

Lib.

**STUDY OF THE ELECTRICAL PROPERTIES OF
POLYVINYLPIRROLIDONE-LITHIUM OXIDE COMPLEX**

BY
SARDAR SAYDUL AMIN

SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF M. PHIL.



DEPARTMENT OF PHYSICS
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY
DHAKA.

MAY, 1995.



BANGLADESH UNIVERSITY OF ENGINEERING & TECHNOLOGY, DHAKA

DEPARTMENT OF PHYSICS

CERTIFICATION OF THESIS WORK

A THESIS ON

STUDY OF THE ELECTRICAL PROPERTIES OF
POLYVINYLPIRROLIDONE-LITHIUM OXIDE COMPLEX

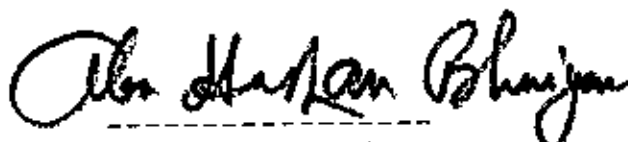
BY

SARDAR SAYDUL AMIN

has been accepted as satisfactory in partial fulfilment for the degree of Master of Philosophy in Physics and certify that the student demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on 18th May, 1995.

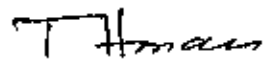
BOARD OF EXAMINERS

(i) Dr. Md. Abu Hashan Bhuiyan
Associate Professor
Department of physics
BUET, Dhaka.



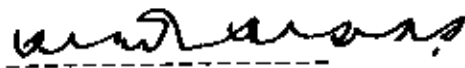
Supervisor and
Chairman

(ii) Prof. Dr. Tafazzal Hossain
Head,
Department of physics
BUET, Dhaka.



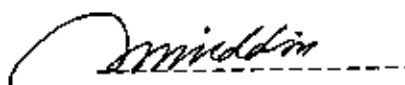
Member

(iii) Prof. M. A. Asgar
Department of Physics,
BUET, Dhaka.



Member

(iv) Prof. Dr. M. Imam Uddin
Department of Physics
Jahangirnagar University
Savar, Dhaka.



Member (External)

CERTIFICATE

This is to certify that the author is solely responsible for the work reported in this thesis and this work has not been submitted to any university or elsewhere for the award of a degree or diploma.

Sardar Saydul Amin

Candidate

(SARDAR SAYDUL AMIN)

Roll no. 9112F

Session : 1989-90.

Abu Hashan Bhuiyan

Supervisor

(DR. MD. ABU HASHAN BHUIYAN)

Associate Professor

Department of Physics

BUET, Dhaka.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my reverend teacher Dr. Md. Abu Hashan Bhuiyan, Associate Professor, Department of Physics, Bangladesh University of Engineering & Technology, Dhaka for his continuous supervision, valuable suggestions and encouragement during my research work.

My deep sense of gratitude is due also to Dr. Tafazzal Hossain, Professor and Head, Department of Physics, Bangladesh University of Engineering & Technology, Dhaka for his kind co-operation and inspiration during the work.

I also express my gratitude to Professor Dr. Gias uddin Ahmad, Professor Dr. M. Ali Asgar and Dr. Mominul Haq of the same department for their encouragement during the work.

I am grateful to Mr. J. Podder, Assistant Professor, Department of Physics, BUET, Dhaka for taking the microphotographs.

I express my indebtedness to Dr. Aktar Uddin Ahmed, Principle Research Officer, Housing and Building Research Institute, Mirpur, Dhaka for taking Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) traces.

I am grateful to My friend Mrs. Jahanara Khanam (Mukta) for encouragement and help in preparation of my thesis. Finally, I am grateful to my family members; particularly my Fufa Jan Mr. Nurul Haque Khan and uncle Sardar Raiful Amin Rouf for their encouragement that made the whole project possible.

ABSTRACT

Polyvinylpyrrolidone (PVP) complexes are prepared with different concentration of lithium oxide (Li_2O) such as 0.5, 1, 2.5, 5, and 10%. One sample of pure PVP and five composition of Li_2O with PVP are investigated. The XRD and IR investigations prove the incorporation of Li_2O in PVP. The DTA/TGA measurements reveal that a structural change occurs at about 90–95°C. The UV–VIS measurement shows that the optical band edge decreases with Li_2O concentration. Surface microphotographs also show different features of the materials. The current voltage (I–V) characteristics are recorded in the voltage range 0–80 volt. D.C conductivity of all the samples is measured in the temperature range 30° to 100°C. The I–V characteristics of all the samples are more or less linear. The d.c. conductivity decreases by 10^3 order of magnitude on heat treatment at 100°C.

