surface, electrochemically deposited on gold at 250x and 1.25x magnifications respectively. The films were deposited as described in the experimental section. Similar surface morphology has been observed for the PPy films deposited on ITO electrodes. Figure 3.9 (A and B) shows the scanning electron micrograph of the Ppy film (in the reduced state, obtained by applying a reducing potential of 0.7 V vs. SCE through aqueous 0.01 M KCl as an electrolyte) surface at 250x and 1.25x magnifications respectively. Figure (3.9A) shows the overall morphology of the Ppy film surface. Several globular structures can be easily seen on the Ppy – reduced film surface which are absent on the Ppy-as deposited film surface. These globular structures becomes more visible in Figure (3.9B). Such type of globular structures has also been observed in the past by several authors [25]. It has also been observed that during electrochemical cycling of the film, these globular structures play an important role. By applying a reducing potential, it has been seen that these globular structures open up and presumably, the intercalated electrolyte ion comes out through these – as proposed and discussed in Ref. [25].



(A)

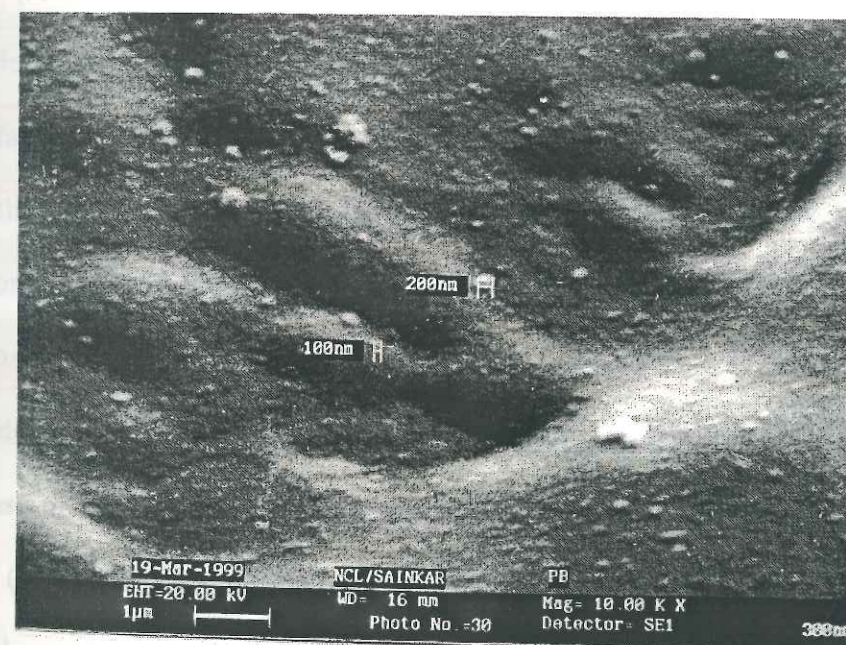


(B)

Figure (3.10) : SEM of the PB as deposited film (A) and SEM of the PB-reduced film (obtained by applying a reducing potential of 0.7 V vs. SCE). Both the films are at the magnifications 100x.



(A)



(B)

Figure (3.11) : SEM of the PB as deposited film (A) and SEM of the PB-reduced film (obtained by applying a reducing potential of 0.7 V vs. SCE). Both the films are at the magnifications 10.0 Kx.

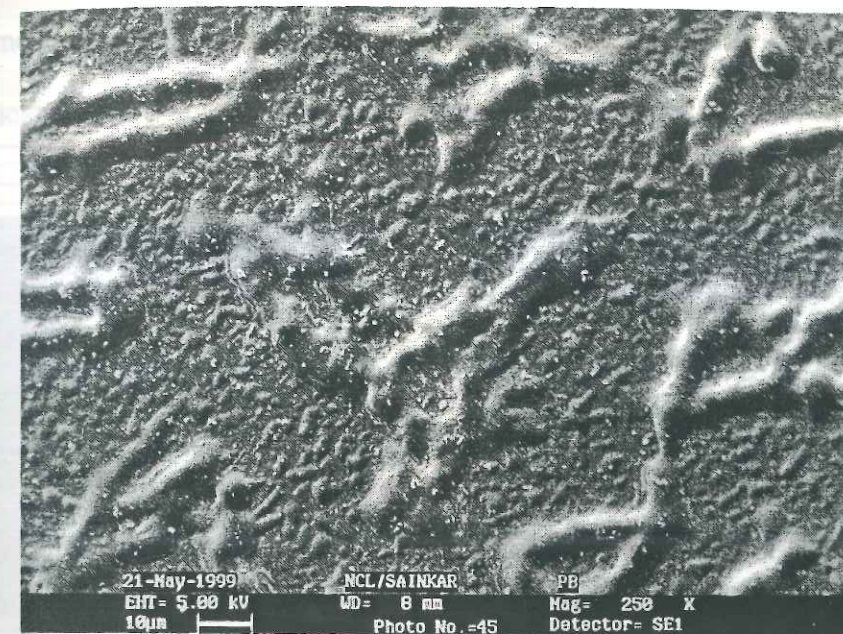


Figure (3.12) : SEM of the PB film in the oxidized form (as deposited) on ITO electrode.

Figure 3.10 (A and B) shows the SEM micrograph of the PB as-deposited and reduced state film, deposited electrochemically on the gold film. Some shrinkages are observable on the surface of PB - as deposited film (as can be seen from Figure 3.10A). By comparing the oxidized and reduced PB film surface morphology, it can be seen that the shrinkages on the film are larger in number in the case of reduced PB film as compared to that of the oxidized form. This can be explained on the basis that the counterions which are intercalated in the PB film (oxidized form) are taken out of the PB film which results in an increase of the shrinkages on the film surface. This becomes more observable in Figure 3.11 (A and B) taken at higher magnifications (at 10.0 Kx). Here, no tearing or opening of the surface has been observed since PB has a zeolite-type structure and does not have a polymer type morphology. The intercalated counterions can move in and out easily via the pores present in the PB film. The PB film deposited on ITO electrode also

has the same morphology as can be seen from Figure (3.12) and also shows the same morphological changes on reverse-cycling i.e. in the reduced state.

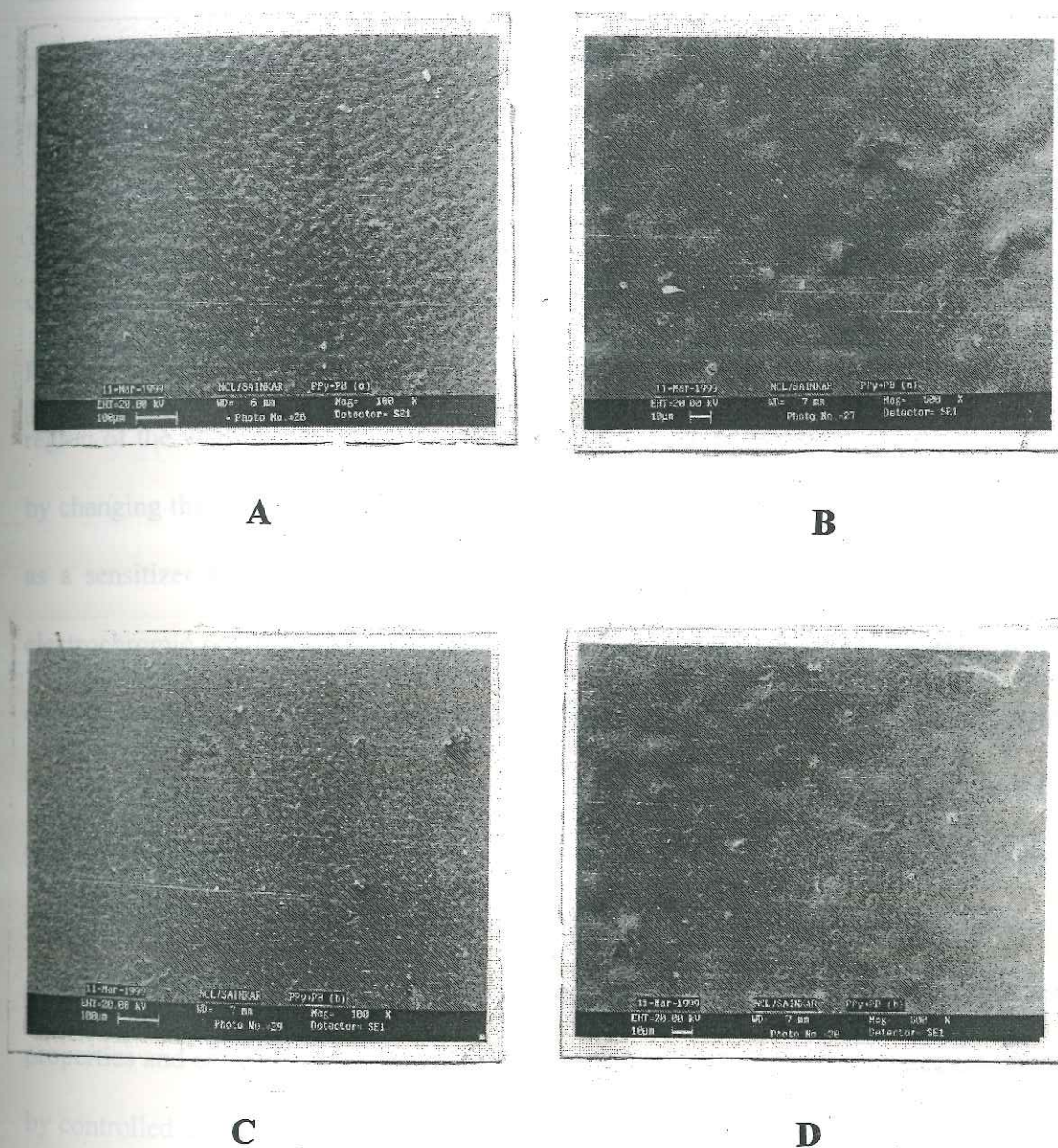


Figure (3.13) : SEM of the Ppy/PB composite films in the oxidized (A and B) and reduced (C and D - obtained by applying a reducing potential of 0.7 V vs. SCE) states.

Figure 3.13 (A and C) presents the surface morphology of the Ppy/PB bilayer films in the as deposited (oxidized state) and reduced form (obtained by applying a reducing potential

of 0.7 V vs. SCE), respectively. It can be seen that several fold surfaces and typical globular structures, similar to the ones observed in case of Ppy film only, are present on the surface of the film. The fold surfaces increase in number when the film is in the reduced state (as can be seen from Figure 3.13C), which becomes clearer at higher magnifications (i.e. 500 x) as shown in Figures 3.13 (B and D).

The studies on the electrochromic response of the conducting polypyrrole (Ppy) films with Prussian blue (PB) films on top and for different electrolytes reveals that the use of PB enhances the electrochromic response of Ppy and also extends the response to wider region of the visible spectrum. The color change can be extended to longer wavelengths by changing the PB content (film thickness) in the composite bilayer films. Thus PB acts as a sensitizer for the electrochromic response of conducting polypyrrole. Also, the electrochromic contrast depends on the nature of the electrolyte, especially the size of the dopant / intercalent ions and their electronegativity. It can be pointed here that the contrast in these films arises from the doping and undoping action due to ion insertion in the Ppy as well as PB moieties. In case of the Ppy film, heavy doping introduces bipolaronic states / band while light doping introduces polaronic states in the band gap. The insertion of these new states changes the electronic structure of the polymer and hence the optical properties and color. Also, the extent of oxidation / reduction of the polymer can be tuned by controlled doping / undoping of the polymer. Polymer with higher oxidation state can be produced with heavy doping and vice versa. Thus, the color of the polymeric film can be tuned continuously from color 1 (in the oxidized state) to color 2 (in the reduced state) by controlling its extent of doping. In case of the PB film, the change of the oxidation

state of Fe occurs by the insertion and the removal of the counterions and is responsible for change of color.

The PB film in fact controls the relative doping levels because it allows ions of certain dimensions to pass through to the back side and dope the Ppy film. Thus, it is possible to tailor the overall electrochromic response of the device by an appropriate choice of the PB film thickness as well as the electrolyte used.

3.3.2 PHOTONSENSITIVITY OF CONDUCTING POLYPYRROLE / PRUSSIAN BLUE BILAYER FILMS :

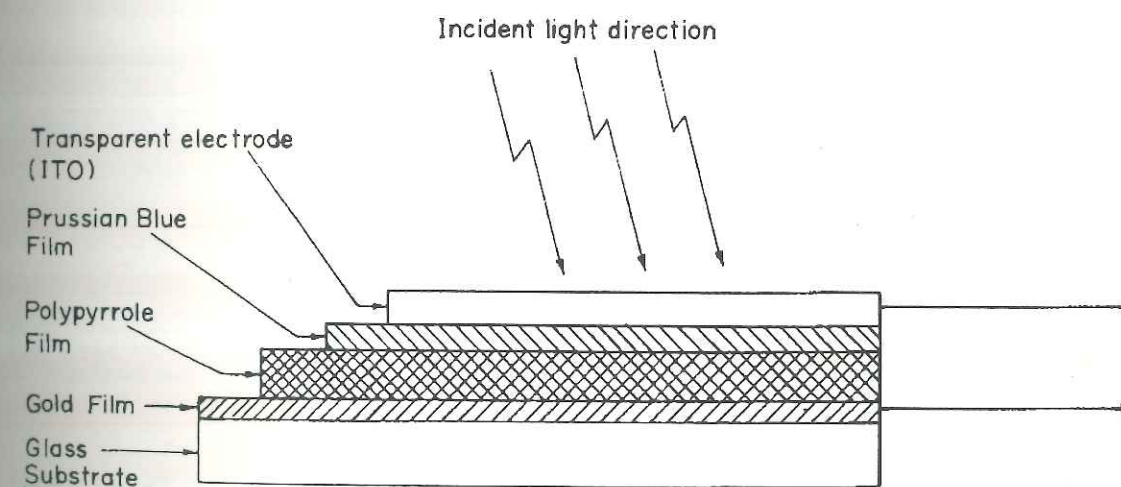


Figure (3.14) : Schematic of the multilayer photocell using conducting Ppy and PB films (Au/Ppy/PB/ITO).

Figure (3.15) : Schematic of the multilayer photocell using conducting Ppy and PB films (Au/Ppy/PB/ITO). This corresponds to PB film.

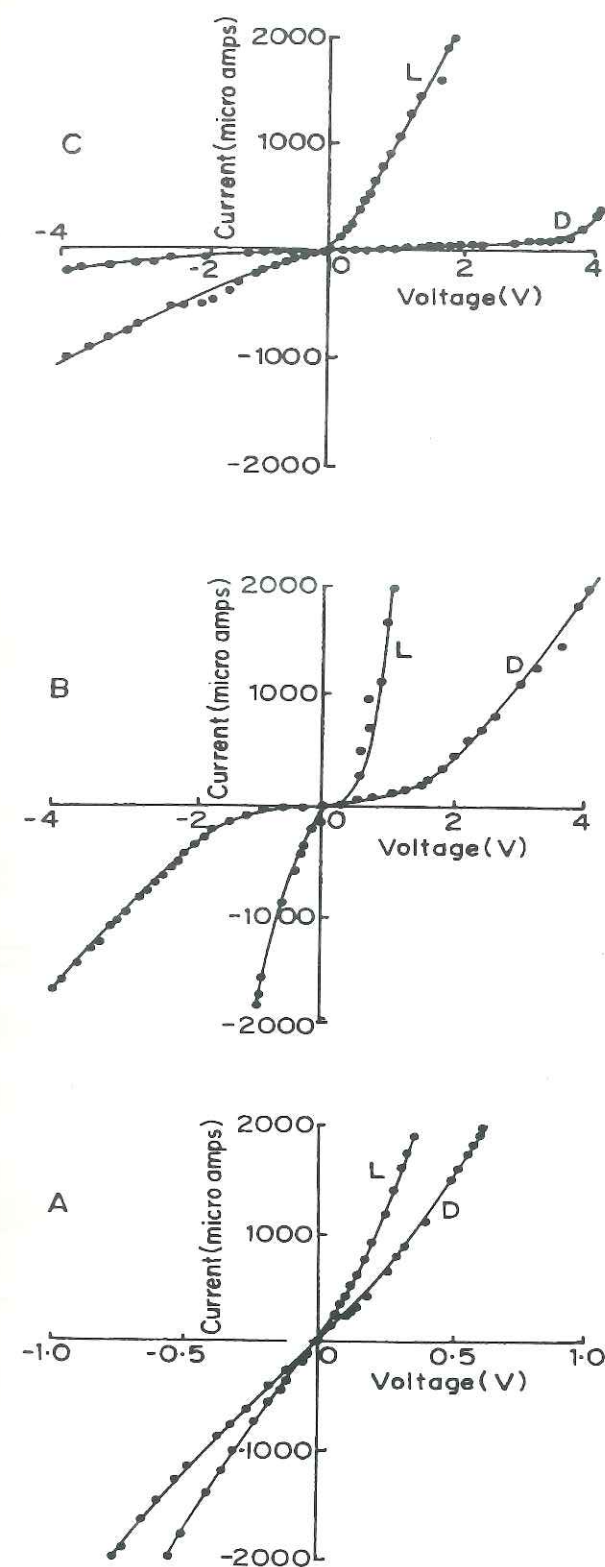


Figure (3.15) : Current-Voltage (I-V) characteristics in dark (D) and light (L) for Au/Ppy/PB/ITO multilayer photocells with different PB film thickness ; (A) to (C) corresponds to PB thickness of 270, 285 and 315 nm respectively.

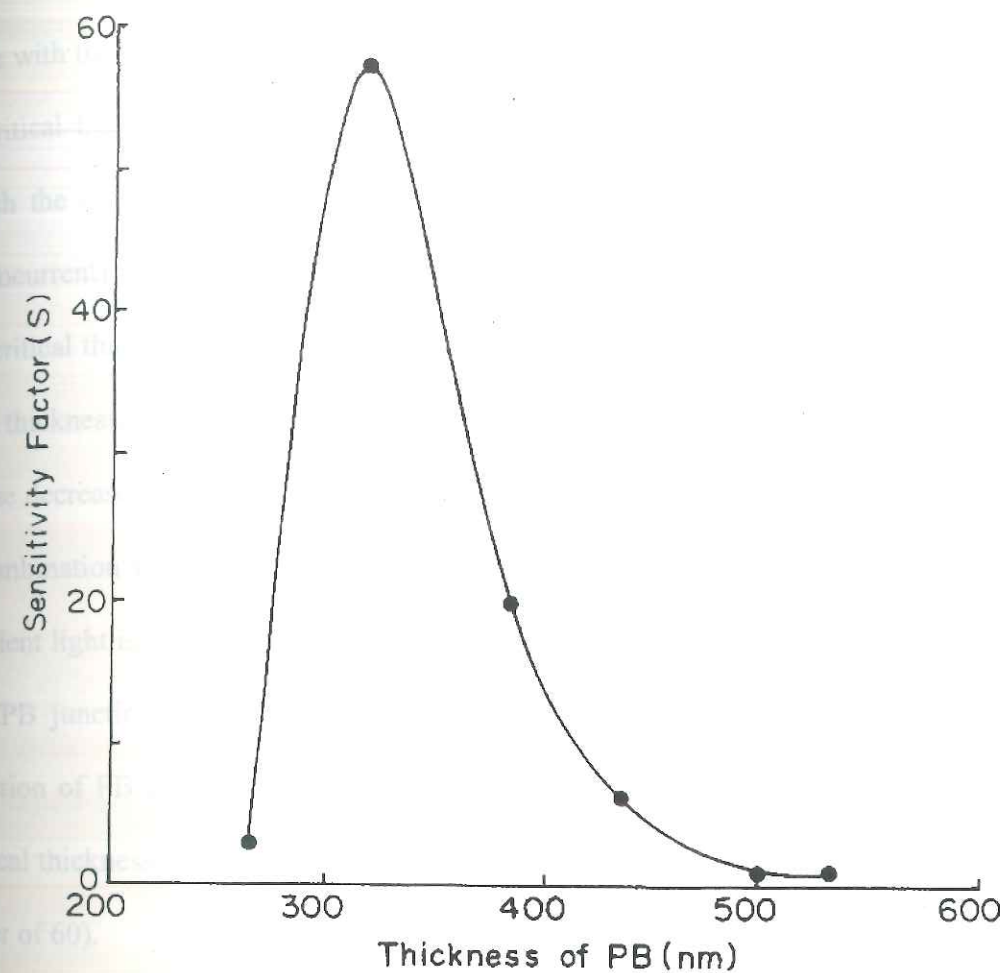


Figure (3.16) : Photosensitivity factor (S) as a function of PB film thickness (in positive, 1st quadrant only).

Figure (3.14) shows the schematic of the solid state sandwich cell using conducting Ppy and PB. The current-voltage (I-V) characteristics of the Ppy/PB photocells in dark and under white light illumination are as shown in Figure (3.15). The curves (A) to (C) corresponds to the PB film thickness of 270, 285 and 315 nm respectively (Ppy film thickness is about 400 nm in all the cases). It is interesting to observe that the current-voltage characteristics are highly non-linear both under illumination (L) as well as in dark

(D). The dark current (I_d) decreases and the photocurrent (I_l) remains more or less the same with the increase in the PB film thickness, up to a certain thickness, can be defined as critical thickness. The critical thickness can be defined as the PB film thickness at which the maximum photosensitivity ($S = I_l/I_d$, I_d is the current in dark and I_l is the photocurrent) has been observed (i.e. here the PB critical thickness is 315 nm). Before the critical thickness, the photosensitivity factor (S) increases with the increase in the PB film thickness. After the critical thickness, the photosensitivity factor decreases because of the decrease of the photocurrent. Above the critical thickness, heavy trapping and / or recombination of the photogenerated charge carriers play an important role. Also, the incident light is absorbed only at the surface and hence photons are unable to reach to the Ppy/PB junction. The photosensitivity factor for these Ppy/PB multiplayer cells as a function of PB film thickness is as shown in Figure (3.16). it is evident that there is a critical thickness of PB at which the photosensitivity is maximum (photosensitivity of the order of 60).

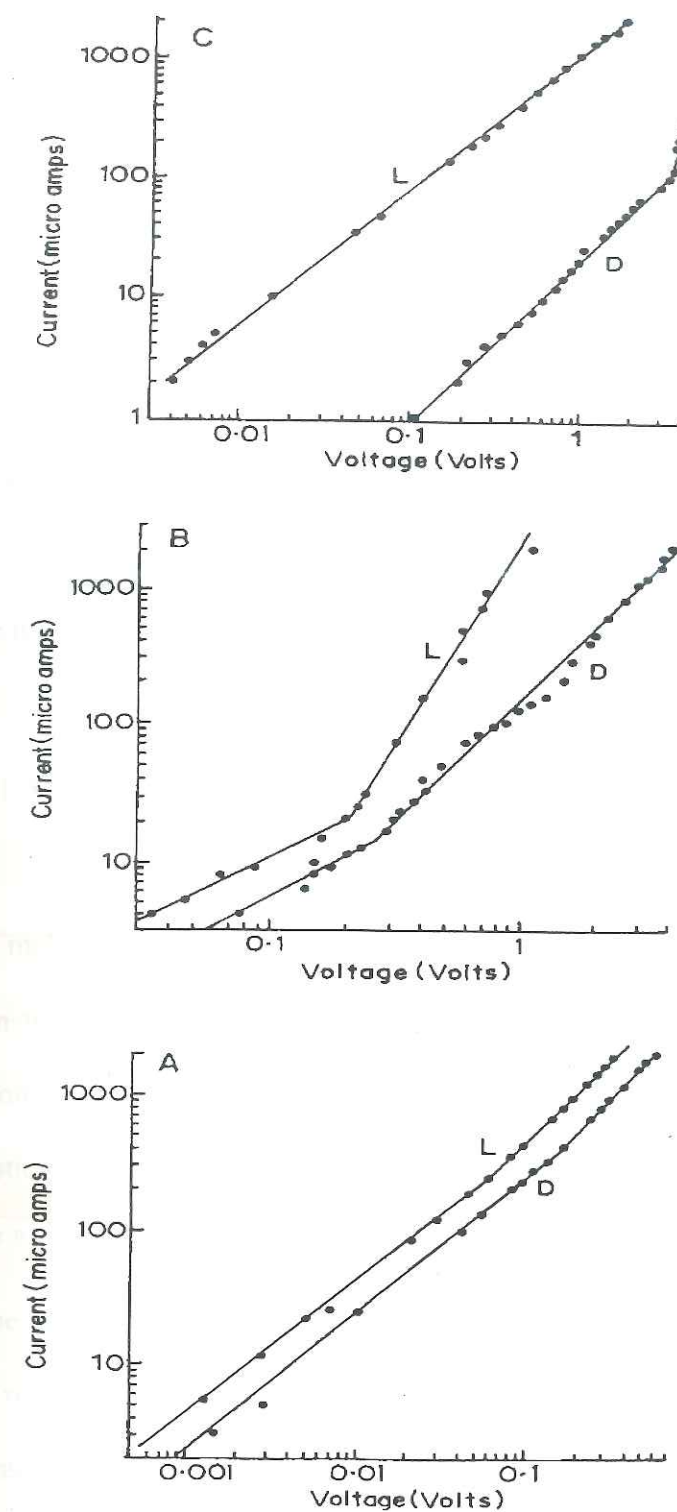


Figure (3.17) : The log-log plot of the I-V curves presented in Figure (19) in the positive quadrant (1st quadrant) only showing the SCLC type behavior with the exponent n ranging from 2 to 3. (A) to (C) corresponds to PB film thickness of 270, 285 and 315 nm respectively.

In order to understand the mechanism involved in the sensitization of photocurrent, one has to first look in the charge transport processes taking place in these structures. The I-V characteristics were analyzed in detailed according to the equations for different types of charge transport processes such as tunneling, Schottky emission, Poole-Frenkel effect, Space Charge Limited Conduction (SCLC) etc. which have been described in chapter 1. In each case, the dependence of current with respect to voltage was verified by plotting appropriate graphs according to equations reported for the effect. The different processes were eliminated on the basis of linearity according to expected relationship. The SCLC appeared to be the most appropriate for the present case in which the current is given by

$$I = (8/9) \mu \theta [V^{(n+1)} / d^{(2n+1)}] \quad \text{-----}(3.3)$$

where μ is the mobility of the charge carriers, d is the PB film thickness, θ is a parameter which takes in to account the concentration of trapping centers (impurity centers) and their distribution and n is an integer indicating the non-linearity. Figure (3.17) shows the I-V characteristics plotted on the log-log scale and it is evident from these curves that the relation $I \propto V^n$ with $n = 3$ is indeed followed. The SCLC curves are usually interpreted in terms of the charge injection and the subsequent filling of the impurity / trapping centers giving rise to the progressively the linear, square and superlinear type dependence of the I-V characteristics.

Figure (3.18) : I-V characteristics of 580 nm thick PB film taken at Rate = 50 mV/s electrochemical window portion of 1.4 V

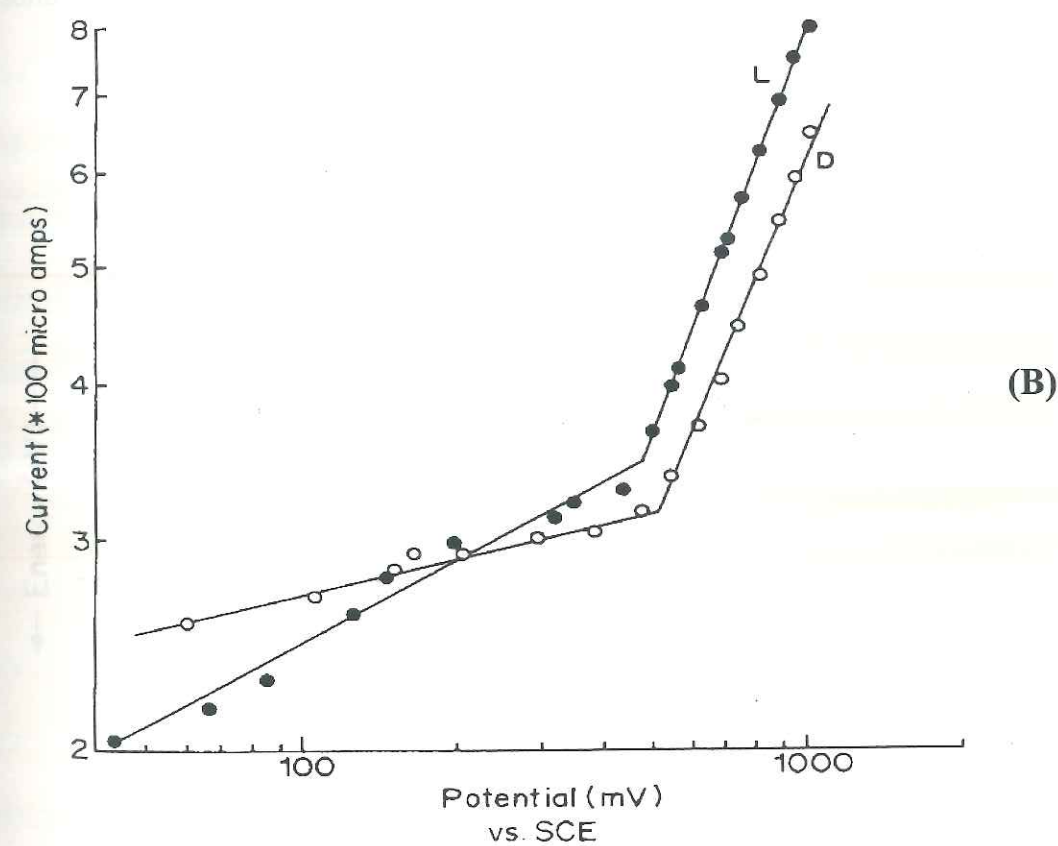
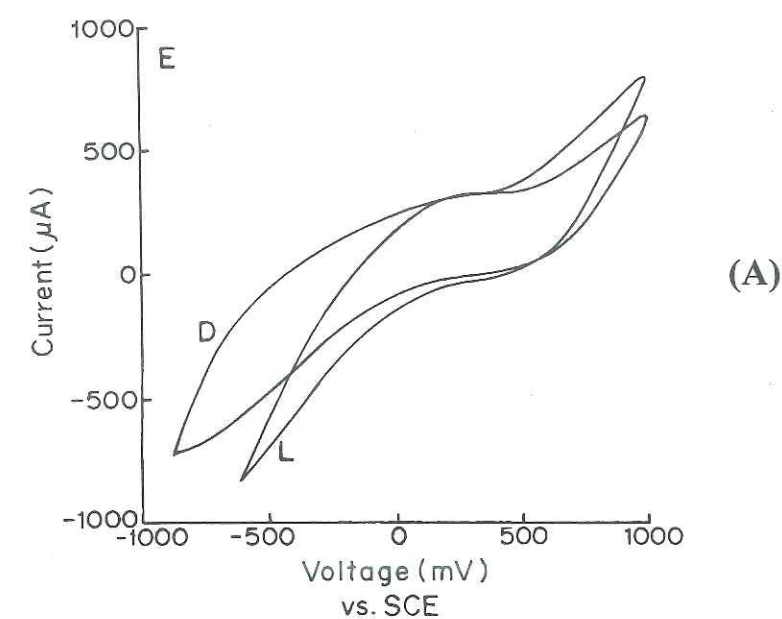


Figure (3.18) : (A) cyclic voltammogram of the Ppy/PB film with the PB film thickness of 580 nm taken using 0.1 M aqueous KCl as an electrolyte in PEC mode (vs. SCE). Scan Rate = 50 mV/s. (B) The current-voltage (I-V) plot of the Ppy/PB composite film in the electrochemical cell configuration with liquid electrolyte (0.1 M KCl) derived from the rising portion of the current in the positive quadrant (PB film thickness of 580 nm).

It is interesting to note here that the space charge effects also play an important role in governing the current-voltage characteristics observed in the liquid electrolyte cell with the Ppy/PB as the working electrode. Figure 3.18 (A) shows the cyclic voltammogram (CV) of the Ppy/PB film (PB film thickness = 580 nm) taken using 0.1 M aqueous KCl as an electrolyte in PEC mode in dark (D) and light (L) with a scan rate of 50 mV/s (vs. SCE). Figure 3.18(B) shows the current-voltage (I-V) characteristics in dark (D) and light (L) derived from the rising portion of the voltammogram [shown in Figure (3.18A)] in the positive quadrant only. It is clearly seen that these are quite similar to those observed for the solid state photocells with a close agreement to the power law equation (3.3).

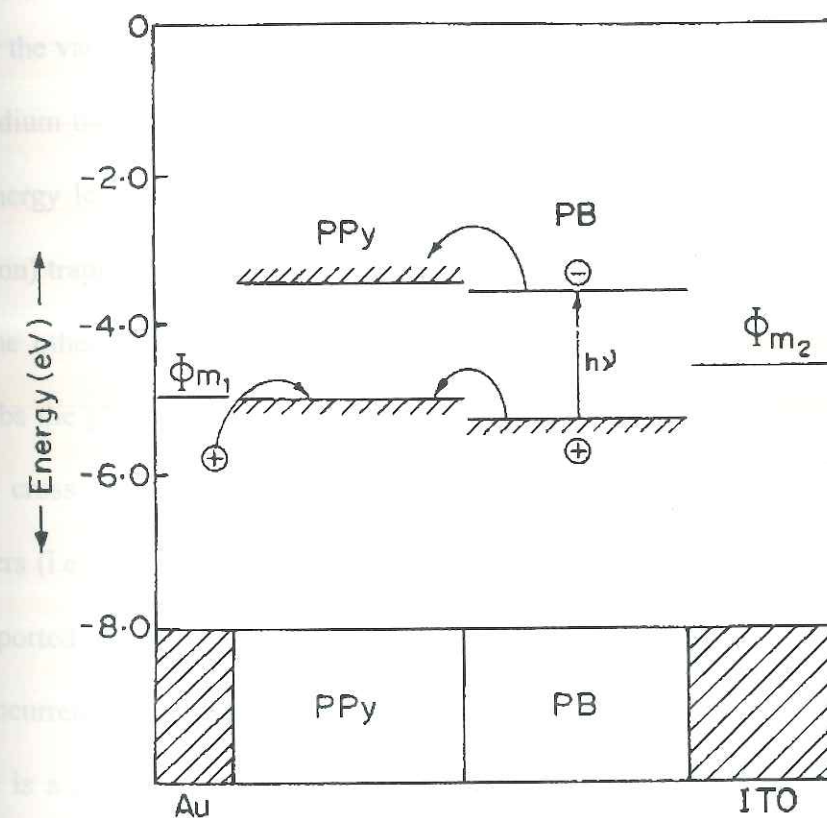


Figure (3.19) : The schematic of the energy level diagram for the materials used in Ppy/PB multilayer photocells.

The sensitization process involves usually photoexcitation of carriers, the trapping of the minority carriers, enhancement of the majority free carrier concentration, carrier mobility and / or its lifetime. In the present case, this can be understood in terms of the energy band diagram for the materials used in forming the Ppy/PB multiplayer system. Figure (3.19) shows the different energy levels for the materials used in the above system. The energy levels of Ppy are those which have been reported in the literature [18] while those for PB are derived from the UV-VIS spectra recorded. Here, Ppy is a p-type material while PB is acting as a n-type material. Also, it can be seen that there is a negligible barrier between Au and Ppy since the work function of Au (5.22 eV) and the highest occupied molecular orbital (HOMO) for Ppy (5.0 eV) are almost at the same position below the vacuum level. On the other hand, the contact at the PB/Ppy interface as well as the indium tin oxide (ITO) is blocking type for both types of the charge carriers. Further, the energy levels of PB are placed in such a way that they act as minority carrier (i.e. electron) trapping centers for Ppy. Thus, in dark, the charge transport is highly restricted. On the other hand, when such a device is exposed to visible radiation, the PB layer absorbs the photons and the photogenerated charge carriers are sufficiently energetic so as to cross the barrier and / or reach the conduction level. The trapping of minority carriers (i.e. electrons from Ppy) facilitates the increase of mobile holes which are easily transported through the Ppy layer. Thus, the addition of PB film gives rise to enhanced photocurrent. However, when the concentration of PB or its film thickness increases, there is a decrease in the dark current and the photo current remains more or less the same. Hence, the apparent photosensitivity factor increases, up to the critical thickness of PB. There after, further increase in the PB film thickness lowers the photosensitivity

factor because of either heavy trapping and / or recombination of the photogenerated charge carriers in the PB film itself (which does not allow them to reach to Ppy) and also the light is only absorbed at the surface of the PB film and is unable to see the junction.

Thus, it can be concluded that the space charge limited conduction is the dominant process of charge transport in conducting Ppy/PB bilayer films which suggests that the photosensitization effect is field dependent due to the formation of the space charge in such materials. This leads to certain value of the thickness of the sensitizing PB layer at which the charge transport is optimized and the photosensitivity is maximum.

ABSORBANCE (Arb. Unit)

300

Figure 0.1
PB H-aggregate
2345 250

3.3.3 PHOTSENSITIVITY OF CONDUCTING POLYPYRROLE SENSITIZED WITH PB DISPERSED IN SOLID POLYMER ELECTROLYTE :

3.3.3.1 PB DYE AGGREGATION :

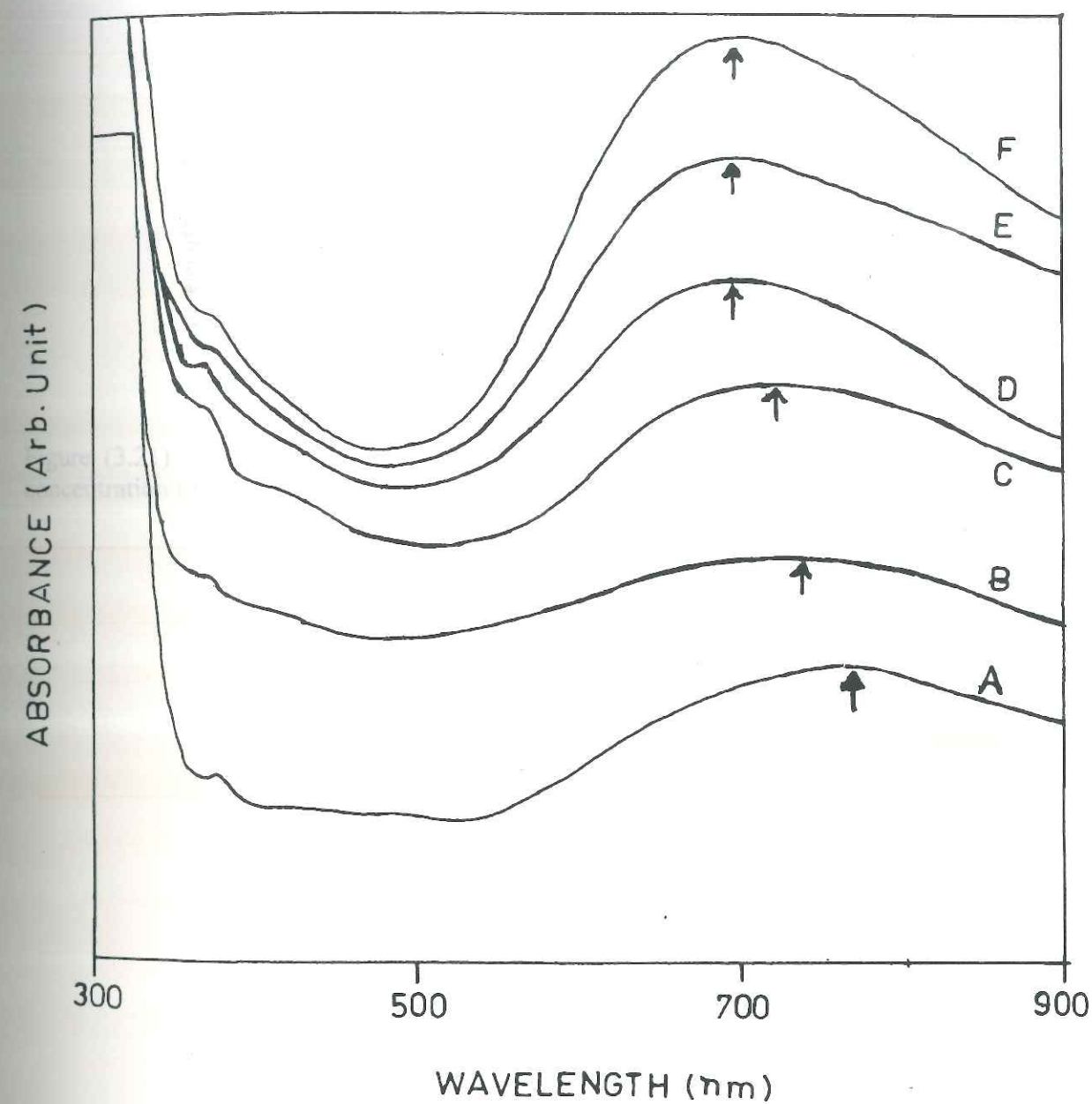


Figure (3.20) : UV-VIS spectra of the PB dispersed in PVA/H₃PO₄ matrix showing the PB H-aggregate formation. Curves (A) to (F) corresponds to the concentration of 2.158, 2.345, 2.564, 2.876, 2.906, 3.01 mM/monomer respectively.

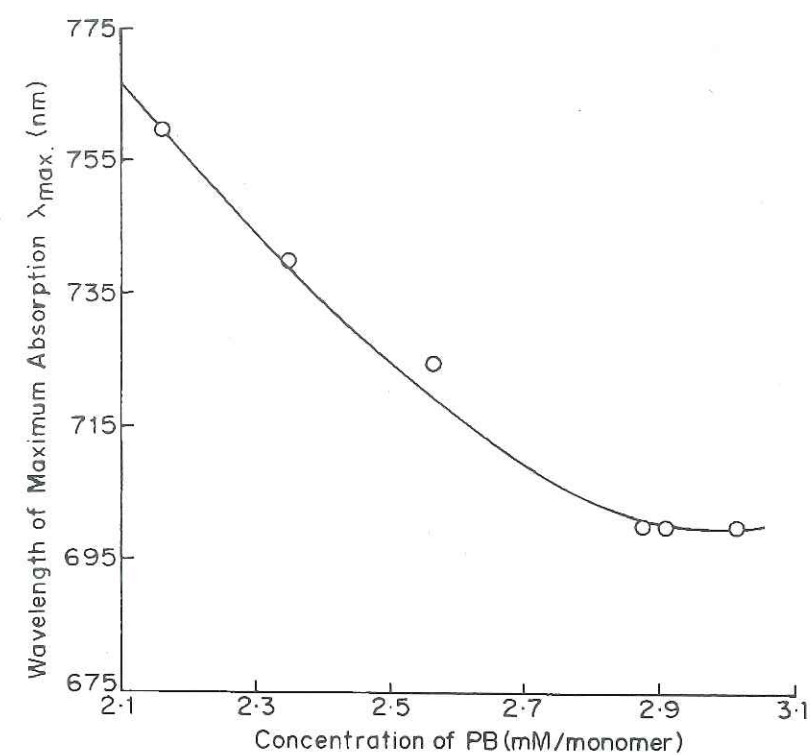


Figure (3.21) : The variation of wavelength of maximum absorption (λ_{max}) with the concentration of PB.

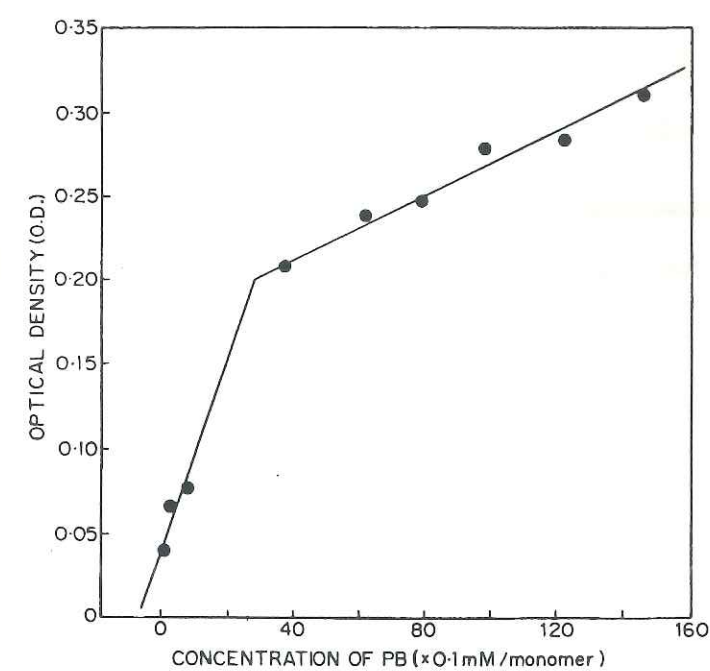


Figure (3.22) : The evidence of PB aggregate formation from the PB concentration vs optical density (OD) plot ; the OD increases non-linearly with the concentration.

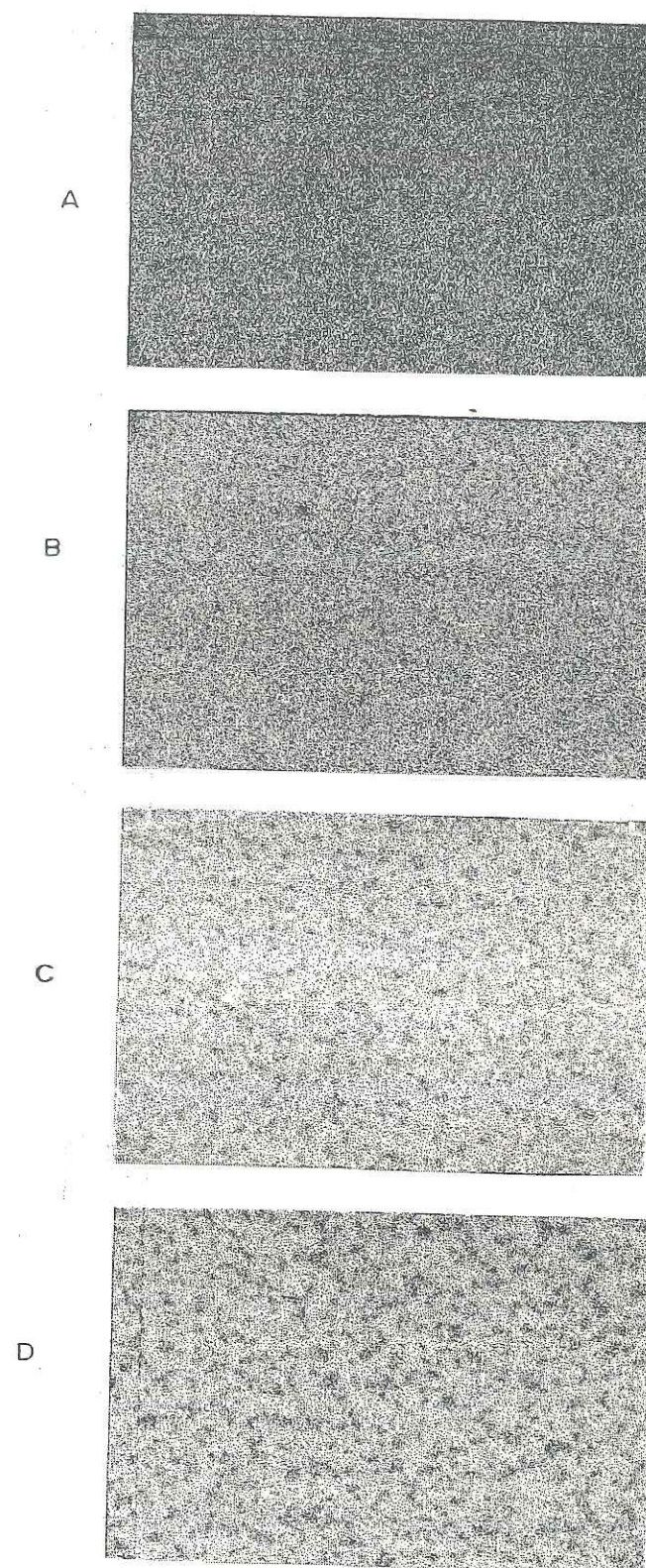


Figure (3.23) : The optical microscope photograph of the PB before aggregation (A, B) and after aggregation (C, D). The PB concentrations are 2.011, 2.315 and 2.906, 3.012 mM/monomer respectively. The magnification used in all case is 400x.

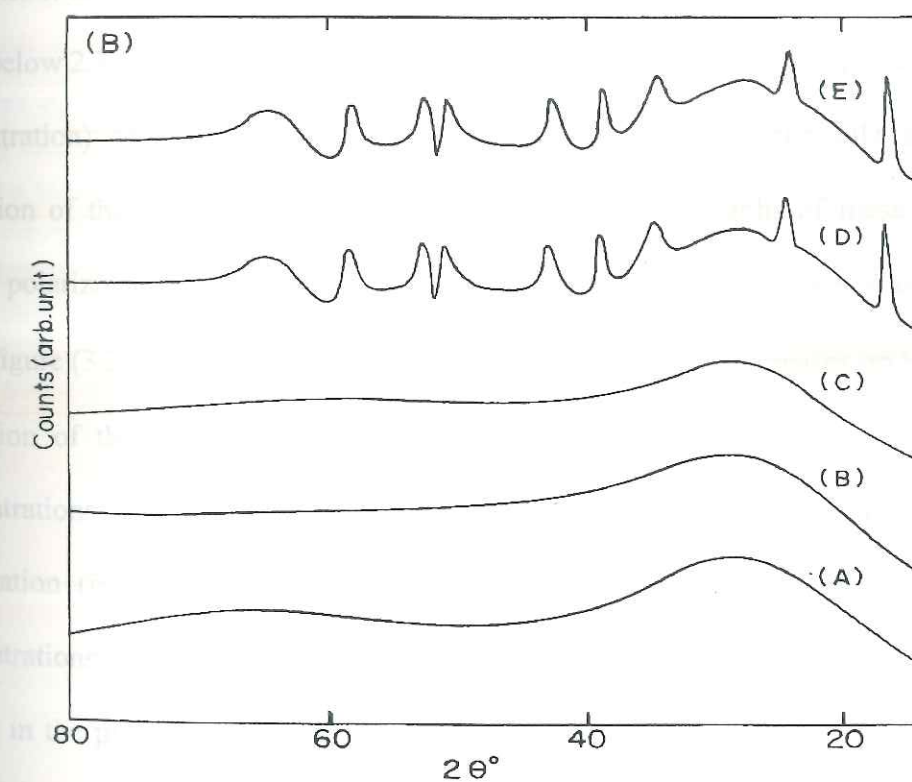
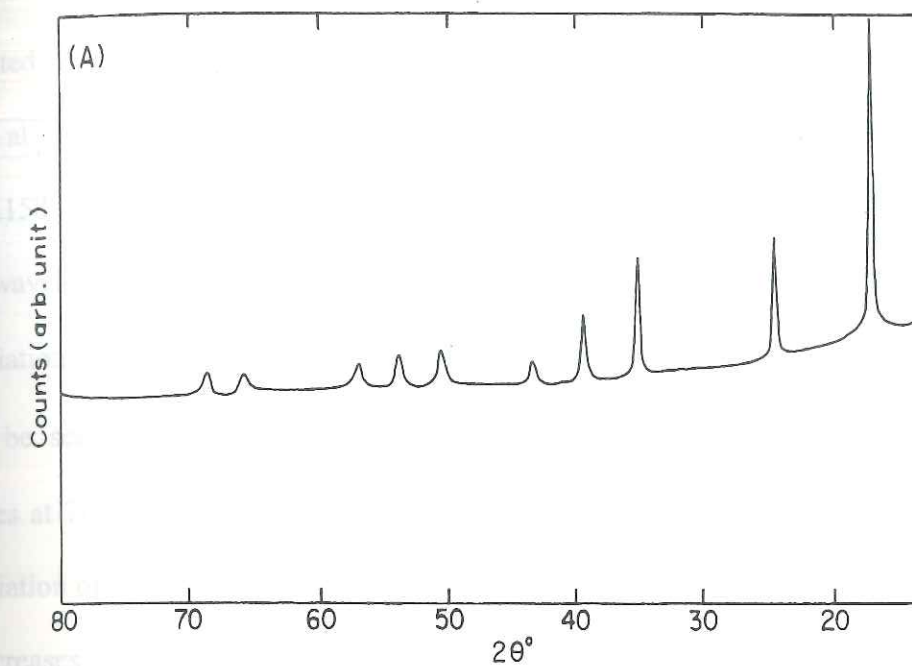


Figure (3.24) : (A) XRD of PB powder. (B) XRD of PVA+H₃PO₄+PB films on glass. (A) to (E) corresponds to PB concentration of 1.0, 1.5, 2.0, 3.3 and 3.7 mM/monomer respectively.

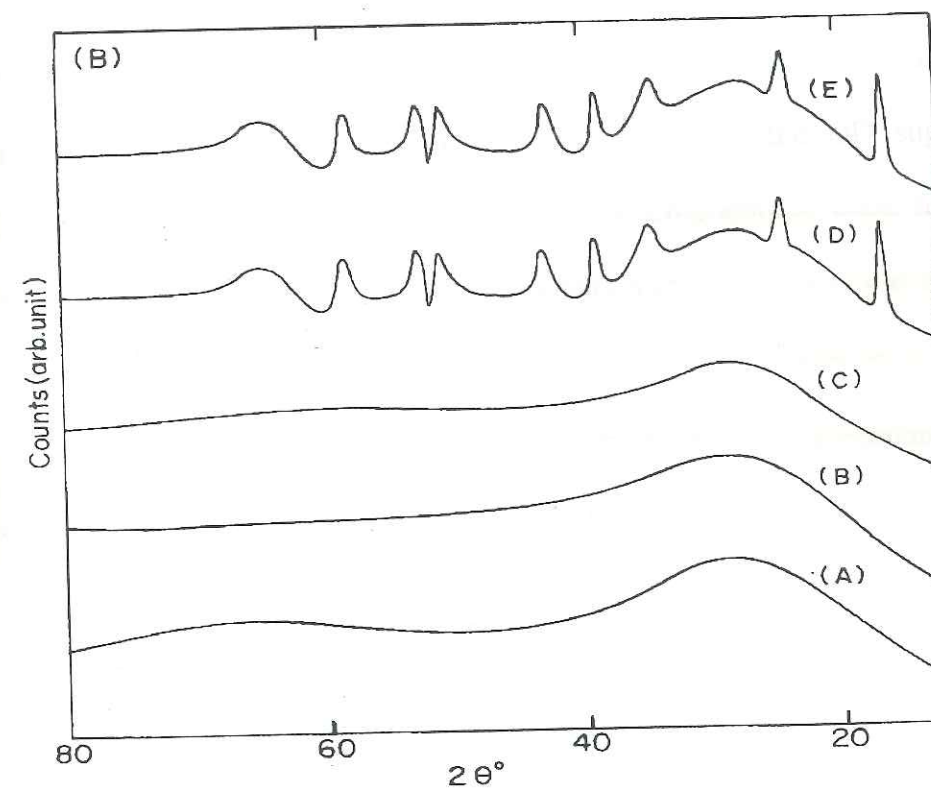
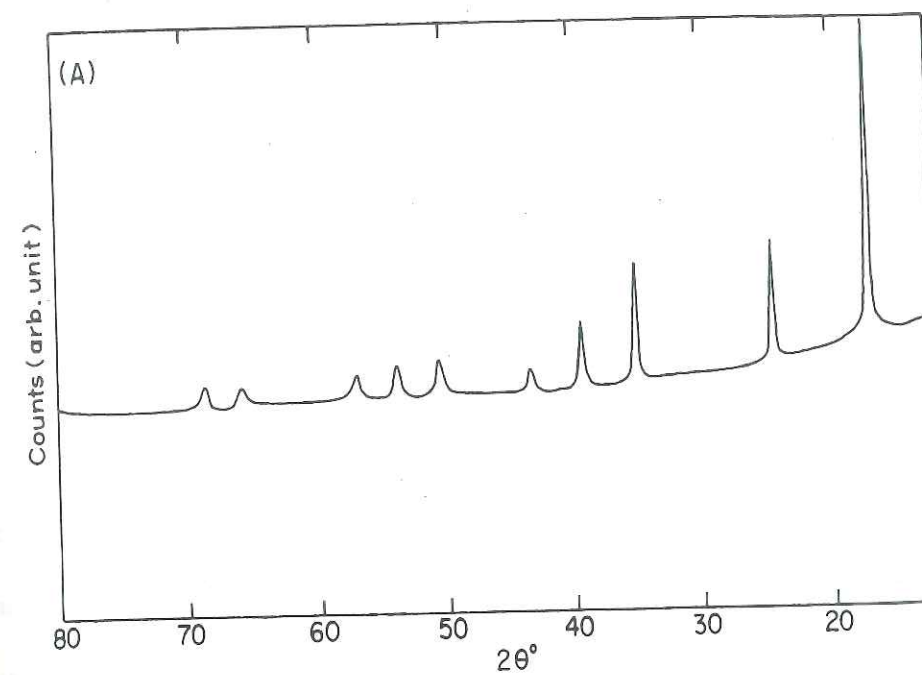


Figure (3.24) : (A) XRD of PB powder. (B) XRD of PVA+H₃PO₄+PB films on glass. (A) to (E) corresponds to PB concentration of 1.0, 1.5, 2.0, 3.3 and 3.7 mM/monomer respectively.