Activation energy values obtained from the plots of $\ln \sigma$ versus $\frac{1}{T}$ suggest that the d.c. conductivity may be due to ion motion.

CONTENTS

CHAPTER 1		INTRODUCTION	Page No
1.1	Composite : An advanced material		1
1.2	Polymers		3
1.2.1	Types of Polymers		6
1.2.2	The Glass Transition temperature (T_g) of Polymer		8
1.3	Polyvinylpyrrolidone (PVP)		11
1.3.1	Properties		12
1.3.2	Application		16
1.4	Lithium and Lithium Oxide (Li_2O)		17
1.4.1	Physical Properties		18
1.4.2	Chemical Properties		18
1.4.3	Application		19
1.5	Objectives of the Present Work		19
CHAPTER 2		THEORY AND LITERATURE SURVEY	
2.1	X-ray Diffraction (XRD)		21
2.1.1	Qualitative Analysis		21
2.1.2	Procedure		22
2.2	Polarizing Microscopy		23
2.2.1	Modes of observation in a Polarizing Microscope		24
2.3	Thermal Analysis		26
2.3.1	Differential Thermal Analysis (DTA)		26
2.3.2	Thermogravimetric Analysis (TGA)		26

2.4	Spectroscopic Analysis	27
2.4.1	Ultra-violet and Visible (UV-VIS) Spectroscopy	27
2.4.2	Infrared (IR) Spectroscopy	28
2.5	D.C. Conductivity	29
2.5.1	Electrical Conduction Mechanism in Solids	31
2.6	Literature Survey	34

CHAPTER 3 EXPERIMENTAL DETAILS

3.1	Materials used in this work	36
3.2	Preparation of the different complexes of PVP and Li_2O	37
3.2.1	Samples for different measurements	37
3.3	Electrode deposition	38
3.4	X-ray diffraction (XRD)	39
3.4.1	X-ray Investigation of the samples	39
3.4.2	Working procedure for taking XRD pattern	39
3.4.3	Calculation of interplanar spacing, d_{hkl}	39
3.5	Polarizing Microscopy	40
3.5.1	Polarizing Microscope	40
3.5.2	Porcedure	41
3.6	Thermal analysis	41
3.6.1	Differential thermal analysis (DTA)	41
3.6.2	Working Principle of DTA	41
3.6.3	DTA apparatus	42
3.6.4	Thrmogravimetric Analysis(TGA)	45
3.7	Spectroscopy	46
3.7.1	Ultraviolet-Visible (UV-VIS) Spectroscopy	46

3.7.2	Infrared (IR) Spectroscopy	46
3.8	D.C. Measurement	46
3.8.1	Instruments used in d.c. measurements	46
3.8.2	Experimental Procedure	50
3.8.3	Working formulas	53

CHAPTER 4 RESULTS AND DISCUSSION

4.1	Structural Analysis	55
4.1.1	X-ray Diffractometric (XRD) Analysis	55
4.1.2	Infrared Spectroscopic Analysis	57
4.1.3	Surface Microscopic Analysis	59
4.1.4	Differential Thermal Analysis (DTA)and Thermogravimetric Analysis(TGA)	62
4.2	Optical Absorption Studies	71
4.3	D.C. Electrical Studies	73
4.3.1	Current-voltage (I-V) Characteristics	73
4.3.2	D.C. Conductivity	77

CHAPTER 5 CONCLUSIONS

5.1	Conclusions	83
5.2	Suggestions for Future Work	84

REFERENCES	85
-------------------	----

APPENDIX	87
-----------------	----

CHAPTER 1
INTRODUCTION

CHAPTER 1

INTRODUCTION



1.1 COMPOSITE : AN ADVANCED MATERIAL

Any one who has taken time to systematically search the literature for a definitive statement on what a composite material, actually there is no proper definitive description exists and this is very controversial area of debate. Thus, a composite material may be defined as substance which is composed by physically combining two or more existing materials to produce a multiphase system with different physical properties from the starting materials but in which the constituents retain their identity. That is, the components do not dissolve in each other and can be physically identified by an interface between the components. Generally, composite materials can be divided into three classes:

- (a) Dispersion - Strengthened composite materials e.g. Alumina dispersed in silver, etc.
- (b) Particulate reinforced composite materials e.g. Rubber reinforced with carbon black, etc.
- (c) Fibre reinforced composite materials e.g. Epoxy resin or polyester reinforced with glass fibres, etc.

We are entering the age of advanced material. The new materials have achieved prominence in the World of engineering materials. Compositing is shown to be a unifying influence in designing new materials for specific functions. Composites have acquired a leading position in the development of new materials because of the realisation that with judicious choice of combinations of materials startling new combinations of properties can be obtained².

Composite materials are used to solve the most acute problems; energy and oil conservation, improvement of the properties of polymer materials etc.

The principle of compositing materials is also used in a very sophisticated way in what is called band gap engineering in microelectronics. The composition of a semiconductor with gallium can change the band gap of the semiconductor to a very small range. So, composite principle suggested that using two materials which have absorption maxima at different optical wavelengths in order to obtain a photovoltaic device of increased efficiency compared with one based on a single absorbing material.

The range of application for polymer composites is broad. The polymer composites have greater flexibility and stability than the virgin polymer. Polymer composites offer great versatility of application and considerable simplicity and convenience in the manufacture of artefacts. So, it is widely used in the building construction, furniture, electric appliances, cars, and other fields³. They suffer however, at least one major disadvantage, that of limited performance at elevated temperatures due primarily to thermal degradation of the polymer matrix. A variety of polymers, both thermosetting and thermoplastic are being developed with a view to increase their glass transition and heat distortion temperatures, but commercially available materials lose a significant proportion of strength and stiffness after a few thousand hours continuous operation in the temperature range 250–300°C. But, polymer composite materials have a maximum operating temperature 400°C. Moreover, many of the polymers with relatively good temperature resistance are expensive compared to polyester and epoxide resins used for the bulk of composite production.

1.2 POLYMERS

Polymers are the substances which are made up of large molecules or macromolecule. These macromolecules or giant molecules are composed of repetition of small repeating units which are called " monomer". Polymers may be natural or artificially synthesized. Natural polymers exist in plants and animals and include starch, proteins, lignin, cellulose, collagen, silk and natural rubber etc. Synthetic polymers derive mainly from oil-based products and include polyethylene, nylon, epoxies, phenolic and synthetic rubbers etc.

Monomers or repeating units can be combined in many ways. If the monomers are connected in a linear fashion it is called linear polymer. Another type of polymers is network polymer. These are based on a different type of monomer which can be chemically joined up not only at each end but elsewhere too . These polymers can therefore form covalently bonded three dimensional networks rather than just linear chains. The repeat unit of the polymer is usually equivalent or nearly equivalent to the monomer or the starting material from which the polymer is formed.

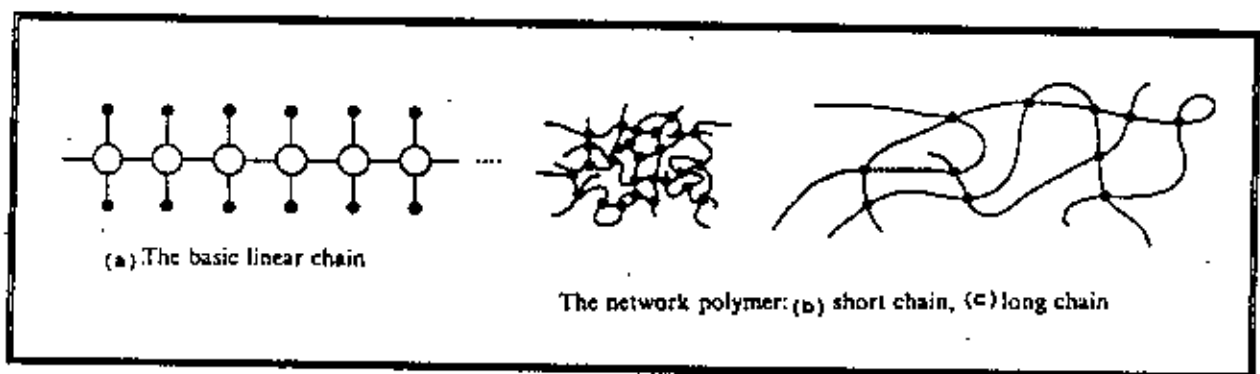
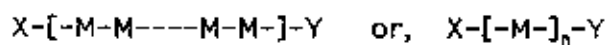


Fig. 1.1 Various Polymers

Number of repeating unit in a giant molecule of polymer gives the degree of polymerization. A high polymer is one in which the number of degree of polymerization is in excess of about one hundred. So, high polymers are substances of very high molecular weight. The molecules of linear polymers have simplest structures and small units are chain like linked.