Figure (3.20) displays the UV-VIS spectra of the PB incorporated SPE (i.e. PVA+H₃PO₄) dip coated films on glass substrates with varying concentration of PB. It can be seen that the PB absorption peak is shifting from about 760 nm to 700 nm at the concentrations from 2.158 to 3.01 mM/monomer. The absorption peak shifts to higher energy side (i.e. lower wavelength), indicating the formation of H-aggregates of PB. Figure (3.21) shows the variation of wavelength of maximum absorption ($\lambda_{\max}$) with the concentration of PB. It can be seen that ($\lambda_{\max}$) decreases with the increase in the PB concentration and saturates at 700 nm at 2.85 mM/monomer PB concentration. Also, Figure (3.22) shows the variation of the optical density (OD) with the PB concentration. It can be seen that the OD increases very rapidly initially up to the PB concentration of 2.3 mM/monomer and thereafter it increases slowly, as can be seen from the two straight lines (having greater slope below 2.3 mM/monomer PB concentration and having a lower slope value after this concentration) in Figure (3.22). The non-linear variation of the OD suggests the formation of the PB aggregates. Further, the optical micrographs of these films under optical polarizing microscope clearly show the formation of PB aggregates as can be seen from Figure (3.23). The particle size which is well below 0.5 μ increases up to 2 μ , on the formation of the PB aggregates. Here, we have observed dye aggregation at higher concentrations (approximately at about 10^{-3} M/monomer). Earlier reports on dye aggregation (in general) shows the formation of the aggregation at relatively lower concentrations (at about 10^{-4} to 10^{-5} M). This must be due to the polymeric medium / matrix in the present case as compared to aqueous or organic solvent media which are used in such studies. Also, it can be seen that as the concentration of PB increases, there is increase in the density of the dye particles.

Figure (3.24A) shows the XRD pattern of the PB powder. Figure (3.24B, B-E) shows XRD pattern of the PB incorporated SPE dip-coated films on glass substrates corresponding to PB concentrations of 1.0, 1.5, 2.0, 3.3 and 3.7 mM/monomer respectively. It is clear that below the critical concentration of PB, the XRD pattern do not show any peaks corresponding to PB indicating thereby that PB is homogeneously dispersed and not present in an aggregate / crystal form. Above the critical concentration, peaks corresponding to PB becomes observable indicating that PB is present in the form of small aggregates / crystals. Thus, XRD studies also support the formation of PB aggregates at high concentrations.

3.3.3.2 EFFECT OF PB AGGREGATION ON PHOTSENSITIZATION :

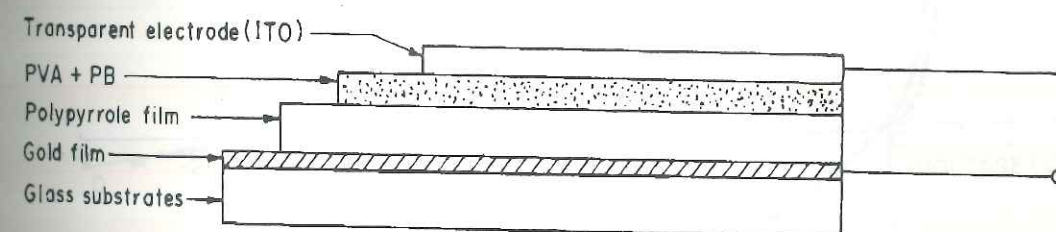


Figure (3.25) : Schematic of the multilayer photocell using conducting Ppy and PB dispersed in SPE (i.e. PVA+H₃PO₄) (Au/Ppy/SPE+PB/ITO).

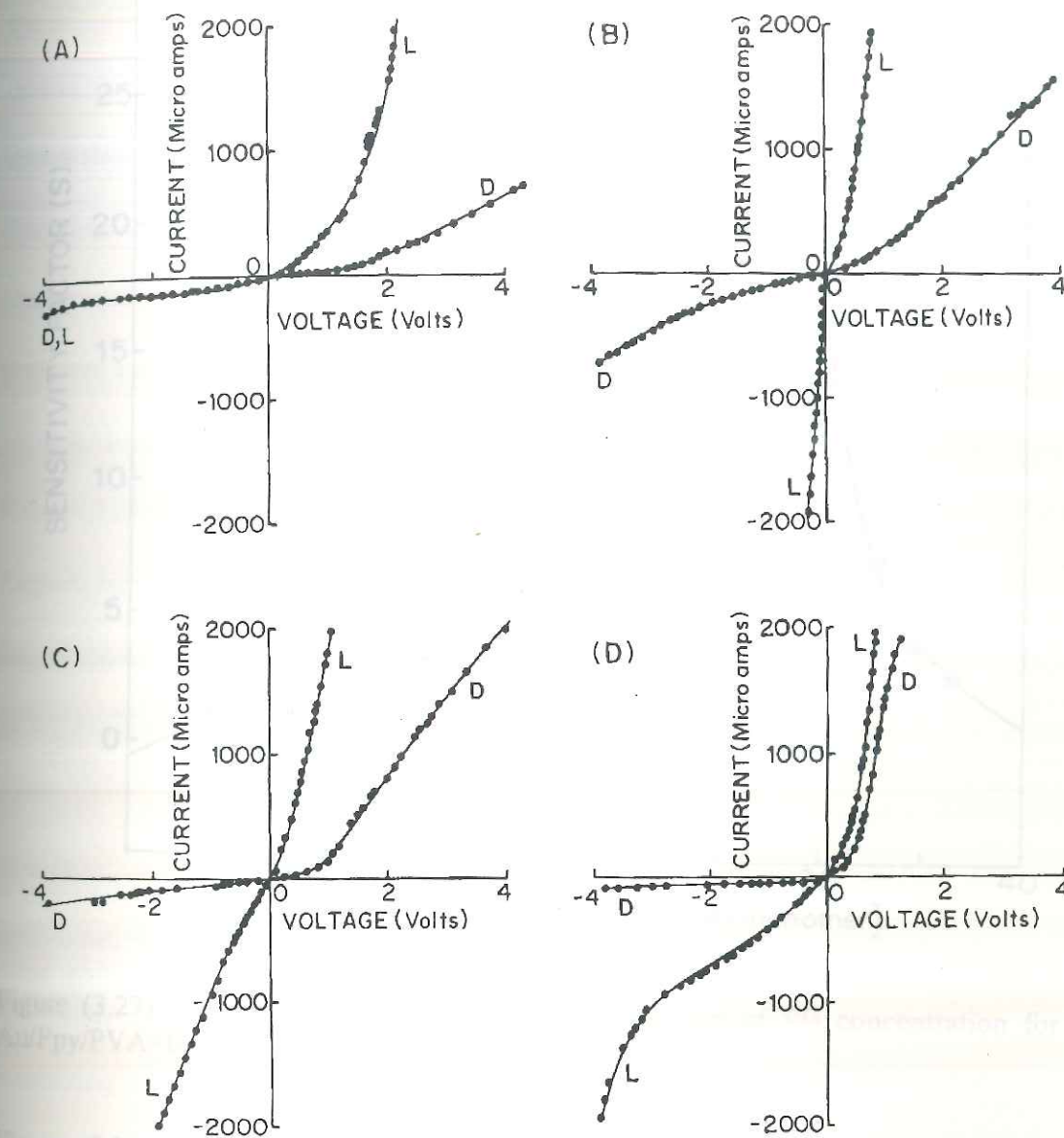


Figure (3.26) : Current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the Au/Ppy/PVA+H₃PO₄+PB/ITO sandwich cell with different PB concentrations. (A) to (D) corresponds to the PB concentrations of 0.769, 2.2, 2.313 and 4.153 mM/monomer, respectively.

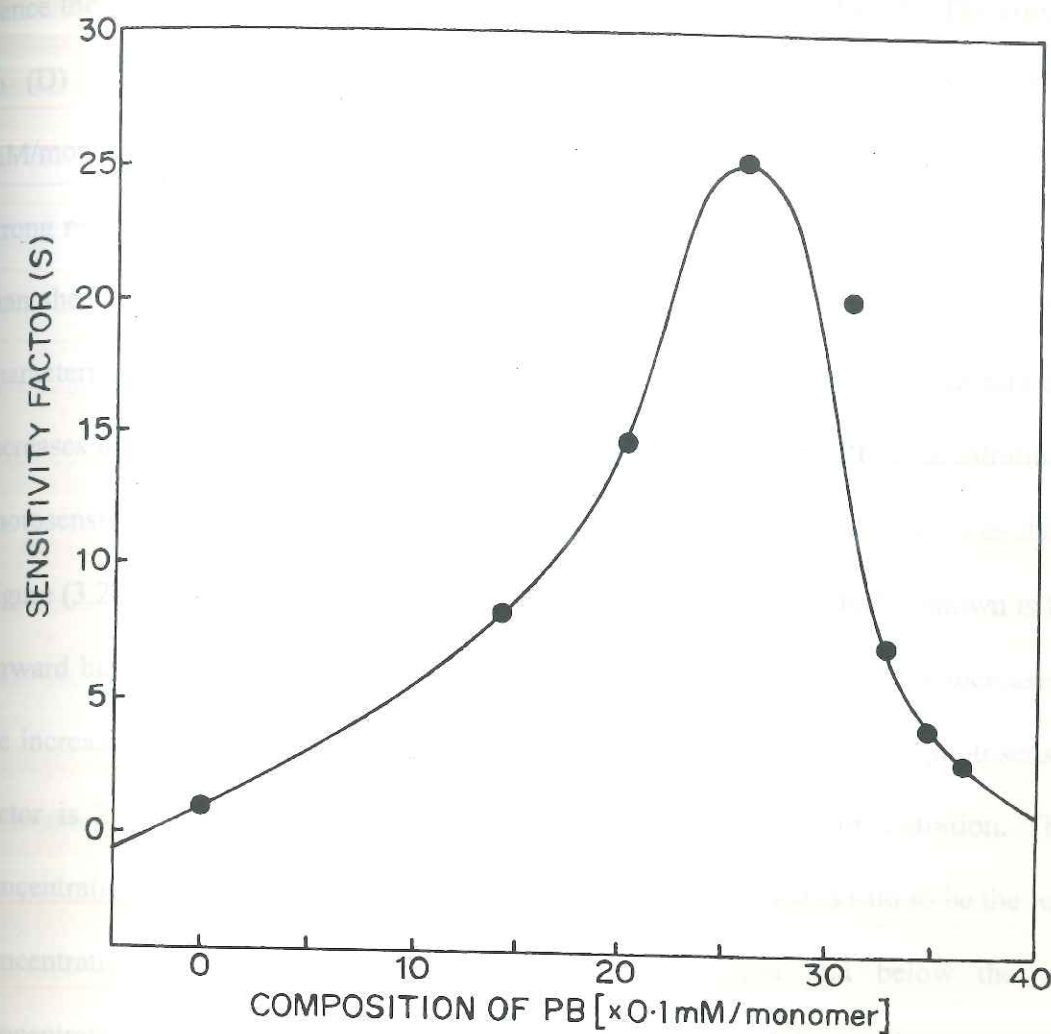


Figure (3.27) : Photosensitivity factor (S) as a function of PB concentration for the Au/Ppy/PVA+H₃PO₄+PB/ITO sandwich cell.

Figure (3.25) shows the schematics of the photocell in which Ppy is sensitized with Prussian blue incorporated / dispersed in SPE. The current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the Ppy/PB sandwich cells (Au/Ppy/PVA+H₃PO₄+PB/ITO) are as shown in Figure (3.26). The I-V characteristics have been recorded by placing the samples in the specially prepared dry box (as discussed in chapter 2) and in the 'dry state' of the solid polymer electrolyte (SPE) and

hence the photocells thus formed can be termed as 'dry state' photocells. The curves (A) to (D) corresponds to the PB concentration of 0.769, 2.307, 3.076 and 4.153 mM/monomer, respectively. It is interesting to observe that the I-V characteristics shows strong rectification i.e. current in one direction (Au + ve, first quadrant) is much higher than the current in the opposite direction (Au - ve, third quadrant). Further, the I-V characteristics are non-linear, both under illumination as well as in dark. The dark current increases and the photocurrent decreases with the increase in the PB concentration. The photosensitivity factor (S) for these cells as a function of PB concentration is as shown in Figure (3.27), for the forward bias only. Here, the photosensitivity factor shown is for the forward bias i.e. first quadrant only. It is evident that the photosensitivity increases with the increase in the PB concentration, reaches to a maximum (maximum photosensitivity factor is 25) and then decreases with further increase in PB concentration. The PB concentration at which the maximum photosensitivity is obtained is said to be the 'critical concentration'. Initially, with increasing PB concentration and below the critical concentration, the photosensitivity increases as the number of the sensitizing centers are increasing. At very low concentration of PB, the photosensitivity is low as the number of sensitizing centers are low in number and hence formation of low number of the photogenerated charge carriers.

Slightly above the critical concentration and thereafter, the photosensitivity is decreasing. This might be because of two reasons : increase in the PB concentration increases the dye aggregation which decreases the actual photosensing surface area and secondly due to the formation of the PB H-aggregates. The actual energy gap [forbidden gap – the difference

hence the photocells thus formed can be termed as 'dry state' photocells. The curves (A) to (D) corresponds to the PB concentration of 0.769, 2.307, 3.076 and 4.153 mM/monomer, respectively. It is interesting to observe that the I-V characteristics shows strong rectification i.e. current in one direction (Au + ve, first quadrant) is much higher than the current in the opposite direction (Au - ve, third quadrant). Further, the I-V characteristics are non-linear, both under illumination as well as in dark. The dark current increases and the photocurrent decreases with the increase in the PB concentration. The photosensitivity factor (S) for these cells as a function of PB concentration is as shown in Figure (3.27), for the forward bias only. Here, the photosensitivity factor shown is for the forward bias i.e. first quadrant only. It is evident that the photosensitivity increases with the increase in the PB concentration, reaches to a maximum (maximum photosensitivity factor is 25) and then decreases with further increase in PB concentration. The PB concentration at which the maximum photosensitivity is obtained is said to be the 'critical concentration'. Initially, with increasing PB concentration and below the critical concentration, the photosensitivity increases as the number of the sensitizing centers are increasing. At very low concentration of PB, the photosensitivity is low as the number of sensitizing centers are low in number and hence formation of low number of the photogenerated charge carriers.

Slightly above the critical concentration and thereafter, the photosensitivity is decreasing. This might be because of two reasons : increase in the PB concentration increases the dye aggregation which decreases the actual photosensing surface area and secondly due to the formation of the PB H-aggregates. The actual energy gap [forbidden gap – the difference

between the bottom of the conduction band (CB) and the top of the valance band (VB)] increases due to the formation of the PB H-aggregates hence results in the reduction of the photosensitivity. Also, it is well known that photo- sensing is a surface dependent phenomenon. So, although in this region, PB concentration is increasing, because of the formation of the PB aggregates, the actual photosensing surface area is decreasing and this might be one of the reasons for decrease of photosensitivity above the critical concentration. Also, at very high concentration of PB the light is being absorbed only at the surface of the film and is unable to penetrate, to see the junction. At high dye concentration the recombination of majority charge carriers (i.e. holes) increases which leads to quenching of the photosensitivity. Also, other factors like carrier life time, thickness of the film are important in such sensitization processes. At the critical concentration, we are getting maximum photosensitivity because this is the concentration at which the formation of the PB aggregates starts. At this concentration, less (or 'NO') formation of the aggregates and enough generation of the charge carriers in presence of light are solely responsible for getting maximum photosensitivity.

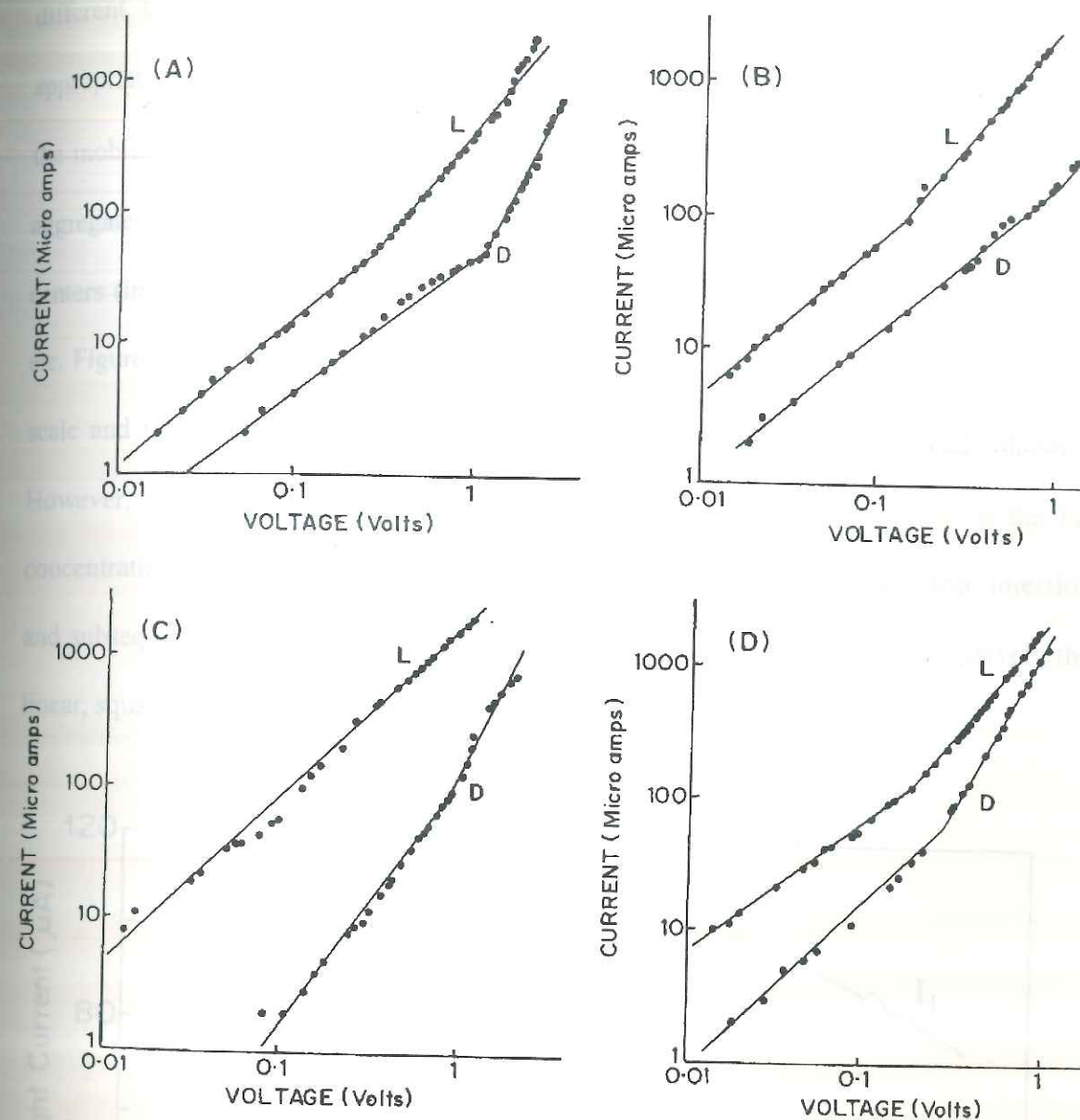


Figure (3.28) : The log-log plot of the I-V curves presented in Figure (26) in the positive quadrant (1st quadrant) only showing the non-linear SCLC type conduction. (A) to (D) corresponds to PB concentration of 0.769, 2.2, 2.313 and 4.153 mM/monomer respectively.

In conducting polymer composites (CPC) and composite film structures like the one under study, the charge transport mechanism is very important and it can be the rate determining factor. The current-voltage (I-V) characteristics were analyzed in detail for

different types of charge transport processes and the SCLC appeared to be most appropriate for the present case in which the current is given by equation (3.3) where μ is the mobility of the charge carriers, d is the average distance between the dye particles / aggregates, θ is a parameter which takes in to account the concentration of the trapping centers (impurity centers) and their distribution and n is an integer having values 0, 1, 2 etc. Figure (3.28) shows the I-V characteristics (shown in Figure 3.26) plotted on log-log scale and it is evident from these curves that the relation $I \propto V^n$ is indeed followed. However, the slope of the graph changes considerably with the variation in the PB concentration. The SCLC curves are usually interpreted in terms of the charge injection and subsequent filling of the impurity / trapping centers giving rise to progressively the linear, square and superlinear type dependence of the I-V characteristics.

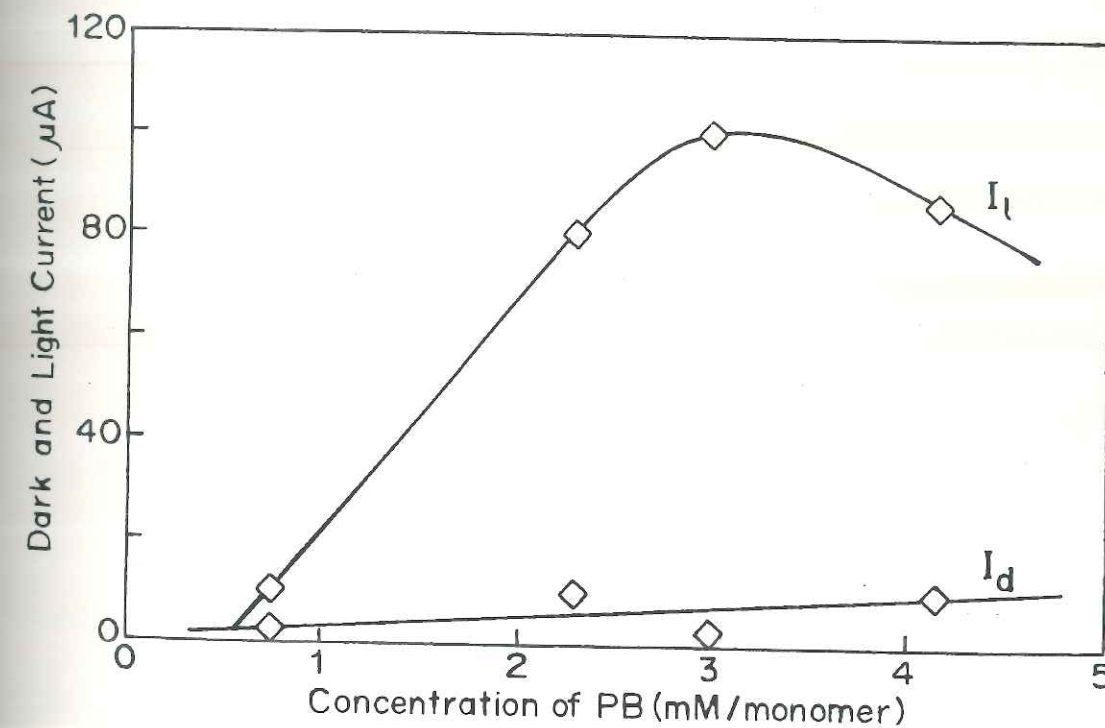


Figure (3.29) : Variation of I_d and I_l with respect to the concentration of PB.

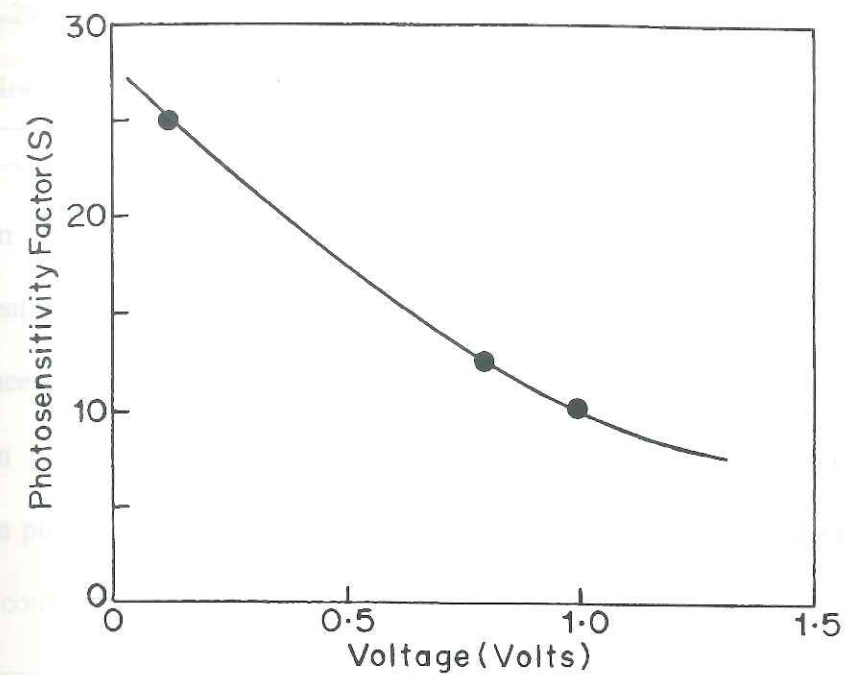


Figure (3.30) : Field dependence of the photosensitivity factor (at the PB concentration at which the maximum photosensitivity is obtained).

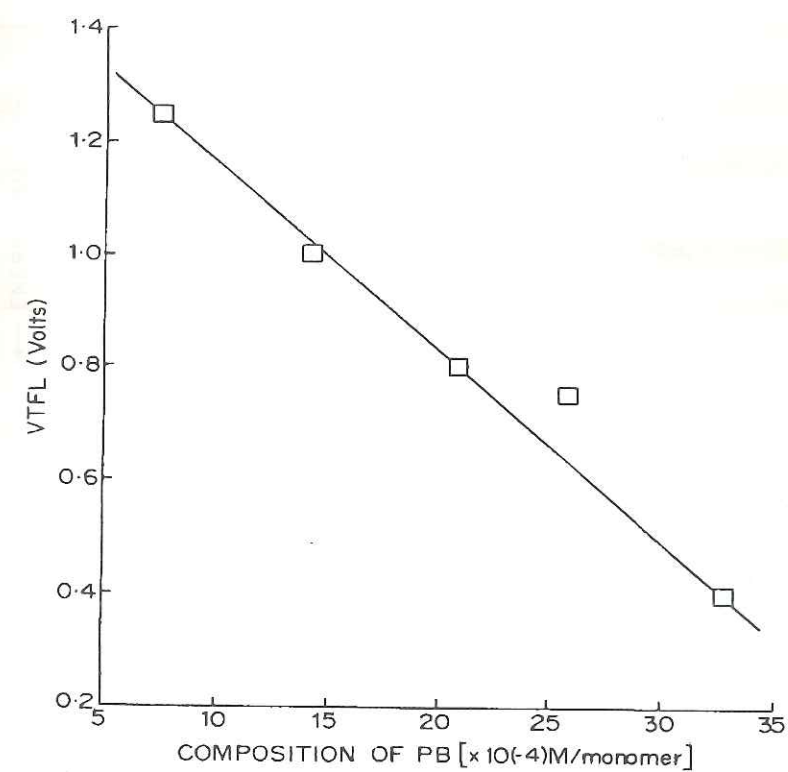


Figure (3.31) : The variation of V_{TFL} with the concentration of PB.

Figure (3.29) shows the variation of I_d and I_l with respect to the PB concentration in the first quadrant only and in the linear portion of the I-V characteristics. It can be seen that the dark current remains practically constant but the photo current goes through a maximum. Thus, it is the variation of the photo current which results in maximum photosensitivity at a particular PB concentration. Figure (3.30) shows the voltage / field dependence of the photosensitivity factor (S), plotted at the PB concentration at which maximum photosensitivity is observed. It can be seen that at a particular voltage maximum photosensitivity can be obtained. Figure (3.31) displays the variation of V_{TFL} with the concentration of PB. It can be seen that as the concentration of PB increases, V_{TFL} decreases.

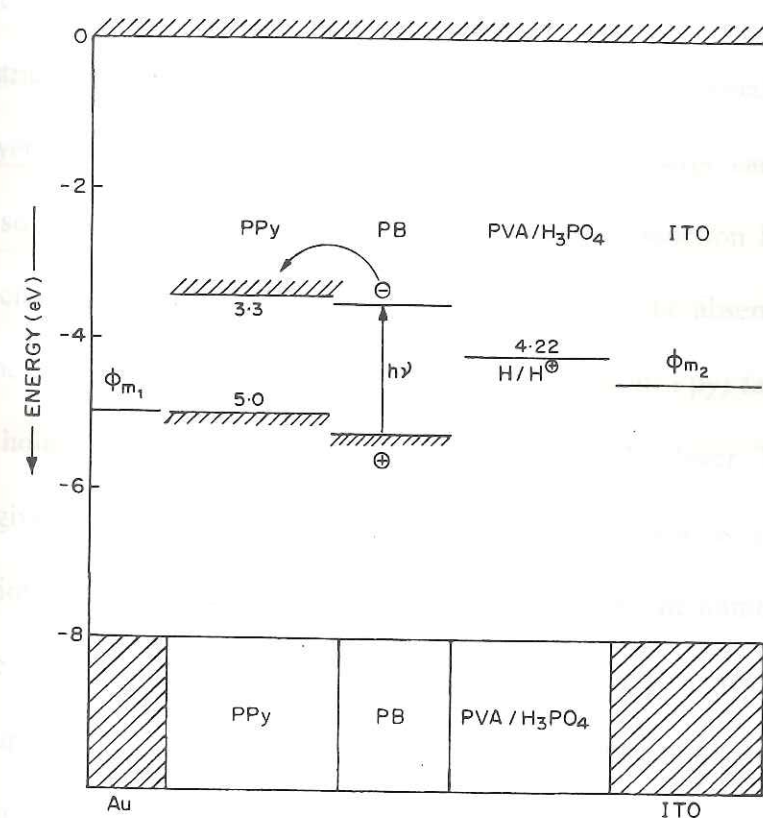
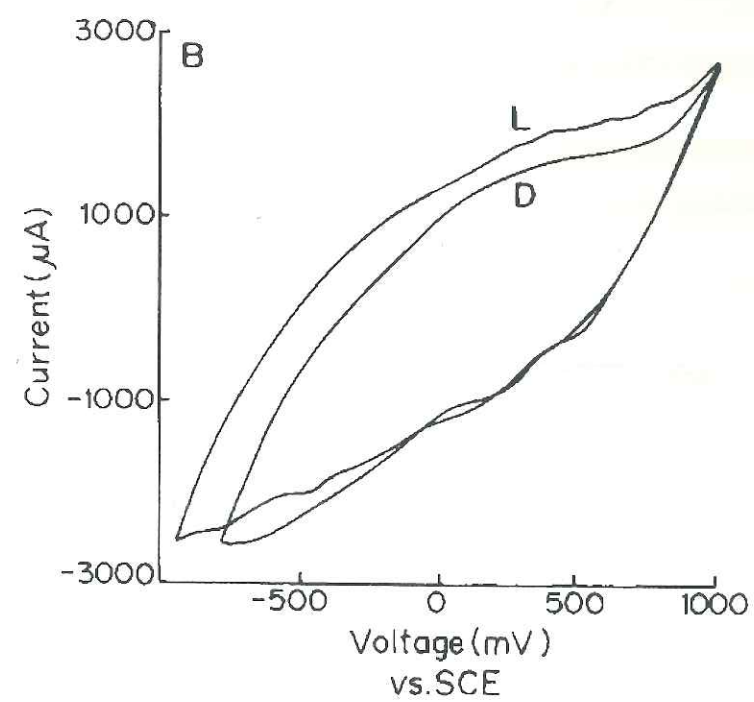
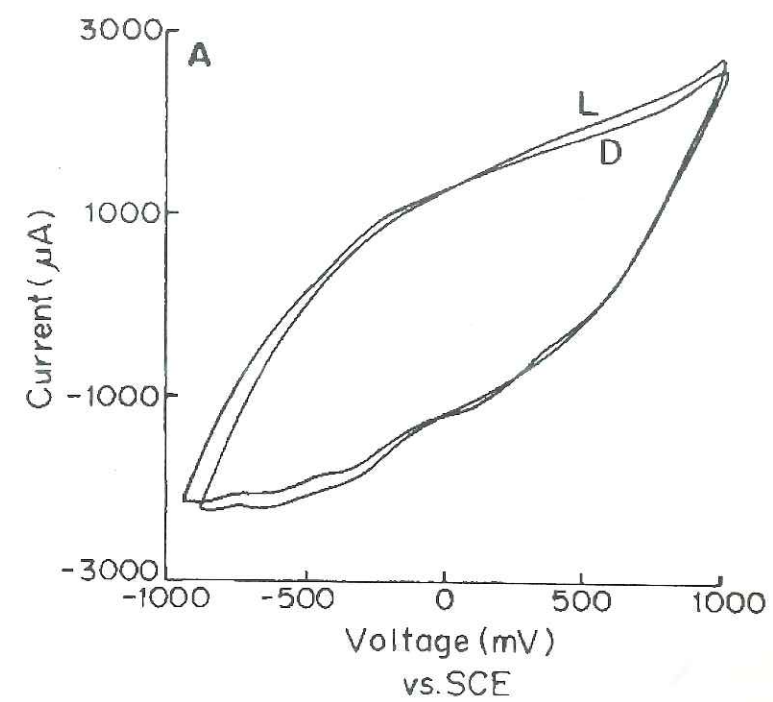


Figure (3.32) : Energy band diagram of the materials forming the sandwich cell (Au/PPy/PVA+H₃PO₄+PB/ITO).

Figure (3.32) shows the energy band diagram for the materials used in forming the photocells. It is basically the same energy band diagram (as that for Ppy/PB bilayer system) but the only difference is that we have considered here the energy level of the SPE. PVA+H₃PO₄ is a proton conductor and hence an energy level corresponding to H/H⁺ can be considered. As stated earlier, Ppy is a p-type material while PB is acting as a n-type material. Also, it can be seen that there is a negligible barrier between Au and Ppy since the work function of Au (5.22 eV) and the highest occupied molecular orbital (HOMO) for Ppy (5.0 eV) are almost at the same position below the vacuum level. On the other hand, the contact at the PB/Ppy interface is blocking type for both types of charge carriers. The energy levels of PB are placed in such a way that they act as minority carrier (i.e. electron) trapping centers for Ppy. Thus, in dark, the charge transport is highly restricted. On the other hand, when such a device is exposed to visible radiation, the PB layer absorbs the photons and the photogenerated charge carriers are sufficiently energetic so as to cross the barrier and / or reach the conduction level. In presence of light, the charge transport is highly facilitated because of the absence / lowering of the barrier. The trapping of minority carriers (i.e. electrons from Ppy) facilitates the increase of mobile holes which are easily transported through the Ppy layer. Thus, the addition of PB film gives rise to enhanced photocurrent and thus acts as a sensitizer. At low concentration of PB the photosensitivity observed is low, as the number of the sensitizing centres are less in number. As the concentration of the PB increases, photosensitivity increases up to critical concentration. The decrease of the photosensitivity after critical concentration is a result of the formation of the H-type of PB aggregates and light is unable to pass through to see the junction. Also, the recombination of the photogenerated

charge carriers plays an important role - as discussed earlier. This leads to certain value of the PB concentration at which the photosensitivity is maximum.

3.3.4 PHOTSENSITIVITY OF CONDUCTING POLYPYRROLE / PRUSSIAN BLUE BILAYER COMPOSITE FILMS IN PEC MODE :



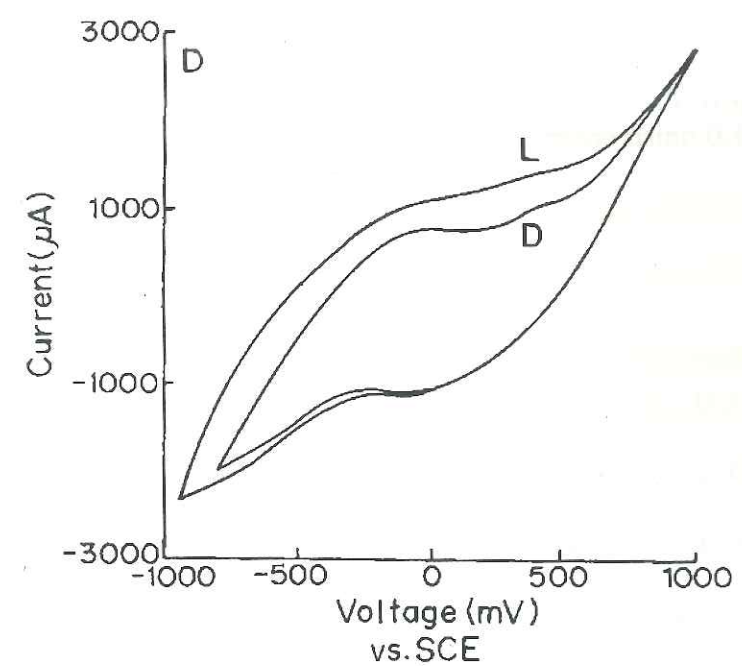
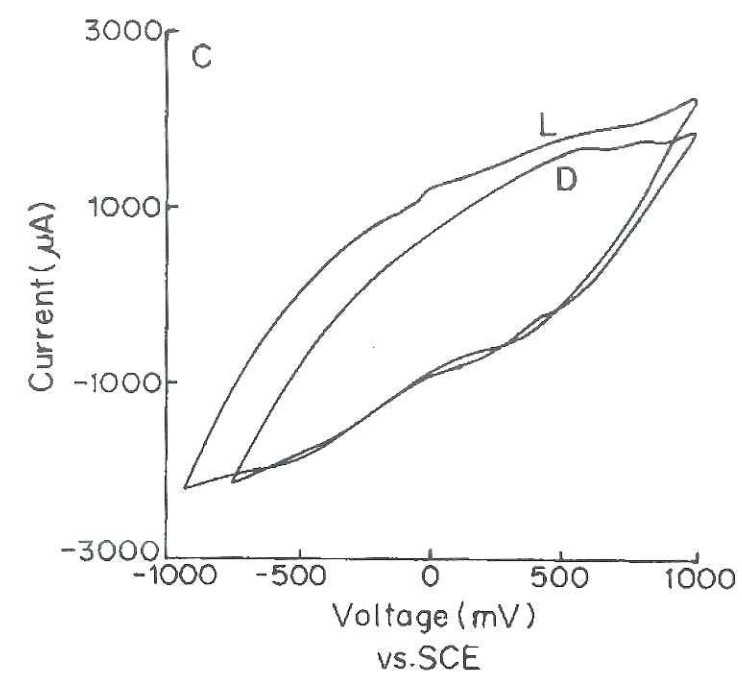


Figure (3.33) : Cyclic voltammogram of the (A) Ppy film and Ppy/PB films with PB film thickness of 265 nm (B), 380 nm (C), 440 nm (D) respectively taken using 0.1 M aqueous KCl as an electrolyte in PEC mode. Scan rate = 50 mV/s.

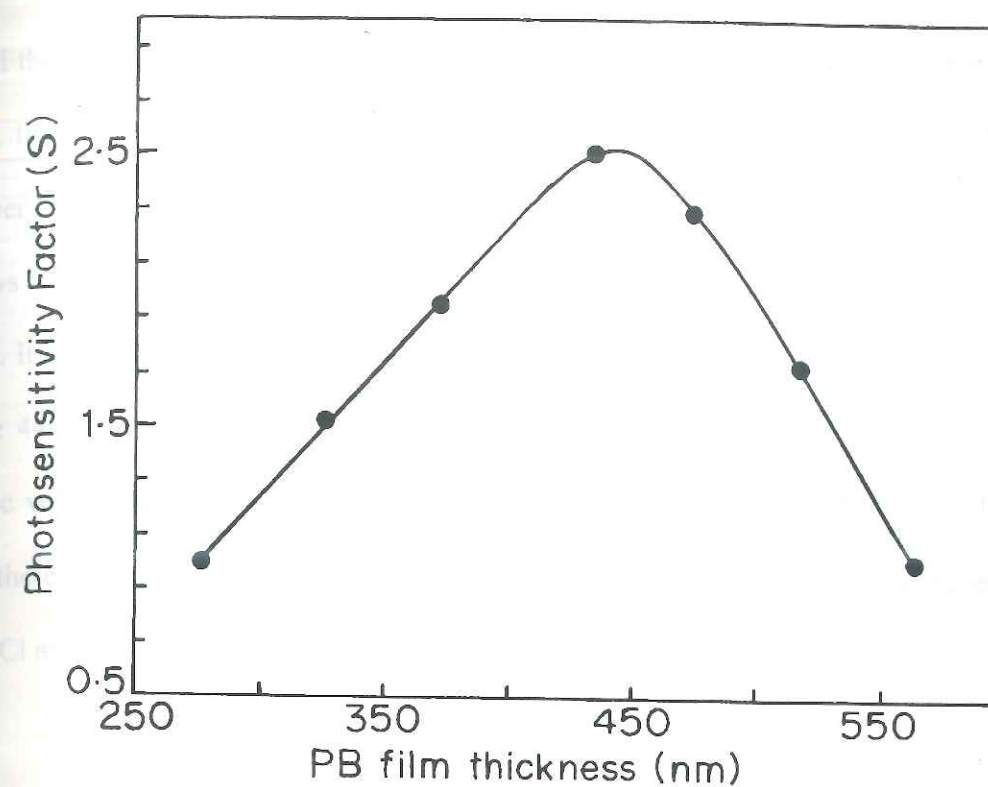


Figure (3.34) : The variation of photosensitivity factor (S) with respect to the PB film thickness for Ppy/PB bilayer composite films in PEC mode using 0.1 M aqueous KCl as an electrolyte.

Figure (3.33A) displays the cyclic voltammogram of the Ppy film deposited electrochemically on gold coated glass in dark (D) and light (L) taken using 0.1 M aqueous KCl as an electrolyte and used in photoelectrochemical (PEC) mode. It is to be noted here that the CV is recorded against SCE. It can be seen that Ppy film displays very poor light sensitivity. Moreover dark current and light current values are almost identical, giving photosensitivity factor of the order of one. Figure (3.33 B, C, D) shows the cyclic voltammogram of the Ppy/PB bilayer films with PB film thickness of 265 nm, 380 nm and 440 nm respectively in dark (D) and light (L), keeping all other experimental

parameters same as for Figure (3.33A). The Ppy film thickness (600 nm) is kept constant in all the cases. By comparison, it can be seen that when a PB film is deposited on Ppy film, the bilayer films show some light sensitivity, although not very high. Also, the bilayer films show more light sensitivity when the film is driven anodically. Figure (3.34) shows the variation of photosensitivity factor (S) with the PB film thickness, at 0 V vs. SCE. It can be seen that the photosensitivity is maximum at a certain PB film thickness (here 440 nm) and decreases on both sides. It is worthwhile to mention here that the cyclic voltammograms reported here are taken using aqueous 0.1 M KCl as electrolyte and the cyclic voltammogram presented in Figure [3.1B(c)] is taken using aqueous 0.01 M KCl as electrolyte, hence the current values are different.

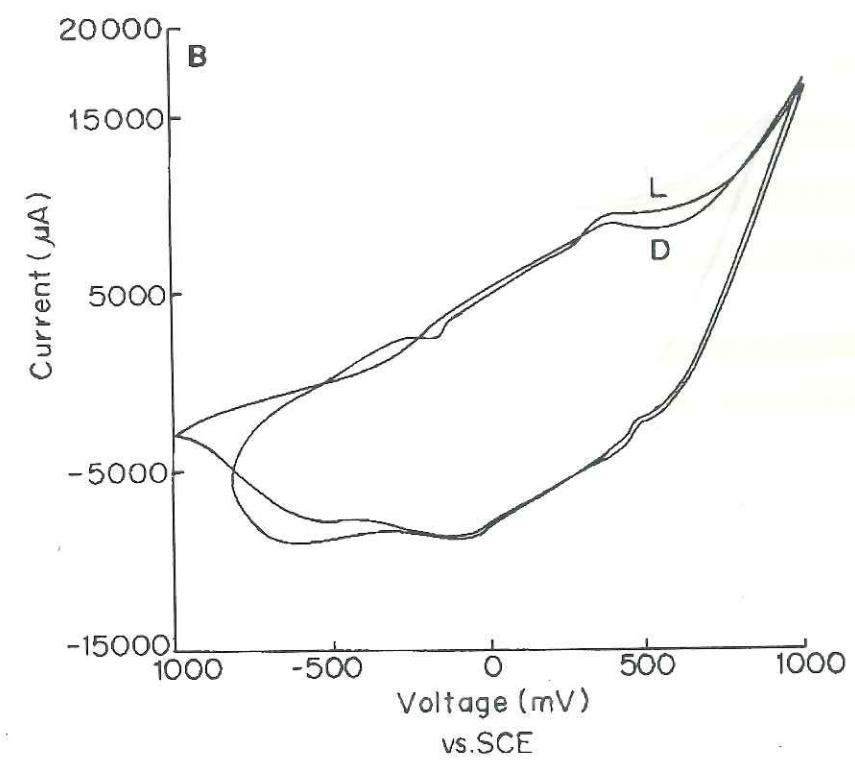
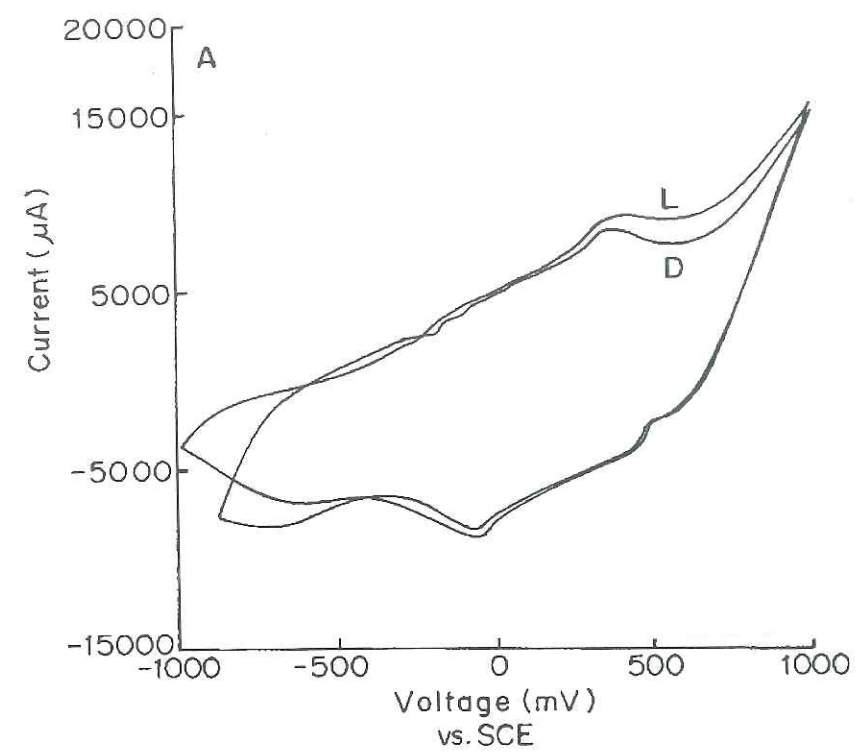


Fig. 1
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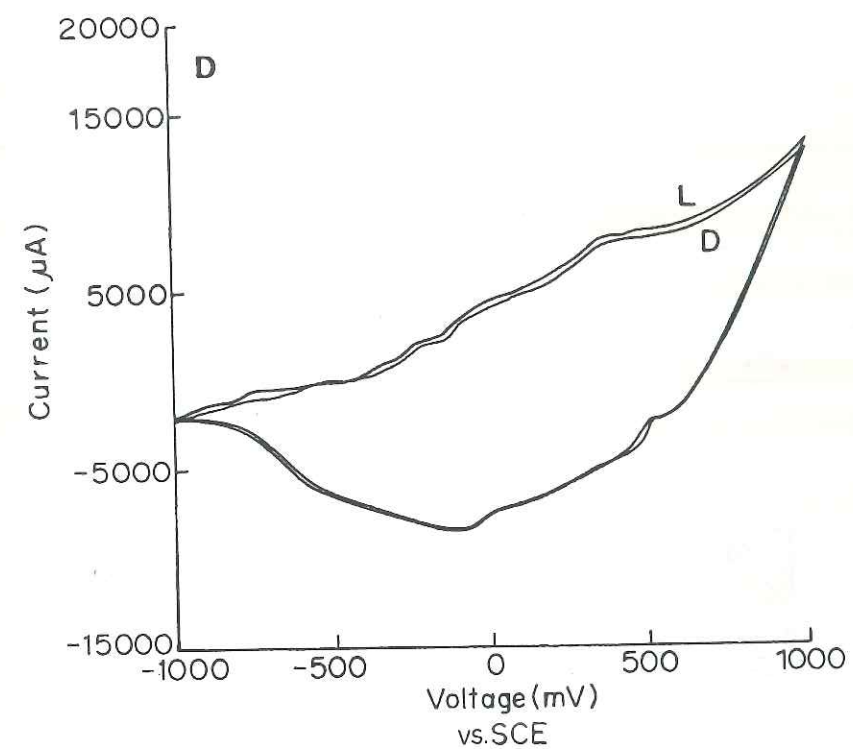
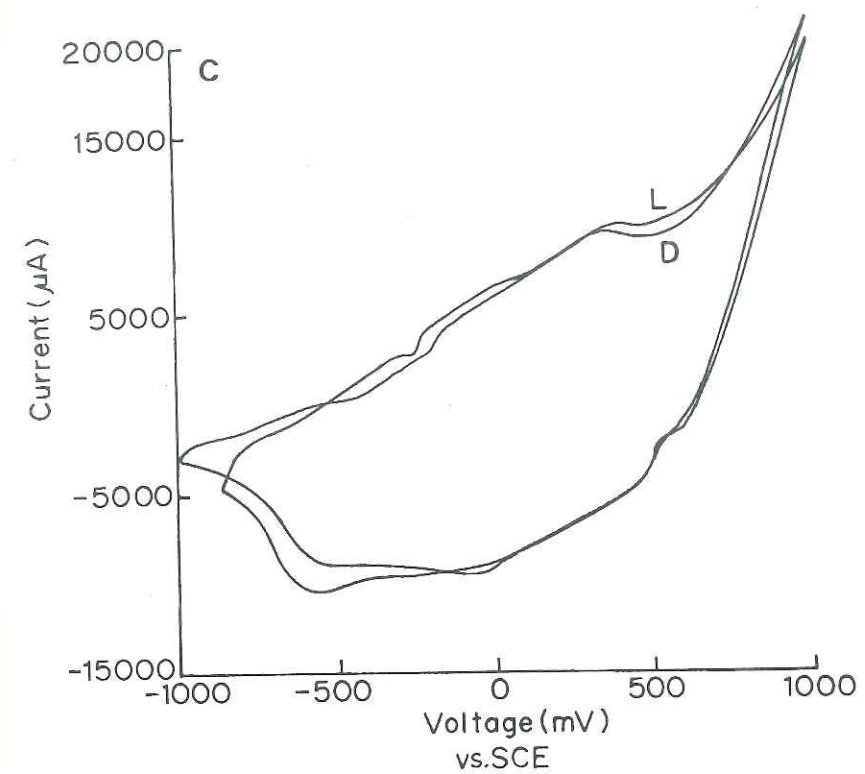


Figure (3.35) : Cyclic voltammogram of the Ppy/PB bilayer composite films with PB film thickness of 380 nm (A), 435 nm (B), 515 nm (C) and 525 nm (D) respectively taken using 0.1 M aqueous LiClO_4 as an electrolyte in PEC mode. Scan rate = 50 mV/s.

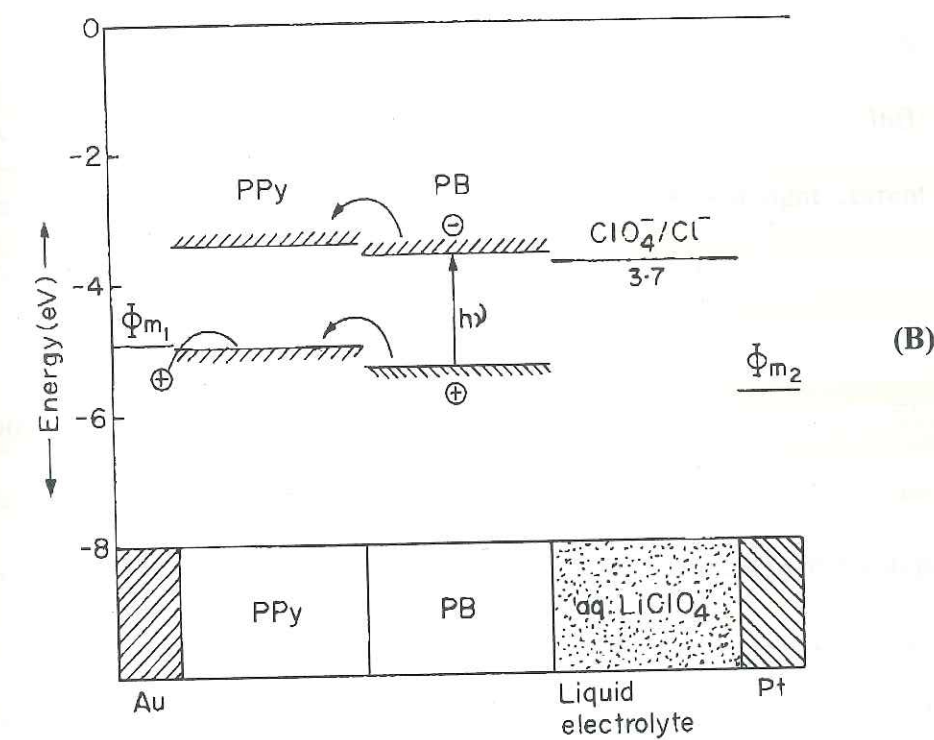
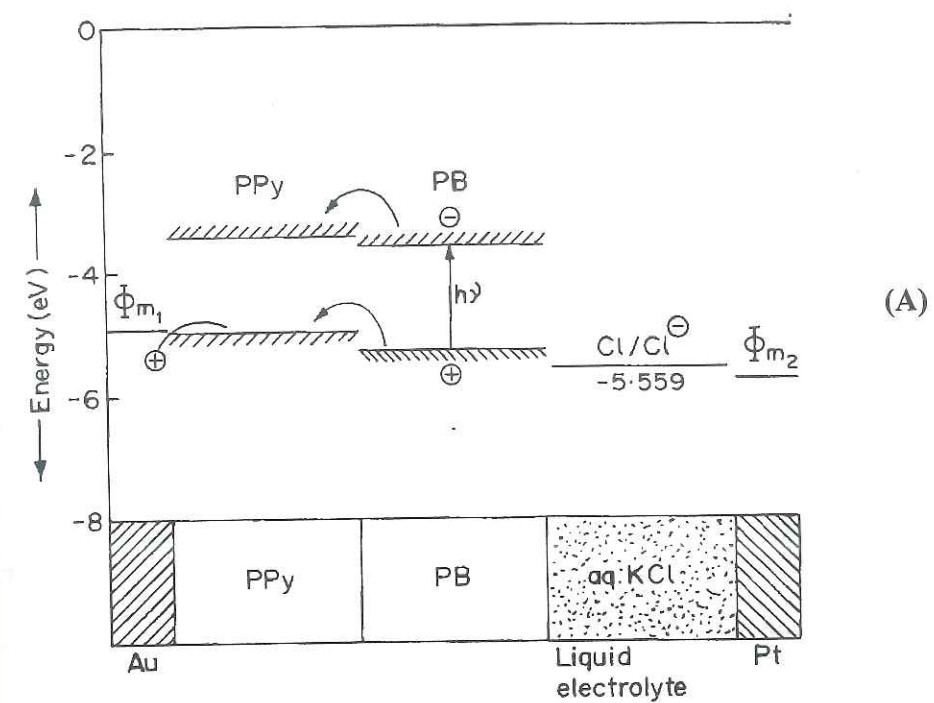


Figure (3.36) : (A) Energy level diagram of the materials used in PEC cell configuration using 0.1 M KCl as an electrolyte.
 (B) Energy level diagram of the materials used in PEC cell configuration using 0.1 M LiClO₄ as an electrolyte.