The length of polymer chain is specified by the number of repeating unit in the chain. The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the degree of polymerization. In the simplest case the polymer may be represented by the formula

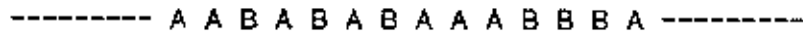


In which a simple, straight chain of n structural units M is terminated by two end groups X and Y which may be same or different. Substances of this kind with uncomplicated structure comprising a single sequence of structural unit are termed as "linear polymer".

In linear polymers if all the structural units are identical, these polymers are called homopolymer, whilst polymer in combining two or more chemically different types of structural units into the chain are termed as copolymers. The most of the synthetic copolymers contain only two types of structural unit and are therefore called "Binary copolymers". Three extreme types of linear binary copolymer structures are as follows.

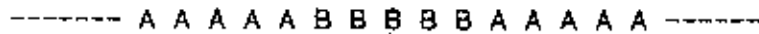
(i) Random copolymers

In this case two different types of chemical structural units A and B are arranged randomly along the chain.



(ii) Block copolymers

In this case the linear polymer chain consists of large group of identical units.

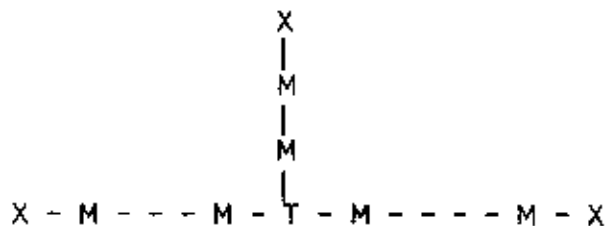


(iii) Alternating copolymers

In this case the structural units are arranged in an alternate fashone.



When the structural units of the side chain are identical to those of the main chain, then it is said to be branched.



The extent to which polymer chain is branched exerts a very large influence on the properties of the polymer, particularly in the solid state where chain branches may restrict the ability of the molecules to align themselves into the crystalline regions. If the side chains of a branched polymer are formed from structural units which are different from those of backbone, the polymer is termed as graft polymer.

The process of formation of polymers is called polymerization. Basically polymerization is of two types.

- (i) Chain reaction polymerization
- (ii) Step reaction polymerization

Chain reaction polymerization is characterized by self-addition of the monomer molecules, to each other, very rapidly through a chain reaction. It produces linear polymers and these products are all thermoplastics. In step polymerization, the polymer build-up proceeds through a reaction between functional groups of the monomers. The reaction takes place in a step-wise manner (i.e., one after another), and the polymer build-up is, therefore, slow. Step polymerization reactions are mostly accompanied by the elimination of small molecules.

1.2.1 Types of Polymers

(a) Homochain polymers

When polymers are made in chain reactions containing only carbon atoms in the main chain called homochain polymers.

(b) Heterochain polymers

The types of polymers made in step reaction may have other atoms, originating in the monomer functional groups, as part of the chain called the heterochain polymers.

(c) Steric isomers

When the repeat unit of a polymer chain are themselves asymmetric, on account of there containing a carbon atom with four different substituents, the large numbers of possible permutations of right handed and left handed units represents a large numbers of steric isomers. This kind of isomerism in polymer is called tacticity. There are three main types of steric isomers.

(i) Isotactic

In this isomer all repeat units are identical, either right handed or left handed form and arranged in a linear, head to tail fashion. In the fully extended chain all the methyl substituents lie on the same side of the chain.

(ii) Syndiotactic

Here successive repeat units alternate in configuration dldldl...., and successive methyl groups along the fully extended chain lie on alternate sides. More elaborate ordering does not often occur in practice.

(iii) Atactic

This describes a completely random arrangements of the repeat units d and l along the chain.

(d) Thermoplastics

Most linear polymers can be made to soften and take on new shapes by the applications of heat and pressure. They are said to be thermoplastics. Natural resin, sealing wax, celluloid, vinyl plastics, polystyrene etc. are examples of thermoplastics.

(e) Thermosetting plastics

The thermosetting plastics can be "set" irrevocably in their final shape by continued heating that is to say the raw materials possess plasticity which enables it to be shaped; but during molding a chemical change occurs in the heated plastics which destroys the essential property of

plasticity. The materials become rigid and will not again become plastic, vulcanized rubber, bakelite and other phenolic type plastics are the examples of thermosetting plastics.

1.2.2 The Glass Transition Temperature(T_g) of Polymer

The glass transition temperature is the temperature at which the molten polymer changes to a hard glass. This transformation occurs over a temperature range that includes the glass temperature, T_g . There is a small temperature region about T_g in which the polymer viscosity varies rapidly with temperature from a very high viscosity characteristics of a glass to a low viscosity characteristic of a more or less viscous liquid. It is the temperature region in which the thermal motion of the molecules become so slow that they are unable to respond within a responsible time to the action of an applied force. Consequently, the material is observed to change from a soft to a hard substance as the temperature is lowered through this region. The glass transition generally occurs in the amorphous state. It does not correspond to any change in the atomic structure. Below T_g , the characteristic time τ of the molecule is large, while above T_g it is small.

In the temperature interval between T_g and the melting point of the crystal T_m , the material could be said to be in a super cooled liquid state and is so viscous that it appears solid, whereas below T_g , the material is solid. Such situation is shown in the figure 1.2 in the cases of the coefficient of expansion and the specific heat capacity; below T_g , the values of one close to those of the crystal, above T_g , to those of the liquid.

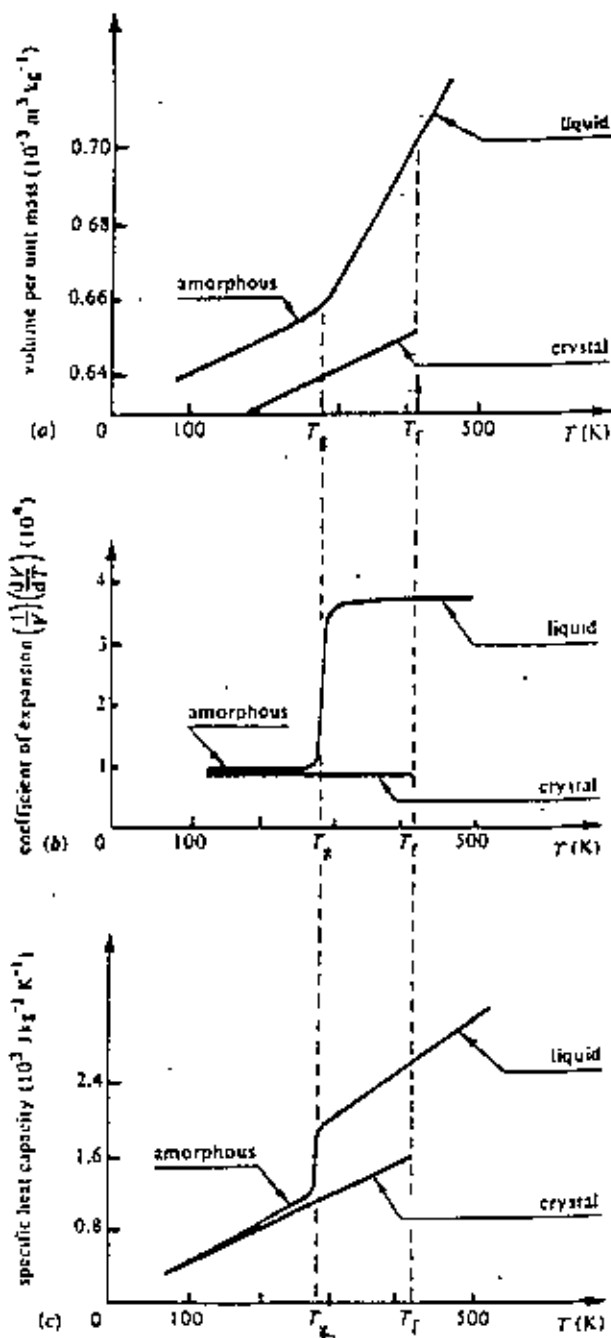


Fig 1.2. Defining the glass transition temperature T_g in (a) the volume per unit mass, (b) the coefficient of expansion and (c) the specific heat capacity for glucose, which exists in both the amorphous and crystalline states.