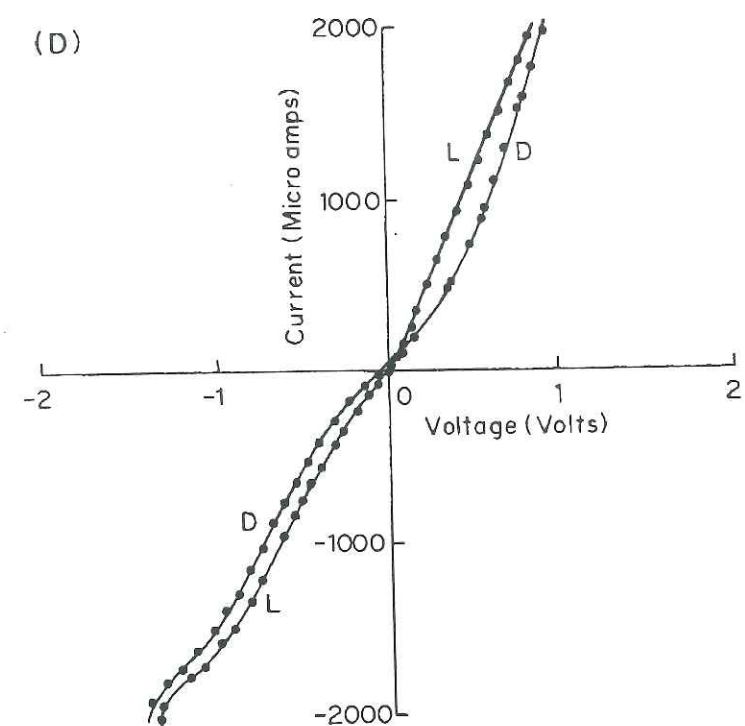
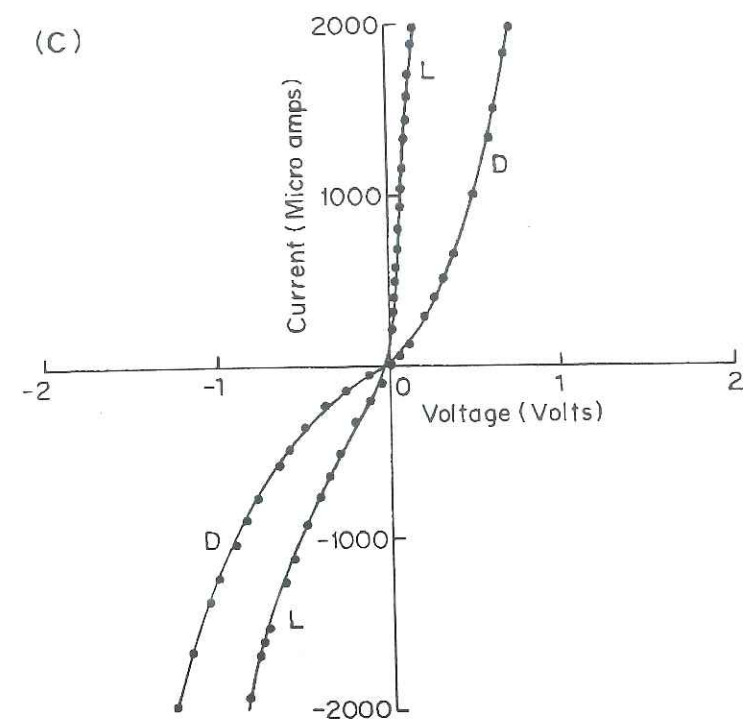
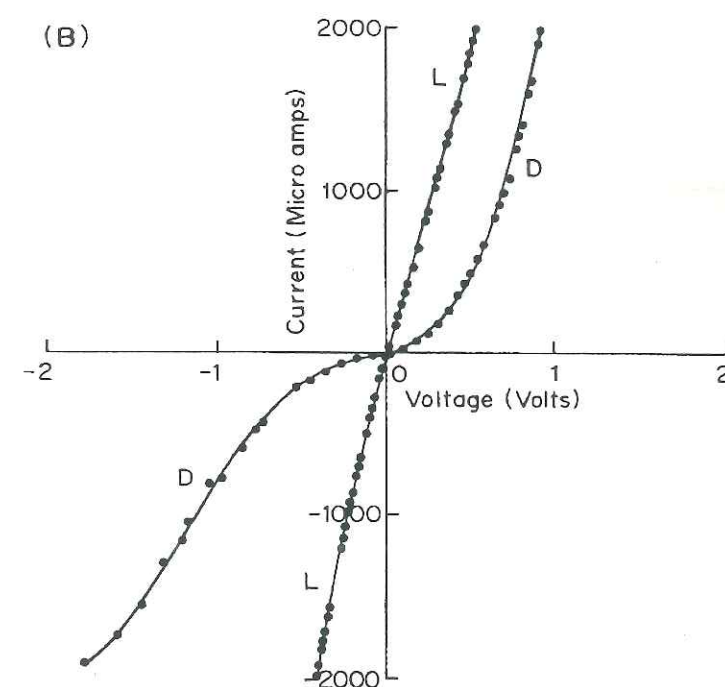
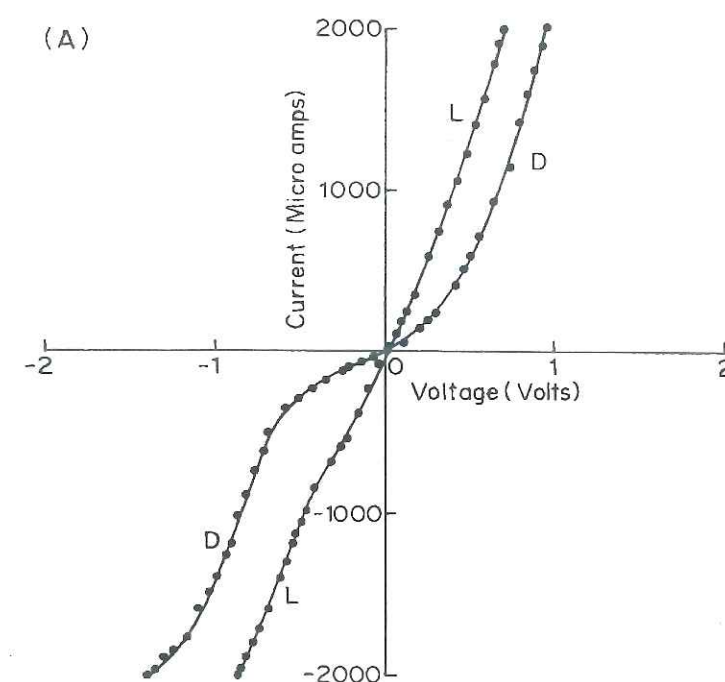


Figure (3.37) : I-V characteristics in dark (D) and under illumination (L) for Au/Ppy/PVA+H₃PO₄+PB/ITO "wet state" photocell with different PB concentrations. (A) to (D) corresponds to PB concentrations of 0.769, 2.307, 3.076 and 4.153 mM/monomer respectively.

3.3.5 PHOTSENSITIVITY OF CONDUCTING POLYPYRROLE SENSITIZED WITH PB DISPERSED IN SOLID POLYMER ELECTROLYTE (WET STATE) :



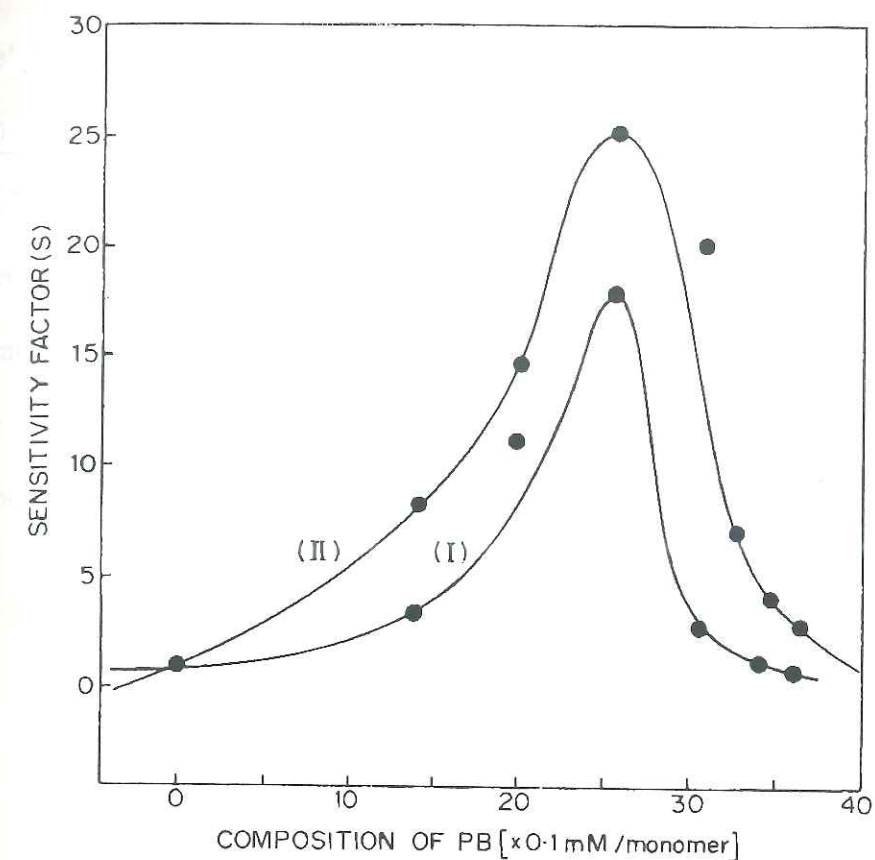


Figure (3.38) : photosensitivity factor as a function of PB concentration in the "wet state photocell"- (I). For comparison, the photosensitivity factor as a function of PB concentration in the "Dry state photocell"-II, is also shown.

The I-V characteristics in dark (D) and under illumination (L) for the Ppy/PB 'wet state' photocells are as shown in Figure (3.37). The curves (A) to (D) corresponds to the PB concentration of 0.769, 2.307, 3.076 and 4.153 mM/monomer, respectively. It is interesting to observe that even in the wet state of the solid polymer electrolyte (SPE, here PVA/H₃PO₄) the I-V characteristics in dark exhibit a rectifying characteristics. However, the photocurrent (I_l) which is dramatically high for low concentration of the PB, decreases progressively while the dark current increases with the increase in the sensitizer concentration. The present 'wet state' system can be described on the parallel

lines (formation of PB H-type aggregates and its effect on photosensitization etc) for the 'dry state' Ppy/PB photocells, as described in the earlier section. The photosensitivity factor (S) for these "wet state" cells as a function of PB concentration is as shown in Figure (3.38). Here, the maximum photosensitivity is of the order of 16. By comparison, it is evident that the photosensitivity in the dry state of the SPE (which is of the order of 25) is greater than in the wet state (which is of the order of 16) . This is due to the fact that in the wet state, the dark current values are very high (since the ionic conductivity of the SPE increases in presence of moisture) in comparison to that of the dry state.

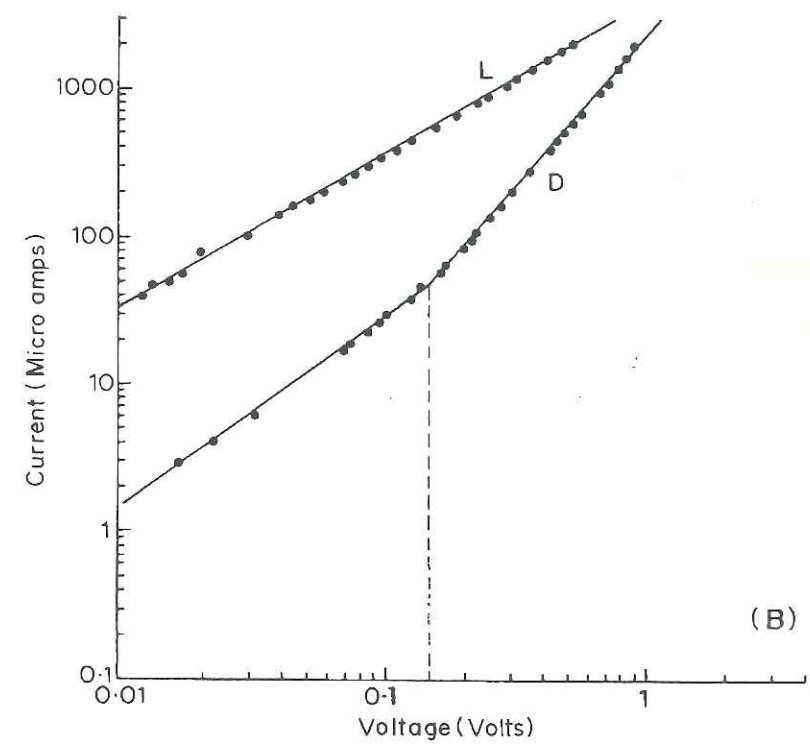
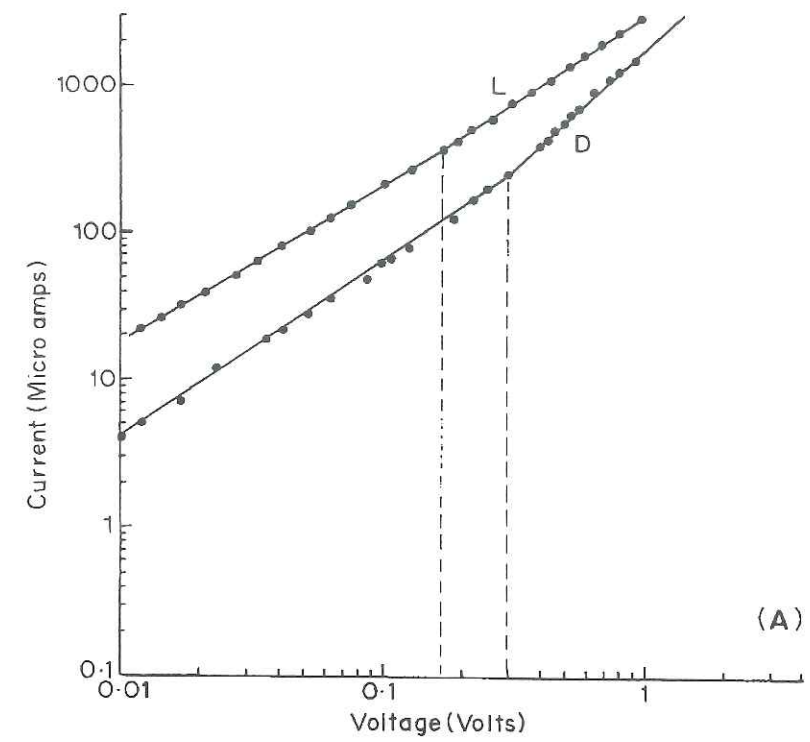


Figure 1
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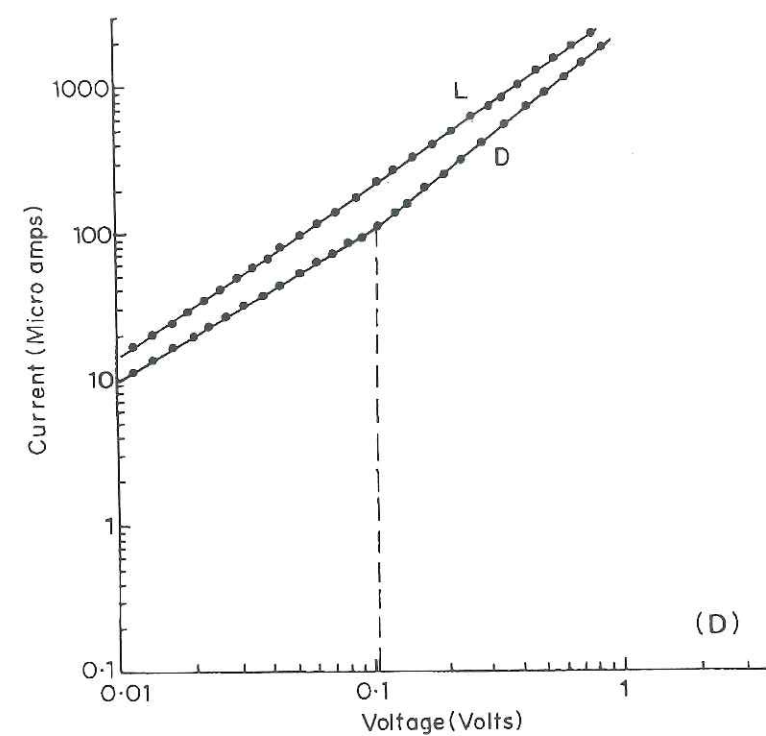
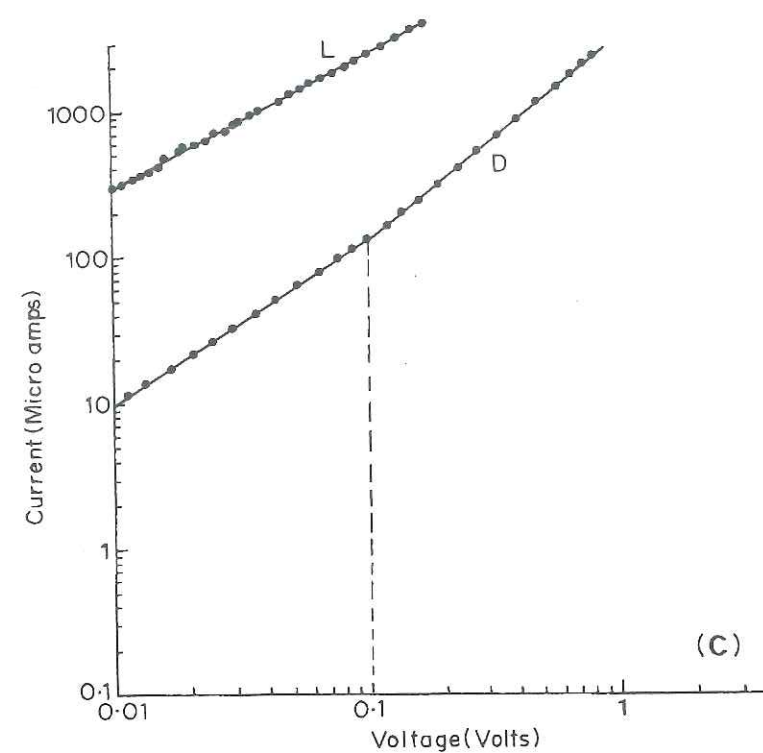


Figure (3.39) : The log-log plot of the I-V curves presented in Figure (36) in the positive quadrant (1st quadrant) only showing the non-linear SCLC type conduction. (A) to (D) corresponds to PB concentration of 0.769, 2.307, 3.076 and 4.153 mM/monomer respectively.

The I-V characteristics plotted on the log-log scale [as shown in Figure (3.39)] shows that SCLC is the dominant charge transport mechanism, where the current is given by equation (3.3).

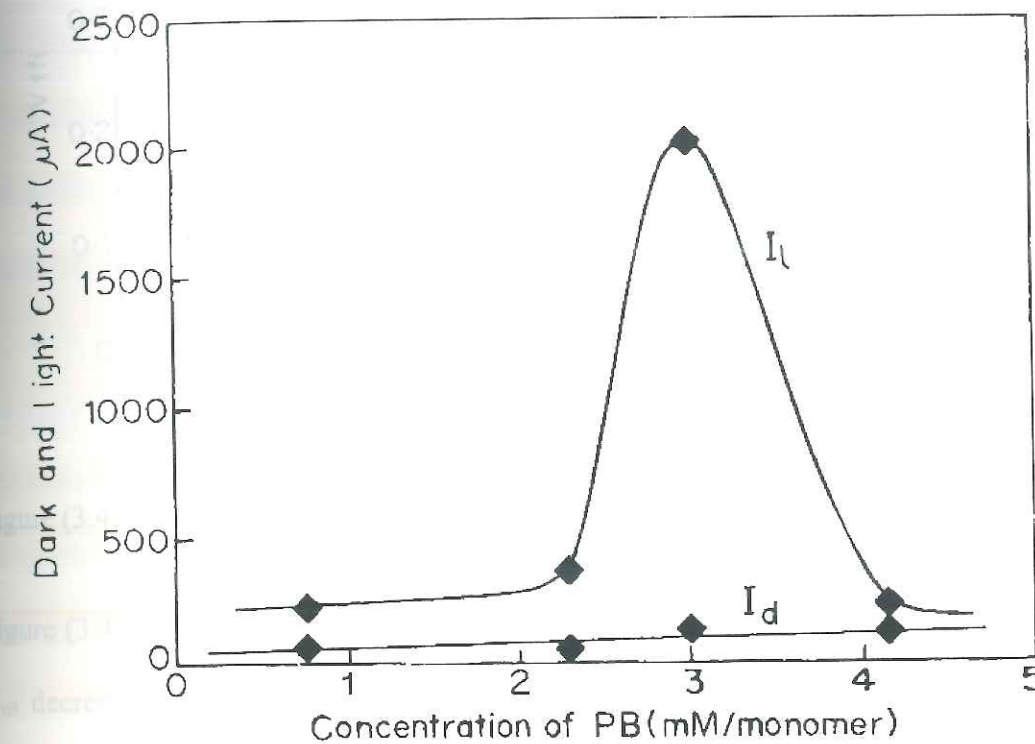


Figure (3.40) : Variation of dark current (I_d) and light current (I_l) with respect to the concentration of the PB.

Figure (3.40) shows the variation of the dark current (I_d) and light current (I_l) with respect to the PB concentration. It can be seen that the dark current remains more or less constant but the light current goes through a maximum. Thus, it is this particular variation of the light current (i.e. going through a maximum) is responsible for obtaining a maximum in the variation of the photosensitivity factor (S) with the PB concentration.

The I-V characteristics plotted on the log-log scale [as shown in Figure (3.39)] shows that SCLC is the dominant charge transport mechanism, where the current is given by equation (3.3).

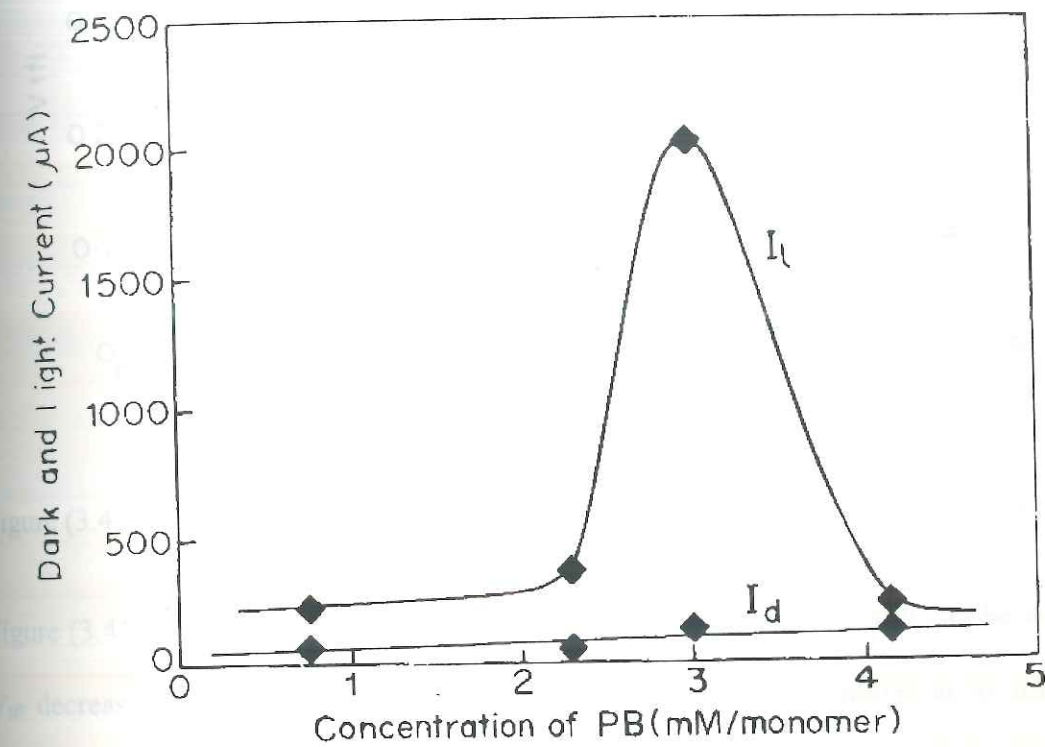


Figure (3.40) : Variation of dark current (I_d) and light current (I_l) with respect to the concentration of the PB.

Figure (3.40) shows the variation of the dark current (I_d) and light current (I_l) with respect to the PB concentration. It can be seen that the dark current remains more or less constant but the light current goes through a maximum. Thus, it is this particular variation of the light current (i.e. going through a maximum) is responsible for obtaining a maximum in the variation of the photosensitivity factor (S) with the PB concentration.

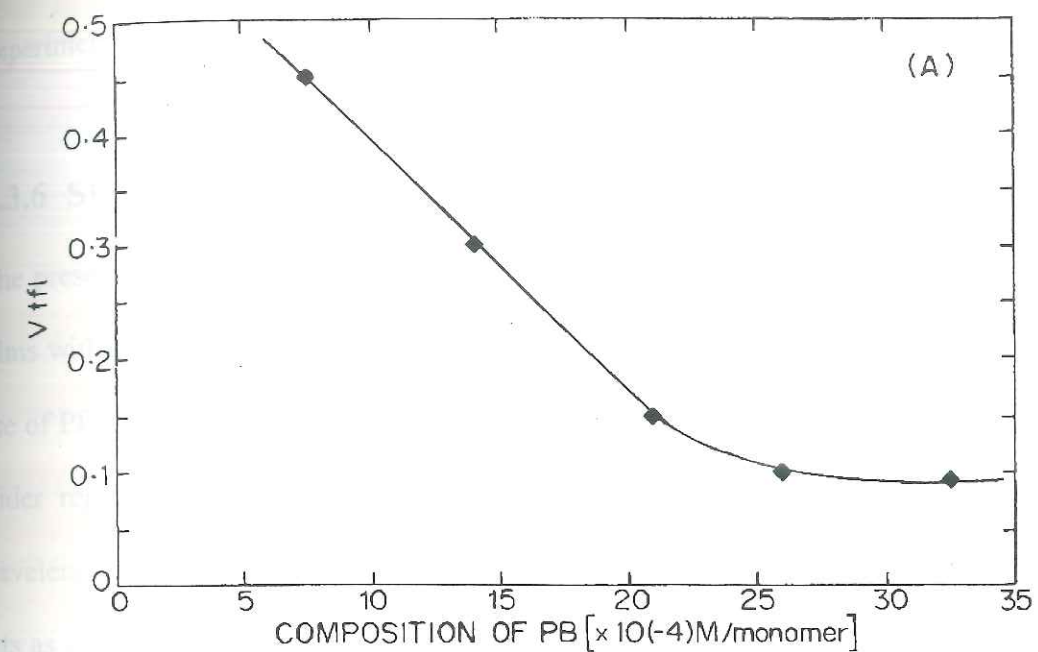


Figure (3.41) : The variation of V_{tf} with the concentration of PB in "wet state" photocell.

Figure (3.41) shows the variation of V_{tf} with the concentration of PB. It can be seen that V_{tf} decreases with the increase in the PB concentration and saturates at its minimum value of 0.1 V at the 2.5 mM/monomer PB concentration. Comparing the V_{tf} values of the corresponding concentrations of the PB in the "wet state" and "dry state" photocells, it is evident that the V_{tf} values shifts to lower voltage side in the "wet state" photocell – as expected.

Hence, it can be concluded that, due to moisture (in SPE), there is an apparent decrease in the photosensitivity of conducting polypyrrole sensitized with PB. As it has been observed and proved (as in present case) that the presence of moisture affects the

photosensitivity in such dye sensitized conducting polymeric photocells, all further experiments were performed in the dry box.

3.3.6 SUMMARY AND CONCLUSION :

The present studies on the electrochromic response of the conducting polypyrrole (Ppy) films with Prussian Blue (PB) films on top and for different electrolytes reveals that the use of PB enhances the electrochromic response of Ppy and also extends the response to wider region of the visible spectrum. The color change can be extended to longer wavelengths by changing the PB content (film thickness) in the composite films. Thus PB acts as a sensitizer for the electrochromic response of conducting polypyrrole. Also, the electrochromic contrast depends on the nature of the electrolyte, especially the size of the dopant/intercalent ions and their electronegativity. By the usage of small size dopant / intercalent ions higher electrochromic contrast can be obtained. It can be pointed here that the contrast in these films arises from the doping and undoping action due to ion insertion in the Ppy as well as PB moieties. The PB film in fact controls the relative doping levels because it allows ions of certain dimensions to pass through to the back side and dope the Ppy film. Thus, it is possible to tailor the overall electrochromic response of the device by an appropriate choice of the PB film thickness as well as the electrolyte used.

In the photosensitization of conducting polypyrrole by Prussian blue in Ppy/PB bilayer film configuration, maximum photosensitivity factor (S) of the order of 60 is observed. The photosensitivity factor (S) is maximum at a certain value of the PB film thickness.

The photosensitivity decreases on both the sides of this PB film thickness. The space charge limited conduction (SCLC) is observed to be the predominant process of charge transport. Due to the presence of space charge effects in such composite film structures, the photosensitivity is observed to be field dependent.

It has been observed and proved that PB can be used as a photosensitizer for conducting polypyrrole. Maximum photosensitivity factor of the order of 25 is obtained when Ppy is sensitized with PB dispersed in SPE. It is observed that PB forms H-type aggregates when dispersed in SPE. From the variation of the photosensitivity factor (S) with PB concentration, it can be seen that maximum photosensitivity factor has been obtained at a certain PB concentration. The photosensitivity factor decreases on both sides of this concentration. The formation of H-type PB aggregates has a negative impact on the photosensitization process and is one of the reason for the decrease of the photosensitivity factor at high dye concentration. It is variation of the photo current (I_l) with the PB concentration which is more important as the dark current (I_d) remains more or less practically constant – in the linear portion of the I-V characteristics. Photo current is maximum at a particular PB concentration. This particular variation of the photo current (I_l) is responsible for getting a maximum in the variation of the photosensitivity factor (S) with PB concentration. The I-V characteristics in such cells reveals that the charge transport is mainly governed by the space charge effects and the SCLC conduction is the predominant process of charge transport. Sensitization effects are due to the lowering of the potential barrier formed at the Ppy/SPE+PB interface under photoexcitation. The photosensitization effects are observed to be field dependent due to

the formation of space charge in such materials. This leads to certain value of the concentration of the sensitizer at which the charge transport is optimized and the photosensitivity is maximum. The maximum photosensitivity factor obtained in such cells is found to depend on the moisture content in the SPE. The presence of moisture in the SPE enhances the ionic conductivity of the SPE thereby increasing the dark current values, resulting in the apparent decrease in the photosensitivity factor as the light current remains more or less the same.

Ppy/PB composite films (with varying PB film thickness) when used in PEC mode using liquid electrolytes, it has been observed that PB does sensitize Ppy but the sensitivity factor obtained is very low (of the order of 2.5 in case of 0.1 M aqueous KCl as an electrolyte).

CHAPTER 4

CHAPTER 4

SENSITIZATION EFFECT IN CONDUCTING POLYPYRROLE AND POLYANILINE BY METHYLENE BLUE

4.1 INTRODUCTION :

Methylene blue (MB, CI basic blue 9, CI solvent blue 8; CI 52015), a redox dye, is one of the most important cationic thiazine based dye. It was discovered by Caro in 1876 and shows many interesting properties such as photochromism, photochemical and electrochemical properties as described in the chapter 1 [1]. It is frequently used as a photosensitizer in free radical polymerizations [2-5]. MB has also been used as polymerization inhibitor for several vinyl monomers [6-9]. A short review on the use of MB as a redox stabilizer has been published by Franke [10]. A mention has also been made where MB acts as a catalyst for the oxidation of glucose to gluconic acid [11].

Since MB absorbs in the visible region with a high absorption co-efficient, it is useful as a photosensitizer. In the present studies, MB is used as a sensitizer for improvement of the photosensitivity of conducting polypyrrole (Ppy) and polyaniline (PANI) in respect of electrical properties rather than photochemical reaction. It would be interesting to see whether this dye can sensitize the photoconduction, electrochromic effect etc. In order to study these effects MB has been incorporated in the solid polymer electrolyte (SPE) to contact with the conducting polymer films.

4.2 EXPERIMENTAL :

The polypyrrole (Ppy) films were deposited on the gold coated glass as described in chapter 2. The Ppy films were subsequently dip-coated with polyvinyl alcohol (PVA, M.W. 10^4 , Loba Chemie) films containing phosphoric acid (1:1) from aqueous solution (1 wt %) which also contained methylene blue (MB) dye (Loba Chemie, microscopic grade) in the concentration range of 0 to 4 mM/monomer. These films were then dried at room temperature and pressed against a transparent conducting ($20 \Omega/\text{sq}$) indium-tin-oxide (ITO) electrode so as to form a photocell with configuration Au/Ppy/PVA+H₃PO₄+MB/ITO.

In order to know whether the sensitization effect depends upon the doped / undoped state of the conducting polymer, the Ppy films were made undoped by applying a reverse potential of 0.7 V vs. SCE for 120 s using aqueous 0.1 M KCl as an electrolyte. The subsequent Ppy films were dip coated with SPE containing MB. The films were dried at room temperature, pressed against a transparent conducting ($20 \Omega/\text{sq}$) ITO electrode so as to form a photocell with configuration Au/Ppy(undoped)/PVA+H₃PO₄+MB/ITO and were used for further study.

In order to know the role of the matrix in which the dye has been incorporated (i.e. SPE) in such sensitization processes, the polymeric material in SPE i.e. PVA is replaced by polyvinyl pyrrolidone (PVP). The doped Ppy films were dip-coated with polyvinyl pyrrolidone (PVP, M.W. 10^4 , Loba Chemie) films containing phosphoric acid (1:1) from aqueous solution (1 wt %) and MB dye (0 to 4.0 mM/monomer). These films were then

dried at room temperature and pressed against a transparent conducting ITO electrode so as to form photocells with configuration Au/Ppy/PVP+H₃PO₄+MB/ITO and were used for further study.

MB has been used as a sensitizer for conducting polyaniline (PANI) in order to know whether it sensitizes other conducting polymers, apart from Ppy, and to the same extent as that for Ppy. The PANI films were deposited electrochemically on gold coated glass electrodes in the same manner as described in chapter 2. These doped PANI films were subsequently dip-coated with polyvinyl alcohol (PVA) films containing phosphoric acid (1:1) from aqueous solution (1 wt %) which also contained MB dye (0 to 4.0 mM/monomer). These films were then dried at room temperature and pressed against a transparent conducting ITO electrode so as to form photocells with configurations Au/PANI/PVA+H₃PO₄+MB/ITO.

The current-voltage (I-V) characteristics of the prepared photocells were studied in the same manner as described in chapter 2. The UV-VIS spectra of the dye in distilled water and SPE+MB dip-coated films on glass were recorded using the Shimadzu UV-240 spectrophotometer.

4.3 RESULTS AND DISCUSSION :

4.3.1 SENSITIZATION EFFECT IN DOPED Ppy BY MB INCORPORATED IN PVA+H₃PO₄ :

4.3.1.1 PHYSICO-CHEMICAL CHARACTERIZATION OF SPE+MB :

4.3.1.1.1 : UV-VIS ABSORPTION STUDY :

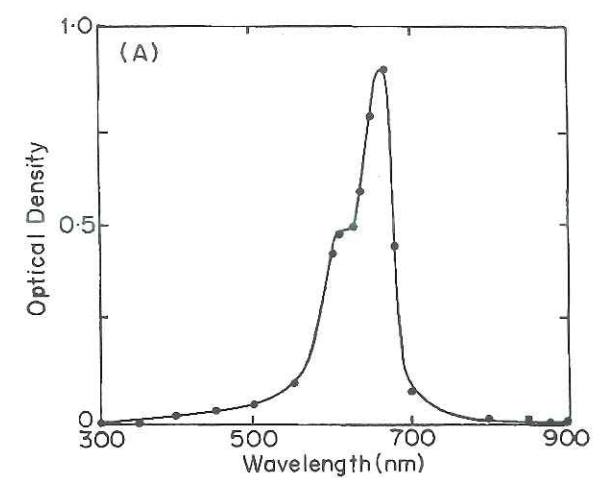


Figure (4.1) : UV-VIS spectra of the MB in water [1×10^{-5} M].

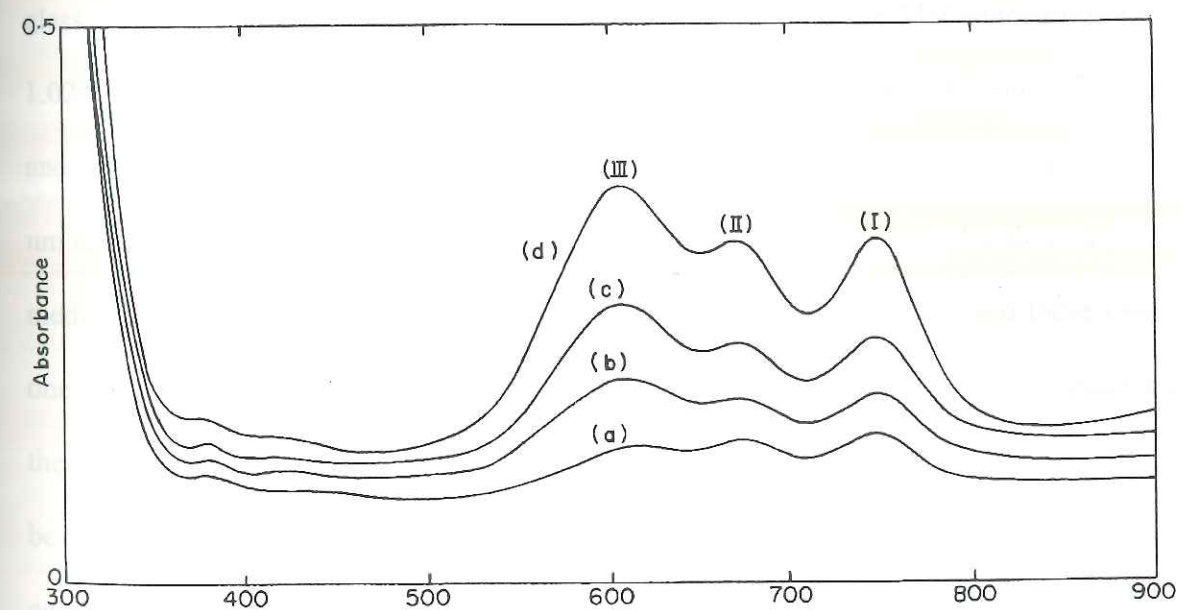


Figure (4.2) : UV-VIS spectra of MB incorporated in SPE (i.e. PVA+ H₃PO₄). (a) to (d) corresponds to the MB concentrations of 1.02, 1.45, 1.87 and 2.32 mM/monomer respectively.

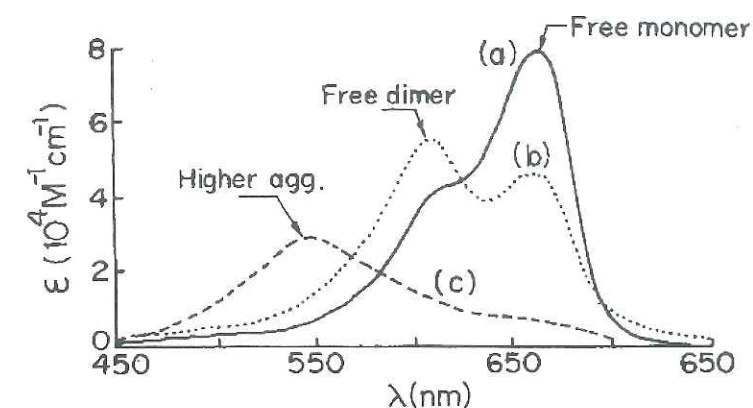


Figure (4.3) : UV-VIS spectra of the aqueous solutions of MB showing the changes in the absorption with MB aggregate formation [1×10^{-5} M (a), 4×10^{-4} M (b)]. Reprinted from Ref. No. [12].

Figure (4.1) shows the UV-VIS spectra of the MB in water [1×10^{-5} M]. It displays a prominent absorption peak at around 660 nm and a hump at around 610 nm. Figure (4.2) represents the UV-VIS spectra of the MB incorporated PVA+H₃PO₄ films deposited on glass by dip-coating method. Spectra (a) to (d) corresponds to the MB concentrations of 1.02, 1.45, 1.87 and 2.32 mM/monomer respectively. Three peaks at around 750, 675 and 605 nm which are marked as I, II and III respectively and a broad band at around 425 nm are observed. It is thus seen that the UV-VIS spectra of the dye molecule in aqueous medium is not the same as in the polymeric matrix. In order to understand these results one has to first look in to the UV-VIS spectra of the dye molecules in different states and the changes it can bring about in the optical absorption. It has been reported that MB can be in different states of aggregation. The UV-VIS spectra of MB in different states of aggregation are shown in Figure (4.3). MB is known to form aggregates of two or more than two molecules in the aqueous phase depending upon the concentration [12-14]. This is manifested in the absorption spectra of MB in water. Aggregation induces

metachromacy i.e. new bands appear on the short wavelength side of the main band which diminishes with increasing concentration and consequently Beer's law is not obeyed, as shown in Figure (4.3) [15-20]. It can be seen from Figure (4.3a) that a free MB monomer has a prominent peak at around 660 nm (I) and a hump at around 610 nm (II). The intensity of the peak (I) is much more than that of (II). In case of a MB dimer (Figure 4.3b), two distinguishable peaks at around 605 nm (II) and 662 nm (I) are observed. Here, the intensity of the peak (II) is more than that of (I). In other words, as we go from a MB monomer to dimer, the intensity of the peak at around 660 nm decreases whereas the intensity of the peak at around 610 nm increases with a slight shift in the peak position towards lower wavelength (by about 5 nm). For higher aggregates (Figure 4.3c), the author reports a broad peak at around 550 nm and a small intensity hump at around 660 nm [15-20]. Alcohols, specially methanol and ethanol, are solvents where the MB dye does not form aggregates and consequently the Beer's law is obeyed in these solvents.

On comparing the above results with those obtained in the present studies, it is quite clear that the changes noted in UV-VIS are not due to aggregate formation. Thus, it can be concluded that MB is not present in an aggregated form in the PVA+H₃PO₄ matrix. The absence of aggregation is also confirmed from the study of these films by optical microscopy. Even at relatively high dye concentration (i.e in the mM [10⁻³] range), aggregation has not been observed. This must be because of the polymeric matrix surrounding the dye molecules rather than the aqueous medium in which the molecules are movable and free to form aggregates.

On the other hand, these observations presented in Figure (4.2) can be explained on the basis of splitting of singlet ground state of MB into a triplet state due to the presence of the PVA+H₃PO₄ matrix. Also, a broad band at around 425 nm indicates a complex formation between the two. As the concentration of MB increases, the intensity of the peaks increases, in general, but no shift in peak positions are observed which is expected for the formation of H type or J-type aggregates. It is worthwhile to note here that at low MB concentrations, the intensity of the peak at around 605 nm (III) was low as compared to the peak at around 750 (I) nm but increases as the dye concentration increases and becomes the dominant in intensity at higher concentrations. The intensity of the peaks at around 675 (II) and 750 (I) nm are practically comparable, latter being slightly higher in intensity.

The splitting of the different levels in molecules due to the interaction with the lattice has been reported by Davidov [21] specially in the case of organic molecular crystals. The interaction between solvent molecules with the chromophores also can lead to different absorption spectra and solvatochromic effects. Thus, the additional bands seen in the present case of MB in PVA+H₃PO₄ matrix arises due to these effects rather than aggregate formation.

4.3.1.1.2 XRD :

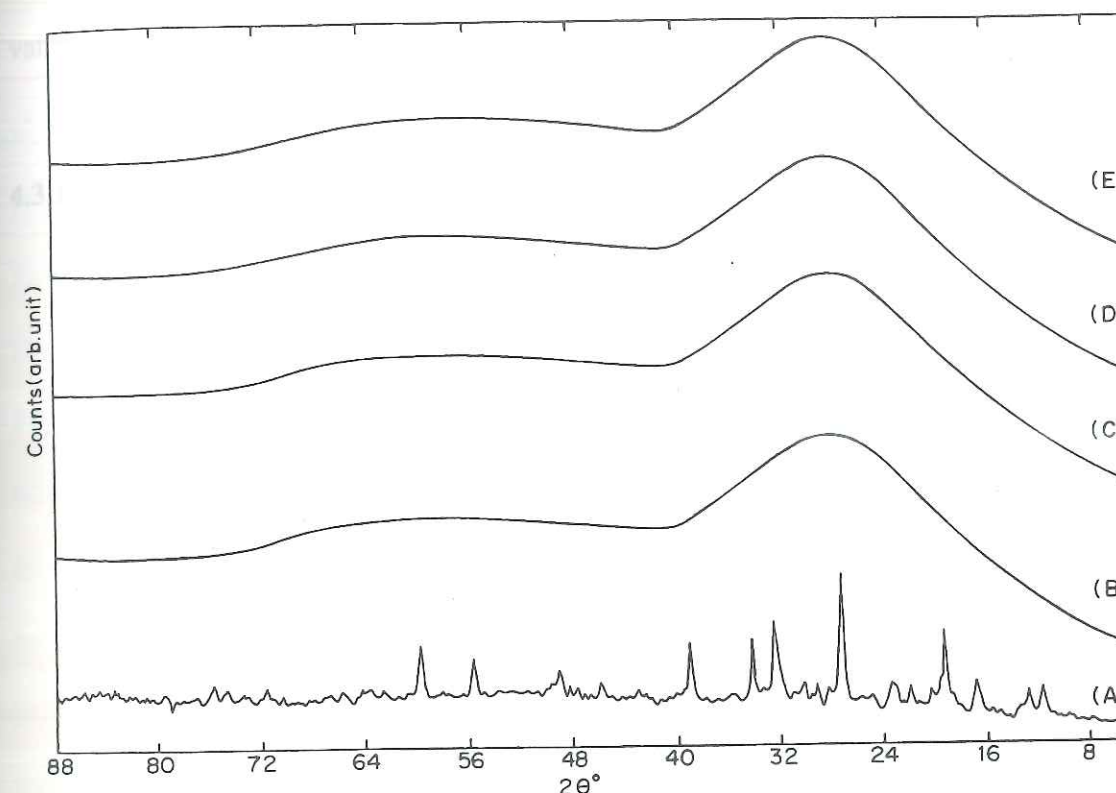


Figure (4.4) : XRD of the MB powder (A) and MB incorporated in SPE (PVA+H₃PO₄) films on glass substrates deposited by dip-coating method. Curves (B) to (E) corresponds to the MB concentration of 1.5, 2.2, 2.9 and 3.5 mM/monomer respectively.

Figure (4.4) shows the XRD of the MB powder (A) and MB incorporated PVA+H₃PO₄ films on glass substrates deposited by dip-coating method (B-E). Spectra (B) to (E) corresponds to the MB concentration of 1.5, 2.2, 2.9 and 3.5 mM/monomer respectively. The XRD of MB is in close agreement with that reported earlier. It can be seen that MB incorporated SPE films do not show any peaks corresponding to MB (unlike that of PB as discussed in chapter 3). In other words, it can be concluded that MB is not present in the aggregate, crystalline or ordered form in the SPE. The study of MB incorporated PVA+H₃PO₄ films by XRD provides another evidence for the absence of the MB

aggregation. Since XRD is used here as a technique to confirm the absence of dye aggregation and not for calculating any structural parameters, the details about the d -values, hkl -values and planes etc. have not been presented here.

4.3.1.1.3 FTIR :

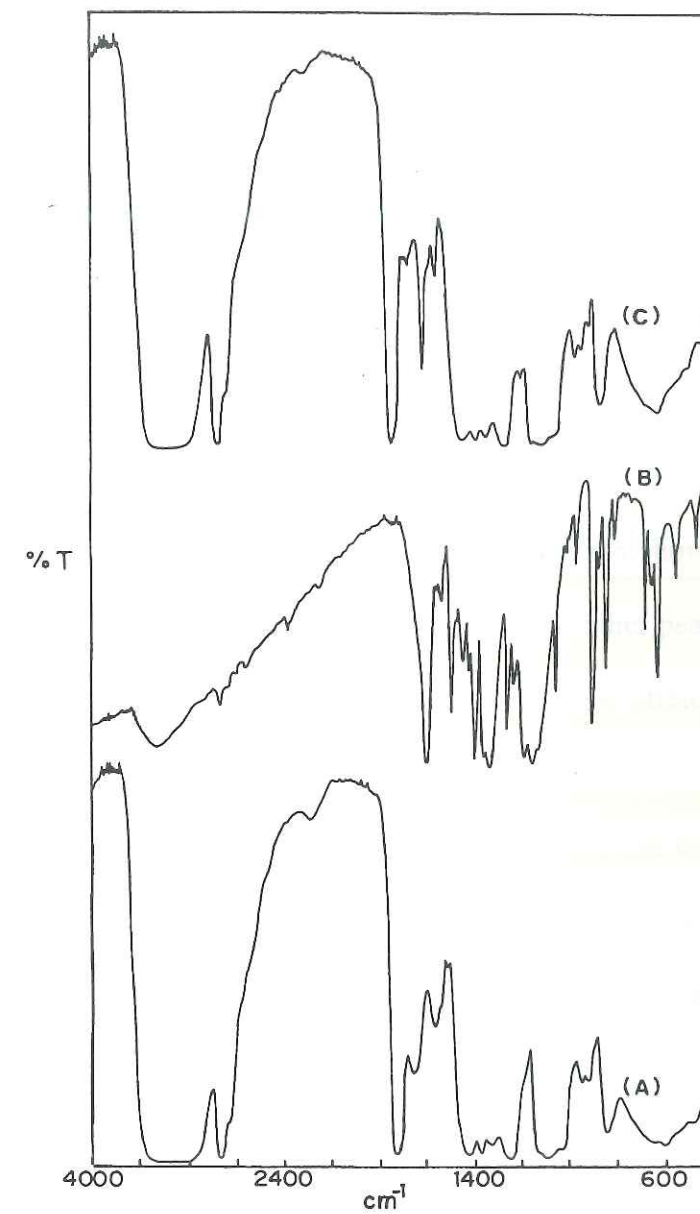


Figure (4.5) : FT-IR spectra of PVA free standing film (A), MB in KBr (B) and MB incorporated PVA free standing film (without H_3PO_4).

Figure (4.5A) shows the FT-IR spectra of the PVA free standing film prepared by first dissolving the polymer in water and then casting the film by evaporating the solvent at room temperature. Figure (4.5B) shows the FT-IR spectra of the MB in KBr. Figure (4.5C) displays the FT-IR spectra of the MB incorporated PVA free standing film prepared by first dissolving the polymer in water, then adding the MB dye in it, followed by evaporating the solvent at room temperature. It should be noted here that the spectra presented in Figure (4.5C) represents that of PVA+MB only i.e. H_3PO_4 is not added in it because the film becomes very much rubbery by the presence of very small amount of acid and hence becomes difficult to record the FT-IR spectra. Table (4.1), (4.2) and (4.3) gives the details of the FT-IR spectra i.e. the peak positions, intensity and their possible assignments for PVA, MB and PVA+MB respectively.

It can be seen from Figure (4.5A), that the FTIR spectra of PVA shows one broad peak at $3400 - 3600 \text{ cm}^{-1}$ corresponding to the O-H vibrations. The other peaks corresponding to C-H stretching occurs at $3163, 2914$ and 2853 cm^{-1} . The C=C stretching vibration peak occur at around 1658 cm^{-1} . The vibrations of the CH_2 group are found at 1420 (bending), 1377 (wagging) and 1246 cm^{-1} (wagging). The skeletal peaks are found between 800 to 920 cm^{-1} . Also, the values are in close agreement with the values reported earlier for PVA. For methylene blue [Figure (4.5B)], vibrations of the aromatic ring are found at 1590 and 1529 cm^{-1} . The C-H 'in plane' vibrations are found between $1243 - 1038 \text{ cm}^{-1}$ and 'out of plane' vibrations are at 990 and 667 cm^{-1} . The C-N stretching vibration is at 1323 cm^{-1} . The peak corresponding to the C-H stretching vibration is found at 2912 cm^{-1} .

Figure (4.5C) displays the FTIR spectra of the PVA+MB free standing film which

suggests that the peaks corresponding to MB have got shifted considerably in presence of the PVA indicating thereby that a considerable amount of the interaction is there between the two. The nature of the interaction becomes clear by looking at the peak positions and comparing them with their close values in presence of PVA. The peak at 1323 cm^{-1} corresponding to C-N stretching in MB have got shifted to 1328 cm^{-1} in presence of the polymer. Similarly, C-H 'in plane' bending vibrations at 1243 and 1166 cm^{-1} have shifted to 1248 cm^{-1} and 1178 cm^{-1} respectively. Vibrations of the aromatic ring at 1590 and 1529 have got shifted to 1600 cm^{-1} and 1536 cm^{-1} respectively. The peak at 2919 cm^{-1} corresponding to C-H stretching has been shifted to 2942 cm^{-1} in presence of PVA. Comparing the peaks corresponding to PVA with that of the PVA+H₃PO₄ it can be seen that the peaks of PVA have also been shifted. The peak at 1096 cm^{-1} corresponding to 'C-O stretch and O-H bend' have shifted to 1092 cm^{-1} . Apart from the various shifts in the peak positions mentioned above, the intensities and the sharpness of the peaks have also been found to be affected. The broad peak at around $3400\text{ to }3600\text{ cm}^{-1}$ in PVA becomes slightly narrow in PVA+MB. The intensity of the peak at about 1658 cm^{-1} corresponding to PVA decreases in PVA+MB.

Thus, it becomes clear that the peaks corresponding to -CN group in MB and -OH group in PVA are getting affected in PVA+MB. Thus, it can be concluded that the -OH group of the polymer interacts with the nitrogen atom on the MB with hydrogen bonding producing a complex. Because of this interaction, the frequencies corresponding to other vibrations in PVA, such as of -CH₂, -CH group, C-O groups, will be affected as observed in the present study. Also, as the nitrogen in MB is taking part in forming a hydrogen

bond with the -OH group of the polymer and since it is linked to the aromatic rings, the vibrational frequencies of the aromatic ring and other groups will be affected - as observed in the present case. In all, it can be concluded that the MB forms a complex with the PVA by an hydrogen bonding interaction between the -OH group of the polymer and the nitrogen on atom of the MB.