When the transitions additional to T_g (and to T_m with crystalline polymers) became apparent it became conventional to label the highest transition (other than T_m where this exists) as an α transition, labelling other transitions β , γ , δ etc., in decreasing order of temperature. In most cases, but not always, the glass transition temperature corresponds to the α transition. Such a formal nomenclature ignored the physical reagents for a transition and it is not surprising that the reason for different transitions vary from one polymer to another. Some mechanism may be common to several materials, others may be highly specific. Hence, a so called β -transition in one polymer may have a quite different origin than a β -transition in a second polymer. At the same time the β -transition the first polymer could have, e.g., the same physical origin as a so called γ -transition in the second polymer. The α , β , γ nomenclature is therefore only a method of labelling a given polymer and no special significance should be attached to such a term as β -transition or γ -transition without reference to a given polymer.

In amorphous polymers transitions occur because of an increase in temperature, a point is reached where the molecules gain sufficient energy to indulge in additional motions. With such amorphous material five types of transition appear possible. In order of increasing temperature they are :

- i) Motion of a side group, e.g., methyle, about an axis at right angles to the chain.

- ii) Motion of two to four carbon moieties in the main chain (the Schatzki crankshaft effect).
- iii) Motion of moieties containing hetero-atoms in the main chain, e.g., the amide group in a polyamide.
- iv) Motion of a chain segments of about 50-100 backbone atoms (which corresponds to T_g).
- v) Motion of the entire chain as a unit.

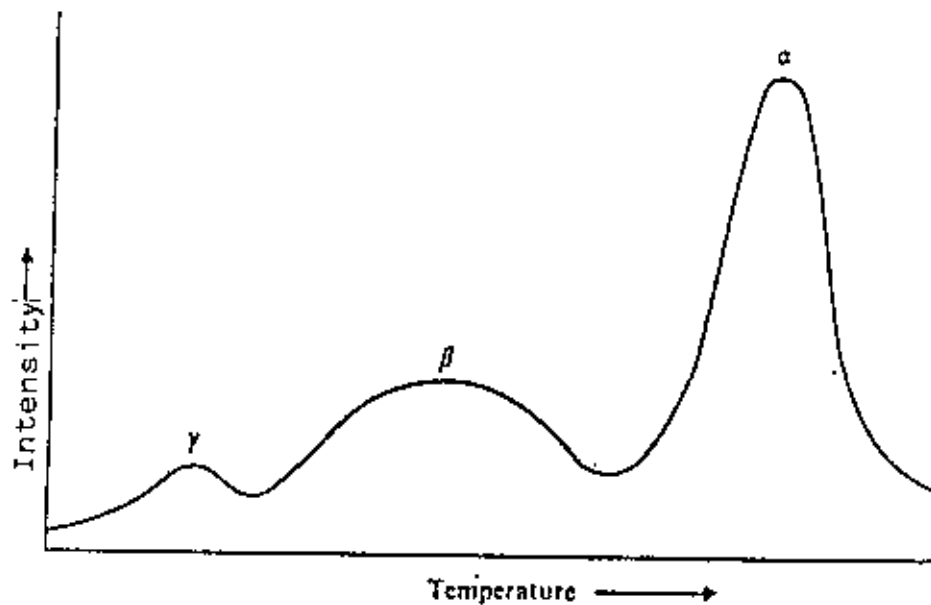
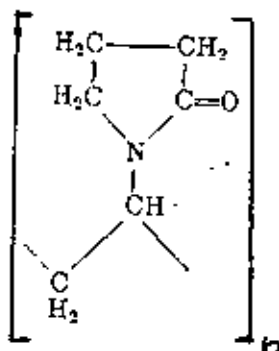


Fig. 1.3 Different transition regions

1.3 POLYVINYLPIRROLIDONE (PVP)

Polyvinylpyrrolidone(PVP) was first developed in Germany in the 1930 and was widely employed by the German as a blood-plasma substitute and extender during

the world war II. PVP is a nonionic homopolymer that is probably best known for its unusual complexing ability, biological compatibility, physiological inertness, low toxicity, film-forming, adhesive characteristics and thermal degradation. PVP is prepared from its monomer N-vinyl-2-pyrrolidinone, commonly called vinylpyrrolidone or VP. The chemical structure of PVP is



That is, PVP consisting of linear vinylpyrrolidone groups of varying degrees of polymerization.