TABLE 4.1 : Polyvinyl alcohol (PVA)

(Intensity nomenclature :- VS : Very Strong, S : Strong, M : Medium,
MS : Medium Strong, W : Weak)

No.	Peak Position (cm^{-1})	Intensity	Assignment
1.	3400 - 3600	VS	OH
1.	3163	S	C-H stretching
2.	2914	S	C-H stretching
3.	2853	Sh	C-H stretching
4.	2172	W	
5.	1717	S	
6.	1658	M	C=C stretching
7.	1568	M	
8.	1420	S	CH ₂ -bending
9.	1377	S	CH ₂ -wagging
10.	1246	S	C-H wagging
11.	1096	S	C-O stretch and O-H bend
12.	918	M	Skeletal
13.	853	M	Skeletal
14.	475	M	
15.	417	M	

TABLE 4.2 : Methylene Blue (MB)

(Intensity nomenclature :- VS : Very Strong, S : Strong, M : Medium,

MS : Medium Strong, W : Weak)

No.	Peak Position (cm ⁻¹)	Intensity	Assignment
1.	3435	M, Broad	O-H stretching
2.	2919	M	C-H stretching
3.	2699	M	
4.	2354	M	
5.	1590	VS	Vibrations of Aromatic Ring
6.	1529	M	
7.	1485	MS	
8.	1438	M	
9.	1409	M	
10.	1385	VS	
11.	1323	VS	C-N stretching
12.	1243	MS	C-H (in plane) bending vibration
13.	1214	M	
14.	1166	S	
15.	1133	S	
16.	1038	M	
17.	990	W	C-H (out of plane) bending vibration
18.	947	W	
19.	880	MS	
20.	823	MS	
21.	790	W	
22.	667	MS	C-H (out of plane) bending vibration
23.	614	MS	
24.	533	M	
25.	447	M	

TABLE 4.3 : Polyvinyl alcohol + Methylene Blue (PVA+MB)

(Intensity nomenclature :- VS : Very Strong, S : Strong, M : Medium,

MS : Medium Strong, W : Weak)

No.	Peak Position (cm ⁻¹)	Intensity	Corresponds to the original component	Assignment
1.	3402	VS		O-H vibration
2.	2942	VS	PVA / MB	C-H stretching
3.	2845	Sh	PVA	C-H stretching
4.	2660	Sh		
5.	2165	W	PVA	
6.	1736	VS		
7.	1657	M	PVA	C=C stretching
8.	1600	MS	MB	Vibration of Aromatic Ring
9.	1536	M	MB	Vibration of Aromatic Ring
10.	1376	VS	PVA	CH ₂ -wagging
11.	1328	VS	MB	C-N stretching
12.	1248	VS	MB and PVA	C-H wagging
13.	1178	MS	MB	C-H (in plane) bending vibration
14.	1092	VS	PVA	C-O stretch and O-H bend
15.	941	M		
16.	917	M	PVA	Skeletal
17.	883	M	MB	
18.	852	MS	PVA	Skeletal
19.	608	MS	MB	
20.	418	M	PVA	

4.3.1.1.4 THERMAL STUDIES :

(A) TG/DTA/DTG ANALYSIS :

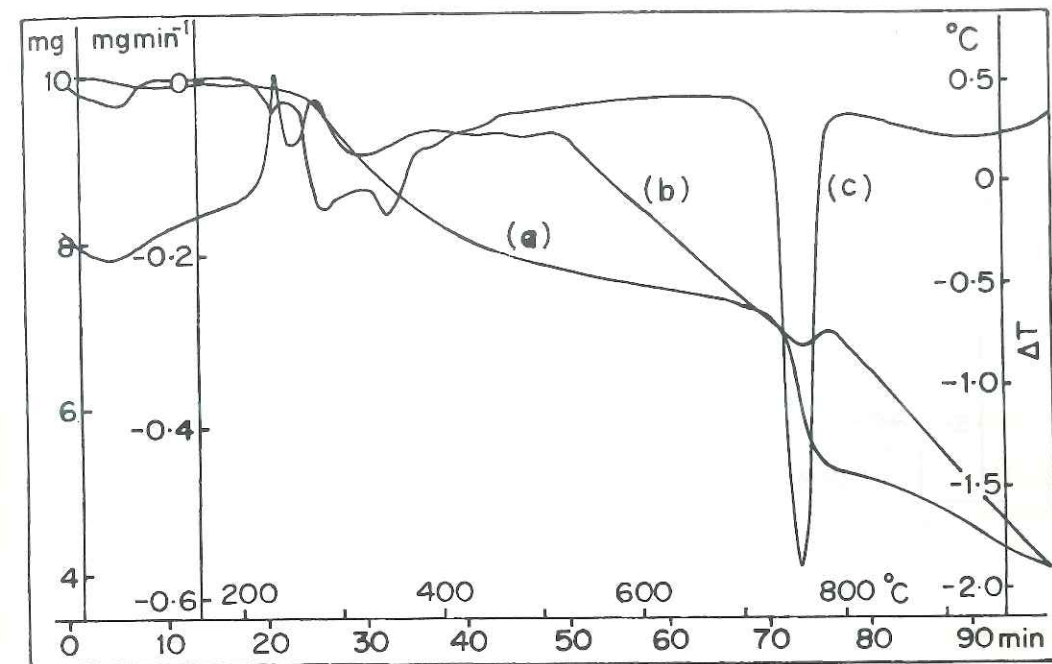
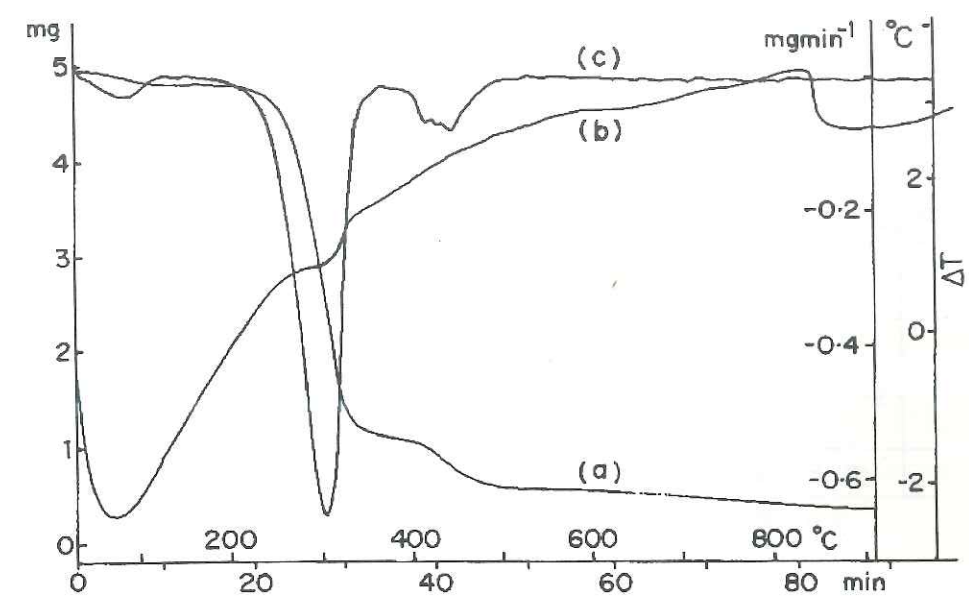
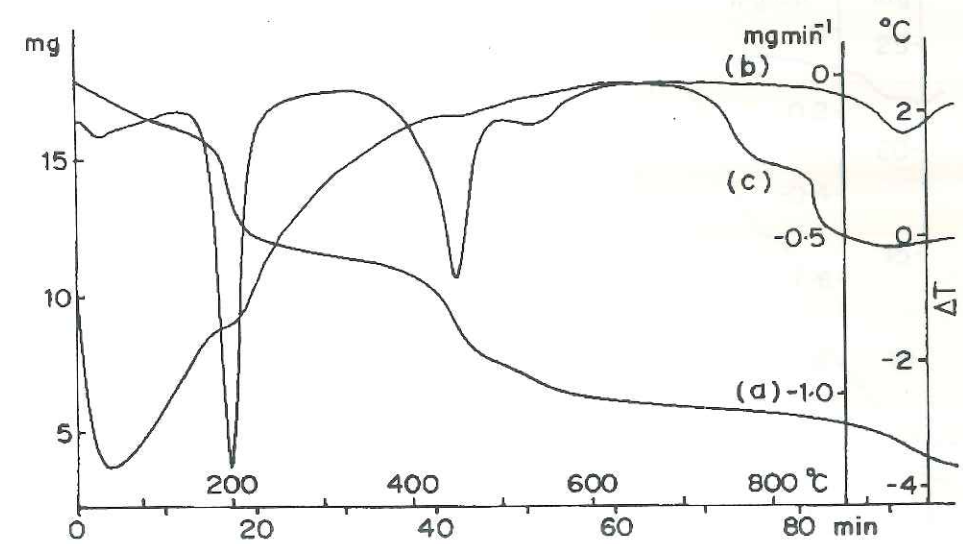


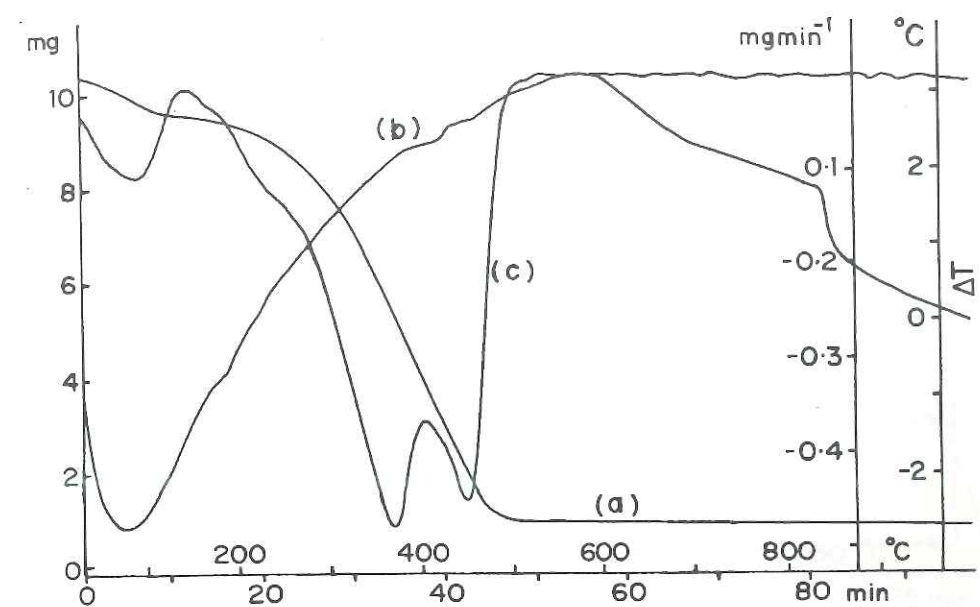
Figure (4.6) : TG/DTA/DTG analysis curves for methylene blue dye (↑exo).



(A)



(B)



(C)

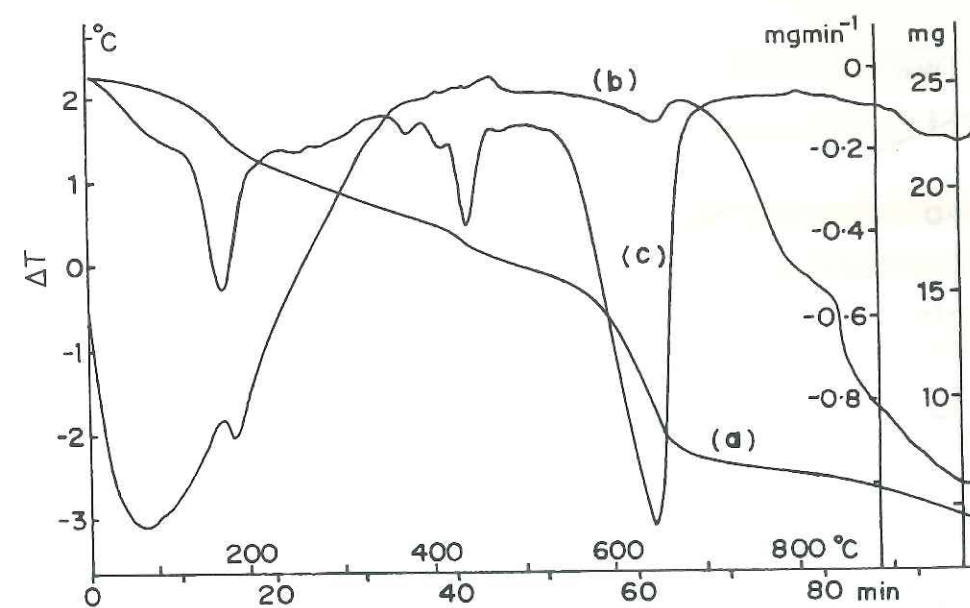
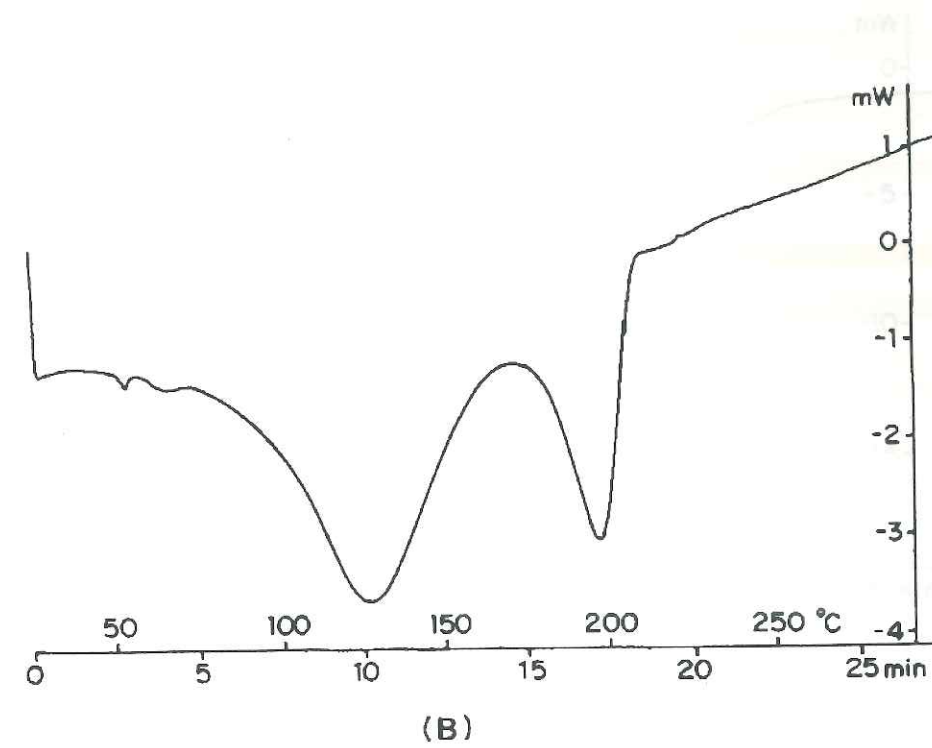
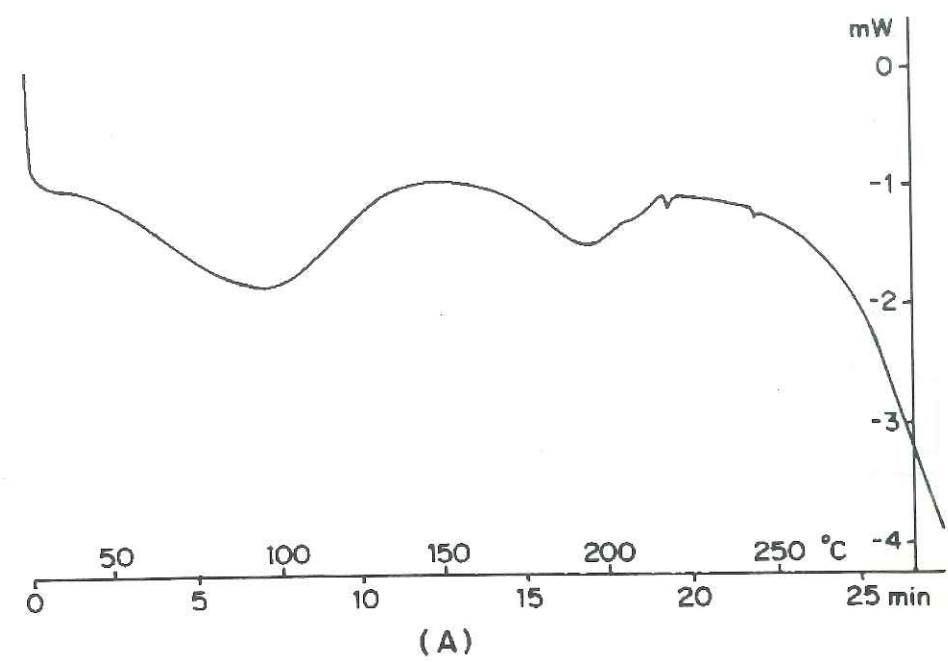


Figure (4.7) : TG/DTA/DTG analysis curves for PVA (A), PVA+H₃PO₄ (B), PVA+MB (C) and PVA+H₃PO₄+MB (D) respectively (↑exo).



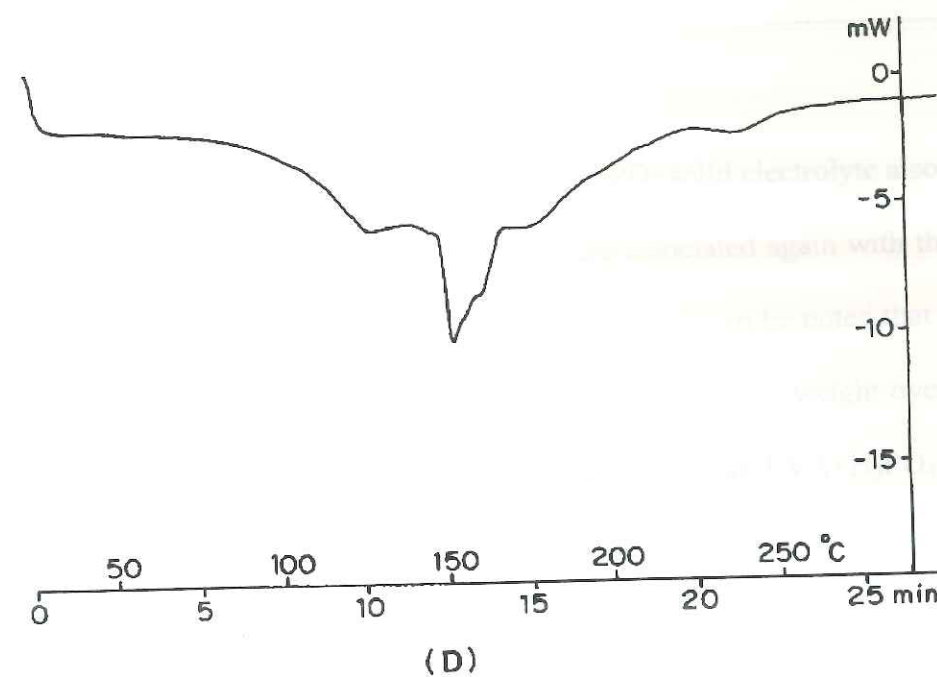
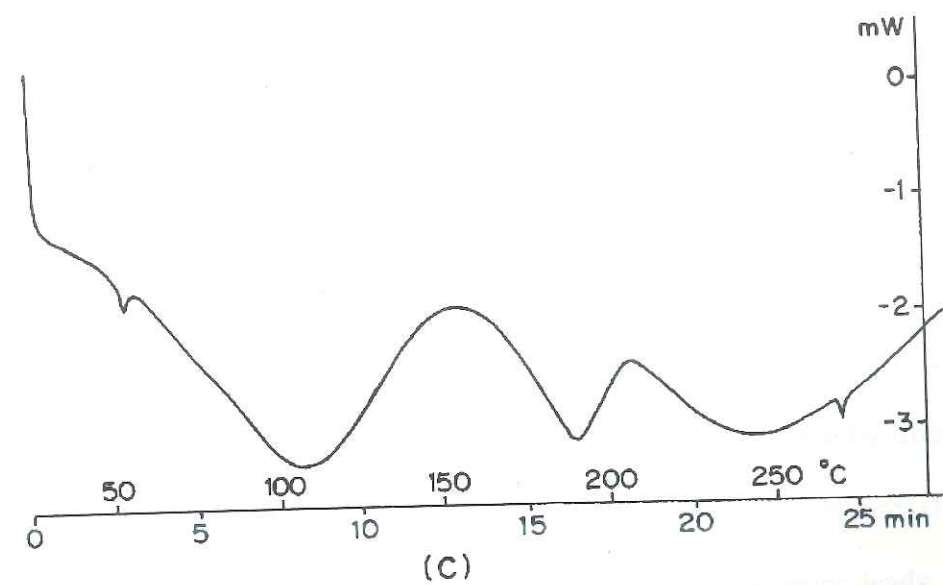
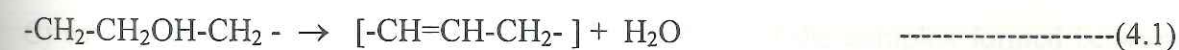


Figure (4.8) : DSC analysis curves for the PVA (A), PVA+H₃PO₄ (B), PVA+MB (C) and PVA+H₃PO₄+MB (D) respectively ($\uparrow$ exo).

Figure (4.6) shows the thermogravimetric analysis of MB alone while Figure (4.7A, B, C and D) represents the thermograms for PVA, PVA+H₃PO₄, PVA+MB and PVA+H₃PO₄+MB respectively. Here, in all, curve (a) represents TG, (b) DTA and (c) DTG. It can be noted that for MB dye there is very little loss in weight up to 270 ° C above which there is a gradual decrease in weight followed by a rapid loss at 740 ° C. Thus, the MB dye itself is stable up to 250 ° C and degrades in two stages : in the first step the Cl atoms gets dissociated and some cyclization also takes place by liberation of N atoms while in the second step the molecule gets fragmented mostly by breakage of C-S bonds. The extent of loss in weight and sharpness of the transitions leads to above conclusions. In the case of PVA the thermal degradation immense at 300 ° C and constitutes two processes viz. Formation of conjugated bonds due to loss of H₂O i.e.



and then final breaking of the main chain. The PVA+H₃PO₄ solid electrolyte also exhibits two major processes during thermal cycling. These are associated again with the loss of H₂O molecules and then breaking of the complex. However, it can be noted that these are comparatively slow processes as can be judged from gradual loss in weight over broader range of temperature. The addition of MB to PVA as well as PVA+H₃PO₄ leads to different thermal behavior.

The weight loss curves together with the DTG clearly show that there are new processes occurring in PVA+MB and PVA+H₃PO₄+MB as compared to these materials without

MB. The peaks at 450 ° C and 650 ° C in the DTG of these samples suggests that there can be complex formation which breaks up at these temperatures in PVA+MB and PVA+H₃PO₄+MB respectively.

The DSC of these films are indicated in Figure (4.8). Curves A to D corresponds to PVA, PVA+H₃PO₄, PVA+MB and PVA+H₃PO₄+MB respectively. In pure PVA, the transition at 85 ° C can be associated with its glass transition temperature and the second transition at 180 - 190 ° C with the crystalline melting point. It is seen that these two transitions in PVA+H₃PO₄ are at much higher temperature due to hydrogen bonding and ionic complex formation. In the case of PVA+MB the peak corresponding to glass transition temperature (T_g) shifts towards higher temperature (> 100 ° C) and so is the case for PVA+H₃PO₄+MB. In these cases, there is transition at much higher temperature (> 200 ° C) which can be associated with the onset of breaking of the complex formed between MB and the matrix. The latter hypothesis is suggested by the TGA data discussed earlier. Thus, these studies on TGA and DSC give indication that MB may be forming a complex with the polymer matrix which is fairly stable.

4.3.1.2 SENSITIZATION OF PHOTOCURRENT :

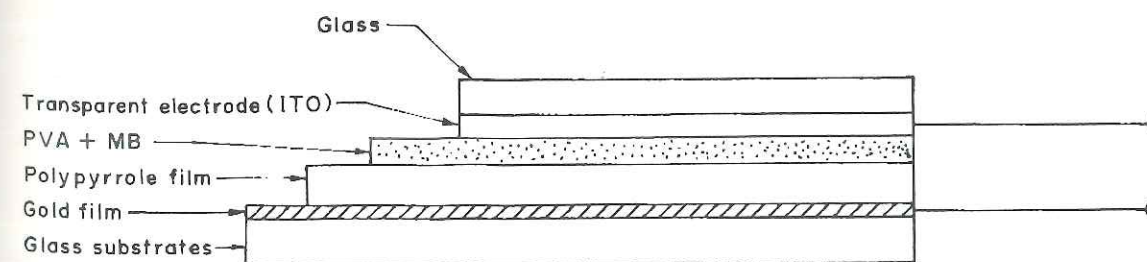
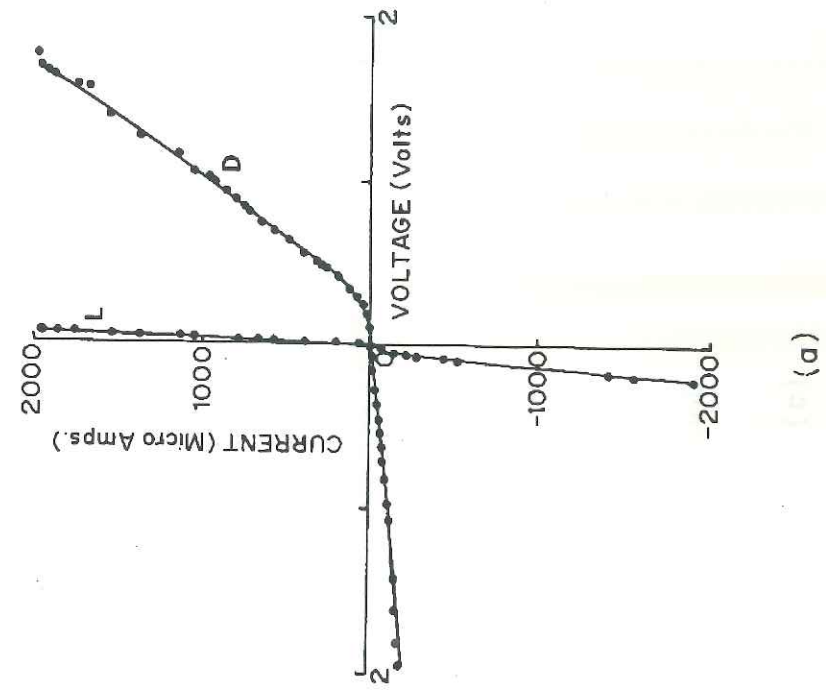
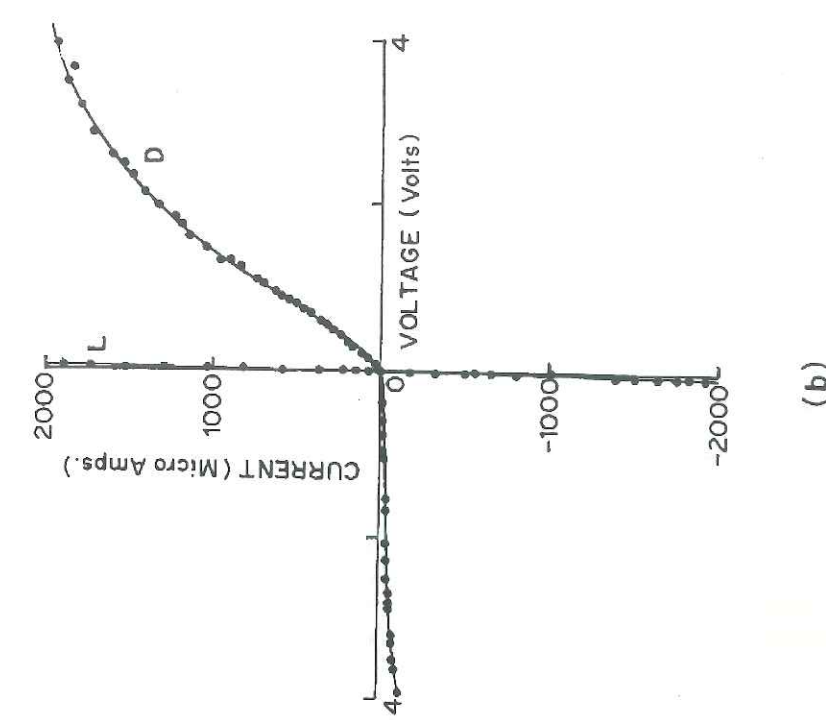


Figure (4.9) : Schematic of the solid state photocell using conducting polypyrrole (Au/Ppy/PVA+H₃PO₄+MB/ITO).



(a)



(b)

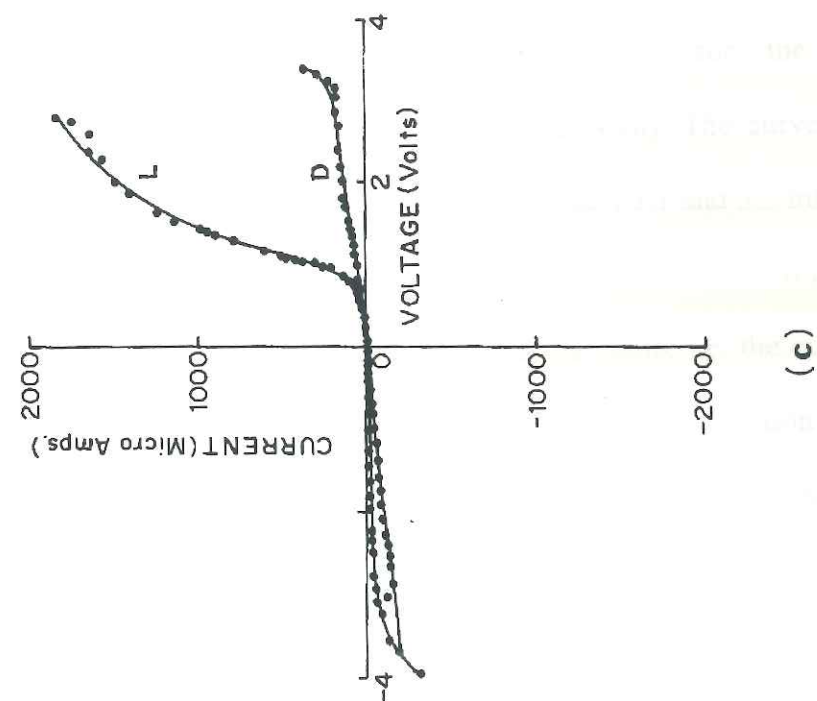
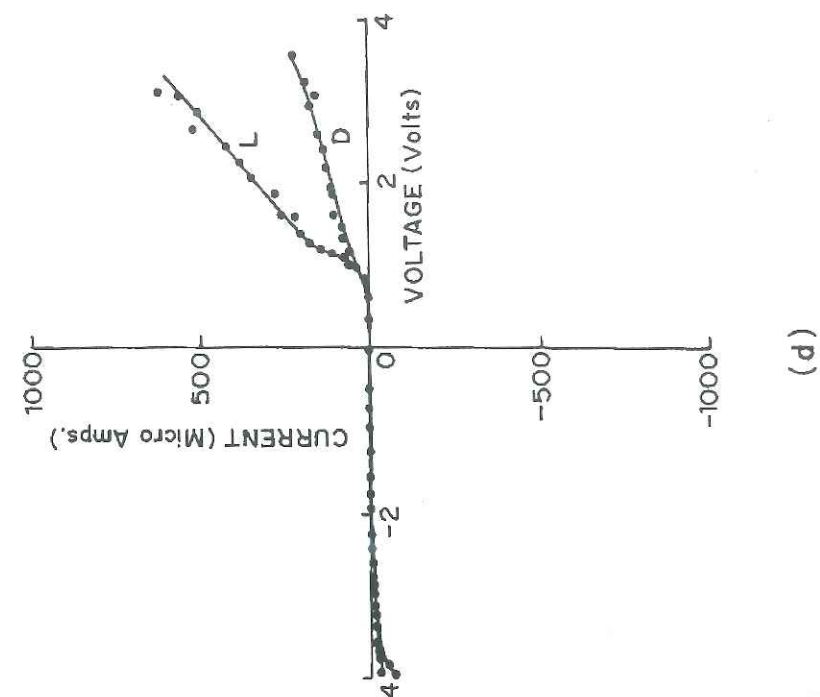


Figure (4.10) : current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocell Au/Ppy/SPE+MB/ITO containing different concentrations of MB; (a) 2.2, (b) 2.5, (c) 3.1 and (d) 3.3 mM/monomer respectively.

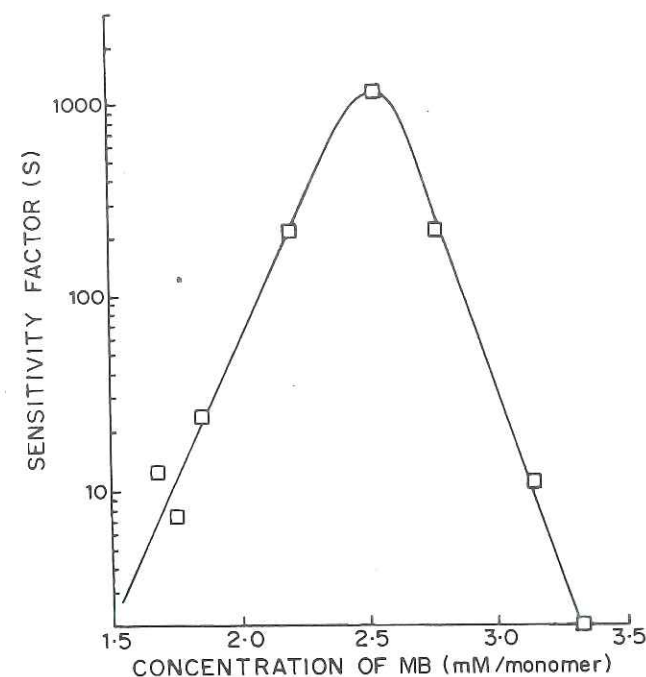


Figure (4.11) : photosensitivity factor (S) as a function of the concentration of MB.

Figure (4.9) shows the schematic of the photocell. The current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocells (Au/Ppy/PVA+H₃PO₄+MB/ITO) are as shown in Figure (4.10). The curves (a) to (d) corresponds to methylene blue (MB) concentration of 2.2, 2.5, 3.1 and 3.3 mM/monomer respectively (all curves have not been shown though recorded). It is interesting to observe that the I-V characteristics in dark (D) exhibit a rectifying nature i.e. the current in one direction (Au +ve, 1st quadrant) is much higher than in the opposite direction (Au -ve, 3rd quadrant). However, the photocurrent (I_l) which is dramatically high for low concentration of MB dye, decreases progressively, while dark current increases with the increase in the sensitizer concentration. The photosensitivity factor ($S = I_l / I_d$, where I_l is the photocurrent and I_d is the dark current) for these cells as a function of dye concentration is as shown in Figure (4.11). It is quite evident that there is a certain MB

concentration (2.5 mM/monomer) at which the photosensitivity is very high (of the order of 10^3). The concentration of the MB dye corresponding to maximum photosensitivity factor is said to be 'critical concentration'.

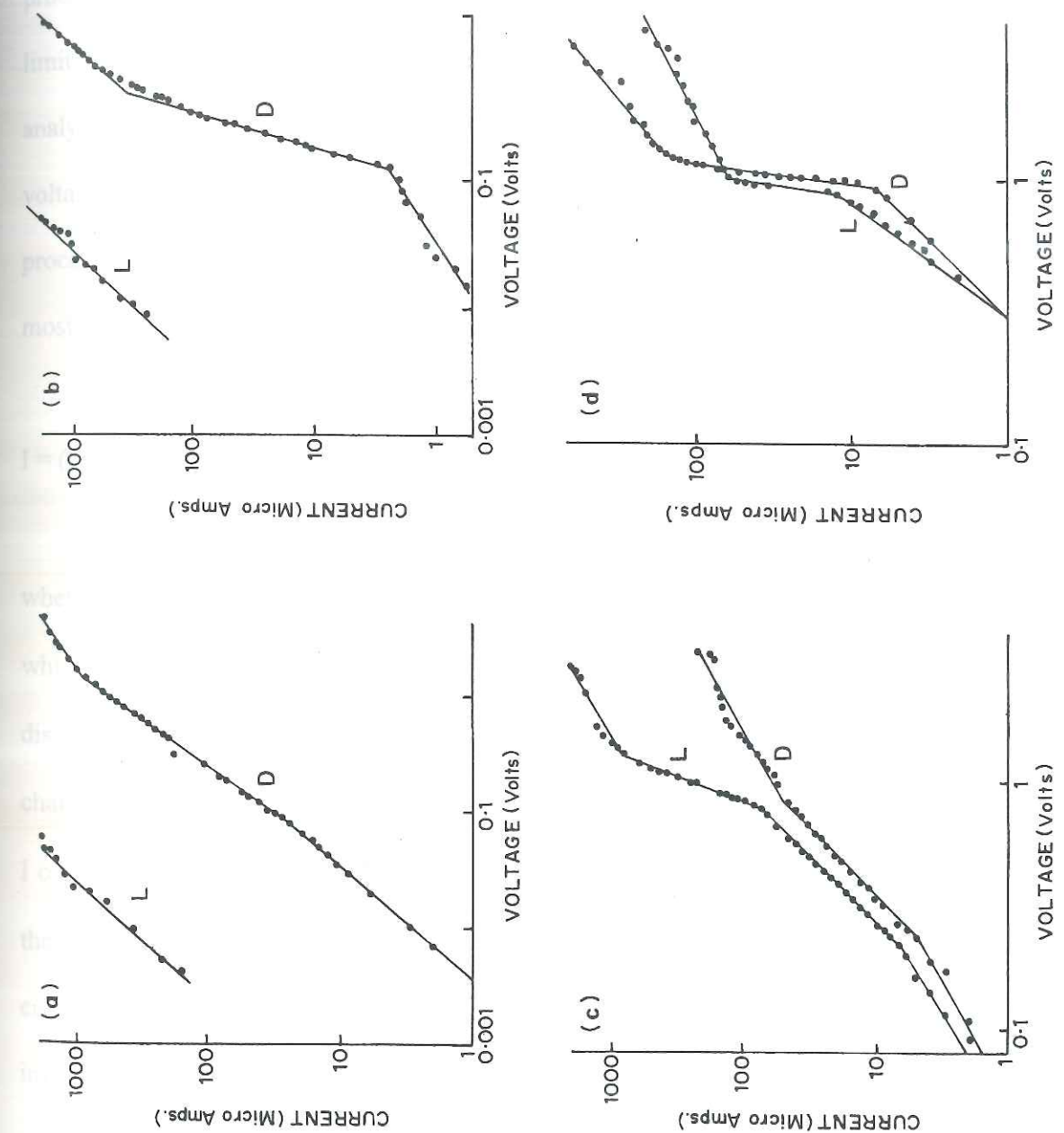


Figure (4.12) : The log-log plot of the I-V curves showing the SCLC type behavior with the exponent 'n' changing by the increase of the dye concentration as well as illumination. Curves (a) to (d) correspond to the MB concentration of 2.2, 2.5, 3.1 and 3.3 mM/monomer respectively.

In order to understand the mechanism involved in the sensitization of photocurrent, one has to first look in to the charge transport process taking place in these cells. The current-voltage (I-V) characteristics were analyzed in detail for different types of charge transport processes such as Schottky emission, Poole-Frankel Effect, Tunneling, space charge limited conduction (SCLC) etc. as described in chapter 1. The experimental data was analyzed according to the expected mathematical relationship between current and voltage for each case. However, Schottky emission, Poole-Frankel and tunneling processes were eliminated due to improper fit. The last case of SCLC appeared to be most appropriate in which the current is given by [22]-

$$I = (8/9) \mu \theta [V^{(n+1)} / d^{(2n+1)}] \quad \text{-----(4.2)}$$

where μ is the mobility of the charge carriers, d is the film thickness, θ is a parameter which takes in to account the trapping centers (impurity centers) concentration and their distribution and n is an integer having values $\geq 1, 2, 3$ etc. Figure (4.12) shows the I-V characteristics plotted on log-log scale and it is evident from these curves that the relation $I \propto V^n$ is indeed followed. However, the slope of the graph changes considerably with the increase of MB concentration as well as the presence of illumination. The SCLC curves are usually interpreted in terms of charge injection and the subsequent filling of impurity / trapping centers giving rise to progressively linear, square / superlinear and again square type dependence of the I-V characteristics. The increase of the impurity centres (MB) increases the dark current and also widens the range of voltage over which the linearity exists (or lowers the value of exponent in equation 4.2). The effect of

illumination is similar to this since the photogenerated carriers also fill the trapping centres in effect giving lower value of the exponent n .

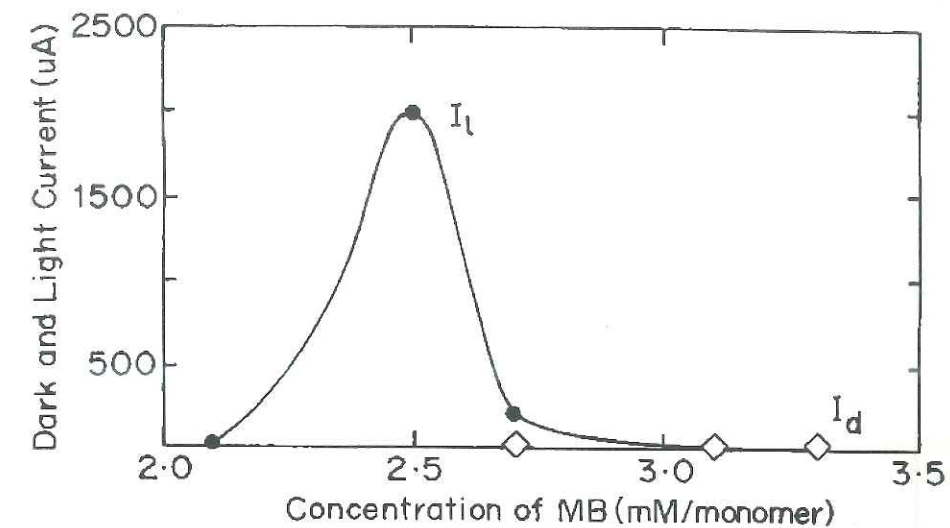


Figure (4.13) : Variation of the dark (I_d) and light (I_l) current with the concentration of the MB in the linear portion of the I-V characteristics at the 0.01 V.

Figure (4.13) displays the variation of the dark (I_d) and light current (I_l) with respect to the MB concentration in the linear portion of the current-voltage (I-V) characteristic at a fixed voltage of 0.01 V. It can be seen that the light current (I_l) increases with the increase in the MB concentration initially, reaches to a maximum and then decreases with further increase in the dye concentration. Hence, the light current (I_l) goes through a maximum in the variation with respect to the MB concentration. The dark current (I_d) increases slowly with the increase in the dye concentration. The initial increase of the light current (I_l) can be attributed to the increase in the number of the sensitizing centres with the increase in the dye concentration. Decrease of the light current (I_l) at high dye concentration can be due to heavy trapping and/or recombination of the photogenerated charge carriers. This particular variation of the light current (I_l) is more important than

that of the dark current (I_d) and is mainly responsible for getting the maximum photosensitivity at a particular dye concentration.

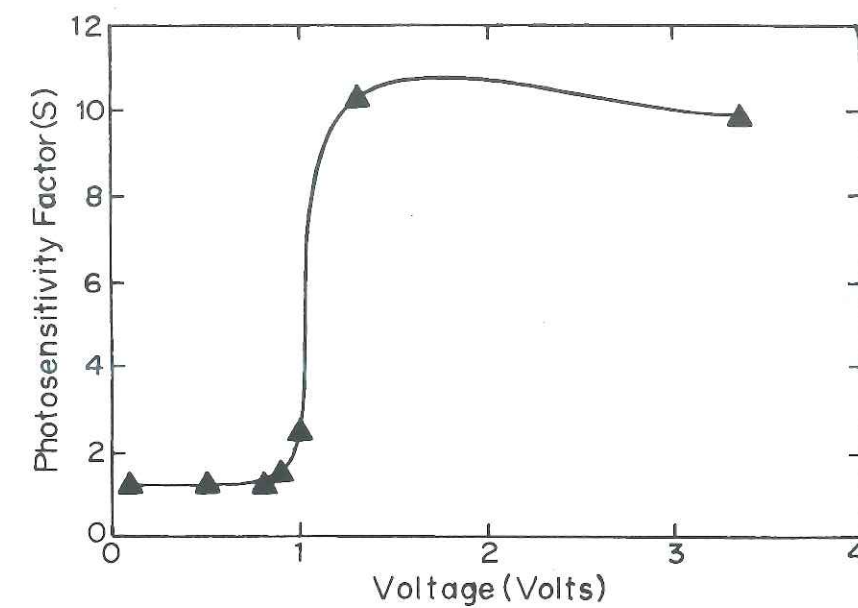


Figure (4.14) : Voltage / field dependence of the photosensitivity factor (S) at 3.1 mM/monomer MB concentration.

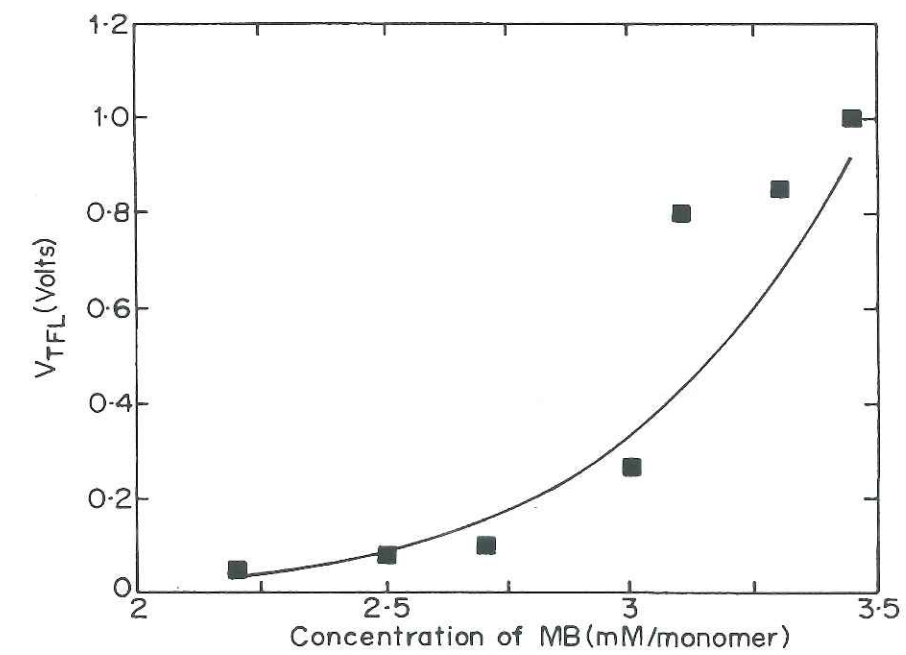


Figure (4.15) : Variation of the V_{th} with respect to the MB concentration.

Figure (4.14) shows the voltage/field dependence of the photosensitivity factor (S), plotted for 3.1 mM/monomer MB concentration. It can be seen that at a particular voltage maximum photosensitivity can be obtained. Figure (4.15) displays the variation of V_{TFL} with the MB concentration. It can be seen that as the concentration of MB increases, V_{TFL} increases.

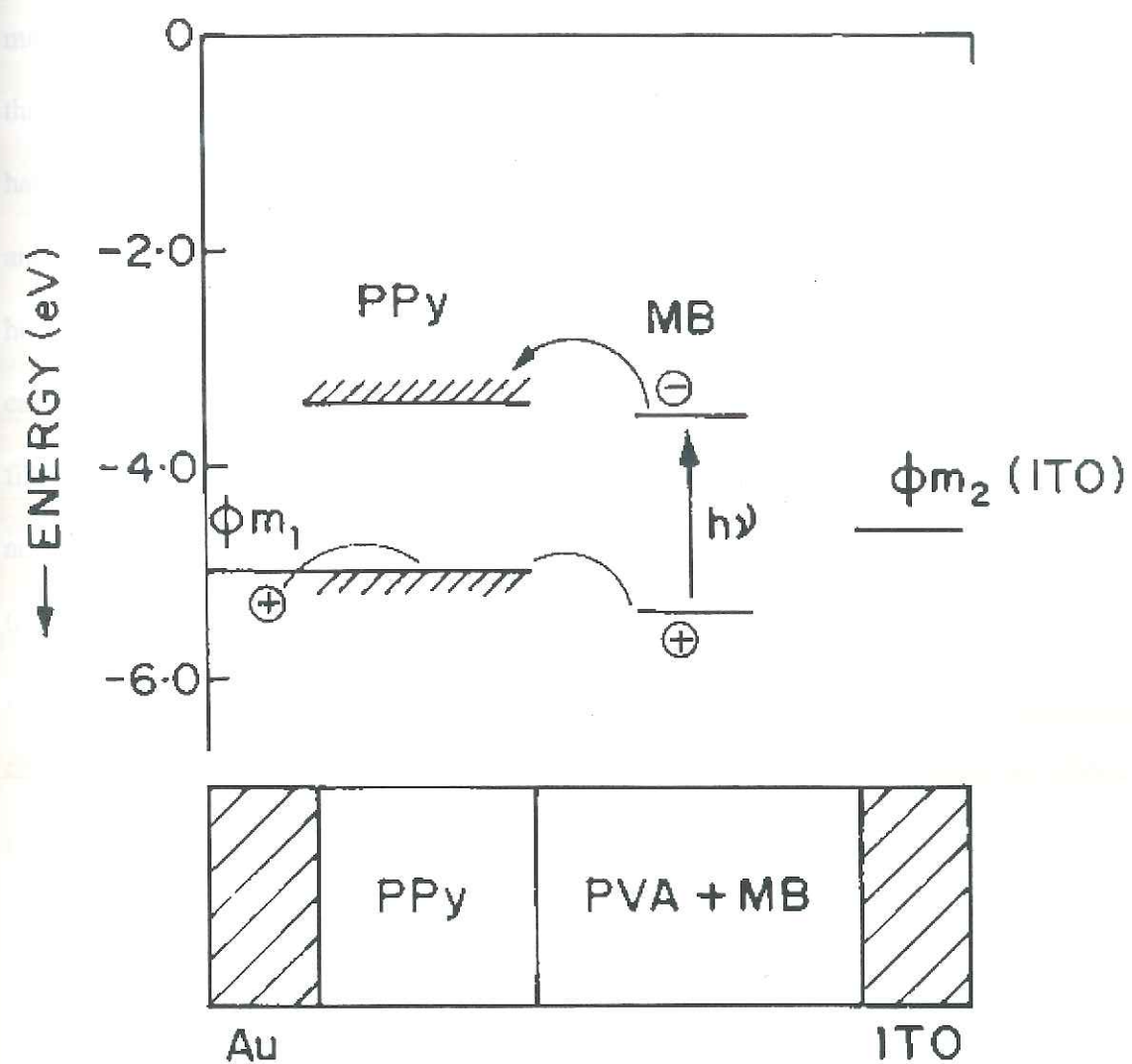


Figure (4.16) : Energy level diagram of the materials used in forming the photocell having Au/PPy/PVA+H₃PO₄+MB/ITO sandwich structure.

The mechanism of the sensitization process can be understood in terms of the energy band diagram for the materials used for forming the cell. Figure (4.16) depicts the different energy levels for the materials used for forming the photocell. The energy levels for Ppy are those which have been reported in the literature [23], while those for MB in PVA are derived from the UV-VIS spectra recorded as above. It must be noted that the PVA containing phosphoric acid is a good proton conductor while Ppy is a p-type material. Thus, when Au is positive, the hole transport via Ppy and the proton transport through PVA are facilitated giving high forward current. On the other hand when Au having negative polarity, the current would be less since electrons are minority carriers and expected a barrier at the Ppy/Au interface (contact blocking to electrons but not to holes). This gives rise to the rectifying type I-V characteristics as noted in the present case. On the other hand, when the cell is under illumination, MB dye absorbs light and fills the higher electronic levels with photoexcited carriers. This facilitates their transport across the potential barrier at the Ppy/PVA interface. It should also be remembered that there are several other energy levels present due to the inherent amorphous nature of the polymer, and hence some of these can act as carrier trapping centres for one type of charge carriers. Thus, when photo-generated electrons are trapped there is an effective increase in the number of holes available for conduction. It is worthwhile to note here that the energy levels of MB are placed in such a way that they act as electron trapping centres for Ppy. Hence, the minority carriers (i.e. electrons) from Ppy are trapped and hence there is an effective increase in the number of the holes available for conduction. In this manner, high photosensitivity is obtained both because of lowering of potential barrier, as well as relative trapping of minority carriers in presence of MB dye. The

decrease of photosensitivity at high MB concentrations can be due to high absorption of light (photons) only at the surface, as well as heavy trapping (followed by recombination) of charge carriers which does not allow them to pass into the bulk of the material.

4.3.2 SENSITIZATION EFFECT IN UNDOPED Ppy BY MB INCORPORATED IN PVA+H₃PO₄ :

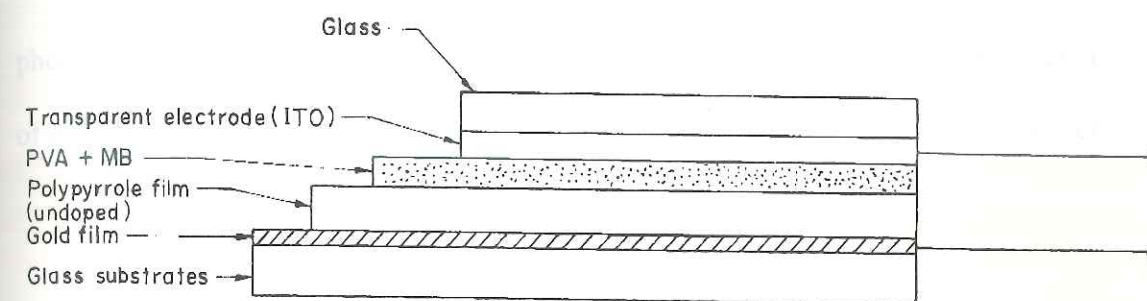
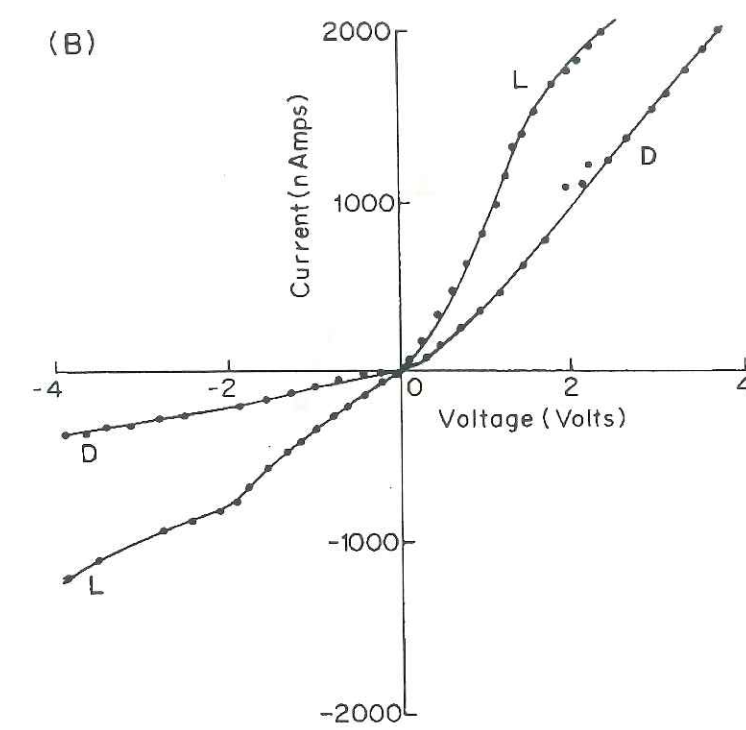
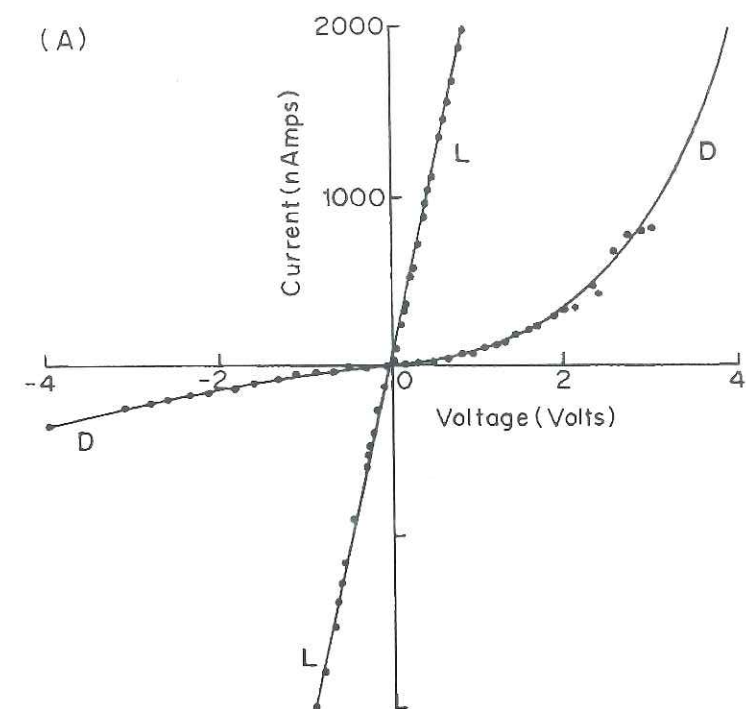


Figure (4.17) : Schematic of the solid state photocell using undoped polypyrrole (Au/Ppy(undoped)/PVA+H₃PO₄+MB/ITO).

MB incorporated in SPE (i.e. PVA+H₃PO₄) has been used as a photo-sensitizer for undoped Ppy, in order to know the difference in the sensitization effect in doped and undoped Ppy. The schematics of the photocells Au/Ppy(undoped)/PVA+H₃PO₄+MB/ITO containing different concentrations of MB are as shown in Figure (4.17). The current-voltage (I-V) characteristics in dark (D) and under illumination (L) for these photocells are as shown in Figure (4.18). The curves (A) to (C) corresponds to MB dye concentration of 3.6, 4.3 and 4.5 mM/monomer respectively. It is interesting to observe that the I-V characteristics in dark (D) exhibit a rectifying nature i.e. the current in one direction (Au +ve, 1st quadrant) is much higher than in the opposite direction (Au -ve, 3rd quadrant). However, the photo-current (I_l) which is dramatically high for low concentration of MB dye, decreases progressively, while dark current increases with the

increase in the sensitizer concentration. The photosensitivity factor ($S=I_l/I_d$, where I_l is the photocurrent and I_d is the dark current) for these cells as a function of MB concentration is as shown in Figure (4.19). It is quite evident that there is a certain MB concentration (3.6 mM/monomer) at which the photosensitivity is very high (of the order of 80). The concentration of the MB dye corresponding to maximum photosensitivity factor is said to be 'critical concentration'. It is worthwhile to note here that maximum photosensitivity is observed at a higher dye concentration (i.e. 3.6 mM/monomer) in case of an undoped Ppy system as compared to the doped Ppy system (2.5 mM/monomer).



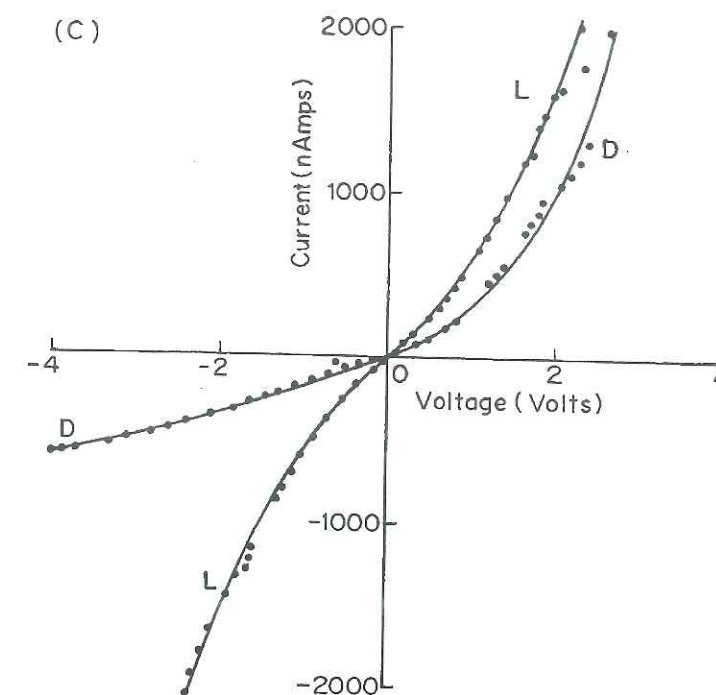


Figure (4.18) : current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocell Au/Ppy(undoped)/PVA+H₃PO₄+MB/ITO containing different concentrations of MB; (A) 3.6 , (B) 4.3 and (C) 4.5 mM/monomer respectively.

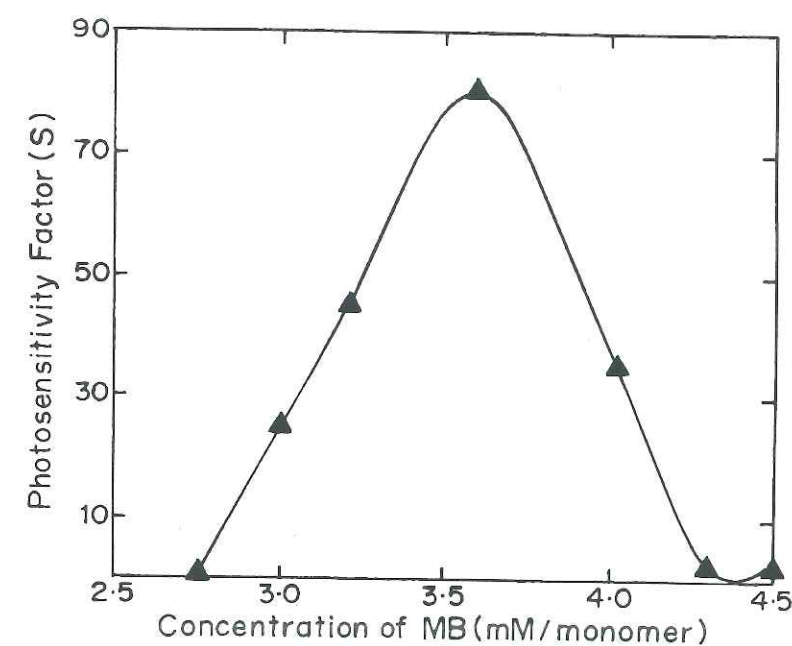


Figure (4.19) : photosensitivity factor (S) as a function of the concentration of MB for the photocell Au/Ppy(undoped)/PVA+H₃PO₄+MB/ITO.

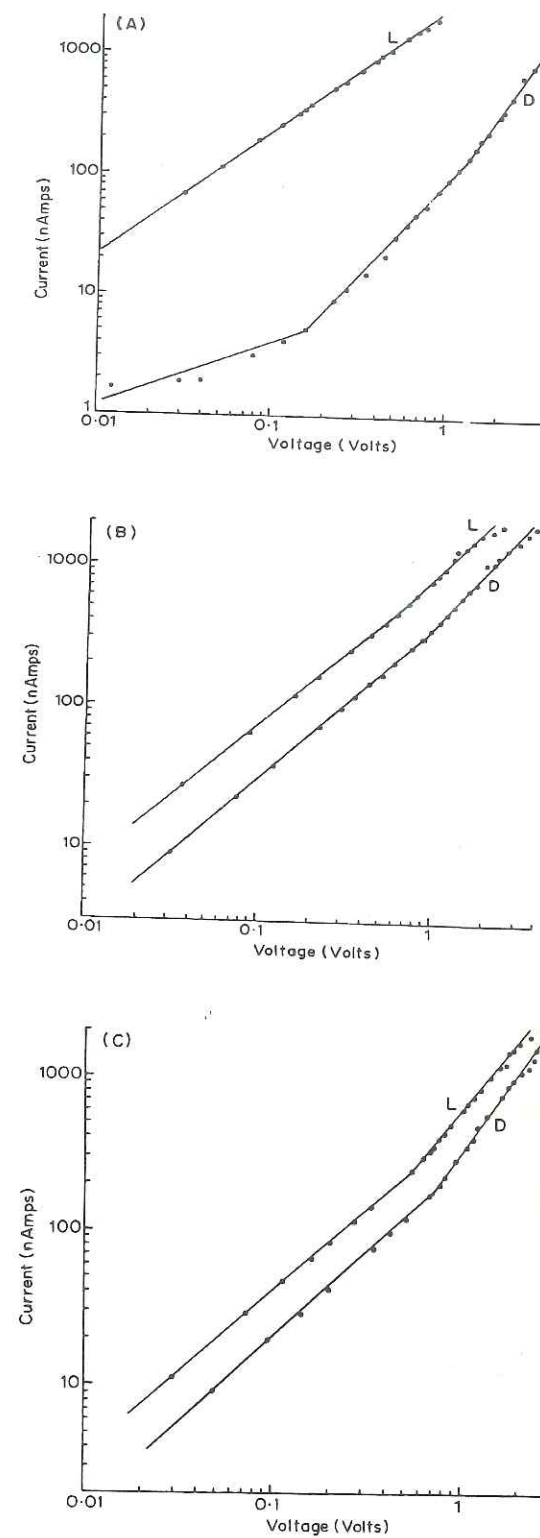


Figure (4.20) : The log-log plot of the I-V curves showing the SCLC type behavior with the exponent 'n' changing by the increase of the dye concentration as well as illumination. Curves (A) to (C) correspond to the MB concentration of 3.6, 4.3 and 4.5 mM/monomer respectively.

The current-voltage (I-V) characteristics were analyzed in detail for different types of charge transport processes. The experimental data was analyzed according to the expected mathematical relation between current and voltage for each case. Space Charge Limited Conduction (SCLC) appears to be the predominant process of charge transport in which the current is given by equation (4.2). Figure (4.20) shows the I-V characteristics plotted on log-log scale and it is evident from these curves that the relation $I \propto V^n$ is indeed followed. However, the slope of the graph changes considerably with the increase of MB concentration as well as the presence of illumination. The SCLC curves are usually interpreted in terms of charge injection and the subsequent filling of impurity / trapping centers giving rise to progressively linear, square / superlinear and again square type dependence of the I-V characteristics. The increase of the impurity centres (MB) increases the dark current and also widens the range of voltage over which the linearity exists (or lowers the value of exponent in equation 4.2).

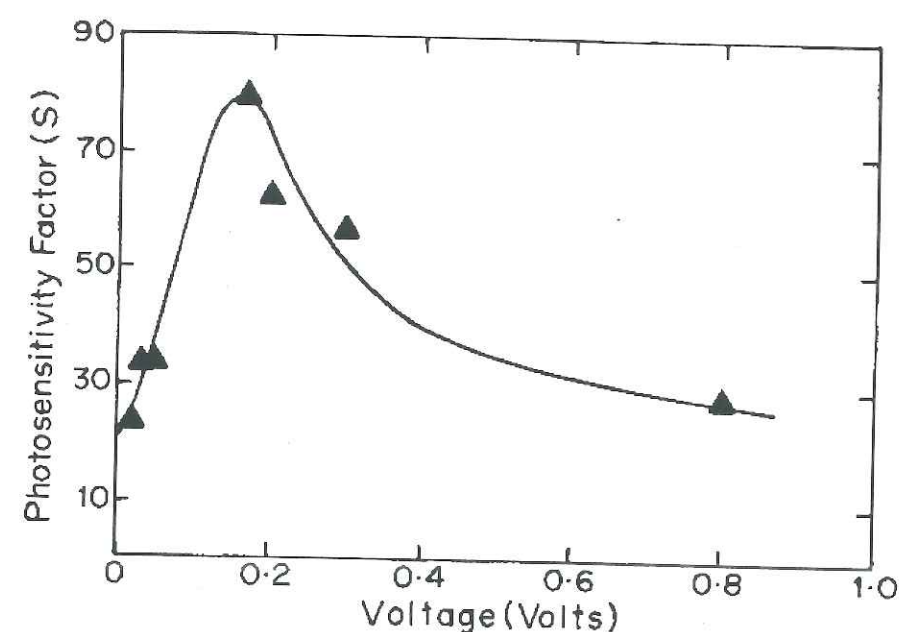


Figure (4.21) : Voltage/ filed dependence of the photosensitivity factor for the photocell Au/Ppy(undoped)/PVA+H₃PO₄+MB/ITO for MB concentration of 3.6 mM/monomer.

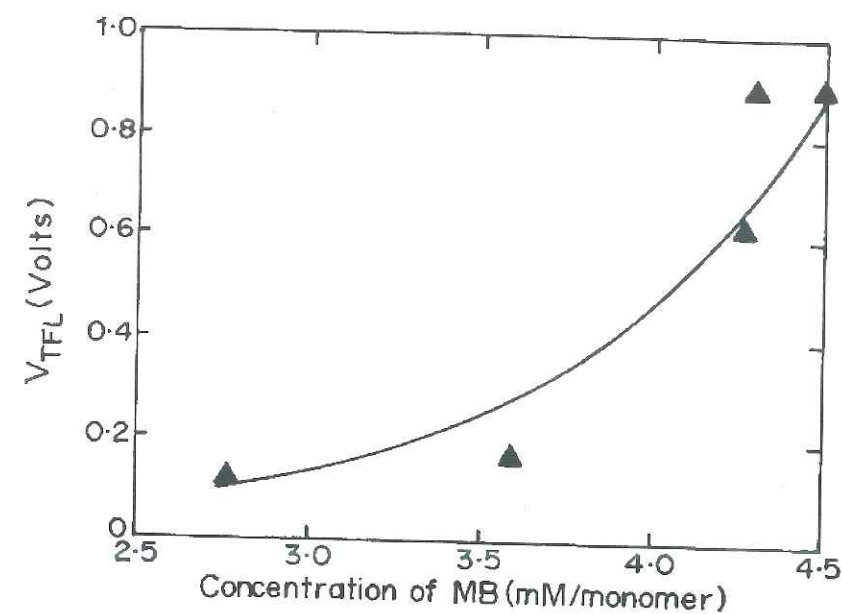


Figure (4.22) : Variation of the V_{TFL} with the MB concentration.

Figure (4.21) shows the voltage / field dependence of the photosensitivity factor (S) at MB concentration of 3.6 mM/monomer. It can be seen that the photosensitivity is maximum (of the order of 80) at a particular voltage (0.19 volts) and decreases on both the sides. Figure (4.22) shows the variation of the V_{TFL} with respect to the MB concentration. It is evident from the figure that the V_{TFL} increases as the dye concentration increases.

Comparing the maximum photosensitivity factor for Ppy in doped and undoped state sensitized with MB, it can be seen that different sensitization effects are observed for the same conducting polymer - dye combination and the photosensitization effect is observed to be more in case of the Ppy doped system. Thus, it can be concluded that the sensitization effect depends upon the doped and / or undoped state of the polymer. The

reason for getting different photosensitization effect becomes obvious by considering the energy level diagram for the materials used in forming the photocells. The energy level diagram for the materials used in forming the photocell Au/Ppy(undoped)/PVA+H₃PO₄+MB/ITO will be the same as that for the Ppy doped system but the only difference is that in case of the Ppy doped system, some additional energy levels and / or bands will be present in the energy gap which will be of solitonic or bipolaronic nature. These energy levels can act as trapping centres for minority charge carriers (i.e. electrons from Ppy) thereby increasing the majority charge carrier concentration and thus enhancing photosensitivity. Since these energy levels are at different places with respect to the energy levels in the dye, the difference between the valance states (i.e. ΔE_v) and the conduction states (i.e. ΔE_c) of the dye and the polymer will be changed as compared to undoped polymer. The charge carriers will face different potential barriers so as to reach to the polymer. Hence, one would expect different sensitization effects for the same polymer / dye combination.

4.3.3 SENSITIZATION EFFECT IN DOPED Ppy BY MB INCORPORATED IN PVP+H₃PO₄ :

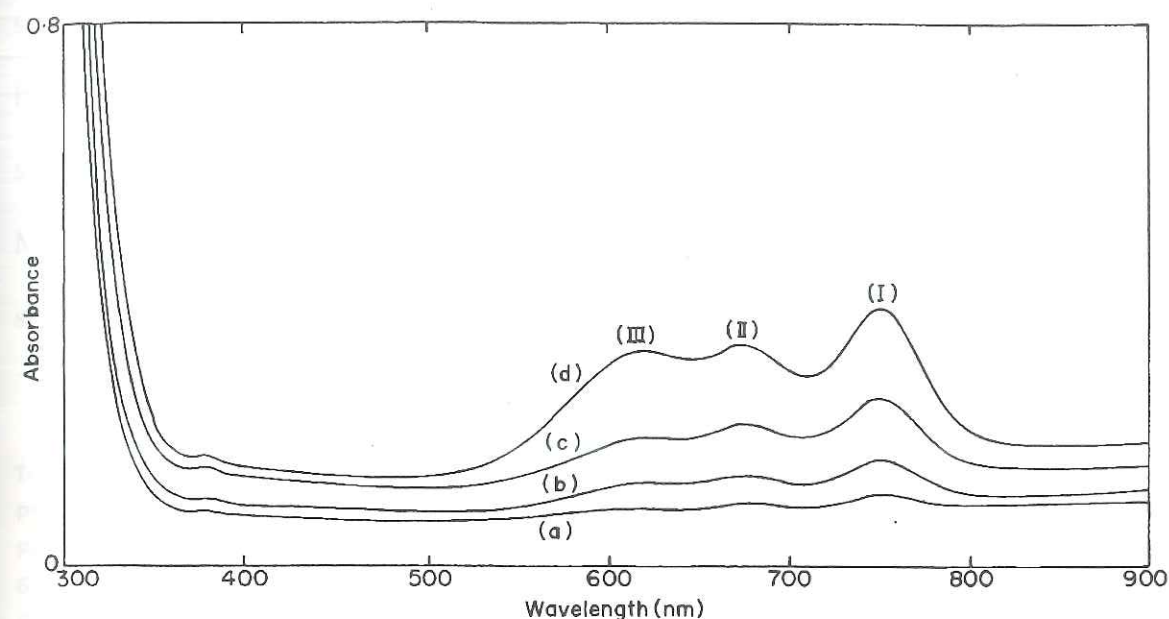


Figure (4.23) : UV-VIS spectra of the MB incorporated PVP+H₃PO₄ films on glass deposited by dip-coating method. Spectra (a) to (d) corresponds to the MB concentrations of 0.965, 1.31, 1.75 and 2.27 mM/monomer respectively.

Figure (4.23) shows the UV-VIS spectra of the MB incorporated PVP+H₃PO₄ films on glass deposited by dip-coating. Curves (a) to (d) corresponds to MB concentrations of 0.965, 1.31, 1.75 and 2.27 mM/monomer respectively. Three distinct peaks at around 750, 675 and 615 nm are observable which are marked in figure as I, II and III respectively along with a small intensity hump at around 425 nm. The intensity of the peak at 750 nm (I) is the high as compared to the two other peaks. Also, the intensity of the peaks increases as the MB concentration increases but no shift in the peak position is observed. On the similar arguments which were given for the UV-VIS spectra of the MB in PVA+H₃PO₄ matrix, it can be concluded that MB is not present in an aggregated, crystalline or ordered form but the optical absorption of the dye has been changed

significantly in presence of the matrix. The singlet ground state of the MB gets splitted into a triplet state by the presence of the PVP+H₃PO₄ matrix. Also, the presence of the small intensity band / hump at around 425 nm indicates the formation of a complex between the two. The observation of these films under the optical microscope also suggests the absence of the dye aggregation. The absence of XRD peaks corresponding to MB in the XRD pattern of MB incorporated PVP+H₃PO₄ dip coated films on glass substrates also confirms the absence of dye aggregation.

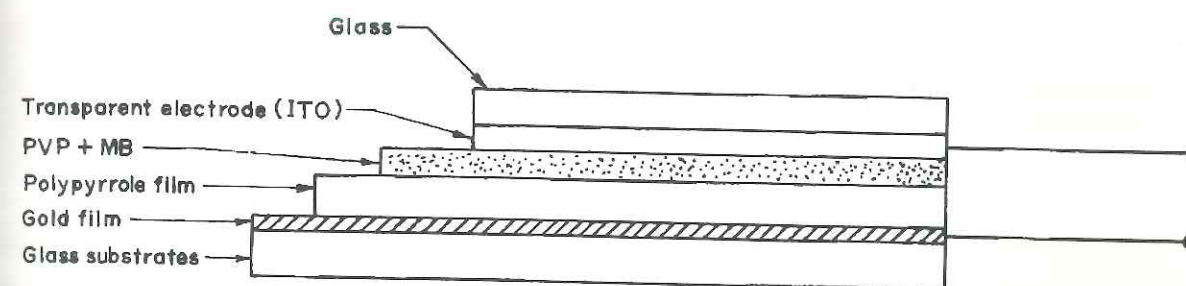


Figure (4.24) : Schematic of the solid state photocell using conducting polypyrrole (Au/Ppy/PVP+H₃PO₄+MB/ITO).

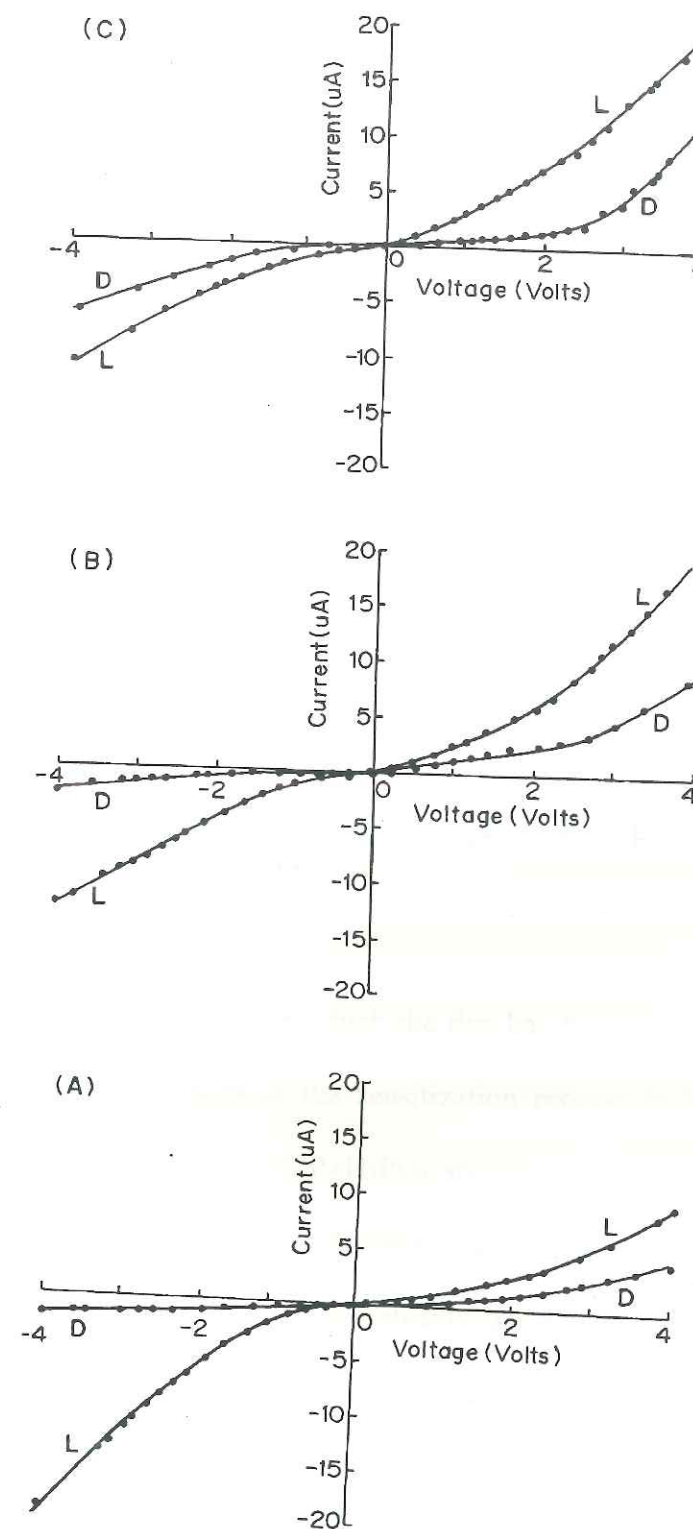


Figure (4.25) : current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocell Au/Ppy/PVP+H₃PO₄+MB/ITO containing different concentrations of MB; (A) 2.25, (B) 2.35 and (C) 2.45 mM/monomer respectively.

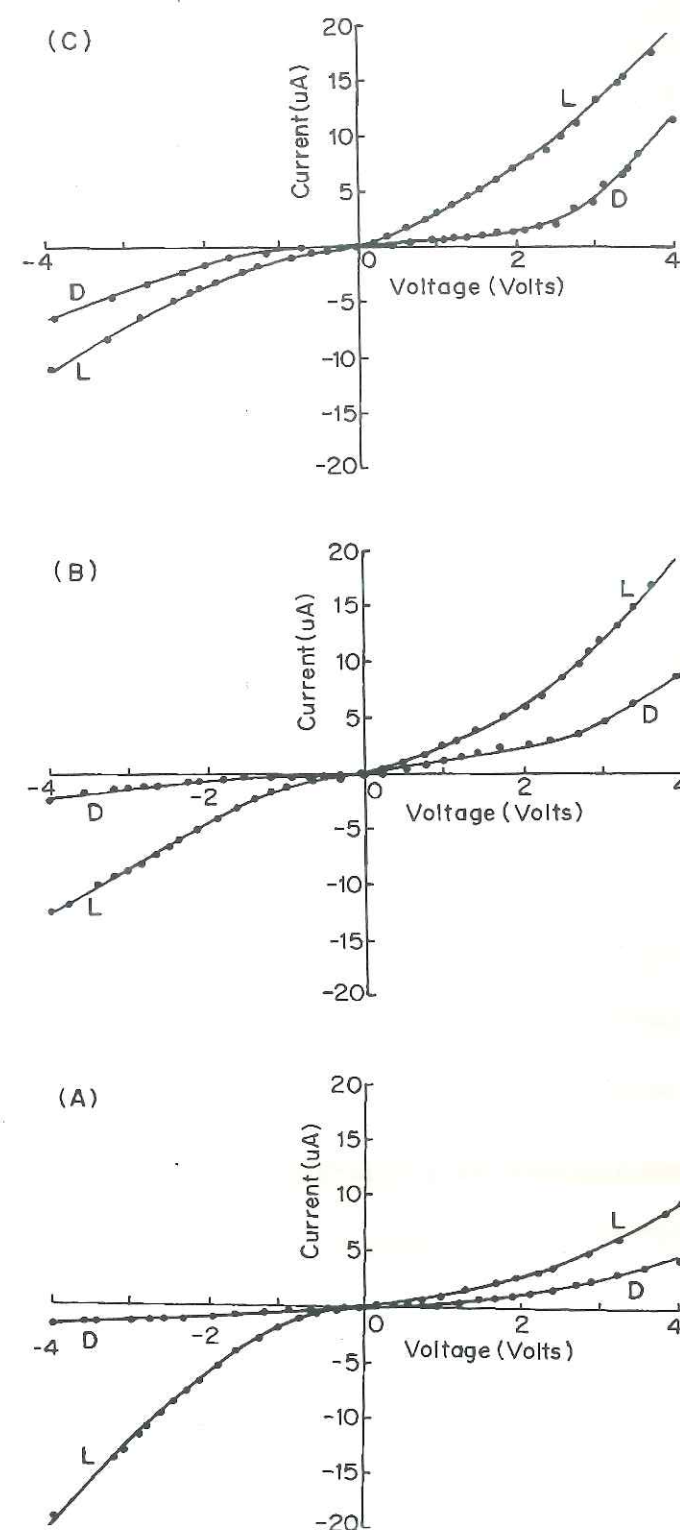


Figure (4.25) : current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocell Au/Ppy/PVP+H₃PO₄+MB/ITO containing different concentrations of MB; (A) 2.25, (B) 2.35 and (C) 2.45 mM/monomer respectively.

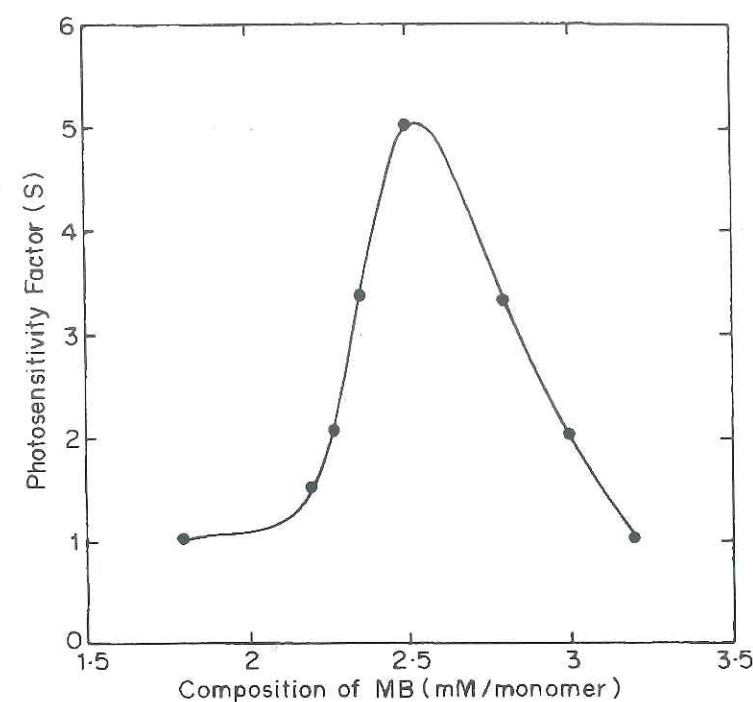


Figure (4.26) : Photosensitivity factor (S) as a function of the MB concentration for the photocell Au/Ppy/PVP+H₃PO₄+MB/ITO.

In order to know whether the matrix in which the dye has been incorporated plays any role in such sensitization processes or the sensitization process is independent of the matrix, MB has been incorporated in PVP+H₃PO₄ and used as a sensitizer for Ppy. The photocells (Au/Ppy/PVP+H₃PO₄+MB/ITO) containing different concentrations of MB were fabricated which can be shown schematically as shown in Figure (4.24). The current-voltage (I-V) characteristics in dark (D) and under illumination (L) for these photocells are as shown in Figure (4.25). The curves (A) to (C) corresponds to MB dye concentration of 2.25, 2.35 and 2.45 mM/monomer respectively. It is interesting to observe that the I-V characteristics in dark (D) exhibit a rectifying nature i.e. the current in one direction (Au +ve, 1st quadrant) is much higher than in the opposite direction (Au

–ve, 3rd quadrant). The variation of the photosensitivity factor (S) with respect to the MB concentration is as shown in Figure (4.26). It is quite evident that there is a certain MB concentration (2.5 mM/monomer) at which the photosensitivity is observed to be maximum (of the order of 5). The concentration of the MB dye corresponding to maximum photosensitivity factor is said to be ‘critical concentration’.

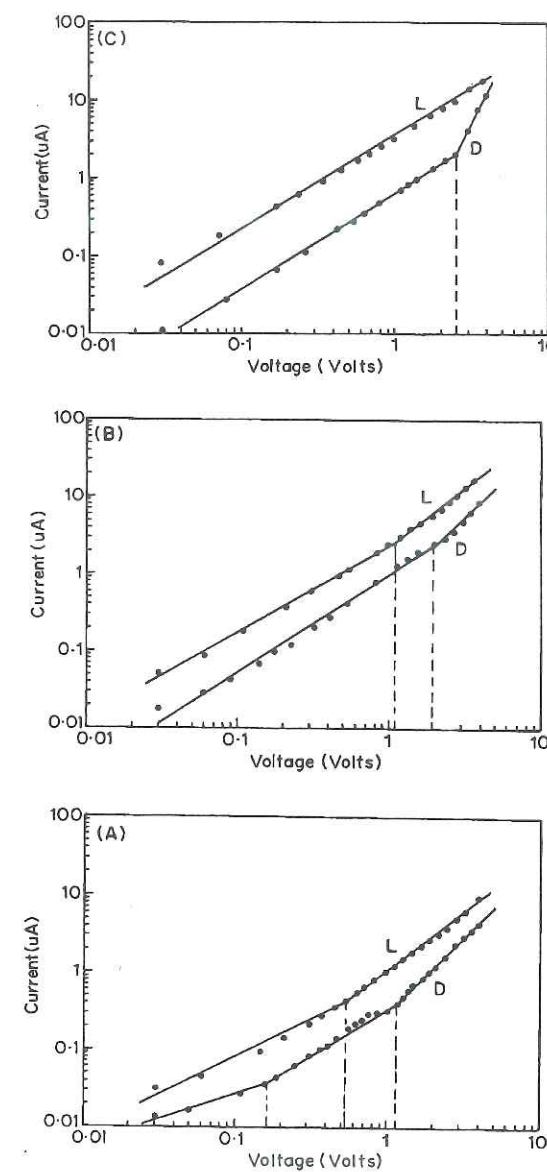


Figure (4.27) : The log-log plot of the I-V curves showing the SCLC type behavior with the exponent ‘n’ changing by the increase of the dye concentration as well as illumination. Curves (A) to (C) correspond to the MB concentration of 2.25, 2.35 and 2.45 mM/monomer respectively.

The current-voltage (I-V) characteristics were analyzed in detail for different types of charge transport processes. Different charge transport processes were eliminated depending upon the mathematical relationship between the current and the voltage. Space Charge Limited Conduction (SCLC) appears to be the predominant process of charge transport in which the current is given by equation (4.2). Figure (4.27) shows the I-V characteristics (presented in Figure 4.25) plotted on log-log scale and it is evident from these curves that the relation $I \propto V^n$ is indeed followed. However, the slope of the graph changes considerably with the increase of MB concentration as well as the presence of illumination. The SCLC curves are usually interpreted in terms of charge injection and the subsequent filling of impurity / trapping centers giving rise to progressively linear, square / superlinear and again square type dependence of the I-V characteristics. The V_{TFL} is also observed to increase with the dye concentration and the photosensitivity is also observed to be field / voltage dependent.

Comparing the Ppy based photocells made by incorporating MB in PVA+H₃PO₄ and PVP+H₃PO₄ matrices, it is evident that high photosensitivity ($S_{max} = 1000$) is obtained for PVA based photocells whereas in case of PVP based photocell photosensitivity is observed to be poor ($S_{max} = 5$). Thus, it can be concluded that the sensitization effect is very much dependent on the matrix in which the dye has been incorporated. The observed low photosensitivity in case of PVP based photocells may be because PVP do not forms a complex with the phosphoric acid and is not as good SPE as PVA+H₃PO₄ with high conductivity. Once the photo generated charge carriers are created by the action of light, they should be able to be transported through the bulk of the material without

recombination. The matrix in which the dye is incorporated should be able to transport the photo-generated charge carriers. From the present study, it can be concluded that the matrix which can efficiently transport the photo-generated charge carriers will be more suitable for dye sensitized devices.

4.3.4 SENSITIZATION EFFECT IN DOPED POLYANILINE BY MB INCORPORATED IN PVA+H₃PO₄ :

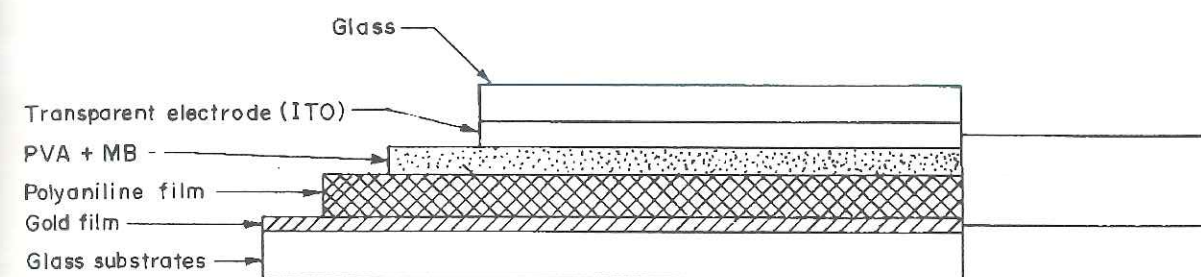
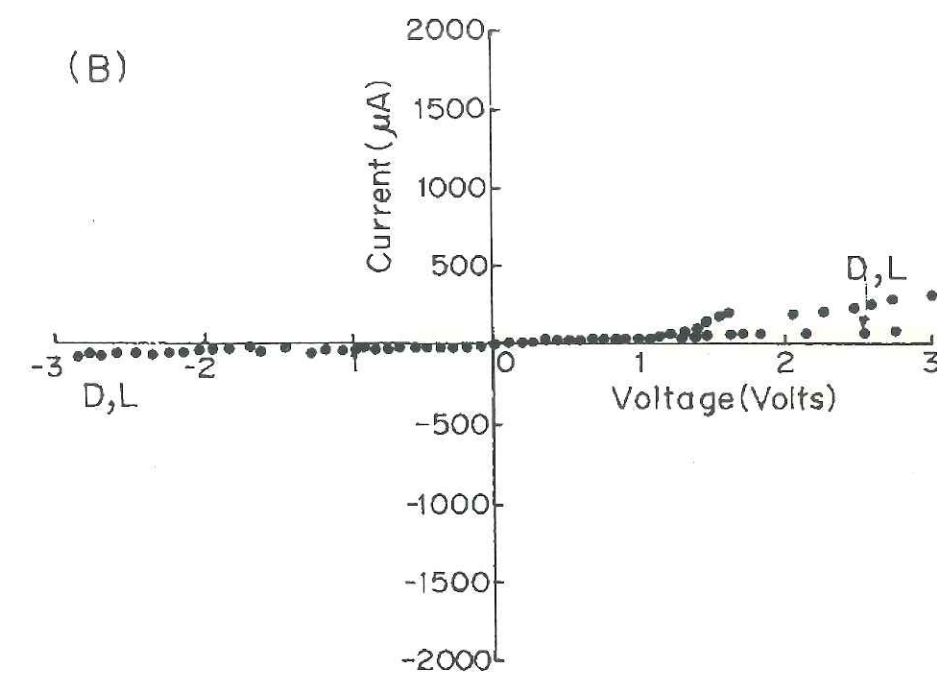
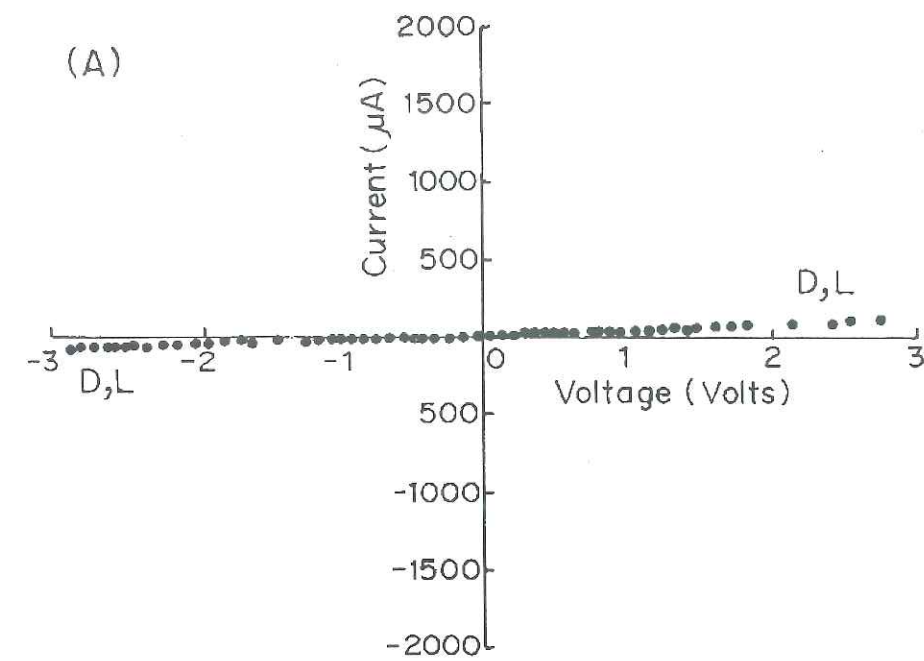


Figure (4.28) : Schematic of the solid state photocell using conducting polyaniline (Au/PANI/PVA+H₃PO₄+MB/ITO).



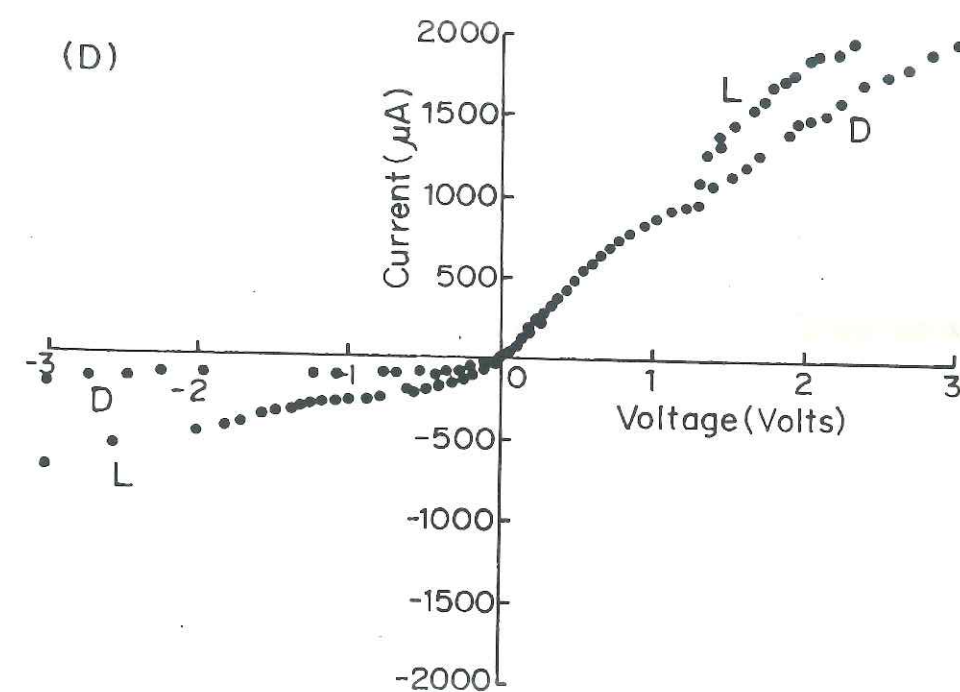
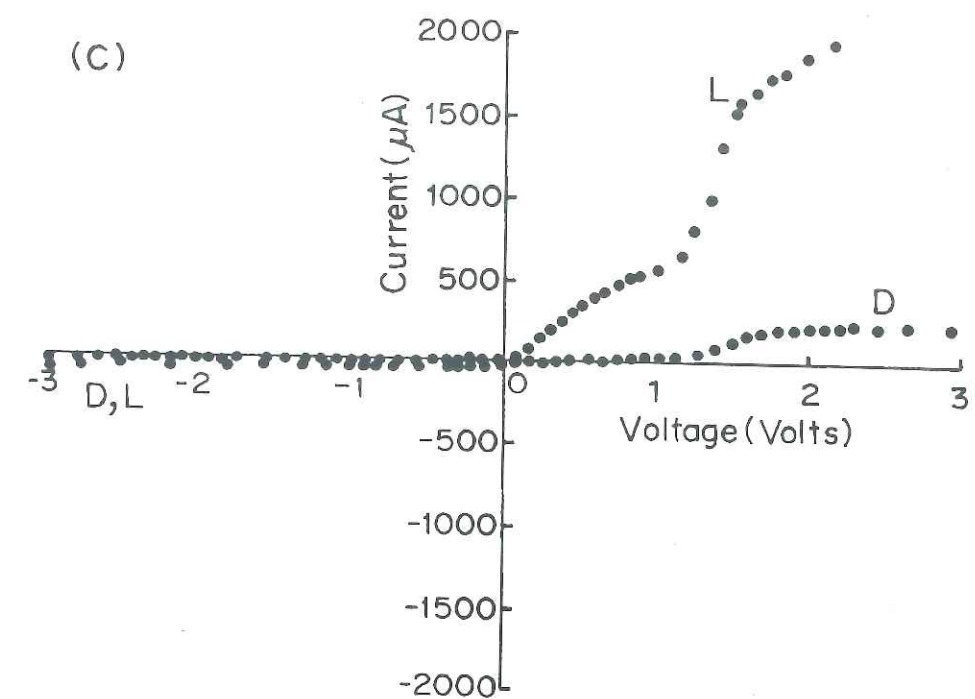


Figure (4.29) : current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocell $\text{Au/PANI/PVA+H}_3\text{PO}_4\text{+MB/ITO}$ containing different concentrations of MB; (A) 2.7, (B) 3.3, (C) 4.1 and (D) 5.3 mM/monomer respectively.

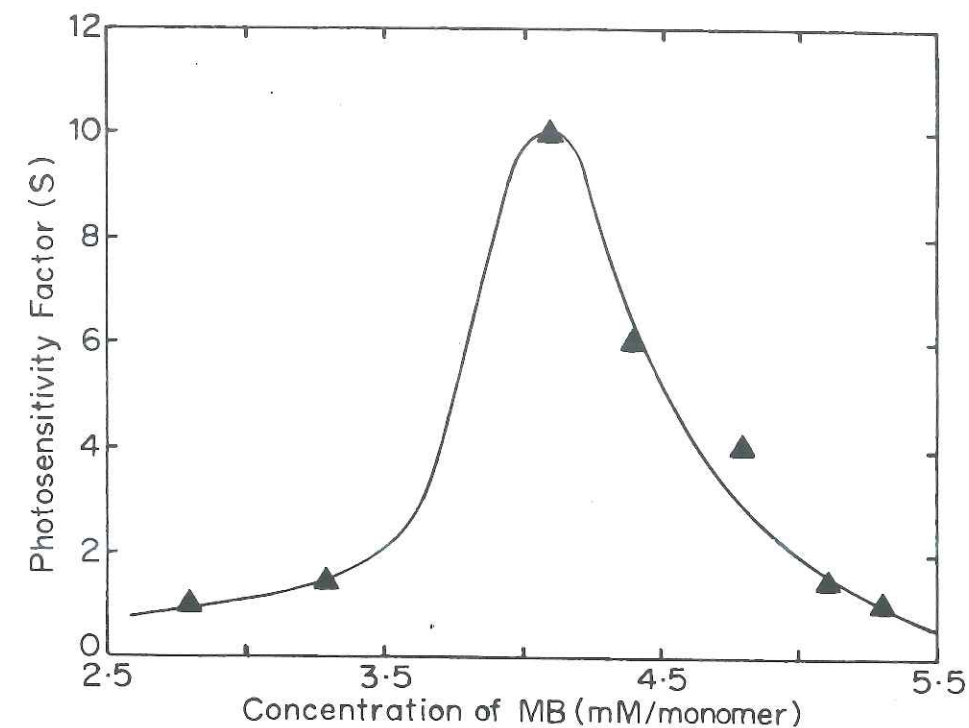
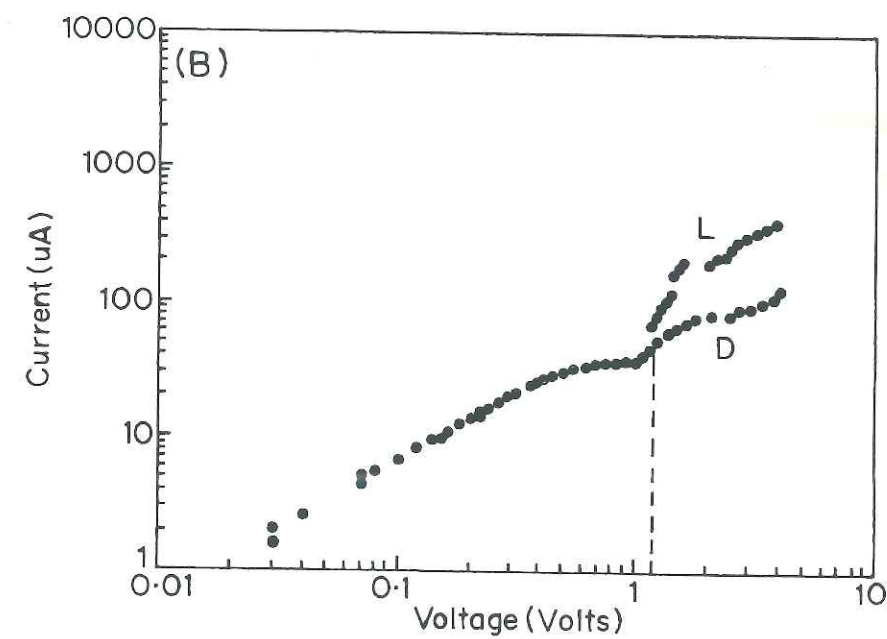
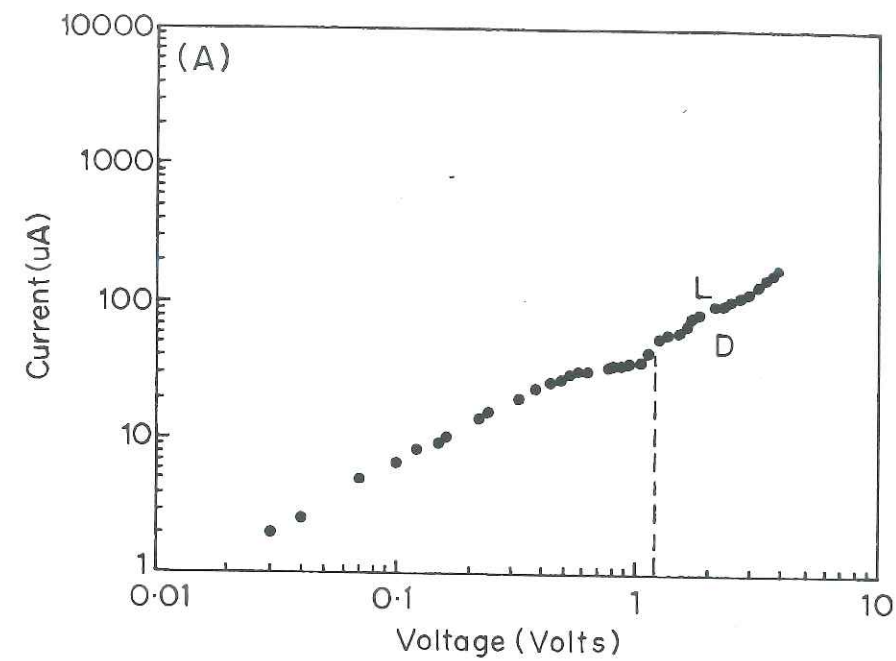


Figure (4.30) : Photosensitivity factor (S) as a function of the concentration of MB for the photocell Au/PANI/PVA+H₃PO₄+MB/ITO.

MB has been used as a sensitizer for polyaniline (PANI) in order to know whether it sensitizes PANI and as efficiently as it does for Ppy. The photocells (Au/PANI/PVA+H₃PO₄+MB/ITO) containing different concentrations of MB were fabricated and can be shown schematically as shown in Figure (4.28). The current-voltage (I-V) characteristics in dark (D) and under illumination (L) for these photocells are as shown in Figure (4.29). The curves (A) to (D) corresponds to MB dye concentration of 2.7, 3.3, 4.1 and 5.3 mM/monomer respectively. It is interesting to observe that the I-V characteristics in dark (D) exhibit a rectifying nature i.e. the current in one direction (Au +ve, 1st quadrant) is much higher than in the opposite direction (Au -ve, 3rd quadrant). The variation of photosensitivity factor (S) with respect to the MB

concentration for these cells is as shown in Figure (4.30). It is quite evident that there is a certain MB concentration at which the photosensitivity is observed to be maximum (of the order of 10). The concentration of the MB dye corresponding to maximum photosensitivity factor is said to be 'critical concentration'.



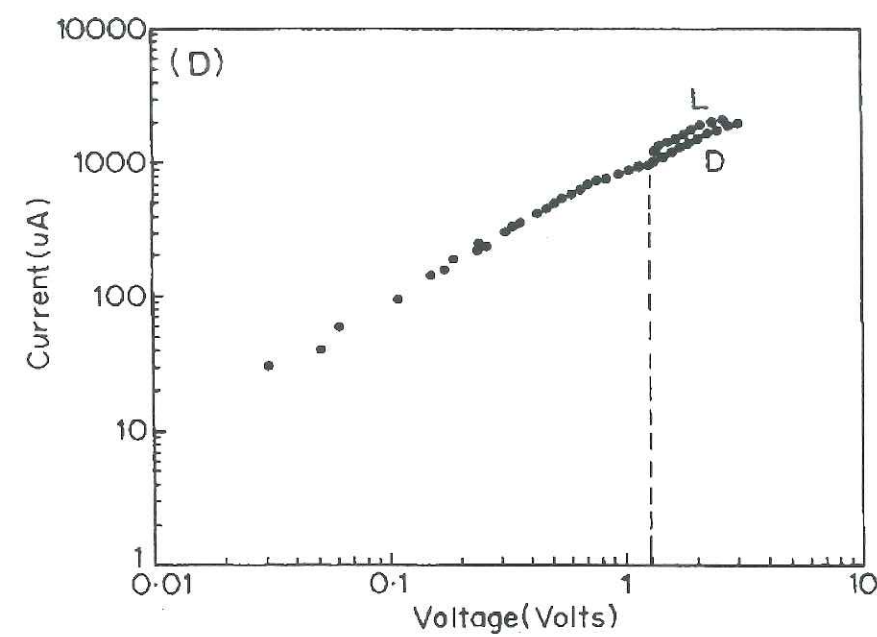
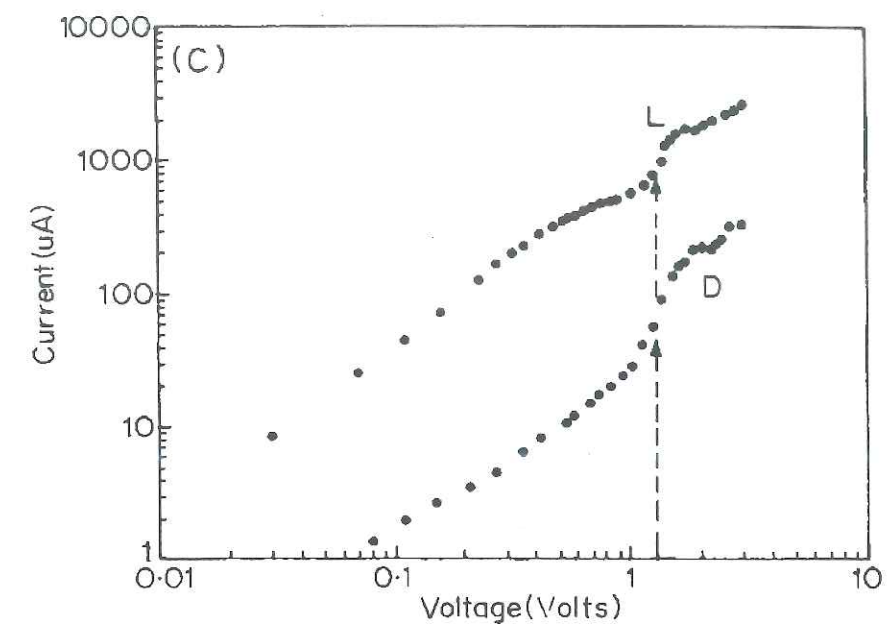


Figure (4.31) : The log-log plot of the I-V curves showing the SCLC type behavior with the exponent 'n' changing by the increase of the dye concentration as well as illumination. Curves (A) to (D) correspond to the MB concentration of 2.7, 3.3, 4.1 and 5.3 mM/monomer respectively.

The I-V characteristics were analyzed in detail for different types of charge transport processes based on the mathematical relationship between the current and the voltage and their best fit. Space charge limited conduction (SCLC) appears to be more appropriate. The I-V characteristics (presented in Figure 4.29) plotted on the log-log scale are as shown in Figure (4.31). These curves are quite interesting and looks to be the superimposition of the space charge limited conduction (SCLC) [obeying equation 4.2] and an electrochemical reaction, as there is a sudden rise of the current values at 1.2 - 1.3 volts which is observed in all the samples and at the same voltage. It should be noted here that MB incorporated in PVA+H₃PO₄ contains Cl⁻ from MB. On application of the positive potential (and at particularly about 1.2 - 1.3 V) to PANI (i.e. when Au is positive), Cl⁻ must be moving from the PVA/MB to PANI with a resultant increase in the doping level of PANI. The conductivity of the PANI will increase as more and more Cl⁻ will come in. As the concentration of the MB dye increases, it has been observed that the current at this particular voltage rises more and more which is in good agreement with the proposed mechanism. This electrochemical reaction must be occurring at 1.2 - 1.3 volts, yielding a rise in the current value at this particular voltage. The presence of illumination is observed to enhance this electrochemical reaction. It is worthwhile to mention here that the conductivity of PANI, in particular, is very much dependent on its doping level and the degree of protonation.

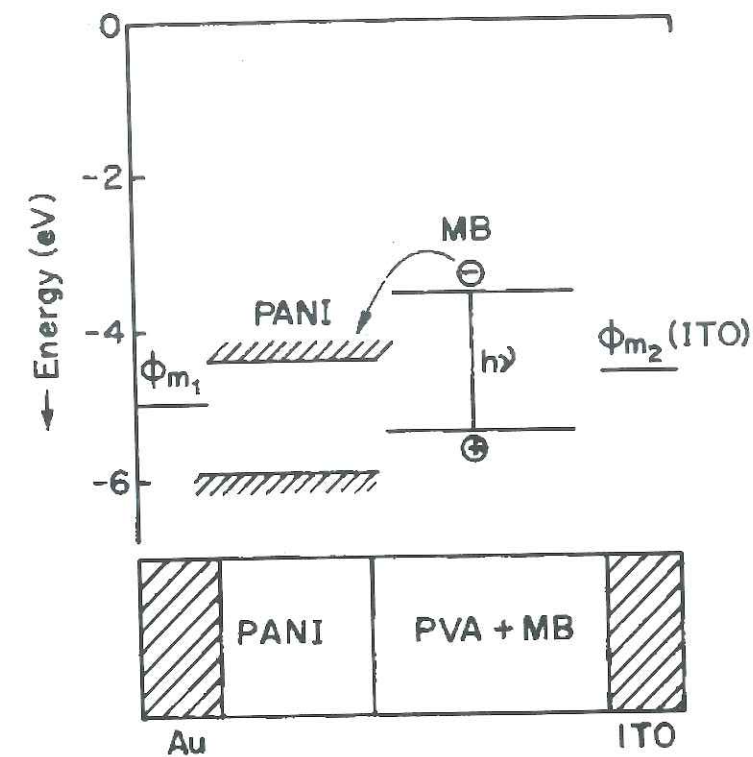


Figure (4.32) : Energy level diagram for the photocell having Au/PANI/PVA+H₃PO₄+MB/ITO type sandwich structure.