1.3.1 PROPERTIES

(a) Physical properties

PVP exhibits a unique combination of properties, including solubility in water and in organic solvents, very low toxicity, high complexing ability, good film-forming characteristics, and the ability to adhere to a number of substrates.

PVP is a white or slightly yellow hygroscopic powder. Physical properties are determined on films or powder. The polymer strongly interacts through dipole-dipole attraction and the melt viscosity of the polymer is therefore

too high for typical thermoplastic-forming operations.

(i) Glass-transition temperature(T_g) of PVP

The glass-transition temperature of linear PVP increases with increasing molecular weight and is calculated by the following equation:

$$T_g(^{\circ}\text{C}) = 175 - \frac{9685}{K^2}$$

where K is the Fikentschen K value of the polymer. The glass-transition temperature of PVP is 175 $^{\circ}$ C,

(ii) Hygroscopicity

The amount of water absorbed is nearly independent of the molecular weight of PVP. The equilibrium water content varies with the ambient relative humidity. Approximately 0.5 mol of water is associated with one monomer unit of PVP.

(iii) Molecular weight

PVP can be prepared in a variety of molecular weights, depending on the conditions of polymerization. The hydrogen peroxide-ammonia process gives a molecular weight range of 2500 to about 1.1×10^6 . The molecular weight range of commercial products are 2500 - 7×10^5 .

(iv) Rheology

It is very difficult to handle melt PVP, the rheology of PVP is investigated in the aqueous media, viscosities can be determined in a variety of solvents, but because of the polar nature of the polymer, measurements are

most conveniently made in water or methanol. From Mark-Houwink equation:

$$\begin{aligned} [\eta]_{\text{CH}_3\text{OH}} &= 2.3 \times 10^{-2} \times M_w^{0.65} \\ [\eta]_{\text{H}_2\text{O}} &= 5.65 \times 10^{-2} \times M_w^{0.55} \end{aligned}$$

This results indicate that methanol is a better solvent than water for PVP.

(v) Solubility

PVP consists of hydrophobic methylene groups and a strongly hydrophilic inside group. As a consequence of the hydrophobic-hydrophilic balance, the polymer is soluble in a variety of organic solvents as well as water. The solid or powder PVP is hygroscopic and quite stable when stored under ordinary conditions.

(vi) Compatibility

PVP is compatible in solutions and in films cast from the solutions with a wide variety of synthetic resins.

(vii) Health hazard

The acute oral lethal dose (LD.) of molecular weight 35000-40000 PVP K-30 is reported to be > 100 g/kg. It is not a skin or eye irritant, or a skin sensitizer. Toleration of PVP K-30 is good by intraperitoneal, intramuscular, and intravenous routes.

(b) Chemical properties

In accordance with the characteristics of vinylpyrrolidone, PVP is chemically inert. The dry polymer can be stored under normal conditions without decomposition, degradation, or structural change. Its heat sensitivity is low, and it is stable at 130°C for short intervals. However, at 150°C in air, solubility is

reduced and colour increased and after an extended period of time, the polymer becomes insoluble.

(c) Complexation

The individual unit in the PVP chain, consisting of the polar imide group, four nonpolar methylene groups, and a methene group, has an amphiphilic character. The dipole moment of this unit must be close to that of its small-molecule analogue, the N-methyl-2-pyrrolidone: $\mu = 13.5 \times 10^{-30}$ cm.

Because of its unique structure, the exposed cyclic imide group and the balance of hydrophilic-hydrophobic segments, PVP forms complexes with a variety of compounds. The hydrophobic character is attributed to the methylene groups in the ring and the linear aliphatic backbone, whereas the hydrophilicity is the result of the polar lactam moiety of the pyrrolidone ring. The complexes are usually formed through hydrogen bonding to which the pyrrolidone structure is highly susceptible. However, in certain cases other forces, such as hydrophobic attraction, van der Waals forces, dipole forces, Debye forces, dispersion forces, ion-dipole forces, and charge transfer interactions may also be responsible for the strong complexing ability of PVP.

(d) Cross-linking

Lightly cross-linked PVP can be prepared by treatment of linear PVP with persulfates, hydrazine and hydroperoxide. Heavily cross-linked polymers can be made by treating vinylpyrrolidone above 100°C with an alkali metal hydroxide and

a small amount of water.