Figure (4.32) shows the energy level diagram for the materials used in forming the photocell Au/PANI/PVA+H₃PO₄+MB/ITO. The energy levels for PANI are those which have been reported in the literature [24], while those for MB in PVA are derived from the UV-VIS spectra recorded as above. It must be noted that the PVA containing phosphoric acid is a good proton conductor while doped PANI is a p-type material. It is worthwhile to note here that Au makes a blocking contact (for both electrons and holes, more for holes) with the PANI. Likewise ITO also makes a blocking contact (for both electrons and holes, more for electrons) with PVA/MB. Thus, when Au is positive, the hole transport via PANI and the proton transport through PVA are facilitated giving high

forward current although some barrier is expected at the Au/PANI interface. On the other hand when Au is having negative polarity, the current would be less since electrons are minority carriers (in both PANI and PVA+MB, since MB is a p-type material) and expected a barrier at the Au/PANI and PANI/PVA+MB interface. This gives rise to the rectifying type I-V characteristics as noted in the present case. On the other hand, when the photocell is under illumination, MB dye absorbs light and fills the higher electronic levels with photoexcited charge carriers. This facilitates their transport across the potential barriers and the required effect is observed. It should also be remembered that there are several other energy levels present due to the inherent amorphous nature of the polymer and due to doping - such as solitonic or bipolaronic states, and hence some of these can act as carrier trapping centres for one type of charge carriers. In this manner, photosensitivity is obtained by lowering of potential barrier at the interface. The decrease of photosensitivity at high MB concentrations can be due to high absorption of light (photons) only at the surface, as well as heavy trapping (followed by recombination) of charge carriers which does not allow them to pass into the bulk of the material.

4.4 SUMMARY AND CONCLUSIONS :

The ground electronic singlet state of MB when incorporated in PVA+H₃PO₄ matrix splits into a triplet state and MB is also observed to form a complex with the matrix as can be seen from an additional absorption band in the UV-VIS at lower energy side of PVA (at the wavelength around 425 nm). MB incorporated in PVA+H₃PO₄ acts as an excellent photosensitizer for doped Ppy giving high photosensitivity factor (S) of the order of 1000. There is a "critical concentration" of the MB dye at which maximum

photosensitivity has been observed (in the present case 2.5 mM/monomer). The photosensitivity decreases on both the sides as we go away from this concentration. The variation of the dark (I_d) and light (I_l) current with the MB concentration, in the linear portion of the I-V characteristics, shows that light current (I_l) goes through a maximum whereas dark current (I_d) remains more or less the same (or increases slowly). This particular variation of the light current (I_l) is more important than that of the dark current (I_d) and is mainly responsible for getting maximum photosensitivity at a particular MB concentration called "critical concentration". Space charge limited conduction (SCLC) is observed to be the dominant process of charge transport. Obviously, the photosensitivity is observed to depend on the voltage / field. V_{TFL} is observed to increase with the dye concentration.

In case of the undoped Ppy sensitized with MB incorporated in PVA+H₃PO₄ matrix, less photosensitivity has been observed as compared to the doped system. Maximum photosensitivity factor (S) of the order of 80 has been observed. There is a "critical concentration" of the dye at which maximum photosensitivity has been observed (in the present case 3.6 mM/monomer). As we go away from this concentration, on both the sides, the photosensitivity decreases. SCLC is the dominant process of charge transport. The photosensitivity factor (S), along with the dye concentration, is also observed to depend on the voltage / field. V_{TFL} is observed to increase with the dye concentration. The creation of polaronic / bipolaronic states in the energy gap of the polymer by doping seems to play an important role in the sensitization process in conducting polymers, as these states can act as trapping centres for one type of the charge carrier (leaving the

other free to move) and also their presence alters the ΔE_v and ΔE_c values. Thus, it can be concluded that the sensitization effect depends very much on the ΔE_v and ΔE_c values and hence on the actual placement of the energy levels of the dye with respect to the polymer to be sensitized. Hence, it can be concluded that the sensitization effect does depend on the doped /undoped state of the conducting polymers.

In case of the doped Ppy sensitized with MB incorporated in PVP+H₃PO₄ matrix, less photosensitivity has been observed as compared to that of Ppy sensitized by MB incorporated in PVA+H₃PO₄ matrix. Maximum photosensitivity factor (S) of the order of 5 has been observed. There is a "critical concentration" of the dye at which maximum photosensitivity has been observed (in the present case 2.5 mM/monomer). As we go away from this concentration, on both the sides, the photosensitivity decreases. SCLC is the dominant process of charge transport. The photosensitivity factor (S), along with the dye concentration, is also observed to depend on the voltage / field. From the present study, it can be concluded that the matrix which can efficiently transport the photo-generated charge carriers will be more suitable for dye sensitized devices. Hence, it can be concluded that the sensitization effect does depend on the matrix in which the dye has been incorporated.

In case of the doped PANI sensitized with MB incorporated in PVA+H₃PO₄ matrix, less photosensitivity has been observed as compared to that of Ppy sensitized by MB incorporated in PVA+H₃PO₄ matrix. Maximum photosensitivity factor (S) of the order of 10 has been observed. There is a "critical concentration" of the dye at which maximum

photosensitivity has been observed (in the present case 4.1 mM/monomer). As we go away from this concentration, on both the sides, the photosensitivity decreases. SCLC is the dominant process of charge transport. An electrochemical reaction (movement of Cl^- from PVA/MB to PANI) is also observed to occur at 1.2 -1.3 volts giving rise to doping of the polymer. The observed I-V characteristics are the superposition of the SCLC and the electrochemical reaction, the role of latter being only to increase the current at the particular voltage mentioned above. The photosensitivity factor (S), along with the dye concentration, is also observed to depend on the voltage / field. Hence, it can be concluded that a dye sensitizes different conducting polymers to different extents.

In all, it can be concluded that the sensitization effect depends on the relative placement of the energy levels of the dye with respect to the polymer to be sensitized. Trapping of the minority carriers thereby increasing the majority carrier concentration, life time etc. plays an important role and is the main reason for getting the maximum photosensitivity in case of Ppy sensitized with MB. The other important factors on which the sensitization effect found to depend are - the concentration of the sensitizer dye, the matrix in which the dye has been incorporated, applied voltage / field, doped / undoped state of the conducting polymer.

CHAPTER 5

CHAPTER 5.

SENSITIZATION EFFECT IN CONDUCTING POLYPYRROLE AND POLYANILINE BY n-TYPE DYES

5.1 INTRODUCTION :

According to certain models suggested for the role of sensitizers, it has been proposed that the n-type dyes are good sensitizers for p-type materials and vice versa [1-3]. On the other hand, the present studies appear to indicate that even p-type dye can be an excellent sensitizer for conducting polypyrrole (Ppy). In order to conform the role of the n-type or p-type dye in the sensitization process studies were carried out using both types of dyes. In the present chapter, n-type dyes viz. crystal violet (CRV), rhodamine B (RB) and rhodamine 6G (R6G) have been employed for sensitizing conducting polypyrrole and polyaniline.

Crystal violet (CRV) as discussed in Chapter 1 is an important cationic dye. It is used as a sensitizer for inorganic semiconductors such as TiO_2 , ZnO in order to improve their photoresponse [4]. It is also used as a sensor for trace elemental detection [5-10], optical humidity detection etc. [11-13]. CRV has been reported to be a n-type dye [14].

Rhodamine dyes have been classified under xanthene dyes. The first and the most important member of this class is the Rhodamine B (RB, CI Basic Violet 10; CI 45170). Rhodamine dyes can be absorbed very well by many polymers such as PMMA etc. Rhodamine dyes are distinguished by a high quantum yield of fluorescence and high photostability. Owing to these characteristics, these dyes are often used for widespread

applications e.g. single molecule detection, fluorescence labeling, dye lasers etc. Rhodamine 6G (R6G) - an analogue - is widely used as a laser dye and is known to possess strong fluorescence, good photostability and fastness to light. Both RB and R6G are known to be n-type materials [15-18].

5.2 EXPERIMENTAL :

The polypyrrole (Ppy) films were deposited on the gold coated glass as described in chapter 2. The Ppy films were subsequently dip-coated with polyvinyl alcohol (PVA, M.W. 10^4 , Loba Chemie) films containing phosphoric acid (1:1) from aqueous solution (1 wt %) which also contained crystal violet dye (CRV, Thomas Baker Chemicals Ltd., India, C.I. 42555, $C_{25}H_{30}ClN_3$, M.W. 407.99) in the concentration range of 0 to 16 mM/monomer. It is worthwhile to note here that PVA containing phosphoric acid is a solid polymer electrolyte (SPE). These films were then dried at room temperature and pressed against a transparent conducting ($20 \Omega/\text{sq}$) indium-tin-oxide (ITO) electrode so as to form a sandwich cell configuration Au/Ppy/PVA+ H_3PO_4 +CRV/ITO.

The current-voltage (I-V) characteristics of these cells were studied by placing the samples in the dry box - in dark and under illumination ($5.0 \text{ mW}/\text{cm}^2$, tungsten lamp source) in the same manner as described in chapter 2. The readings were taken instantaneously and at room temperature. The UV-VIS spectra of the SPE+CRV dip-coated films on glass were recorded using the Shimadzu UV-240 spectrophotometer.

The Ppy/RB photocells (Au/Ppy/PVA+H₃PO₄+RB/ITO) were prepared in the same manner as that of the Ppy/CRV system except that instead of CRV the dye was RB (Central Drug House (P) Ltd.; India, C.I. 45170, C₂₈H₃₁N₂O₃Cl, M.W. 479.02). The concentration of RB was varied from 0 to 6 mM/monomer. The I-V and other physico-chemical characteristics for this system are studied in a similar manner as that for the Ppy/CRV system.

The polyaniline (PANI) films were deposited on the gold coated glass as described in chapter 2. The PANI films were subsequently dip-coated with polyvinyl alcohol (PVA, M.W. 10⁴, Loba Chemie) films containing phosphoric acid (1:1) from aqueous solution (1 wt %) which also contained rhodamine 6G dye (R6G, Loba Chemie Industries Ltd.; India, C. I. 45160, C₂₈H₃₁ClN₂O₃, M.W. 479.02) in the concentration range of 0 to 15 mM/monomer. These films were then dried at room temperature and pressed against a transparent conducting (20 Ω/sq) indium-tin-oxide (ITO) electrode so as to form a sandwich cell configuration Au/PANI/PVA+H₃PO₄+R6G/ITO. The I-V and other physico-chemical characteristics for this system are studied in a similar manner as that for the Ppy/CRV system.

5.3 RESULTS AND DISCUSSION :

5.3.1 SENSITIZATION EFFECT IN DOPED Ppy BY CRV INCORPORATED IN PVA+H₃PO₄ :

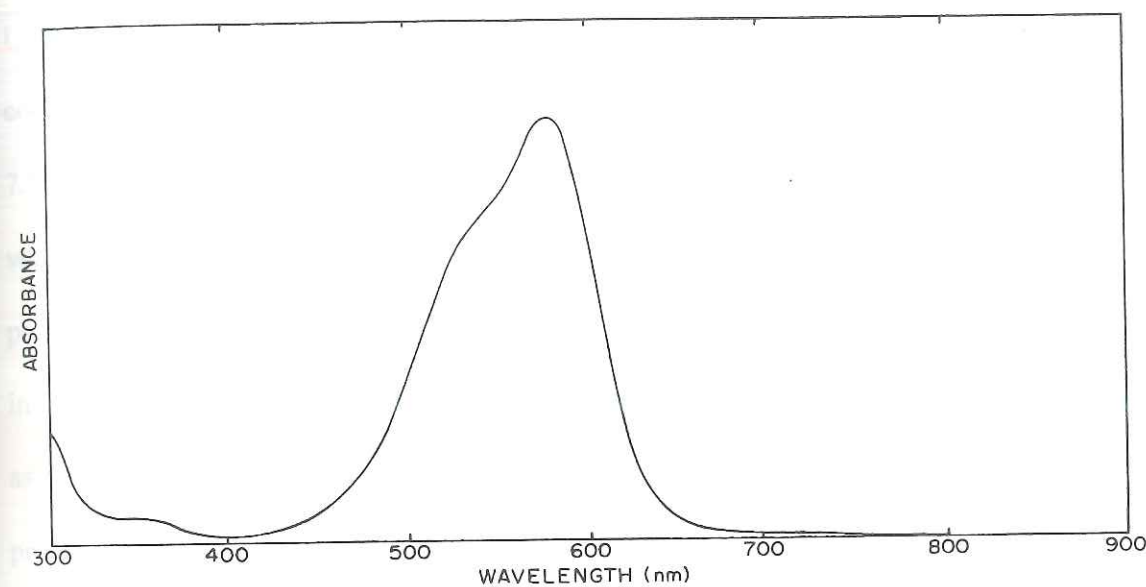


Figure (5.1) : UV-VIS spectra of the CRV in water [1×10^{-5} M].

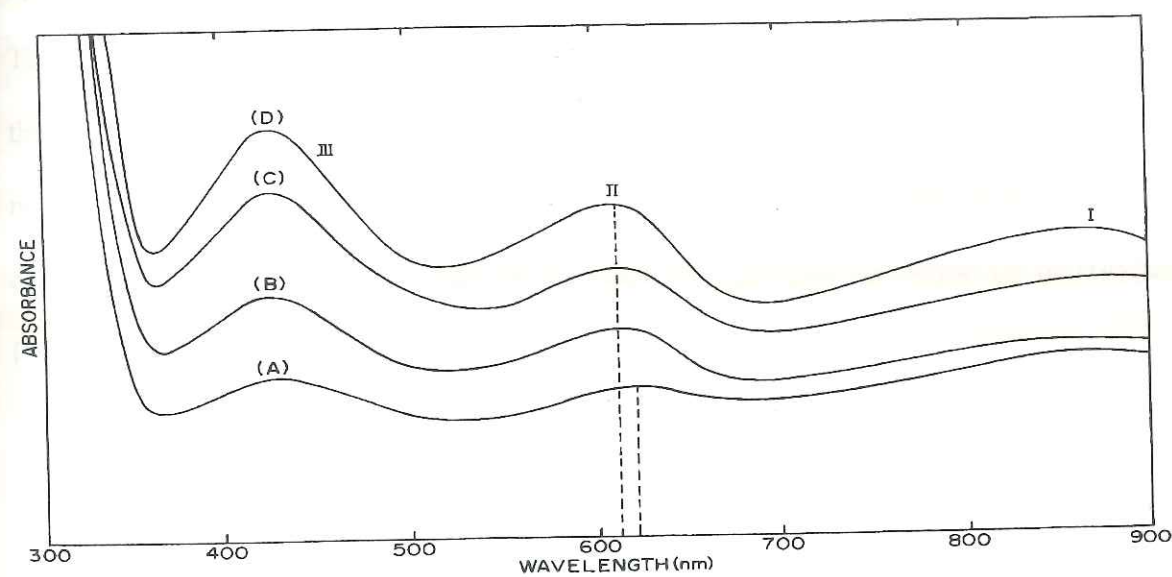


Figure (5.2) UV-VIS spectra of CRV incorporated SPE (i.e. PVA+H₃PO₄) films deposited on glass by dip-coating method. (A) to (D) corresponds to the CRV concentrations of 2.01, 4.34, 7.56 and 8.35 mM/monomer respectively.

Figure (5.1) shows the UV-VIS spectra of the CRV in water [1×10^{-5} M]. It is observed that CRV dissolves in water. It shows a peak at around 575 nm and a shoulder at around 530 nm. A small intensity peak at around 360 is also observed. Figure (5.2) represents the UV-VIS spectra of the CRV incorporated PVA+H₃PO₄ films deposited on glass by dip-coating method. Spectra (A) to (D) corresponds to the CRV concentrations of 2.01, 4.34, 7.56 and 8.35 mM/monomer respectively. Three peaks at around 870, 610 and 430 nm which are marked as I, II and III respectively are observed. The presence of the new peaks suggests that the CRV forms a charge transfer complex with the SPE. The CRV is in a strong acidic environment and must be in a protonated form similar to CRV in nafion as reported earlier [19-21]. The color of the film is yellow in the dry state because of the presence of CRV in the protonated form. In other set of our experiments (not reported here) we have shown that films of CRV incorporated SPE possess humidity dependent optical properties which can be useful for the detection of humidity by optical method. The color of such films changes from yellow to violet depending upon the humidity in the surrounding atmosphere, thereby indicating that CRV changes from protonated to neutral form. There are no large shifts in the main absorption peak (610 nm) with concentration of CRV which would be expected for aggregate formation (J- or H-type) [19-21].

The CRV containing PVA+H₃PO₄ films when observed under optical microscope revealed no aggregates formation. The XRD studies show that the CRV by itself and the SPE films doped with it are all amorphous. Thus, overall conclusion is that the CRV is

not present in the aggregate form in the SPE but it is well mixed at the molecular levels with the same.

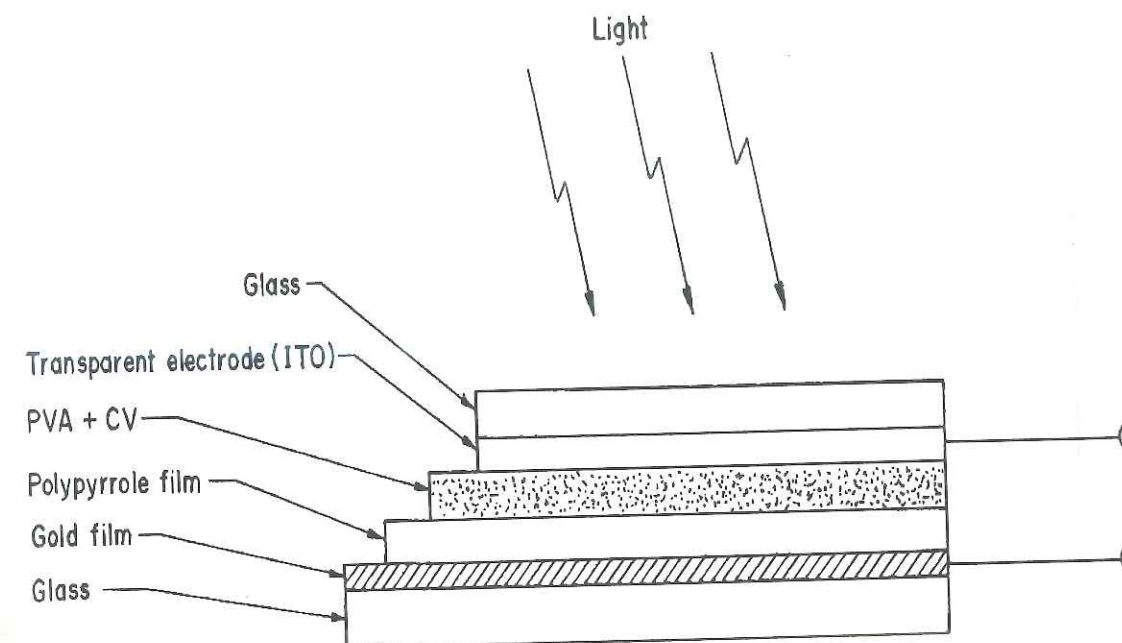
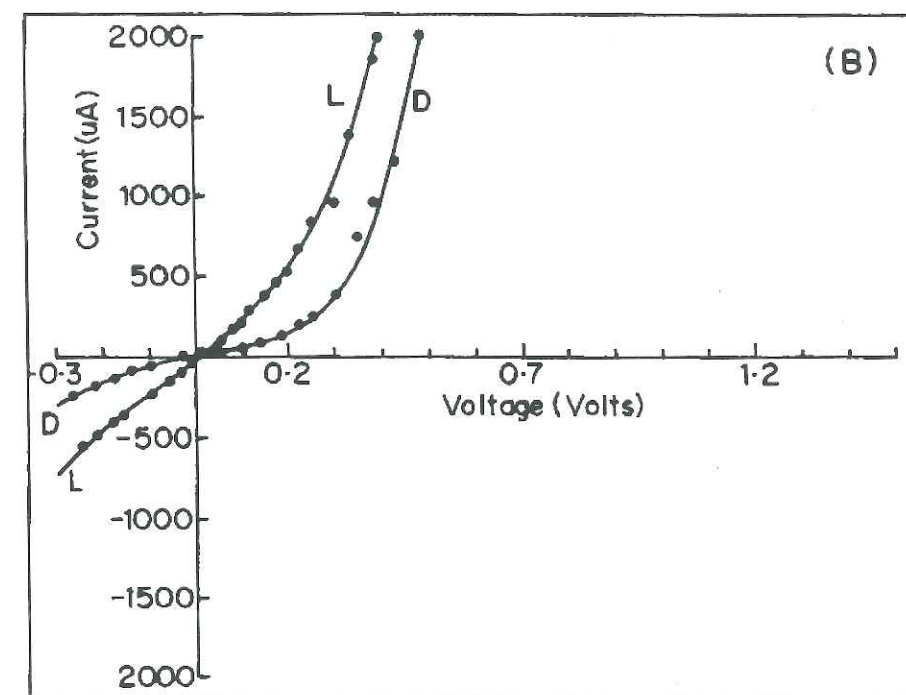
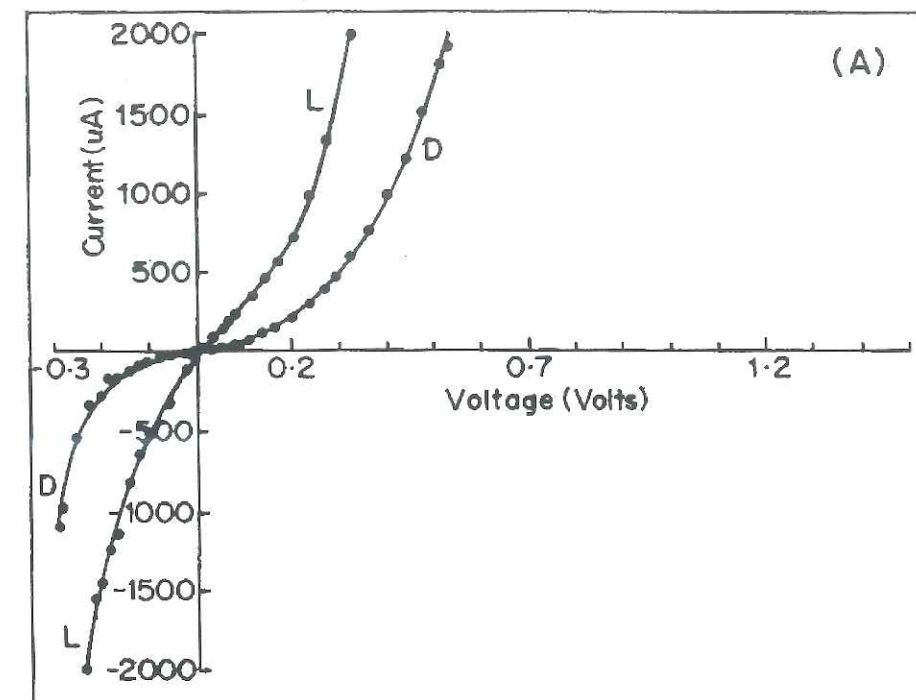
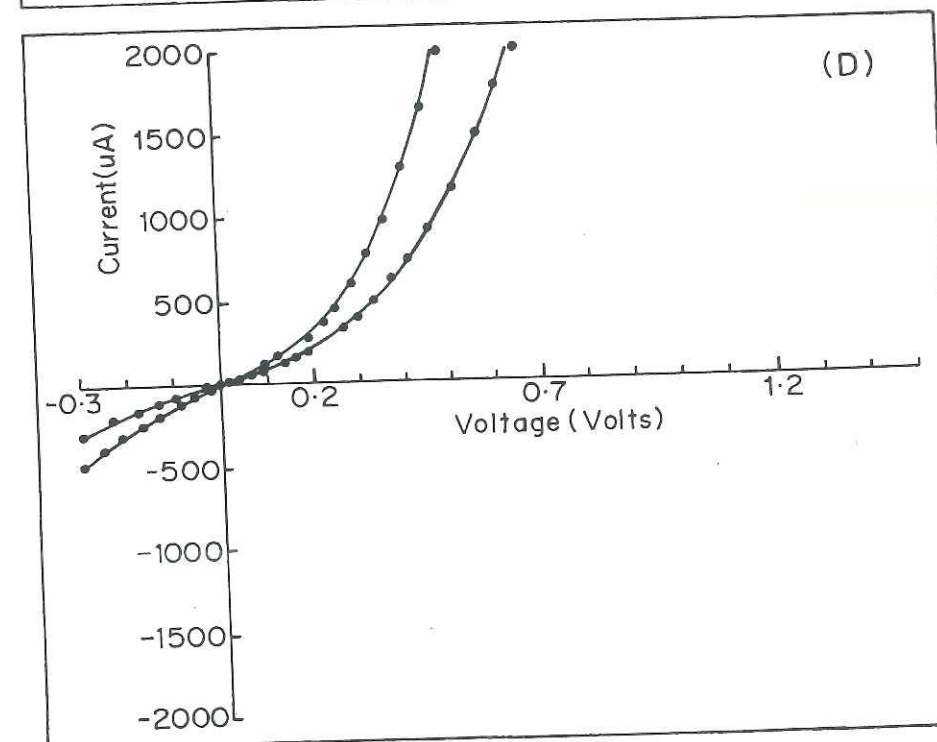
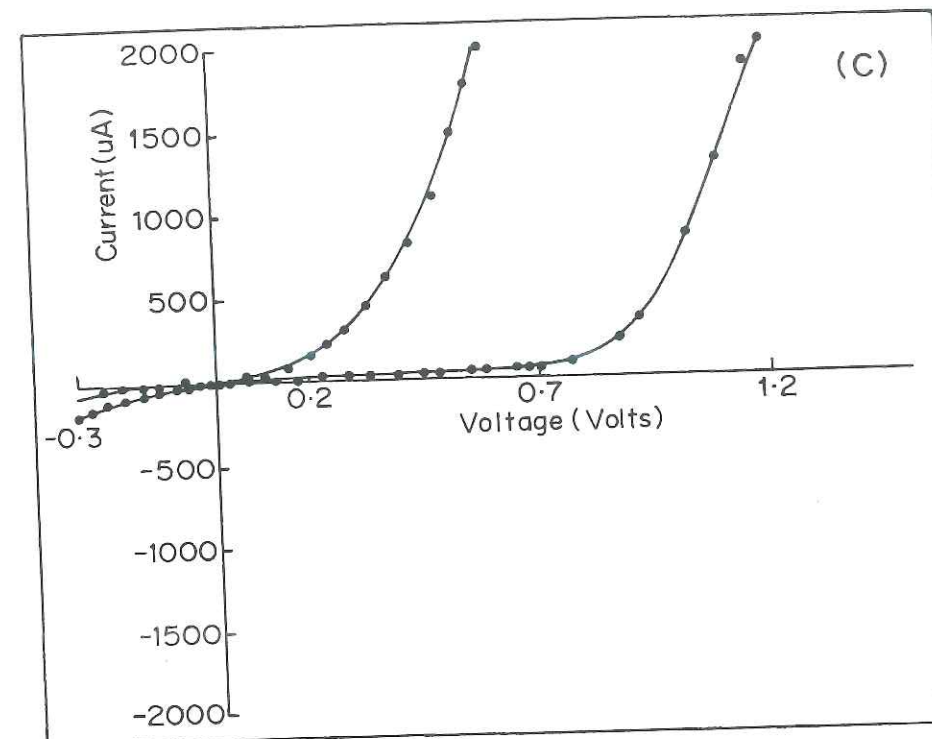


Figure (5.3) : Schematic of the solid state photocell using conducting polypyrrole (Au/Ppy/PVA+H₃PO₄+CRV/ITO).





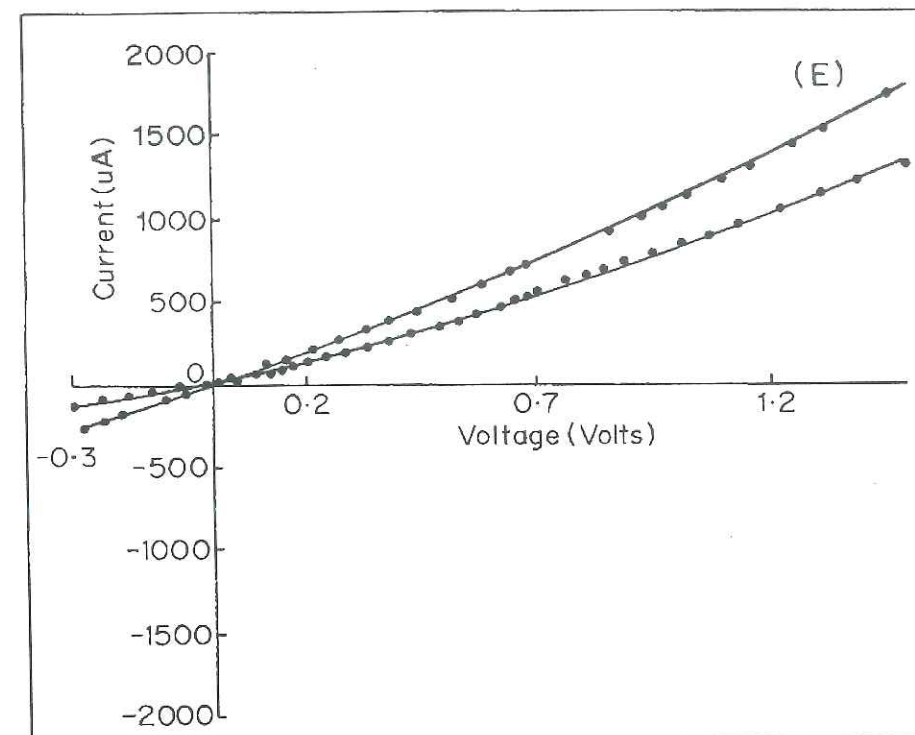


Figure (5.4) : current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocell Au/Ppy/PVA+H₃PO₄+CRV/ITO containing different concentrations of CRV ; (A) 1.111, (B) 2.998 , (C) 5.797 , (D) 14.47 and (E) 15.76 mM/monomer respectively.

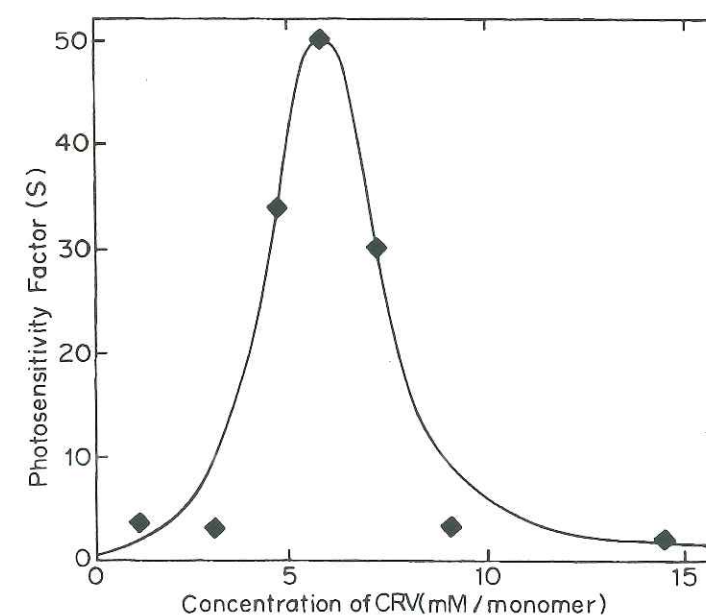


Figure (5.5) : Photosensitivity factor (S) as a function of the concentration of CRV.

The current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocells having sandwich structure Au/Ppy/PVA+H₃PO₄+CRV/ITO [schematically shown in Figure (5.3)] are as shown in Figure (5.4). The curves (A) to (E) corresponds to CRV concentration of 1.111, 2.998, 5.797, 14.47 and 15.76 mM/monomer respectively. It is interesting to observe that the I-V characteristics in dark (D) as well as in light (L) exhibit a rectifying nature and the rectification behavior becomes more pronounced with the increase of the dye concentration. The outset of non-linearity also increases with the increase in CRV concentration. The dark current decreases dramatically especially at low voltages. This suggests that the n-type dye form p-n junctions with the p-type Ppy. The photosensitivity factor ($S=I_l/I_d$, where I_l is the photocurrent and I_d is the dark current) for these cells as a function of dye concentration is as shown in Figure (5.5). It is quite evident that there is a certain CRV concentration (5.79 mM/monomer) at which the photosensitivity is very high (of the order of 50). The concentration of the CRV dye corresponding to maximum photosensitivity factor (S) is said to be 'critical concentration'.

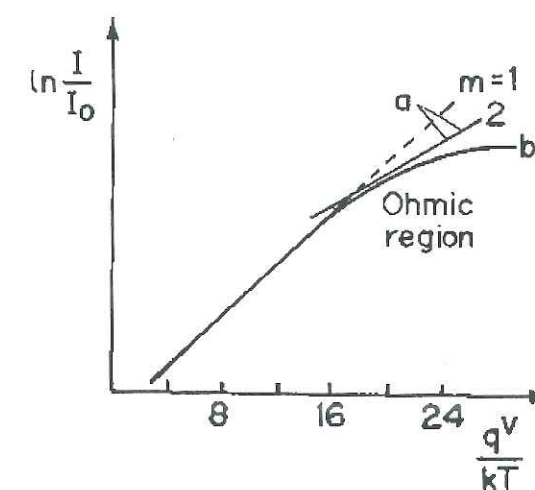


Figure (5.6) : Schematic of the Semilog plot of a p-n junction forward current-voltage characteristic. (a) design curve (b) experimental curve.

The above finding suggests that the I-V characteristics in the present case have to be analyzed according to the p-n junction rather than the conventional mechanisms. The current-voltage characteristic of a ideal p-n junction diode is described by [22] -

$$I = I_0 (e^{qV/kT} - 1) \quad \text{-----}(5.1)$$

where V is the voltage applied at a temperature T, k is the Boltzman's constant and q is the charge on the carrier. It is assumed that the p-n junction is sufficiently thin and therefore the generation and the recombination of the carriers in the semiconductor is disregarded. When the junction is forward biased and when $V \gg kT/q$, the current grows rapidly with increasing voltage. When $|-V| \gg kT/q$, the current through the p-n junction tends to reach a constant value I_0 , called thermal current. Also, higher the minority carrier density, the larger will be the value of the thermal current. This, it is expected that the semi-log plot of the I-V characteristic (i.e. log I vs.V) will be a straight line for a p-n junction diode in the forward bias.

In deriving equation (5.1), the voltage drop across the semiconductor bulk resistance has not been taken in to account. This bulk resistance causes redistribution of the applied voltage. Owing to the additional voltage drop across the bulk of the semiconductor and the injected carrier space-charge region, the forward current-voltage curve becomes less steep. Taking into account the voltage drop across the bulk of the semiconductor, the current-voltage relation can be given by -

$$V = (kT/q) \ln [I/I_0 + 1] + I r_t \quad \text{-----}(5.2)$$

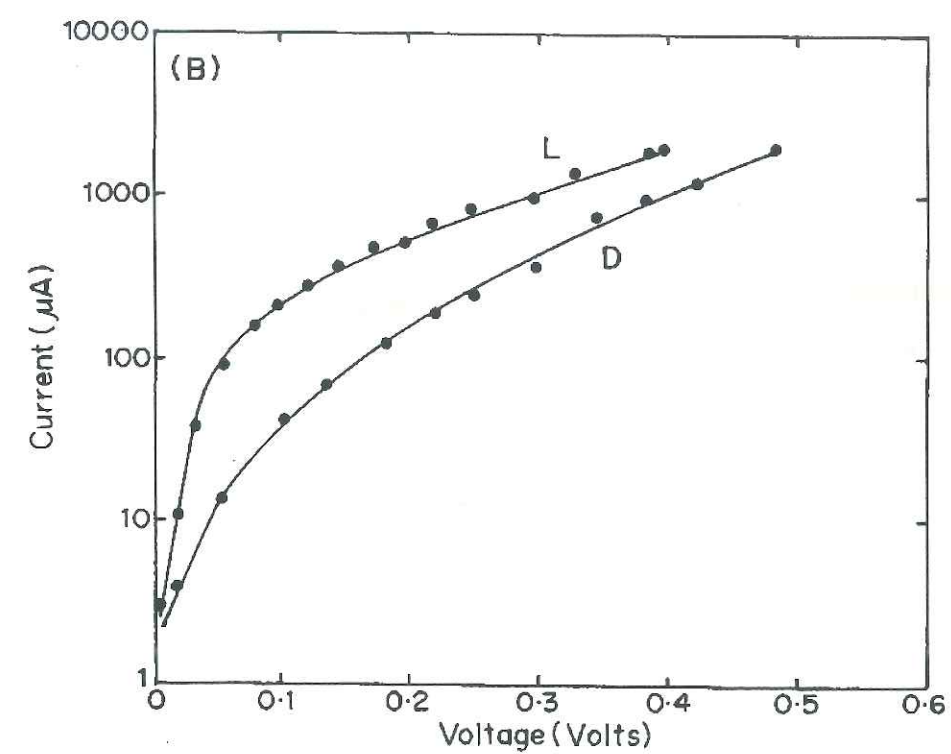
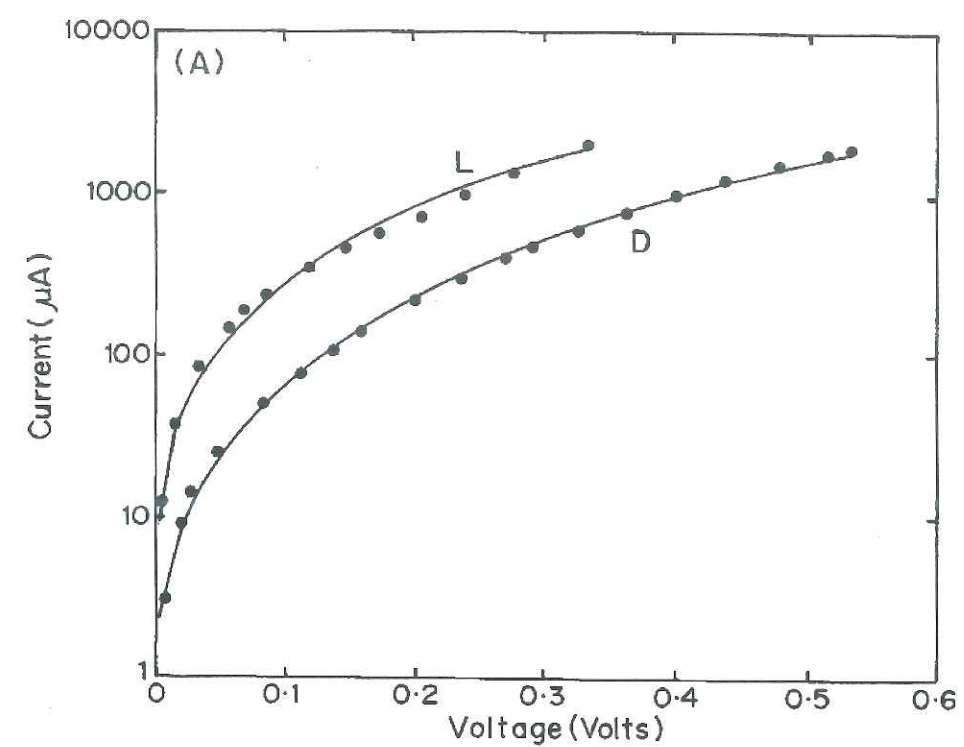
Thus, as long as the voltage is small, the current is also small and the forward current obeys equation (5.1). But as the current increases, the linear dependence of the current on voltage V_r becomes more pronounced than the logarithmic dependence of current on voltage at the junction.

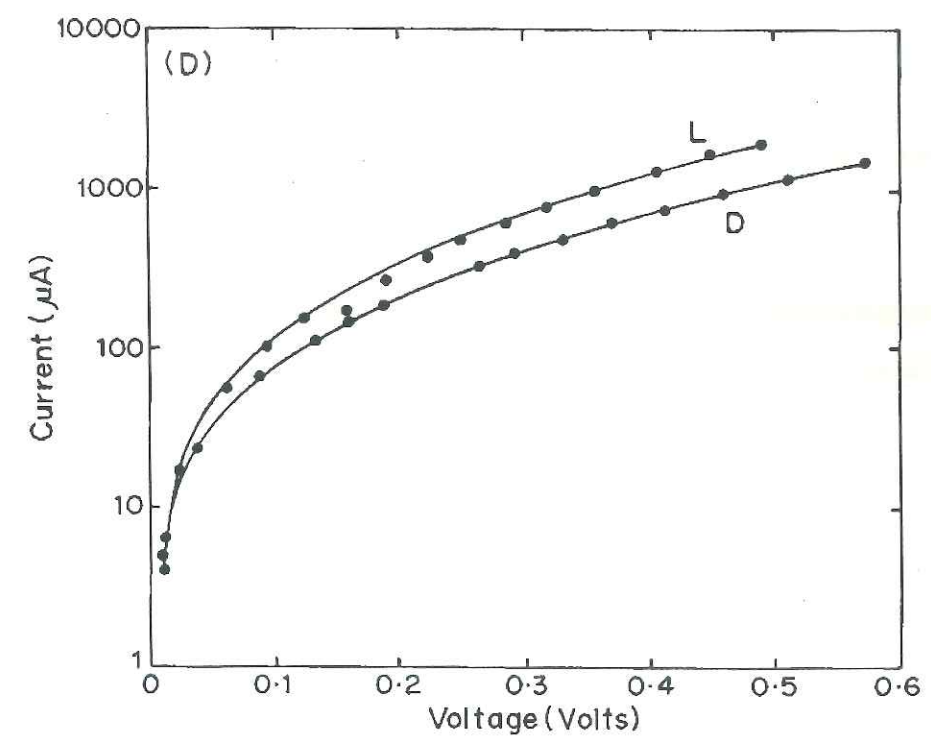
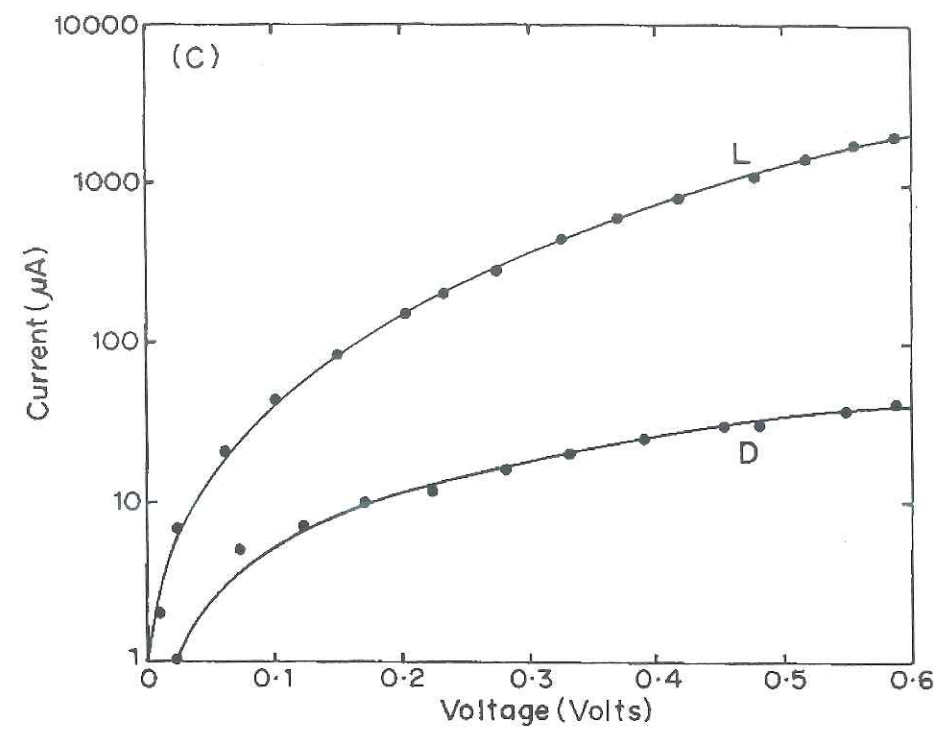
The forward current-voltage characteristics of a p-n junction in non-ideal case is given by

$$I_{\text{for}} = (2h/\gamma) I_0 \exp [qV/mkT] \quad \text{-----}(5.3)$$

$$\text{where } h = [I_i/b \cdot I_0]^{(m-1)/m} ; \quad m = 1 + (W/b \cdot L_p) \quad \text{-----}(5.4)$$

where W is the thickness / width of the n-type region (here, in the present study, it will indicate the concentration of the n-type dye) and b is the ratio of the mobilities of the charge carriers. Here, $L_p = \text{sq. root of } (D_p \cdot \tau)$, where D_p is the diffusion co-efficient for electrons and τ is the lifetime of the charge carriers. From the above equations, it can be seen that the value of m is related to the concentration of the sensitizer dye. Thus, in a non-ideal case, the value of the change in slope of the I-V characteristics will depend upon m and hence on the dye concentration. Figure (5.6) shows the schematic of the forward current-voltage characteristic of a p-n junction plotted on a semilog scale with regard for the voltage drop across the injected -carrier space charge region and the resistance within the bulk of the semiconductor [22].





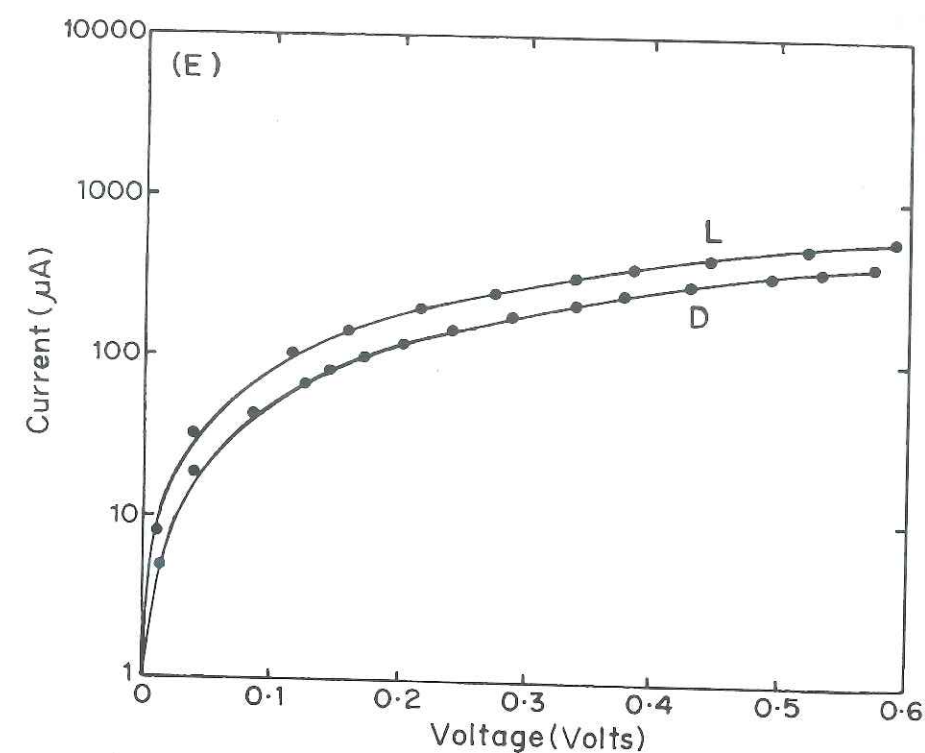


Figure (5.7) : The Semilog plot of the I-V curves for the Ppy/CRV system . Curves (A) to (E) correspond to the CRV concentration of 1.111 , 2.998 , 5.797 , 14.47 and 15.76 mM/monomer respectively.

The semi-log plot of the I-V curves (i.e $\log I$ vs. V) for the system under study is as shown in Figure (5.7). Curves (A) to (E) corresponds to the CRV concentration of 1.111, 2.998, 5.797, 14.47 and 15.76 respectively. The I-V curves were analyzed in detail for their relationship such as $\log I$ - $\log V$, $\log I$ - $\text{Sq. root } V$ etc. From all this study it has been concluded that the I-V curves resemble more like a p-n junction. This is behaving like a non-ideal p-n junction with change in slope in the I-V characteristics depending upon the dye concentration. Also, it can be seen that the curves exactly matches with those predicted from equation (5.3). Thus, it can be concluded that there is a formation of a p-n junction at the Ppy/CRV interface, Ppy being p-type and CRV being n-type, behaving like a conventional p-n junction diode - the only difference being is that the conventional

p-n junction diodes are usually made from only one semiconductor crystal doped with p and n-type impurities (i.e normally trivalent and pentavalent impurities). Also, it is worthwhile to note here that the doping of these impurities is normally done at a very small level in conventional semiconductors like Si, Ge. On the other hand, Ppy here is heavily doped. In this sense the p-n junction diode prepared here differs from the conventional one.

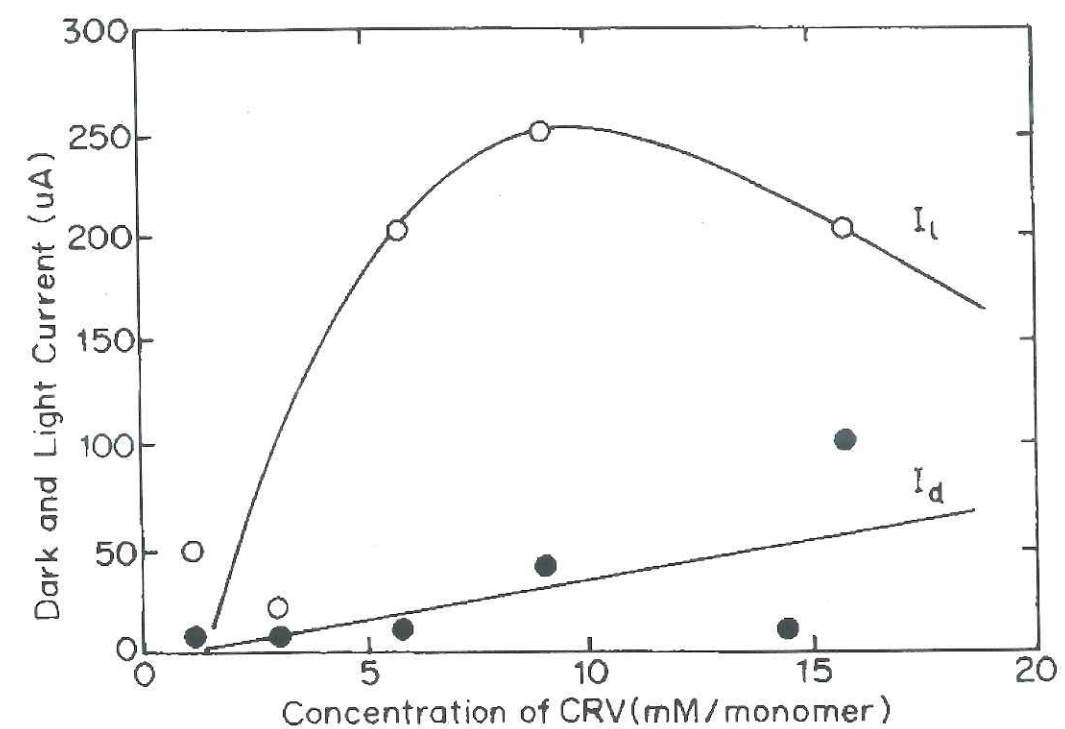


Figure (5.8) : Variation of the dark (I_d) and light (I_l) current with the concentration of the CRV in the linear portion of the I-V characteristics at about 0.2 V.

Figure (5.8) displays the variation of the dark (I_d) and light current (I_l) with respect to the CRV concentration in the linear portion of the current-voltage (I-V) characteristic at a fixed voltage of 0.2 V. It can be seen that the photo-current (I_l) increases with the increase in the CRV concentration initially, reaches to a maximum and then decreases

with further increase in the dye concentration. Hence, the photo-current (I_l) goes through a maximum in its variation with respect to the CRV concentration. The dark current (I_d) increases slowly with the increase in the dye concentration. The initial increase of the photo-current (I_l) can be attributed to the increase in the number of the sensitizing centres with the increase in the dye concentration. Decrease of the photo-current (I_l) at high dye concentration can be due to heavy trapping and / or recombination of the photogenerated charge carriers. This particular variation of the photo-current (I_l) is more important than that of the dark current (I_d) and is mainly responsible for getting the maximum photosensitivity at a particular dye concentration.

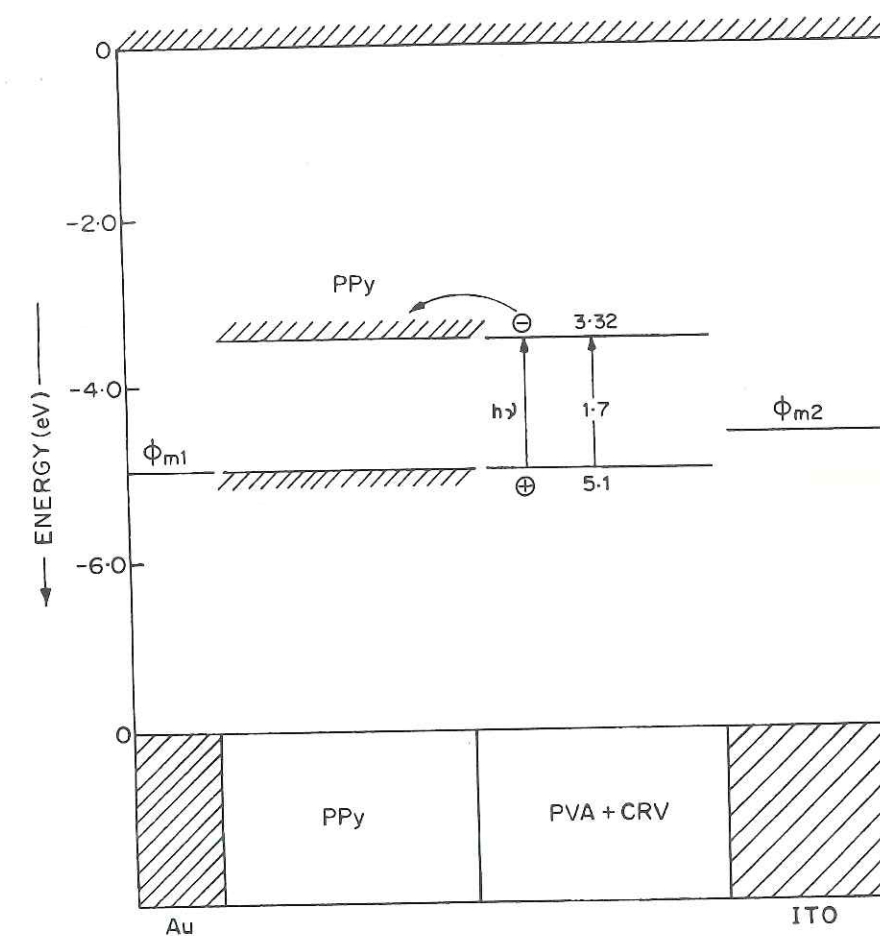


Figure (5.9) : Energy level diagram of the materials used in forming the photocell Au/PPy/PVA+H₃PO₄+CRV/ITO.

The mechanism of the sensitization process can be understood in terms of the energy band diagram for the materials used for forming the cell. Figure (5.9) depicts the different energy levels for the materials used in forming the photocell. The energy levels for Ppy are those which have been reported in the literature [23], while those for CRV in PVA are derived from the UV-VIS spectra recorded and using the reported energy levels of CRV. It must be noted here that the PVA containing phosphoric acid is a good proton conductor while Ppy is a p-type material and CRV is n-type. A p-n junction is formed at the Ppy/PVA+CRV interface - as discussed earlier. Thus, when Au is positive, the p-n junction is forward biased and the high current observed is due to the majority carriers. Also, the hole transport via Ppy and the proton transport through PVA are facilitated giving high forward current. On the other hand when Au is having negative polarity, the current would be less since the p-n junction is reverse biased and the current is due to the minority carriers only. Electrons are minority carriers and will experience a barrier at the Ppy/Au interface (contact blocking to electrons but not to holes, as the work function of Au and the HOMO of Ppy are almost at the same level). This, in all, it will give rise to a typical p-n junction diode I-V characteristic as observed in the present case. When such a cell is under illumination, CRV dye absorbs light and fills the higher electronic levels with photoexcited carriers. This facilitates their transport to Ppy. It should be noted here that there is almost no barrier for electrons at the Ppy/PVA+CRV interface. Holes will experience a barrier of about 0.1 eV at the Ppy/PVA+CRV interface which is also considerably small. In other words, the energy levels of Ppy closely matches with that of the CRV dye and hence the charge carriers (either electrons or holes) will be able to move freely from Ppy to CRV and vice versa. In other words, we can say that CRV

does not act as a trapping centre for the minority carriers (i.e. electrons) from the Ppy. This could be one of the reason for the low photosensitivity observed in the present case because high photosensitivity is generally achieved by trapping of the minority carriers thereby enhancing the majority carrier concentration, lifetime etc. It should also be remembered that there are several other energy levels present due to the inherent amorphous nature of the polymer and hence some of these can act as carrier trapping centres for one type of charge carriers. Thus, when photo-generated electrons are trapped there is an effective increase in the number of holes available for conduction. The decrease of photosensitivity at high CRV concentrations can be due to high absorption of light (photons) only at the surface as well as recombination of charge carriers which does not allow them to pass into the bulk of the material.

5.3.2 SENSITIZATION EFFECT IN DOPED Ppy BY RB INCORPORATED IN PVA+H₃PO₄ :

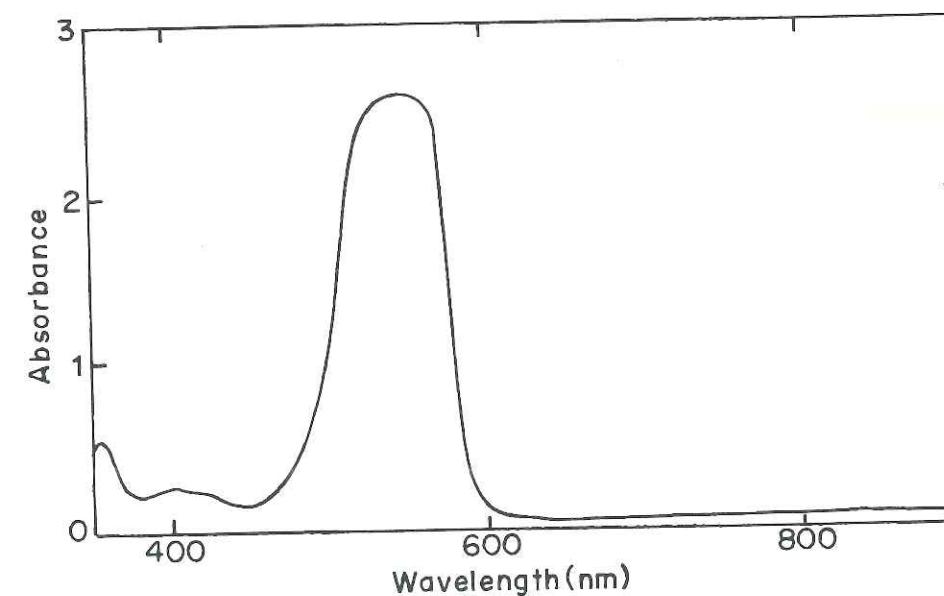


Figure (5.10) : (A) UV-VIS spectra of the RB in water.

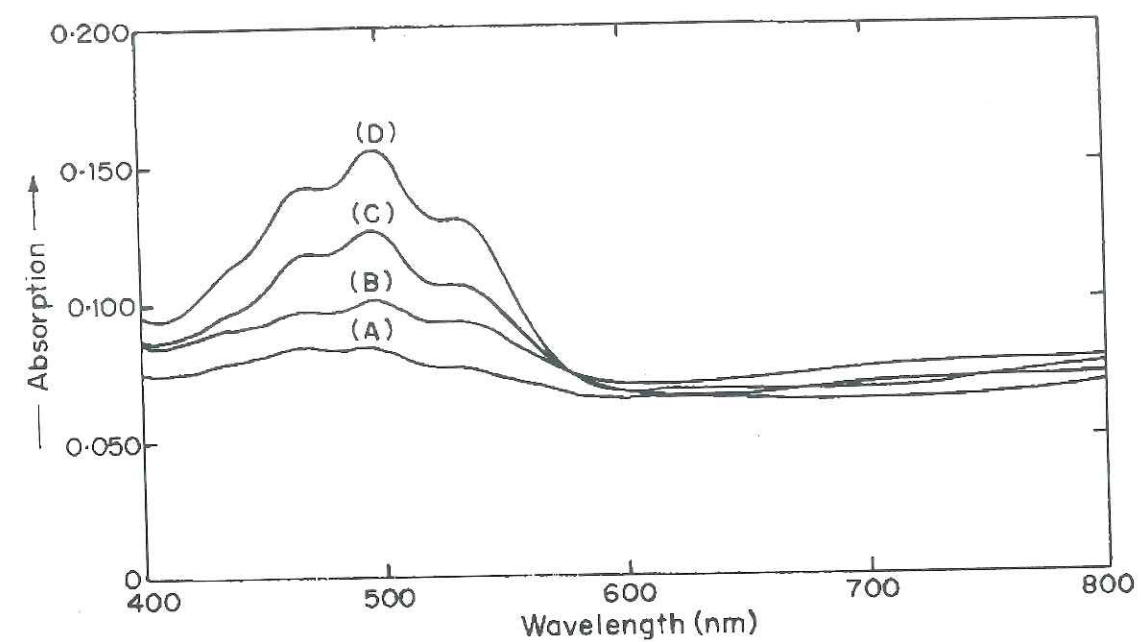


Figure (5.10) (B)UV-VIS spectra of RB incorporated SPE (i.e. PVA+ H_3PO_4) films deposited on glass by dip-coating method. (A) to (D) corresponds to the RB concentrations of 0.211, 0.361, 0.482 and 0.604 mM/monomer respectively.

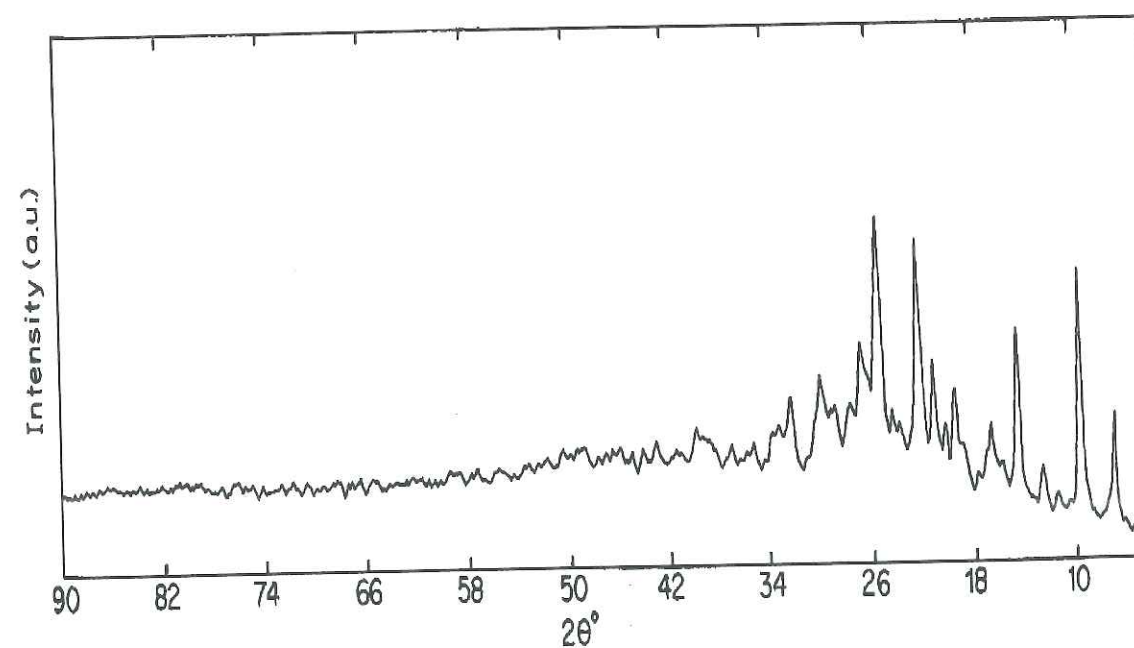


Figure (5.11) (A) XRD of the RB powder.

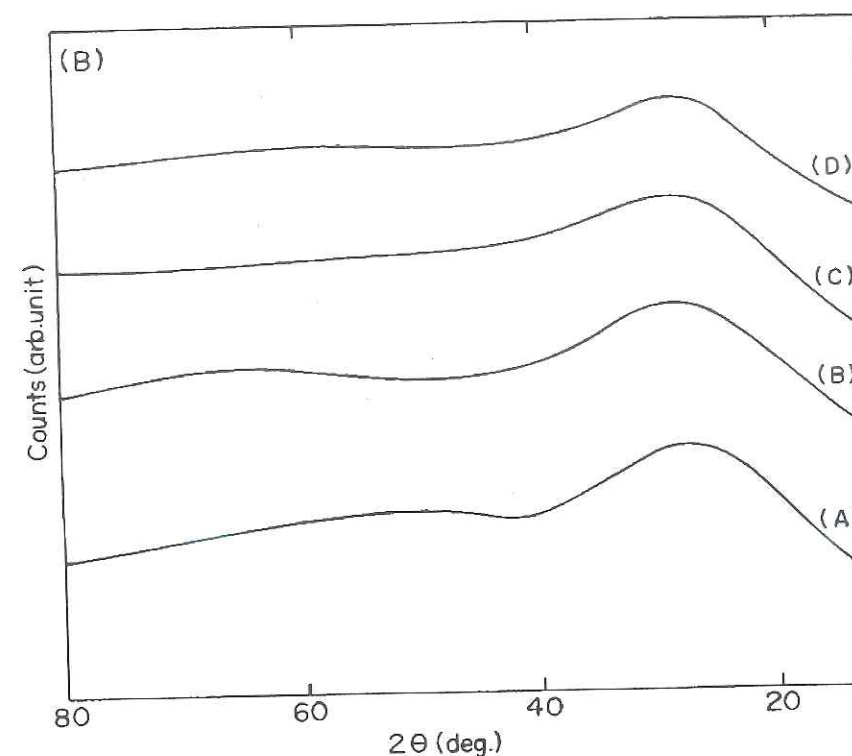


Figure (5.11) (B) XRD of the RB incorporated SPE films on glass substrates. Curves (A) to (D) corresponds to the RB concentrations of 2.45, 4.45, 6.08 and 8.15 mM/monomer respectively.

Figure (5.10A) shows the UV-VIS spectra of the RB in water. It has been observed that RB dissolves in water. Two peaks at about 550 and 400 nm are observable. The maximum wavelength of absorption ($\lambda_{\max}$) for RB is 550 nm. Figure (5.10B) shows the UV-VIS spectra of the RB incorporated PVA+H₃PO₄ dip-coated films on microscopic grade glass substrates. Curves (A) to (D) corresponds to the RB concentrations of 0.211, 0.361, 0.482 and 0.604 mM/monomer respectively. It can be seen that there is a broad absorption band between 400 nm to 550 nm which consists of four peaks centered at around 535, 500, 465 and 435 nm marked as I, II, III and IV respectively. Also, it is observable that the absorption increases with the increase in the RB concentration and at higher RB concentrations, the peak becomes visibly distinct. The maximum wavelength

of absorption ($\lambda_{\max}$) for RB incorporated in PVA+H₃PO₄ films is 500 nm. There are no large shifts in the main absorption peak with the RB concentration which would be expected for aggregate formation (J- or H-type). Since RB absorption peak which was earlier at 550 nm shifts to about 500 nm in SPE (lower wavelength region), the possibility of formation of complex between the dye and the SPE is low. Since UV-VIS of RB in SPE possess 3 to 4 components, it can be concluded that the ground state remains as it is whereas the first excited state splits due to the interaction between the dye molecules and the matrix. Splitting of the states due to the interaction with the matrix is known as Davydov splitting.

Figure (5.11A) presents the XRD of the RB powder. It can be seen that RB by itself is crystalline. The XRD of the RB incorporated PVA+H₃PO₄ dip-coated films on glass substrates (as shown in Figure 5.11B) indicates absence of any XRD peaks corresponding to RB suggesting that RB is not present in an aggregate, crystal or ordered form in the SPE. The absence of RB aggregation in SPE is also confirmed by studying the RB incorporated PVA+H₃PO₄ films under optical microscope. Thus, it can be concluded that RB is not present in an aggregate form in SPE but it is well mixed at the molecular levels with the same.

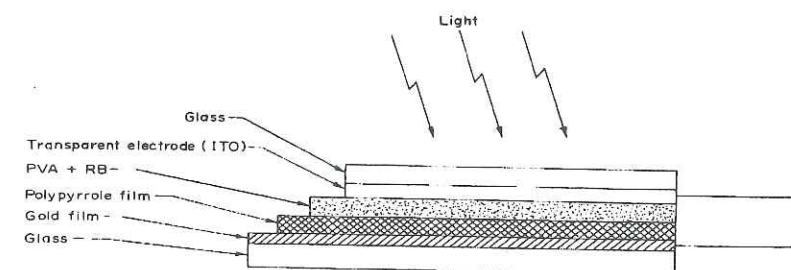
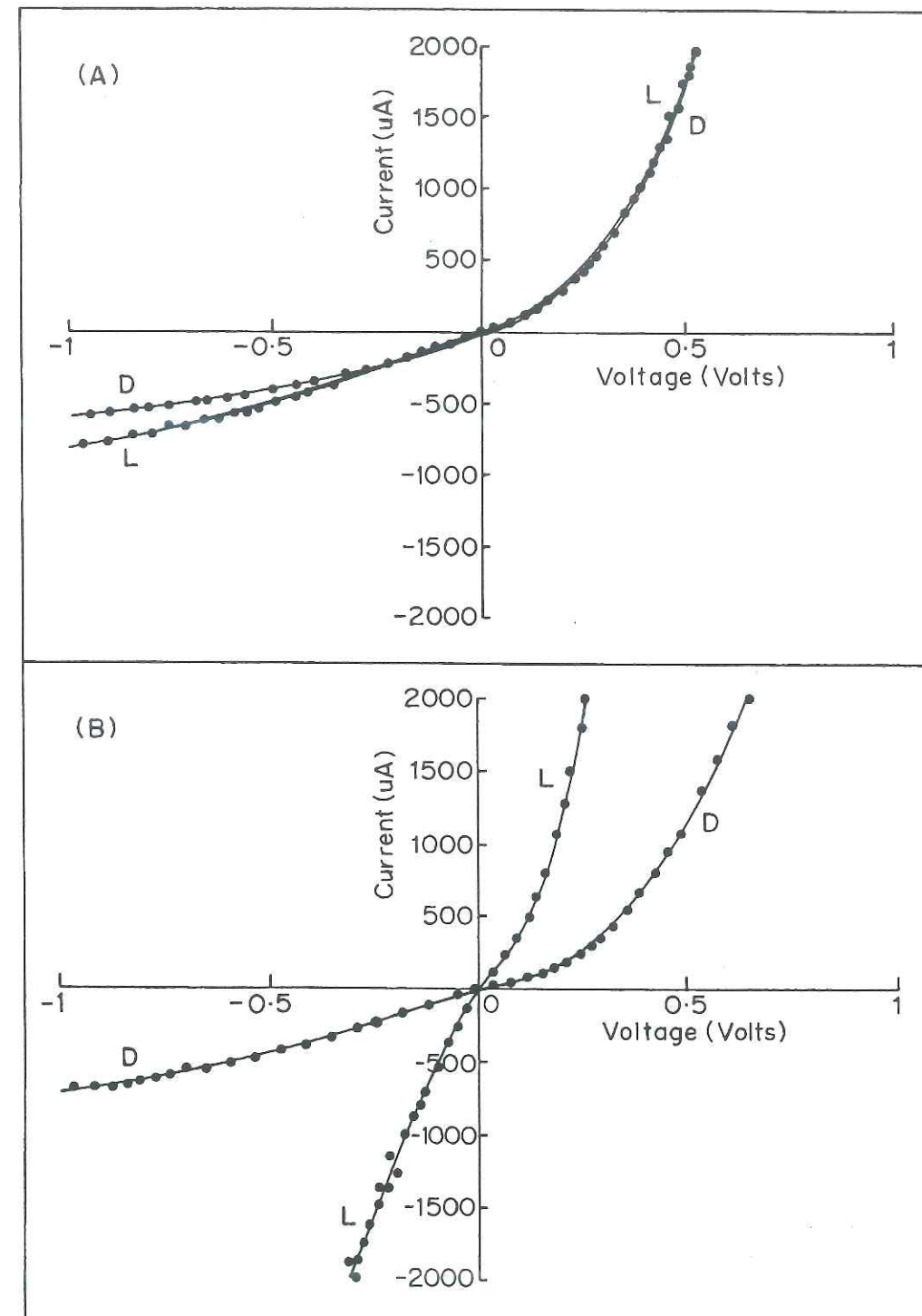


Figure (5.12) : Schematic of the solid state photocell using conducting polypyrrole (Au/Ppy/PVA+H₃PO₄+R6G/ITO).



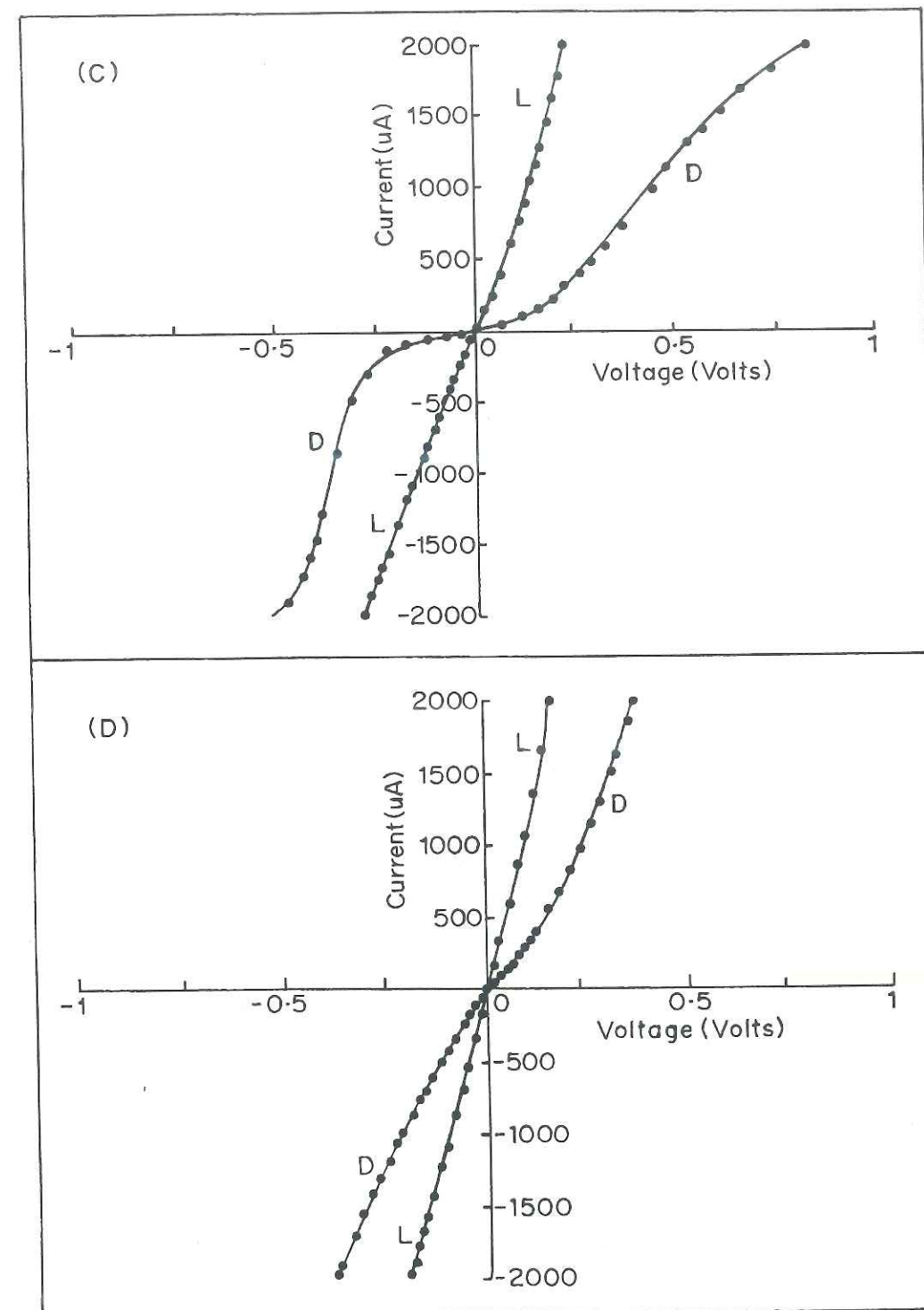


Figure (5.13) : current-voltage (I-V) characteristics in dark (D) and under illumination (L) for the photocell Au/Ppy/PVA+H₃PO₄+RB/ITO containing different concentrations of RB; (A) 0.477 , (B) 1.411, (C) 3.228 and (D) 4.111 mM/monomer respectively.

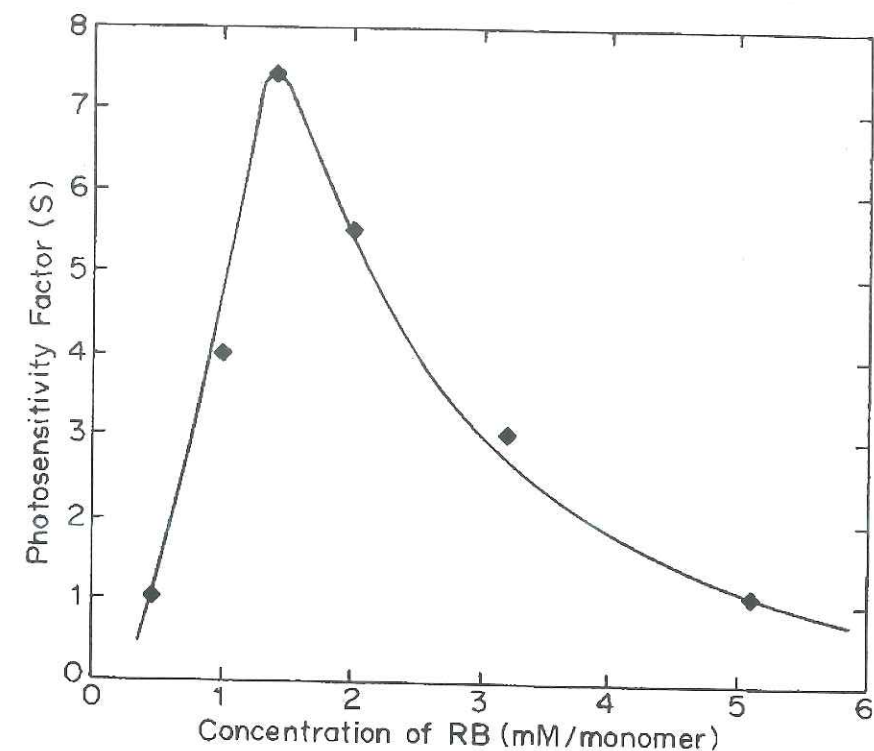
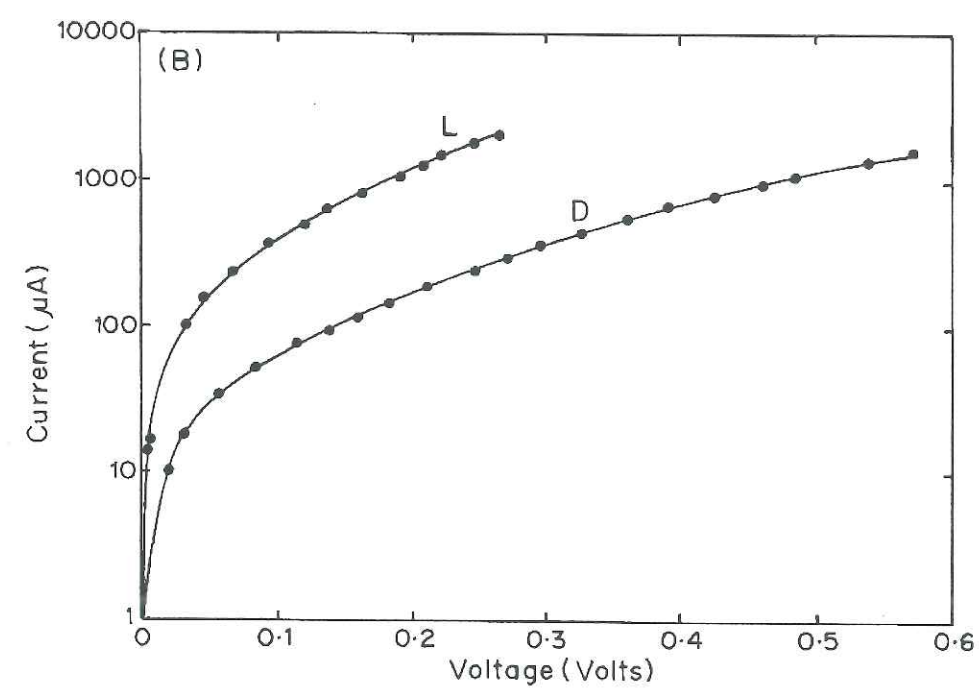
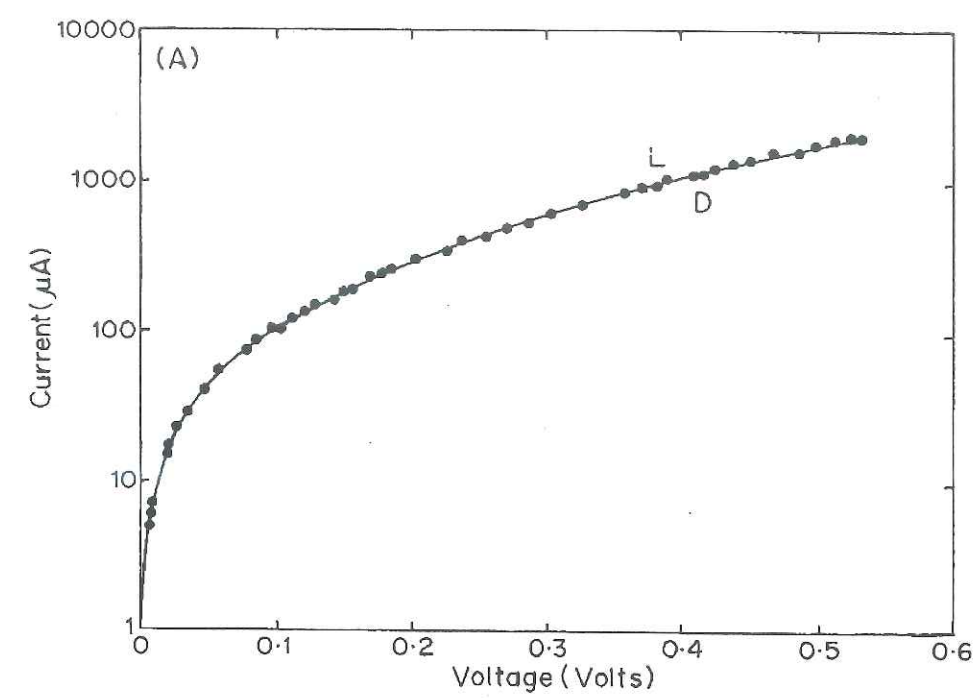


Figure (5.14) : Photosensitivity factor (S) as a function of the concentration of RB for the photocell Au/Ppy/PVA+H₃PO₄+RB/ITO.

The schematic of the photocells (Au/Ppy/PVA+H₃PO₄+RB/ITO) fabricated using conducting polypyrrole sensitized with RB incorporated in SPE are as shown in Figure (5.12). The current-voltage (I-V) characteristics in dark (D) and under illumination (L) for these photocells are shown in Figure (5.13). The curves (A) to (D) corresponds to RB dye concentration of 0.477, 1.411, 3.228 and 4.111 mM/monomer respectively. It is interesting to observe that the I-V characteristics in dark (D) exhibit a rectifying nature i.e. the current in one direction (Au +ve, 1st quadrant) is much higher than in the opposite direction (Au -ve, 3rd quadrant) and the rectification behavior becomes more pronounced with the increase of the dye concentration. The dark current decreases with the increase in the dye concentration. The variation of the photosensitivity factor (S) with respect to

the RB concentration is shown in Figure (5.14). It is quite evident that there is a certain RB concentration (1.411 mM/monomer) at which the photosensitivity obtained is maximum (of the order of 7.4). The concentration of the RB dye corresponding to maximum photosensitivity factor is said to be 'critical concentration'.



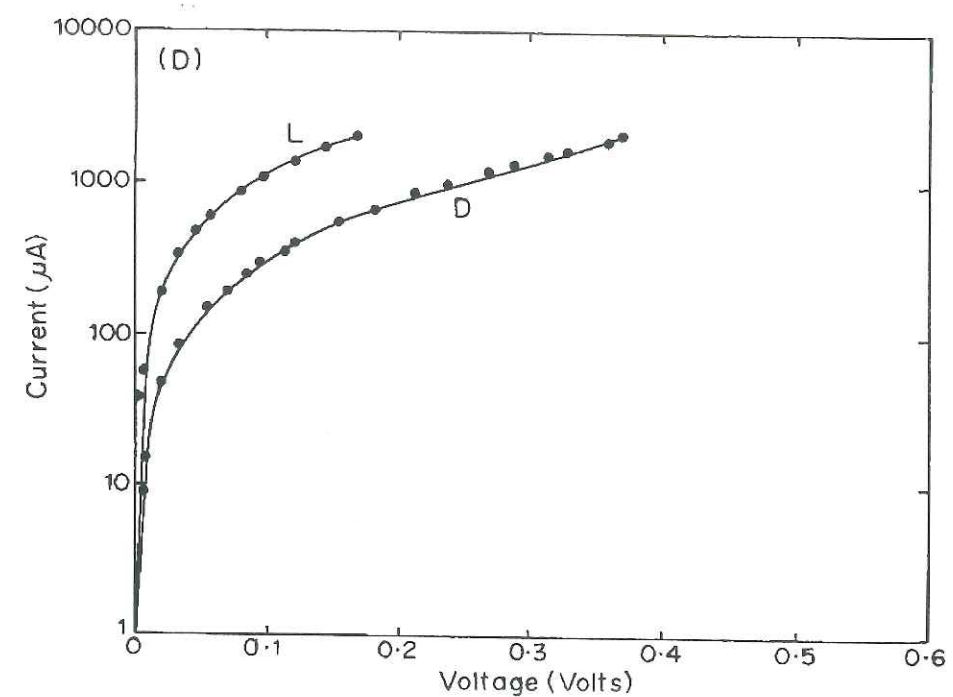
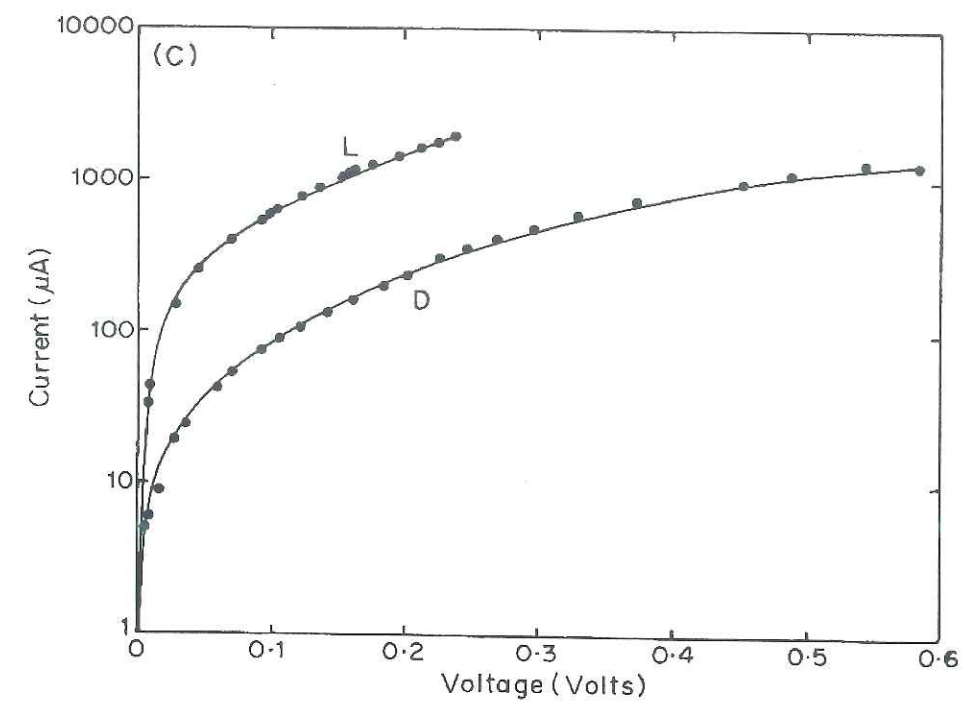


Figure (5.15) : The Semilog plot of the I-V curves showing the p-n junction diode type behavior. Curves (A) to (D) correspond to the RB concentrations of 0.477, 1.411, 3.228 and 4.111 mM/monomer respectively.

The semilog plot of the I-V curves (i.e. $\log I$ vs. V) for the system under study are as shown in Figure (5.15). Curves (A) to (D) corresponds to the RB concentrations of 0.477, 1.411, 3.228 and 4.111 mM/monomer respectively. The I-V curves were analyzed in detail for their relationship such as $\log I - \log V$, $\log I - \text{Sq. root } V$ etc. From all this study it has been concluded that the I-V curves resembles more like a p-n junction diode characteristics. Also, it can be seen that the curves exactly matches with those predicted from equation (5.3). Thus, it can be concluded that there is a formation of a p-n junction at the Ppy/PVA+RB interface, Ppy being p-type and RB being known as a n-type dye, behaving like a conventional p-n junction diode. The photosensitivity observed in the forward biased p-n junction can be due to reduction of the barrier height (in presence of light) as discussed for the earlier Ppy/CRV system.

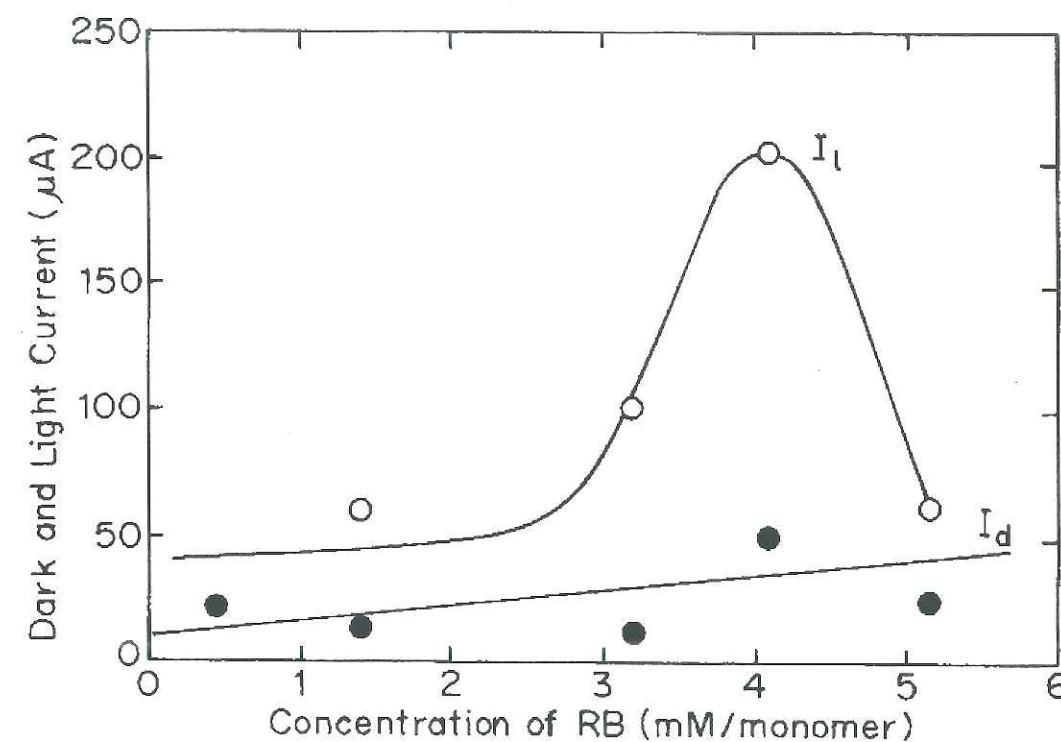


Figure (5.16) : Variation of the dark (I_d) and light current (I_l) with the concentration of the RB in the linear portion of the I-V characteristics at the 0.02 V.

Figure (5.16) displays the variation of the dark (I_d) and light (I_l) current with respect to the RB concentration in the linear portion of the current-voltage (I-V) characteristics at a fixed voltage of about 0.02 V. It can be seen that the photocurrent (I_l) increases with the increase in the RB concentration initially, reaches to a maximum and then decreases with further increase in the dye concentration. Hence, the photocurrent (I_l) goes through a maximum in its variation with respect to the RB concentration. The dark current (I_d) increases slowly with the increase in the dye concentration. The initial increase of the photocurrent (I_l) can be attributed to the increase in the number of the sensitizing centres with the increase in the dye concentration. Decrease of the photocurrent (I_l) at high dye concentration can be due to heavy trapping and / or recombination of the photogenerated charge carriers. This particular variation of the photocurrent (I_l) is more important than of the dark current (I_d) and is mainly responsible for getting maximum photosensitivity at a particular dye concentration.

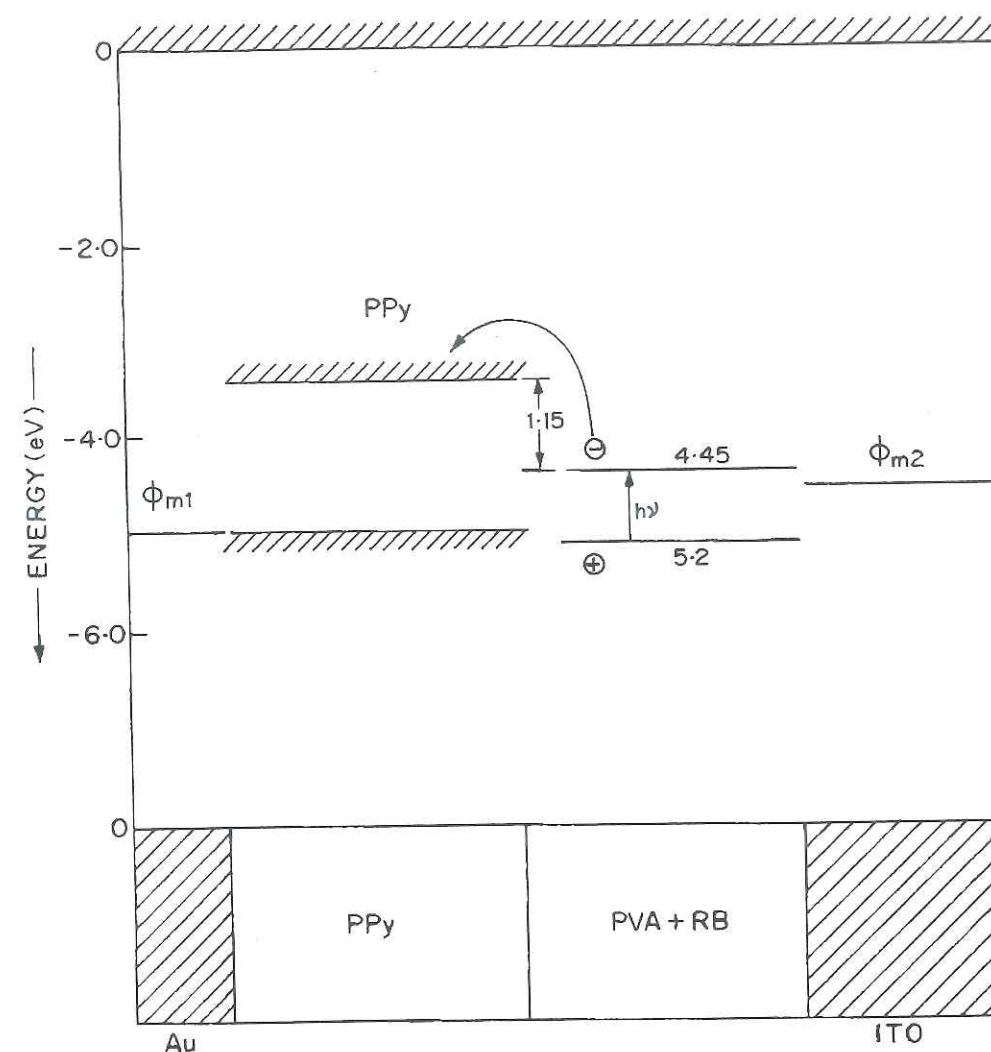


Figure (5.17) : Energy level diagram for the photocell having Au/PPy/PVA+H₃PO₄+RB/ITO sandwich structure.

The mechanism of photosensitization process can be understood in terms of the energy band diagram for the materials used in forming the photocell. Figure (5.17) depicts the different energy levels for the materials used in forming the photocell. The energy levels for Ppy are those which have been reported in the literature [23], while those for RB in PVA are derived from the UV-VIS spectra recorded and using the reported energy levels of RB. It must be noted here that the PVA containing phosphoric acid is a good proton

conductor while Ppy is a p-type material and RB is known to be a n-type dye. A p-n junction is formed at the Ppy/PVA+RB interface - as discussed earlier. Thus, when Au is positive, the p-n junction is forward biased and the high current observed is due to the majority carriers. Also, the hole transport via Ppy and the proton transport through PVA are facilitated giving high forward current. On the other hand when Au is having the negative polarity, the current would be less since the p-n junction is reverse biased and the current is due to the minority carriers only. Electrons are minority carriers and will experience a barrier at the Ppy/Au interface (contact blocking to electrons but not to holes, as the work function of Au and the HOMO of Ppy are almost at the same level). Electrons will also experience a barrier at the Ppy/PVA+RB interface (of the order of 1.15 eV which is considerably large). This, in all, will give rise to a typical p-n junction diode I-V characteristics as observed in the present case. When such a cell is under illumination, RB dye absorbs light and fills the higher electronic levels with the photoexcited carriers. The photogenerated electrons will experience a barrier of the order of 1.15 eV at the Ppy/PVA+RB interface and hence will not be easily transmitted to Ppy to yield high photosensitivity. Here, it is worthwhile to mention that the energy levels of RB are placed (in comparison with that of the Ppy) in such a way that it can act as an excellent trapping centre for the minority carriers (i.e. electrons) in the Ppy. Even though low photosensitivity has been observed (maximum photosensitivity factor of the order of 7.4) in the present case. This is because RB is not capable of efficiently transferring the photogenerated charge carriers (particularly electrons) to Ppy because of a large potential barrier at the Ppy/PVA+RB interface. Thus, it is not only the trapping of the minority charge carriers (i.e. electrons) from the Ppy is important but the dye should be able to

efficiently transfer the photogenerated charge carriers to the Ppy. In other words, the actual placement of the energy levels of the dye in comparison with that of the polymer is more important. A close observation of the energy level diagram of the present system suggests that the system can be efficiently photovoltaic and indeed some work has already been done on the same system in this regard.

5.3.3 SENSITIZATION EFFECT IN DOPED PANI BY R6G INCORPORATED IN PAV+H₃PO₄ :

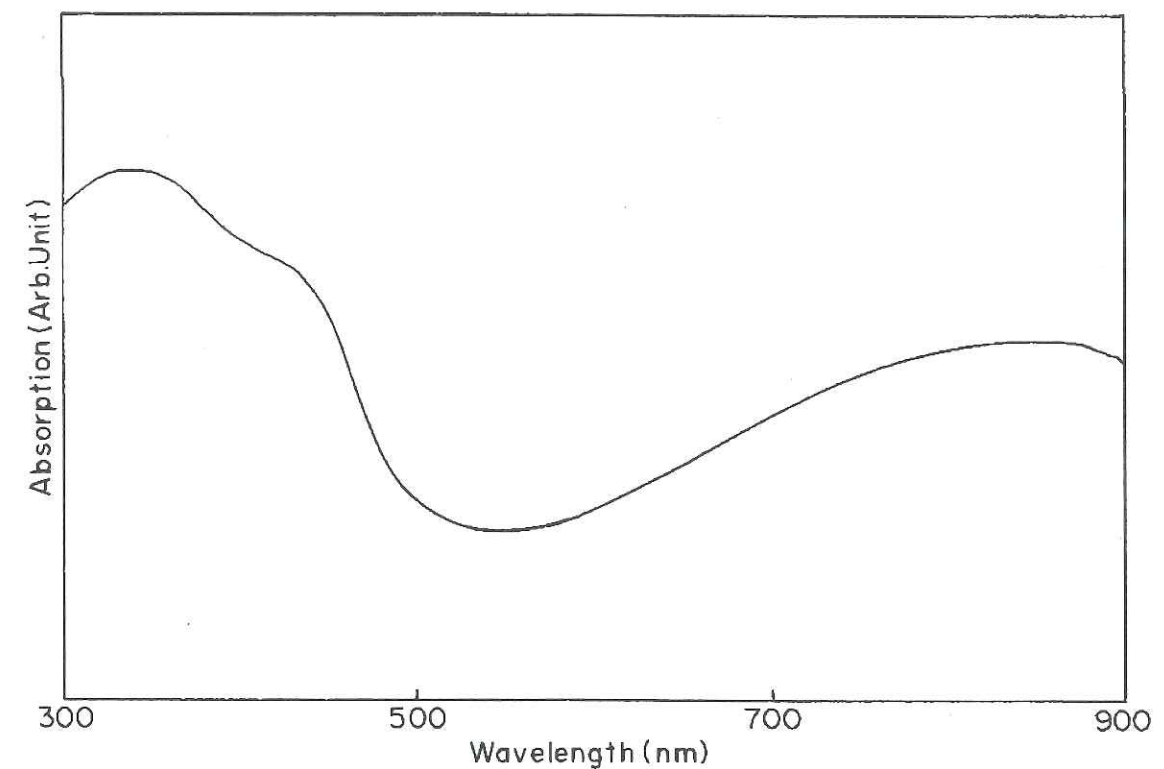


Figure (5.18) : (A) UV-VIS spectra of the PANI on ITO (film thickness = 500 nm).

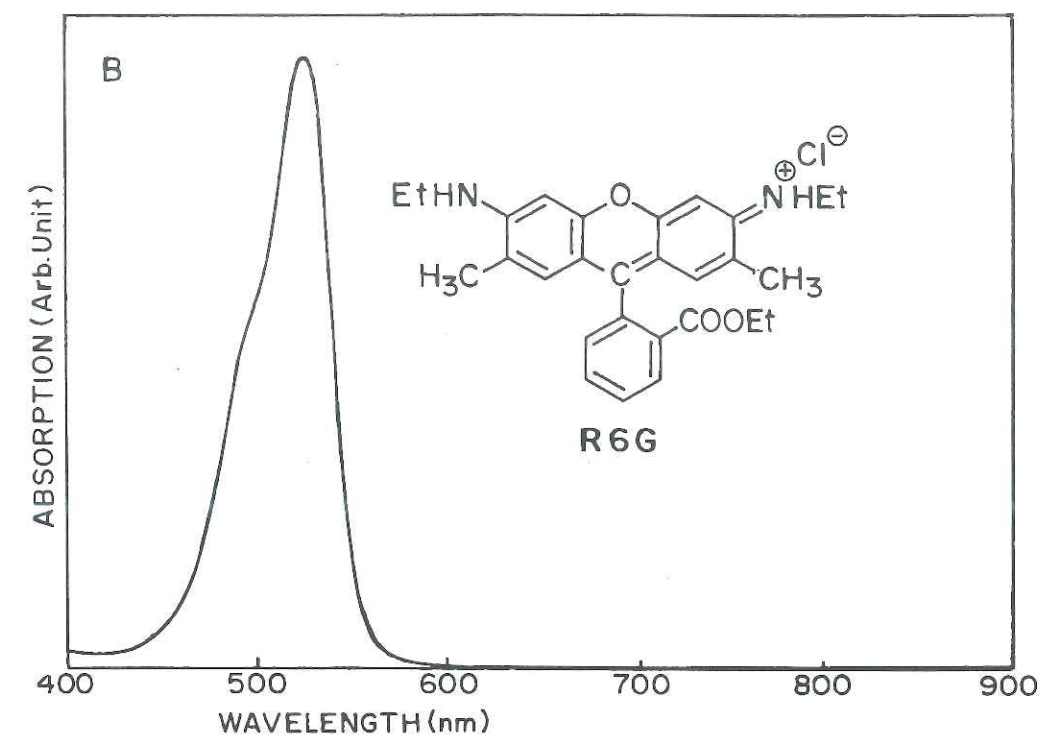


Figure (5.18) : (B) UV-VIS spectra of R6G in water (10^{-5} M).

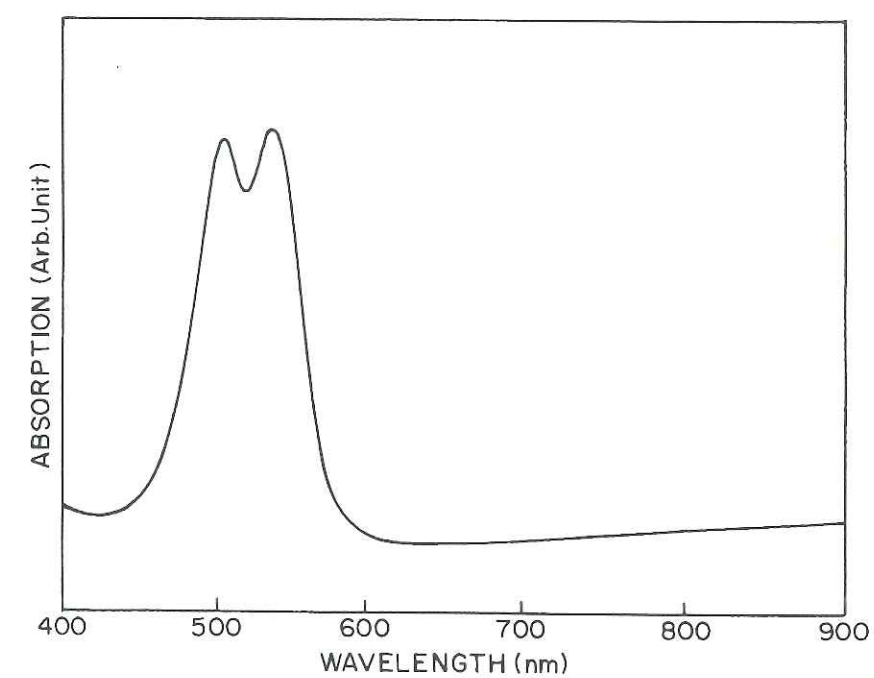


Figure (5.18) : (C) UV-VIS spectra of R6G incorporated PVA+H₃PO₄ film on glass deposited by dip-coating method.

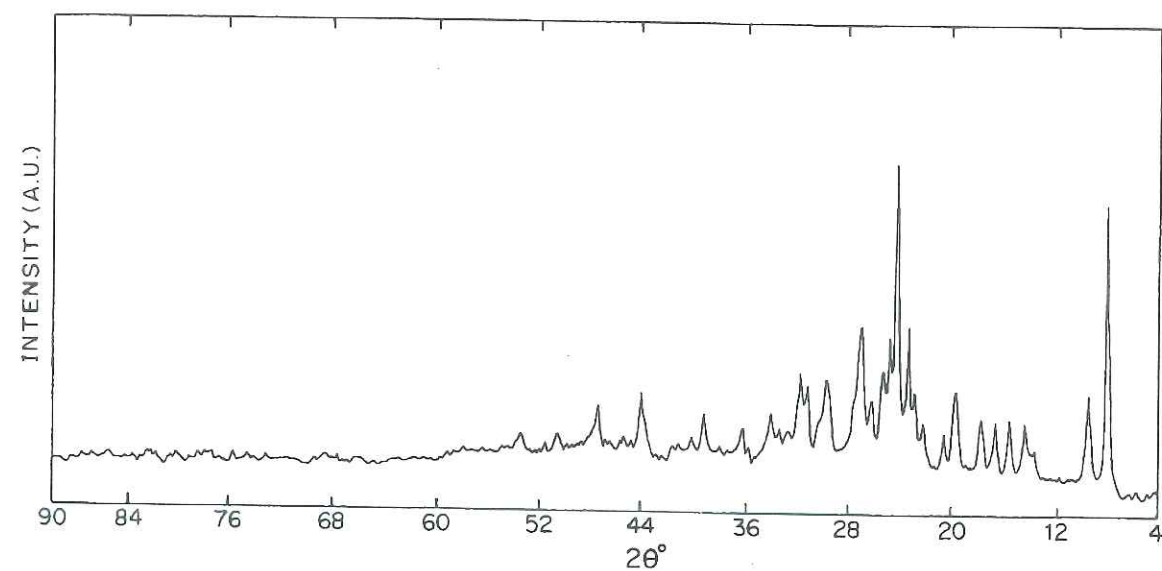


Figure (5.19) : (A) XRD of the R6G powder

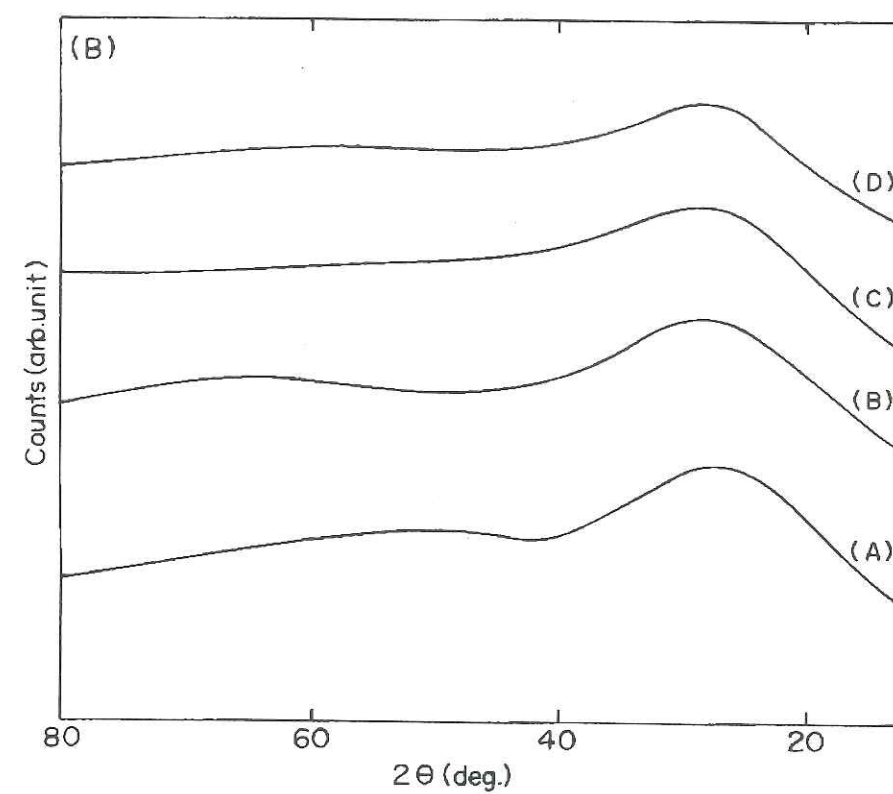


Figure (5.19) : (B) XRD of the R6G incorporated SPE films deposited by dip coating on glass substrates. Curves (A) to (D) corresponds to R6G concentrations of 3.01, 6.62, 9.85 and 13.56 mM/monomer.

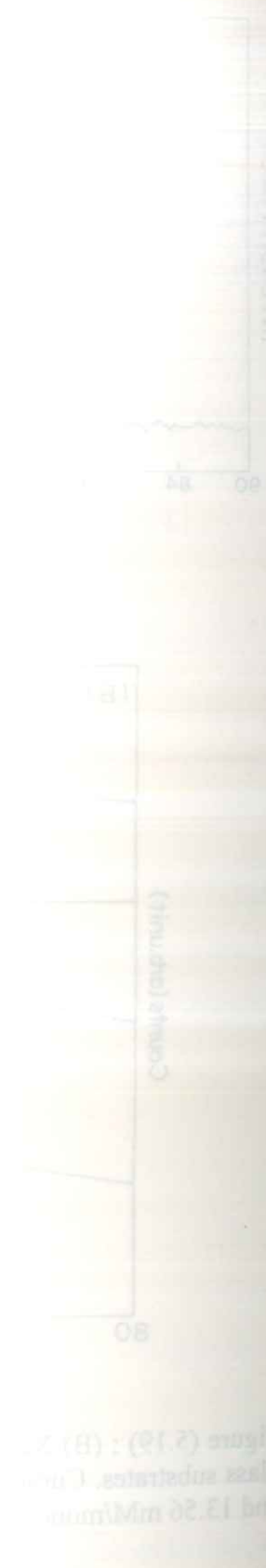


Figure (5.18A) shows the UV-VIS spectra of the PANI film deposited on ITO by electrochemical polymerization of aniline as described in chapter 2. It possess a broad absorption band at around 850 nm and two peaks at around 425 nm and 345 nm. Figure (5.18B) shows the UV-VIS spectra of the R6G in water (10^{-5} M). A sharp, prominent peak at around 525 nm with a small shoulder at around 505 nm is observed. Figure (5.18C) show the UV-VIS spectra of the R6G incorporated PVA+H₃PO₄ film deposited by dip coating on the glass substrates. It is observable that it shows two peaks in the visible region centered at around 545 nm and 505 nm. Thus, it can be concluded that there is a significant interaction between the dye and the polymer matrix. It can be seen that the peak at 525 nm for R6G has shifted to 545 nm (by about 20 nm) while the shoulder at around 505 nm remaining at the same position. Also, it is observable that the intensity of the shoulder which is small in case of R6G has increased in comparison with that of the peak at around 525 nm. Such type of splitting by the matrix is earlier reported and is called as "Davidod Splitting". Also, it can be observed that R6G has absorption in the spectral region (450 - 550 nm) where PANI has minimum (or less) absorption (480 - 600 nm). Thus, the photons which will not be absorbed by PANI will be captured by R6G and hence is expected to show sensitization effect.

Figure (5.19A) displays the XRD of the R6G powder. It is observable that R6G by itself is crystalline. XRD of the R6G incorporated PVA+H₃PO₄ dip-coated films on the glass substrate (as shown in Figure 5.19B) is amorphous and shows no peaks corresponding to R6G suggesting thereby that R6G is not present in an aggregated, crystalline or ordered form in SPE. Also, the study of such films under optical microscope shows absence of

R6G aggregates. Thus, it can be concluded that the R6G is not present in an aggregated / particulate form in SPE.

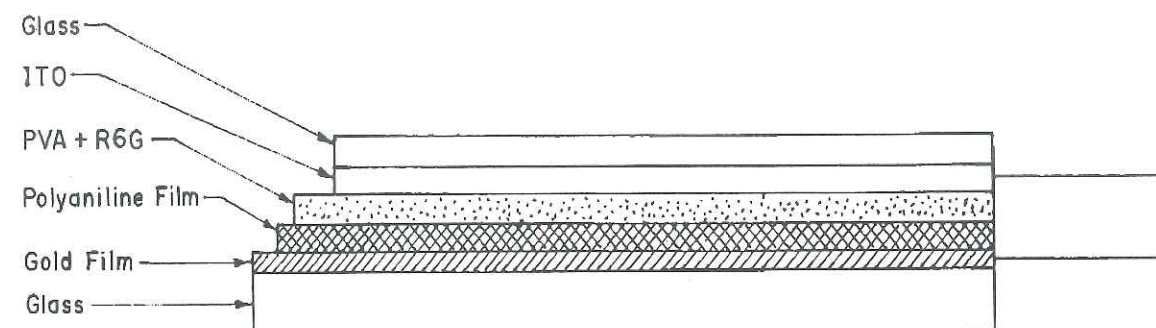
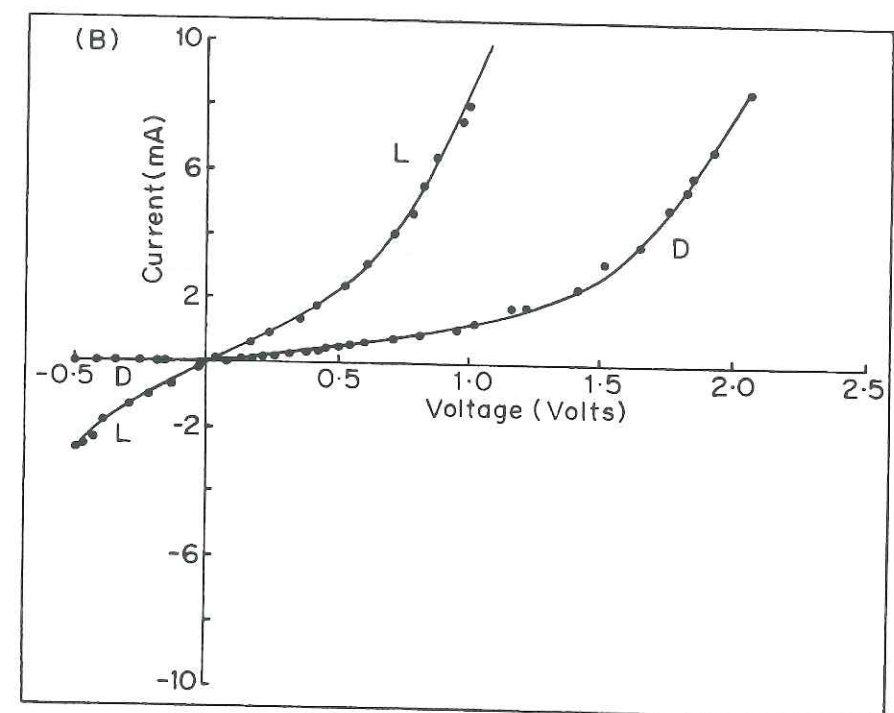
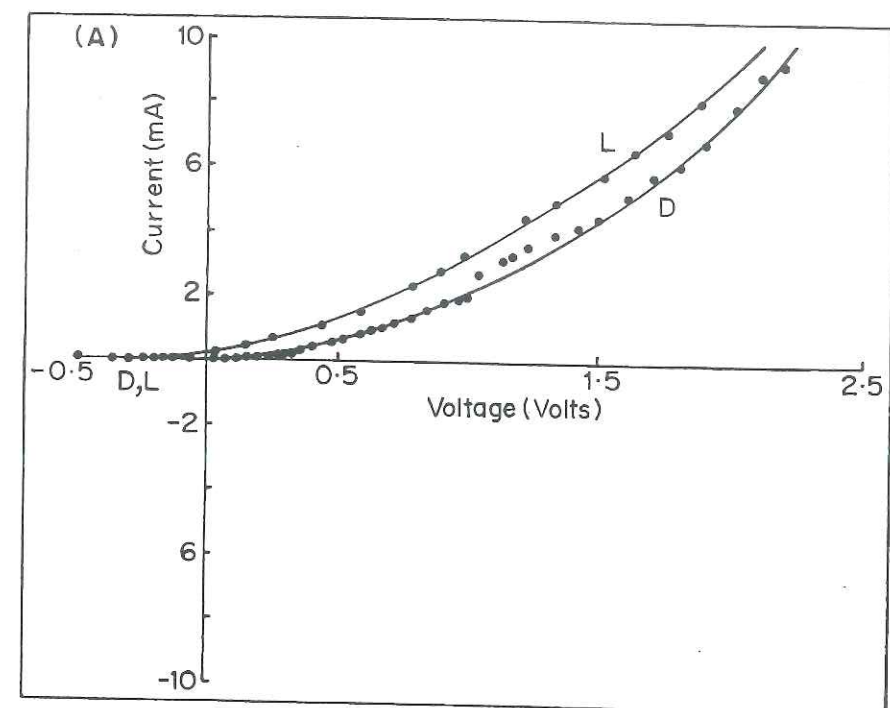


Figure (5.20) : Schematic of the solid state photocell using conducting polyaniline and R6G (Au/PANI/PVA+H₃PO₄+R6G/ITO).



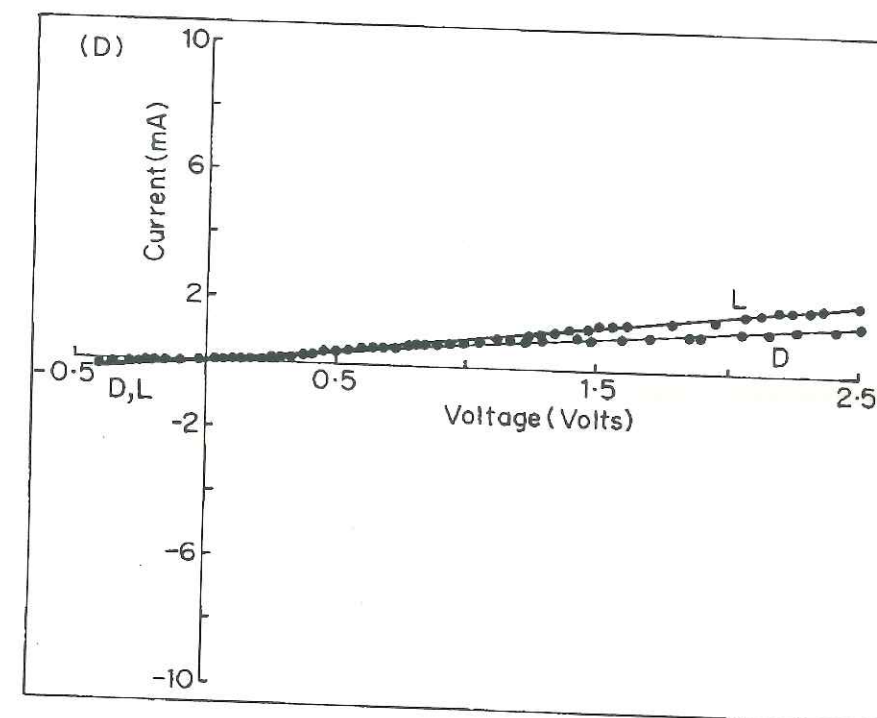
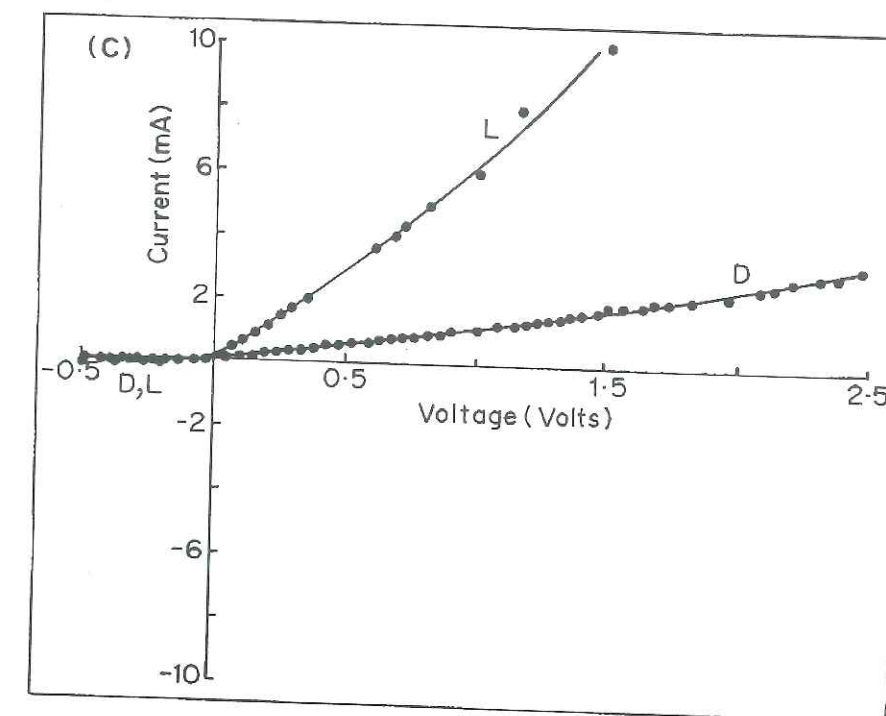


Figure (5.21) : current-voltage (I-V) characteristic in dark (D) and under illumination (L) for the photocell $\text{Au/PANI/PVA+H}_3\text{PO}_4\text{+R6G/ITO}$ containing different concentrations of R6G ; (A) 4.0, (B) 6.3, (C) 8.0, and (D) 13.0 mM/monomer respectively.

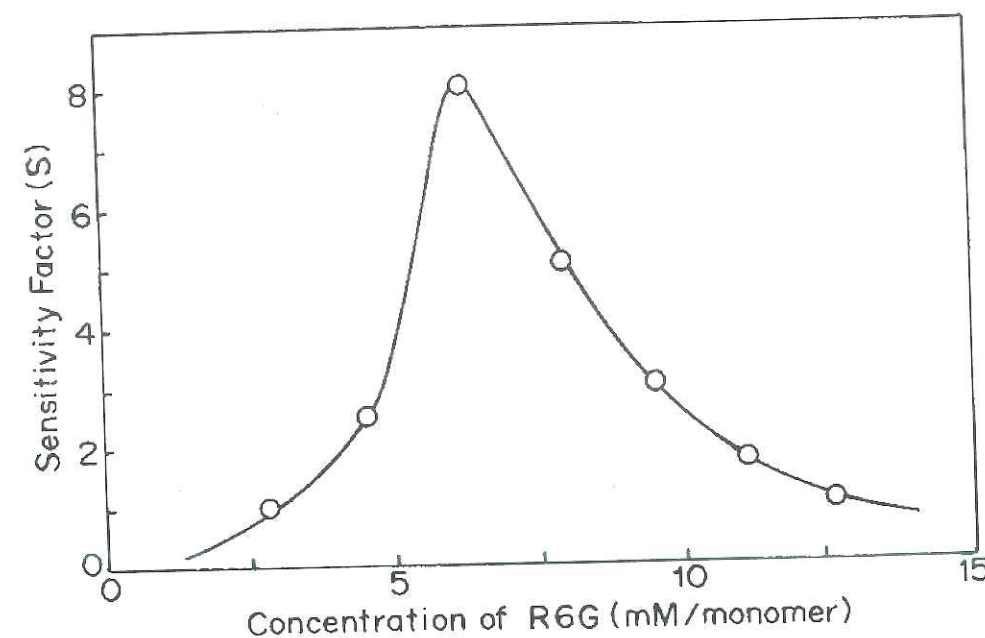


Figure (5.22) : Photosensitivity factor (S) as a function of the R6G concentration.

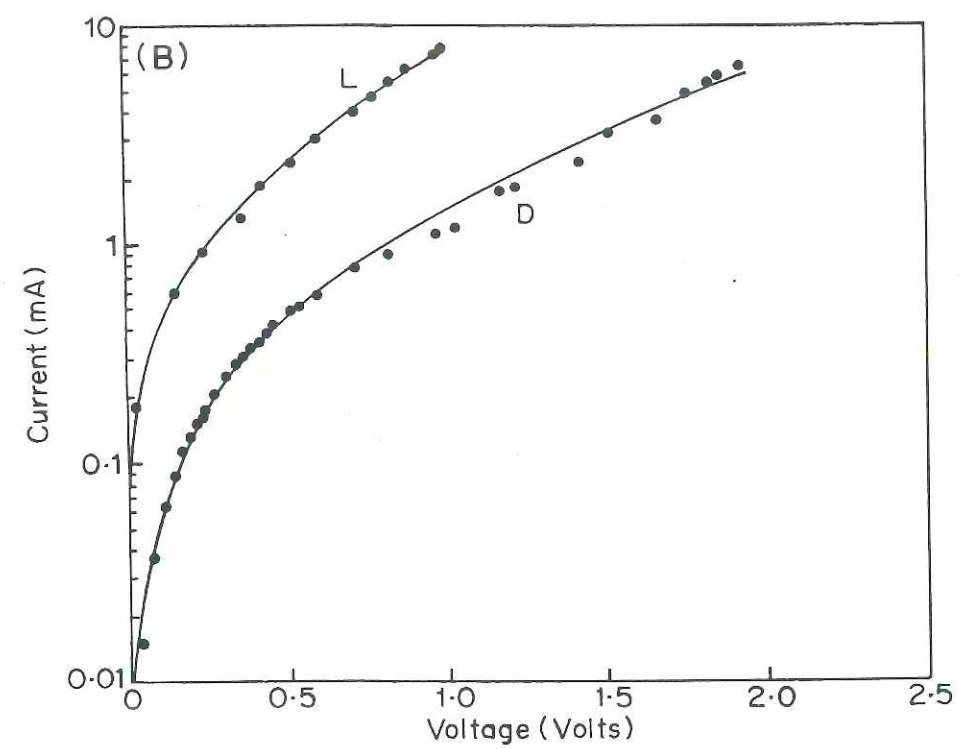
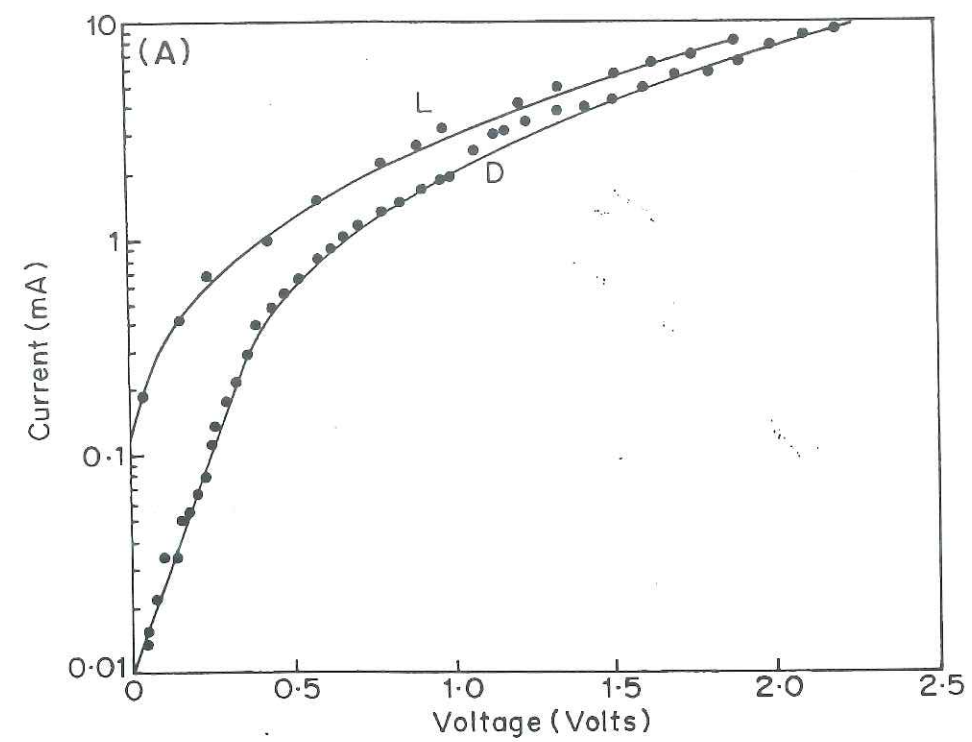
Figure (5.20) shows the schematic of the photocell Au/PANI/PVA+H₃PO₄+R6G/ITO. The current-voltage (I-V) characteristics in dark (D) and under illumination (L) for these photocells are as shown in Figure (5.21). The curves (A) to (D) corresponds to R6G dye concentration of 4.0, 6.3, 8.0 and 13.0 mM/monomer respectively. It is interesting to observe that the I-V characteristics in dark (D) as well as in light (L) exhibits a rectifying nature i.e. the current in one direction (Au +ve, 1st quadrant) is much higher than in the opposite direction (Au -ve, 3rd quadrant). The onset of the non-linearity increase with the increase of R6G concentration. Also, it is observed that the dark current (I_d) decreases with the increase in the dye concentration. The photocurrent (I_l) which is drastically high for low concentration of the R6G decreases gradually with the increase in the dye concentration. It is worthwhile to point out here that the currents observed in this system are quite high. The variation of the photosensitivity factor (S) with respect to the dye



Figure (5.22)

The current-voltage ($I-V$) characteristics of the photoconductor are shown in Figure (5.20). It is observed that the $I-V$ curve is non-linear, i.e. the current increases in the opposite direction (An increase of R6G concentration with the increase in the concentration of R6G dye is quite high. The

concentration is as shown in Figure (5.22). It is quite evident that there is a certain R6G concentration (6.3 mM/monomer) at which the photosensitivity is observed to be maximum (of the order of 8). The concentration of the R6G dye corresponding to maximum photosensitivity factor is said to be 'critical concentration'.



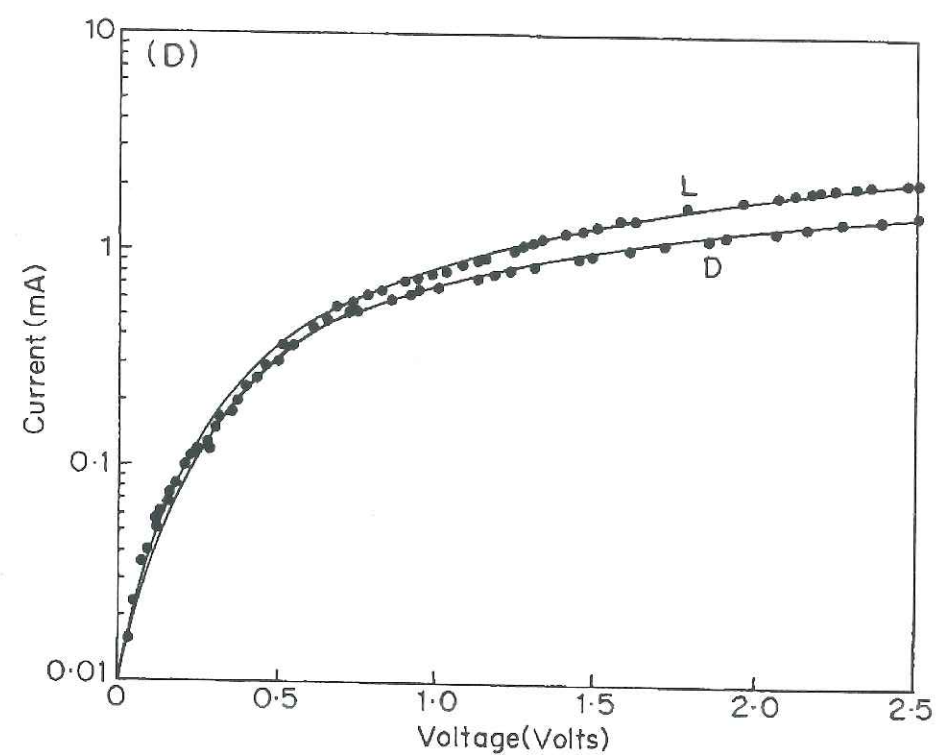
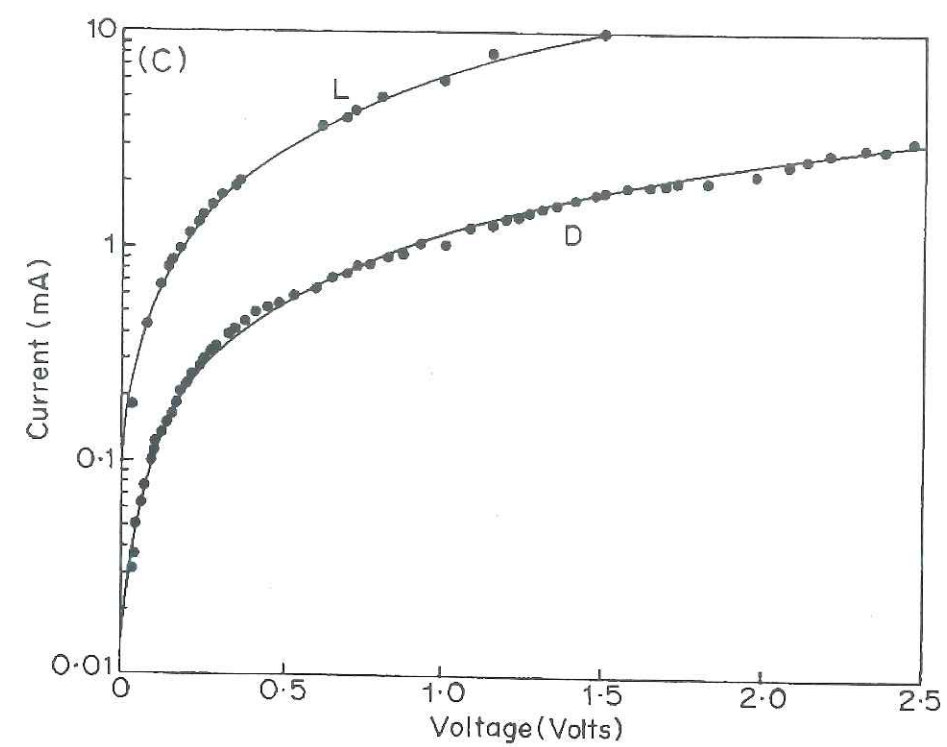


Figure (5.23) : The Semilog plot of the I-V curves showing a typical p-n junction diode type behavior. Curves (A) to (D) correspond to the R6G concentrations of 4.0, 6.3, 8.0 and 13.0 mM/monomer respectively.

The semilog plot of the I-V curves (i.e. $\log I$ vs. V) for the system under study are as shown in Figure (5.23). Curves (A) to (D) corresponds to the R6G concentrations of 4.0, 6.3, 8.0 and 13.0 mM/monomer respectively. The I-V curves were analyzed in detail for their relationship such as $\log I - \log V$, $\log I - \text{Sq. root } V$ etc. From all this study it has been concluded that the I-V curves resembles more like a p-n junction diode characteristics. Also, it can be seen that the curves exactly matches with those predicted from equation (2). Thus, it can be concluded that there is a formation of a p-n junction at the PANI/PVA+R6G interface, PANI being p-type and R6G being known as a n-type dye, behaving like a conventional p-n junction diode. The photosensitivity observed in the forward biased p-n junction can be due to reduction of the barrier height (in presence of light) as discussed for the earlier Ppy/CRV system.

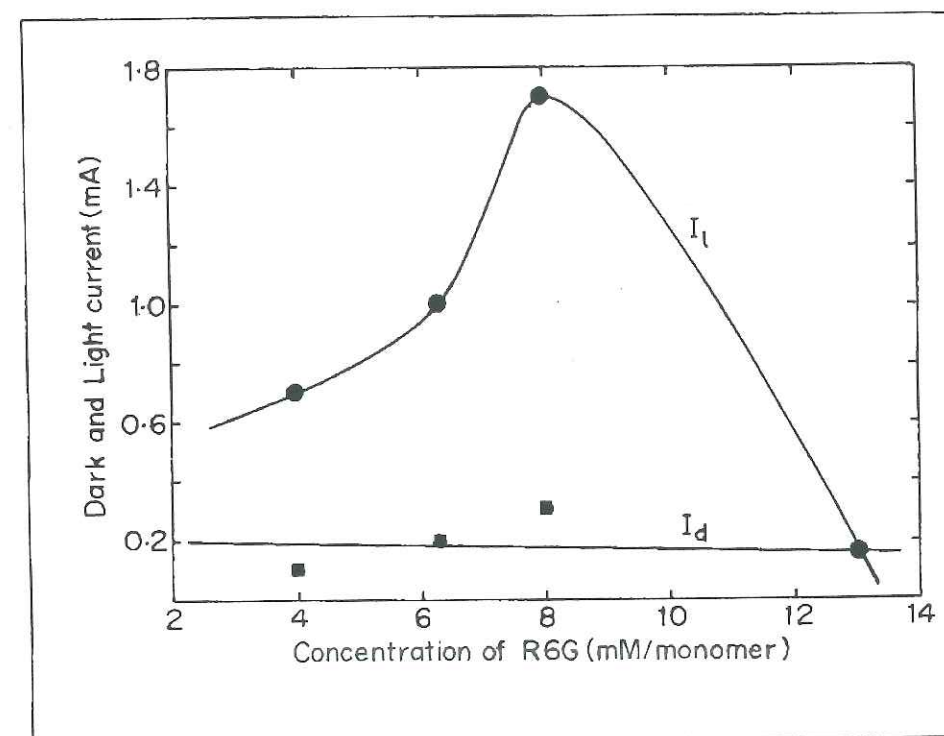


Figure (5.24) : Variation of the dark (I_d) and light (I_l) current with the R6G concentration in the linear portion of the I-V characteristics at the 0.25V.

Figure (5.24) displays the variation of the dark (I_d) and light (I_l) current with respect to the R6G concentration in the linear portion of the I-V characteristic at a fixed voltage of 0.25 V. It can be seen that the photocurrent (I_l) increases with the increase in the R6G concentration initially, reaches to a maximum and then decreases with further increase in the dye concentration. Hence, photocurrent (I_l) goes through a maximum in its variation with respect to the R6G concentration. The dark current (I_d) increases slowly with the increase in the dye concentration. The initial increase of the photocurrent (I_l) can be attributed to the increase in the number of the sensitizing centres with the increase in the dye concentration. Decrease of the photocurrent (I_l) at high dye concentration can be due to heavy trapping and/or recombination of the photogenerated charge carriers. This particular variation of the photocurrent (I_l) is more important than that of the dark current (I_d) and is mainly responsible for getting the maximum photosensitivity at a particular dye concentration.

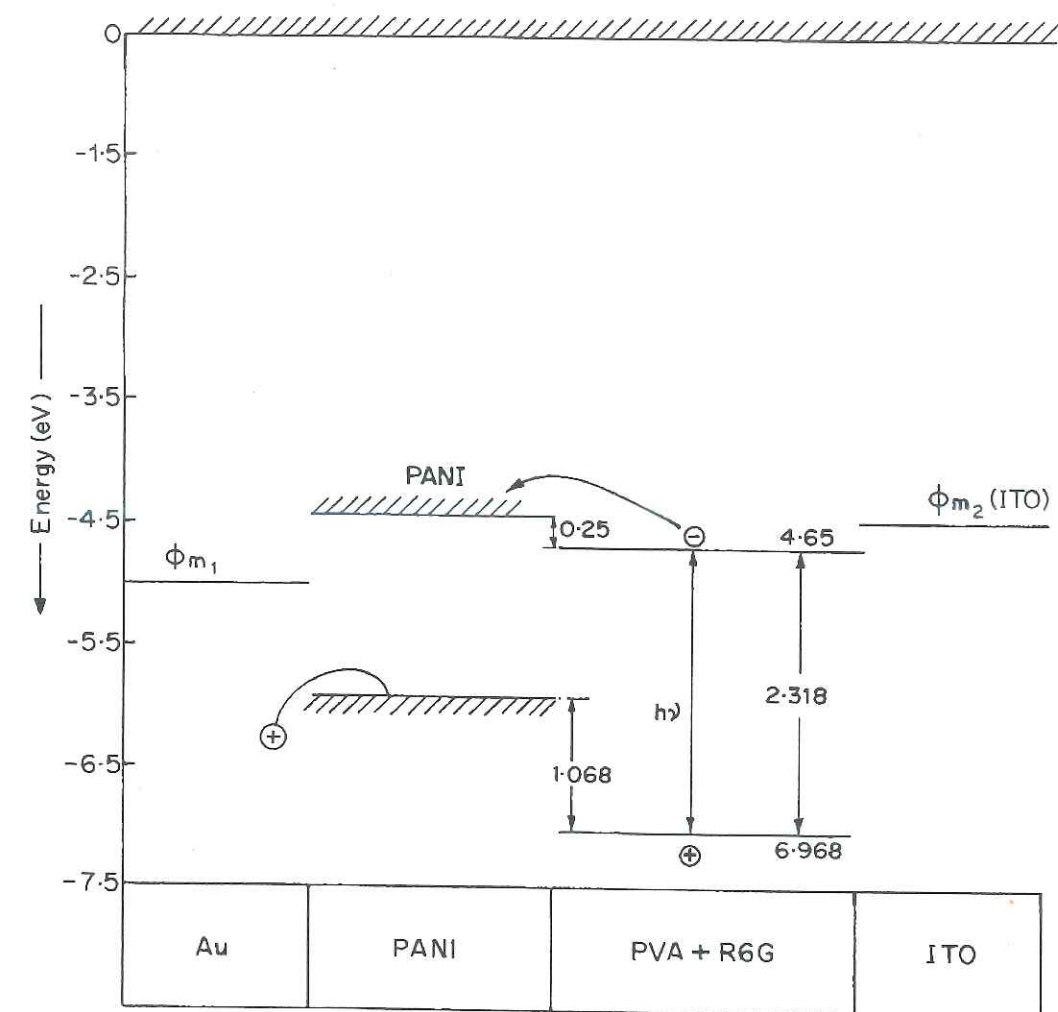


Figure (5.25) : Energy level diagram for the photocell using PANI and having Au/PANI/PVA+H₃PO₄+R6G/ITO type sandwich structure.

The mechanism of the sensitization process can be understood in terms of the energy band diagram for the materials used for forming the photocell. Figure (5.25) depicts the different energy levels for the materials used in forming the photocell. The energy levels for PANI are those which have been reported in the literature [24], while those for R6G in PVA are derived from the UV-VIS spectra recorded and using the reported energy levels of R6G. It must be noted here that PVA containing phosphoric acid is a good

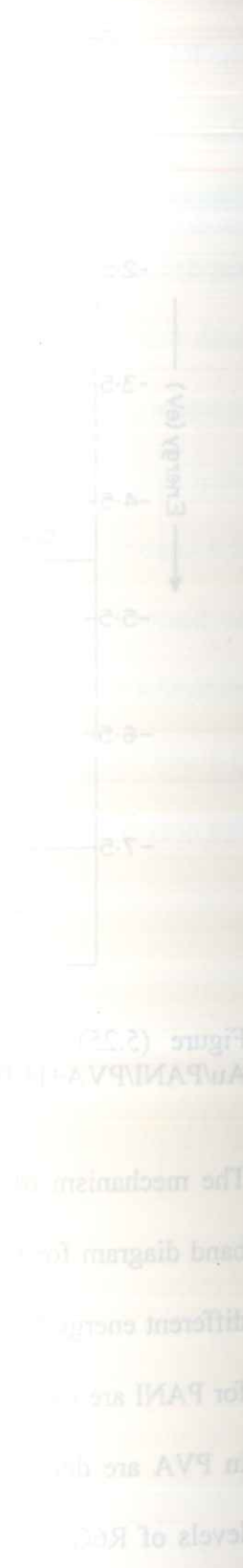


Figure (5.25)
Au/PANI/PVA+R6G
The mechanism of
band diagram for
different contacts
for PANI and
in PVA and the
levels of R6G

proton conductor while PANI is a p-type material and R6G is known to be a n-type dye. A p-n junction is formed at the PANI/PVA+R6G interface - as discussed earlier. Thus, when Au is positive, the p-n junction is forward biased and the high current observed is due to the majority carriers. Also, the hole transport via PANI and the proton transport through PVA are facilitated giving high forward current. On the other hand when Au is having the negative polarity the current would be less since the p-n junction is reverse biased and the current is due to the minority carriers only. Electrons are minority carriers and will experience a barrier (of about 0.25 eV) at the PANI/PVA+R6G interface. The work function of Au is placed (in comparison with the PANI energy levels) in such a way that it forms a blocking contact for both the types of charge carriers (less for electrons and more for holes). Also, holes will also experience a large barrier (of about 1.068 eV) at the PANI/PVA+R6G interface. Here, the energy level (C.B) of R6G is placed in such a way that it can act as minority carrier trapping centre (i.e electrons) from the PANI. But the hole will experience barriers at Au/PANI and PANI/PVA+R6G interfaces. Thus, even though R6G can act as an excellent minority carrier trapping centre, the holes which are the majority carriers experiences large barriers at several stages in the photocell. Generally, high photosensitivity is achieved by the trapping of the minority carriers thereby increasing the majority carrier concentration, life time, mobility etc. In the present system under investigation, even though trapping of the minority carriers takes place, effective increase in majority carrier concentration or there life time and mobility etc. has not been achieved and this could be the reason that very high photosensitivity is not observed.

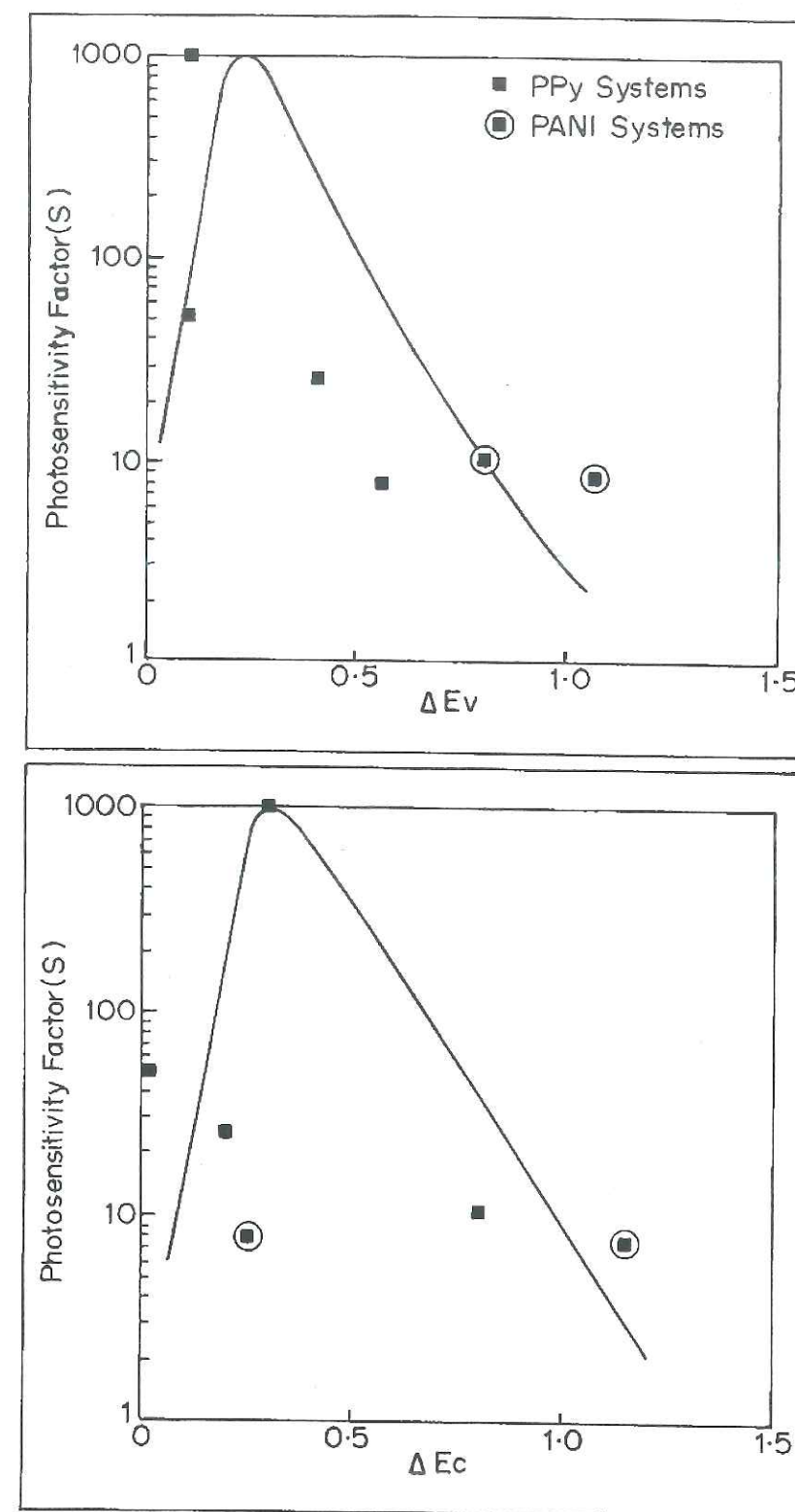


Figure (5.26) : Dependence of the photosensitivity factor (S) on the ΔE_v and ΔE_c values.

Table 5.1 : Ppy : LUMO : 3.3 eV and HOMO : 5.0 eV

PANI : LUMO : 4.4 eV and HOMO : 5.9 eV

Sr. No	Polymer	Dye (type)	VB (eV)	CB (eV)	ΔE_v (eV)	ΔE_c (eV)	Photosensitivity factor (S)	Critical Concentration (mM/monomer)
1	Ppy	MB (p)	5.1	3.60	0.10	0.30	1000	2.50
2	Ppy	PB (n)	5.4	3.50	0.40	0.20	25	2.50
3	Ppy	CV (n)	5.1	3.32	0.10	0.02	50	5.79
4	Ppy	RB (n)	5.2	4.45	0.55	1.15	7.4	1.41
5	PANI	MB (p)	5.1	3.6	0.8	0.8	10	4.10
6	PANI	R6G (n)	6.968	4.65	1.068	0.25	8	6.30

Table 5.1 gives the details of the energy levels for different materials used in the present study [23-26]. These energy levels are used to calculate ΔE_v and ΔE_c values. ΔE_c is the difference between the LUMO of the polymer and the first excited state of the dye similarly ΔE_v is the difference between the HOMO of the polymer and the top of the valance band of the dye. Figure (5.26) shows the dependence of the photosensitivity factor (S) on the ΔE_v and ΔE_c . It can be seen that photosensitivity factor (S) goes through a maximum in the variation of both ΔE_v as well as ΔE_c . In case of Ppy sensitized with different dyes, maximum photosensitivity has been observed when the ΔE_v and ΔE_c values are in between 0.2 to 0.3 eV. As we go away from this value on both the sides, it is observed that the photosensitivity factor (S) decreases. From Figure (5.26) it can be

concluded that when ΔE_v and ΔE_c values will be in between 0.2 to 0.3 eV, for any conducting polymer / dye combination, excellent photosensitization effects will be observed. As discussed earlier, high sensitization can be obtained by trapping of the minority carriers thereby increasing the effective number of free, mobile majority carriers, their lifetime and / or mobility etc. Photosensitivity is also observed to depend on the concentration and / or thickness of the sensitizer, voltage / field. Also, it does not matter whether the dye is p- or n- type or its band gap but the actual placement of the energy levels of the dye in comparison with that of the polymer to be sensitized (and hence ΔE_v and ΔE_c value) is very important.

5.4 SUMMARY AND CONCLUSIONS :

From the present studies, n-type dyes are observed to form a non-ideal p-n junction when used with p-type conducting polymers giving typical p-n junction diode (graded) I-V characteristics. The rectification depends upon the dye concentration. The onset of the non-linearity is observed to depend upon the concentration of the dye and increases as the dye concentration increases. The value of the change in slope of the I-V characteristic is observed to depend upon the dye concentration. The dark current values are observed to decrease as the concentration of the sensitizing dye increases. Maximum photosensitivity factor (S) is observed at a certain dye concentration called "critical concentration". The variation of the dark and the light current with the concentration of the sensitizer suggests that light current goes through a maximum and this particular variation of the light current is more important than that of the dark current especially in the linear portion of

the current-voltage characteristics. The sensitization process is due to the lowering of the potential barrier under the action of light.

CHAPTER 6

CHAPTER 6

SUMMARY AND CONCLUSIONS

Historically, considerable work has been done on dye sensitization of inorganic semiconductors such as TiO_2 , ZnO , CdS etc. R. H. Bube et. al. and Minoria et. al. have significantly contributed in this area. Various models have also been suggested for the dye sensitization processes. Recently, dye sensitization of nano-sized inorganic semiconductors like TiO_2 , ZnO etc. have gained lot of attention for possible application in high efficiency solar cells. Organic dye have also been used as photo-sensitizers for insulating polymers such as polyvinylcarbazole. Such materials are promising for electrophotography (Xerography), photo-sensors etc. because of their cost effectiveness, high processibility etc. Conducting polymers in itself is a relatively new area and as far as our knowledge goes, there are no detailed reports on dye sensitization in conducting polymers. One of the advantage of conducting polymers is that most of the polymers absorbs in the visible region. Further, their response can be enhanced by sensitizing them with suitable dyes and pigments. Dye can not only be used as photo-sensitizers but they can also be used as sensitizers for other interesting properties such as electrochromism, photovoltaic, catalytic etc. Hence, the work (presented in this thesis) was undertaken to study the optoelectronic properties i.e. electrochromism and the photosensitivity (to visible light) of the conducting polypyrrole sensitized with organic dyes and pigments. The effect of different types of dyes (i.e. p- or n-type having different optical properties and hence energy band diagrams) on the photosensitivity of conducting polypyrrole was aimed to be investigated. The main aim of the present work undertaken was to know the important factors that govern the sensitization process and how they affect the

sensitization phenomena. This chapter summarizes the important results obtained by doing various experiments which are presented in earlier chapters in the thesis. The chapter also concludes the important factors observed in such dye sensitization processes such as trapping of minority carriers, type of the dye (i.e. p- or n-type), concentration / thickness of the dye etc. and how they affects / controls the sensitization effect.

The present studies on the electrochromic response of the conducting polypyrrole (Ppy) films with Prussian blue (PB) films on top and for different electrolytes reveal that the use of PB enhances the electrochromic response of Ppy and also extends the response to broader wavelength region of the visible spectrum. The color change can be extended to longer wavelengths by changing the PB content (film thickness) in the composite films. Thus PB acts as a sensitizer for the electrochromic response of conducting polypyrrole. Also, the electrochromic contrast depends on the nature of the electrolyte, especially the size of the dopant / intercalating ions and their electronegativity. By the usage of small size dopant / intercalating ions higher electrochromic contrast can be obtained. It can be pointed here that the contrast in these films arises from the doping and undoping action due to ion insertion in the Ppy as well as PB moieties. The PB film in fact controls the relative doping levels because it allows ions of certain dimensions to pass through to the back side and dope the Ppy film. Thus, it is possible to tailor the overall electrochromic response of the device by an appropriate choice of the PB film thickness as well as the electrolyte used.

In the photosensitization of conducting polypyrrole by Prussian blue in Ppy/PB bilayer film configuration, maximum photosensitivity factor of the order of 60 is observed. The photosensitivity is maximum at a certain value of the PB film thickness. Space charge limited conduction is observed to be the predominant process of charge transport. Due to the presence of the space charge effects in such composite film structures, the photosensitivity is observed to be electric field dependent.

In certain devices such as photoelectrochemical (PEC) cells, electrochromic displays (ECD), it is often essential to employ the solid state electrolytes. Hence, studies were carried out by incorporating the dye sensitizer in such materials as solid polymer electrolytes (SPE). In this case, PB remains in a dispersed form in the SPE (PVA+H₃PO₄). It is observed that the photosensitivity is maximum (maximum photosensitivity factor of the order of 25) at a particular PB concentration defined as "critical concentration". It is observed that PB forms H-type aggregates when dispersed in SPE. The formation of H-type PB aggregates has a negative impact on the photosensitization process and is one of the reason for the decrease of the photosensitivity at high dye concentration. From the variation of the dark and light current with respect to the PB concentration we found that it is the variation of the light current (I_l) which is more important as the dark current (I_d) remains more or less practically constant (or increases slowly) – in the linear portion of the I-V characteristics. Light current is maximum at a particular PB concentration. This particular variation of the light current (I_l) is responsible for getting maximum photosensitivity at a particular PB concentration. The I-V characteristics in such cells reveals that the charge transport is

mainly governed by the space charge effects and the SCLC is the predominant process of charge transport. Sensitization effects are due to the lowering of the potential barrier formed at the Ppy/SPE+PB interface under photoexcitation. The photosensitization effects are observed to be field dependent. This leads to certain value of the concentration of the sensitizer at which the charge transport is optimized and the photosensitivity is maximum.

In Ppy/PB bilayer films (with constant Ppy but varying PB film thickness) used in PEC mode with liquid electrolytes such as aqueous KCl, LiClO₄ etc., it has been observed that PB sensitizes Ppy even in PEC mode but with low photosensitivity. Maximum photosensitivity factor of the order of 2.5 was obtained in case of 0.1 M aqueous KCl as an electrolyte.

It is observed that the use of solid polymer electrolyte (SPE) (as in PB dispersed system) and liquid electrolyte (as in Ppy/PB bilayer films in PEC mode) yields different results regarding photosensitization. The two can be considered as limiting cases in the sense that when the moisture content in the SPE is very high, it can be treated as equivalent to a liquid electrolyte. It is interesting to know what happens when an electrolyte in between solid state and liquid state is used and also whether the moisture content in the SPE plays any role in such sensitization processes. Hence, the experiments were performed on the effect of moisture on photosensitization of PB. The system configuration is exactly same as that of the PB dispersed system in dry state but the only difference is that the SPE is in the wet state. It is observed that the presence of moisture in SPE enhances the ionic

conductivity which results in increase in the dark current values while the photocurrent remains more or less the same. Hence, there is an apparent decrease of the photosensitivity factor due to presence of the moisture.

Thus, it can be concluded that PB sensitizes conducting polypyrrole in different configurations such as in bilayer film configuration, bilayer films used in PEC mode, dispersed in SPE and used to form multilayer structures. The actual sensitivity factor depends on the configuration used. The important factors on which the sensitization process is found to depend are - the type of the configuration used, concentration / film thickness of the dye, voltage / field applied, formation of the dye aggregation (H- or J-type), moisture present in the SPE.

The most outstanding results in the present studies were obtained for methylene blue (MB). MB when incorporated in SPE (i.e. PVA+H₃PO₄) is found to act as an excellent photosensitizer for Ppy giving high photosensitivity factor (of the order of 1000). MB is observed to form a complex with the SPE. There is a "critical concentration" of the MB dye at which maximum photosensitivity has been observed (in the present case 2.5 mM/monomer). The variation of the dark (I_d) and light (I_l) current with the MB concentration, in the linear portion of the I-V characteristics, shows that light current (I_l) goes through a maximum whereas dark current (I_d) remains more or less the same (or increases slowly). This particular variation of the light current (I_l) is more important than that of the dark current (I_d) and is mainly responsible for getting maximum photosensitivity at a particular MB concentration called "critical concentration". SCLC is

observed to be the dominant process of charge transport. The photosensitivity is observed to depend on the voltage / field. V_{TFL} is observed to increase with the dye concentration. From the energy band diagram of the materials used in forming the photocell, it can be seen that the energy levels of MB are placed in such a way that they act as excellent trapping centres for the minority carriers (i.e. electrons) from the polypyrrole. Trapping of the minority carriers in turn enhances the free majority carrier concentration yielding high photosensitivity.

MB is also observed to sensitize the undoped polypyrrole. Low photosensitivity has been observed as compared to the doped system [maximum photosensitivity factor (S) of the order of 80]. The "critical concentration" of the dye at which maximum photosensitivity has been observed in the present case is 3.6 mM/monomer. SCLC is the dominant process of charge transport. The photosensitivity factor (S), along with the dye concentration, is also observed to depend on the voltage / field. The V_{TFL} at which the current goes to non-linear regime is observed to increase with the dye concentration. Hence, it can be concluded that the sensitization effect depends also on the doped / undoped state of the conducting polymers.

In order to know the role of the matrix in which the dye is incorporated, MB was incorporated in PVP+H₃PO₄ and used as a sensitizer for Ppy. Low photosensitivity [maximum photosensitivity factor (S) of the order of 5] has been observed. This may be because PVP do not forms a complex with the phosphoric acid and is not as good a SPE as PVA+H₃PO₄ with high conductivity. Once the photo generated charge carriers are

created by the action of light, they should be able to be transported through the bulk of the material without recombination. The matrix in which the dye is incorporated should be able to transport the photo-generated charge carriers. From the present study, it can be concluded that the matrix which can efficiently transport the photo-generated charge carriers will be more suitable for dye sensitized devices.

In order to know whether MB sensitizes other conducting polymers to the same extent as that for Ppy, MB is incorporated in SPE (i.e. PVA+H₃PO₄) and used as a sensitizer for polyaniline (PANI). Low photosensitivity (maximum photosensitivity factor of the order of 10) has been observed as compared to that of Ppy. There is a "critical concentration" of the dye at which maximum photosensitivity has been observed (in the present case 4.1 mM/monomer). SCLC is the dominant process of charge transport. An electrochemical reaction (movement of Cl⁻ from PVA/MB to PANI) is also observed to occur at 1.2 -1.3 volts giving rise to additional doping of the polymer. The observed I-V characteristics are the superposition of the SCLC and the electrochemical reaction, the role of latter being only to increase the current at the particular voltage mentioned above. The photosensitivity factor (S), along with the dye concentration, is also observed to depend on the voltage / field. From the energy level diagram, it is observable that MB do not act as a trapping centre for the minority carriers (i.e. electrons) of PANI. Hence, it can be concluded that MB does sensitizes conducting polyaniline but not to the extent as it sensitizes Ppy. Overall it can be concluded that a dye may sensitize many polymers but to the different extents.

In order to know whether the sensitization effect depends on the type of the dye (i.e p- or n-type), n-type dyes such as CRV, RB, R6G are used as sensitizers. CRV, RB, R6G are observed to form a complex with the SPE. All n-type dyes are observed to form a p-n junction (graded) when used with p-type conducting polymers (i.e. Ppy or PANI) giving typical p-n junction diode I-V characteristics. Maximum photosensitivity is observed at a certain dye concentration called "critical concentration". The variation of the dark and the light current with the concentration of the sensitizer suggests that light current goes through a maximum and this particular variation of the light current is more important than that of the dark current especially in the linear portion of the current-voltage characteristics. From the energy band diagram of the materials used in forming the photocell using CRV dye, it can be seen that the energy levels of CRV and that of the Ppy are almost at the same positions (with a little or no barrier). Hence, both majority and minority charge carriers do not feel any barrier and can move easily from or to the polymer. Here, no trapping of minority charge carriers from Ppy is expected which results in low photosensitivity - as expected. This increases their recombination probability and hence lowers the photosensitivity. By comparing the photosensitization effect in Ppy sensitized with MB and CV [both having approximately similar electronic structure but one (i.e. MB) is p-type and other (i.e. CV) is n-type] it can be concluded that the sensitization effect does not depend on the type of the dye (i.e. p- or n-type). When Ppy is sensitized with RB, low photosensitization is observed. From the energy level diagram of the materials used in forming the photocell using RB dye, it can be seen that both the differences in energy levels at valance (ΔE_v) and conduction band (ΔE_c) are very high. The photogenerated charge carriers (both in conduction and valance band) will

feel very high potential barrier and hence not easily transported at all. This in turn results in low photosensitivity factor. Hence, it can be concluded that very high or very low values of ΔE_v and ΔE_c results in low photosensitization. There is an optimum at around 0.2 to 0.3 eV, for both, when maximum sensitization will be obtained (as discussed in chapter 5). Thus, the sensitization effect is not only depend on the trapping of the minority carriers from the polymer but the relative placement of the energy levels of the dye with respect to the polymer to be sensitized is very crucial. Studies on PANI sensitized with R6G incorporated in SPE yields similar results.

Thus, overall it can be concluded that dyes and pigments can be used as sensitizers for improving the optoelectronic properties such as electrochromism and photosensitivity of the conducting polymers. Thickness of the film, size of the counterions, electronegativity are important factors and should be considered in improving the electrochromic response of the polymer by dyes and pigments.

The type of the dye (i.e p- or n-type), its band gap are less important in photosensitization processes but the exact placement of the energy levels of the dye in comparison with that of the polymer to be sensitized plays a crucial role. Photosensitivity is observed to be maximum when the ΔE_v and ΔE_c values are about 0.2 to 0.3 eV. As we go away from this value on both the side (higher or lower), the photosensitivity is observed to decrease. Trapping of the minority carriers thereby increasing the free / mobile majority carrier concentration and their lifetime in the polymer to be sensitized by the dye is the most important factor which governs the photosensitization process. The

other factors are the configuration of the photocell, the concentration / film thickness of the dye, the matrix in which the dye is incorporated, dye aggregation and / or complexation, presence of moisture, field/voltage etc. It is also observed that the sensitization effect depends on the state of the conducting polymer (i.e. doped or undoped) which again confirms the above hypothesis regarding the placement of energy levels. In doped conducting polymer, additional energy levels are created within the energy gap - solitonic or bipolaronic. Since these are at different places with respect to the energy levels in the dye, ΔE_v or ΔE_c will be changed as compared to undoped polymer. Hence, one would obtain different sensitization effects for the same polymer / dye combination which conclusively proves the suggested correlation as made above.

FUTURE DIRECTIONS :

The present studies with different dyes and p-type conducting polymers revealed that good p-n junctions can be formed by the appropriate choice of material. Such type of organic p-n junction diodes do show photovoltaic effect and can be used for the conversion of sunlight into electricity. Recently, there are some reports on organic solar cells. The main advantage of organic solar cells and particularly polymer based ones is their cost effectiveness and easy processibility. Further, these can be easily made on large area panels just by coating processes used in paint industry. It will be interesting to study these possibilities in dye sensitized polymers so that one may obtain cheaper solar energy conversion in near future.

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REFERENCES

CHAPTER 1

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3. OPTOELECTRONIC PROPERTIES OF CONDUCTING POLYPYRROLE SENSITIZED WITH ORGANIC DYES
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7. STUDY OF CONDUCTING POLYMER COMPOSITES FOR PRESSURE SENSOR APPLICATIONS
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8. DYE SENSITIZED CONDUCTING POLYMERS FOR PHOTODENSOR APPLICATIONS

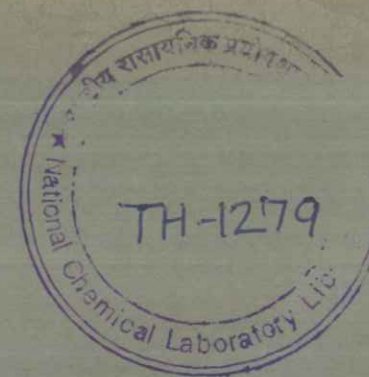
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(III) Patents (granted) :

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