1.3.2 APPLICATION OF PVP

Because of its unique physical and chemical properties, particularly its good solubility in water and organic solvents, its outstanding chemical stability, its strong complexing ability toward both hydrophobic and hydrophilic substances, PVP is one of the most widely used specialty polymers.

PVP has a wide variety of application in the industries. Its film-forming and adhesive properties are utilized in hair sprays, adhesives and photographic and lithographic coatings. As a protective colloid, it is used in drug and detergent formulations, emulsions and suspensions, and in pigment and dyestuff dispersions.

Its complexing ability is utilized in the textile industry for improving dye ability and dye stripping, in the pharmaceutical industry and agriculture for drug dissolution and sustained release of drugs and chemicals, and the food industry for the clarification of beer and wine⁴.

PVP finds excellent use in life-saving substances such as blood-plasma. An appropriate solution with a concentration of 3.5% of the PVP can be used as a substitute for blood plasma. This solution is very stable over a long period of time and can be given to patients, irrespective of their blood groups⁵.

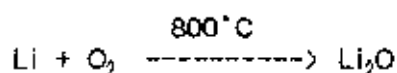
1.4 LITHIUM AND LITHIUM OXIDE (Li_2O)

The group I metals are extremely reactive and electropositive and exist in combination with other elements or radicals as positive ions (Li^+ Cl^-); they are therefore never found in the free state in nature. They all adopt the body centered cubic structure in which each atom is surrounded by eight nearest neighbours with six more atoms only slightly further distant. Among the metals lithium is a chemical element of atomic number 3 and atomic weight 6.939. In nature it is a mixture of the isotopes Li^6 and Li^7 . Lithium, the lightest solid element, is a soft, low-melting, reactive metal. Although all metal atoms have one electron in the outer shell preceded by a closed shell containing eight electrons but lithium has a closed shell of two. In chemical combination this single electron is very readily transferred, giving a unipositive metal ion with the stable electronic configuration of a noble gas.

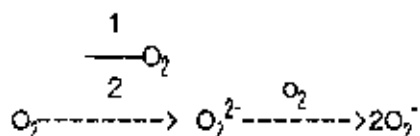
Lithium, because of the small size of its atom and unipositive ion, tends to form compounds in which there is some degree of covalent character. Lithium undergoes a large number of reactions with both organic and inorganic reagents. Lithium only forms the monoxide (Li^+)₂ O^{2-} when heated in oxygen. The lithium ion, by virtue of its small size is not able to surround itself by sufficient peroxide ions to give a stable crystal lattice and only the monoxide exists.

Lithium oxide, Li_2O , can be prepared by heating pure lithium hydroxide to about 800°C in vacuum; however, a more convenient method is thermal decomposition

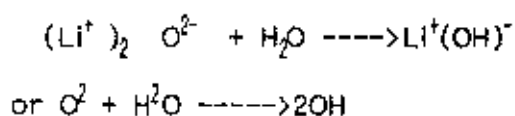
of lithium peroxide (Li_2O_2).



Three oxide ions are related as follows:



All three oxide ions are unstable in the presence of water. e.g.



The above reaction involve the abstraction of protons from water molecules; the oxide ions thus function as strong bases.

1.4.1 PHYSICAL PROPERTIES

Lithium is a colorless or silvery white. It is extremely good conductors of heat and electricity. It is harder than sodium but is extremely light. Its density which is 0.534 at 20°C is the lowest of all the metals. When volatilized, it imparts a red colour to the flame. It forms an amalgam and alloys with a number of other metals.

1.4.2 CHEMICAL PROPERTIES

Lithium has some chemical behavior that resembles the chemistry of Mg. Anomalous properties of Li^+ results mainly from the small size of the atom and the ion; the polarization power of Li^+ is the greatest of all the alkali metal ions and

leads to a singularly great tendency toward solvation and covalent bond formation. The ionic radii of Li^+ and Mg^{+2} are quite nearly the same (0.60 - 0.65Å)⁸.

The reactivity of the group I metals toward all chemical reagents except nitrogen increases with increasing electropositive nature (Li-C_s). Lithium is usually the least reactive. It is only rather slowly attacked by water at 25°C.

1.4.3 APPLICATION

The most important application of lithium and its compounds are given below:

Lithium is mostly used in the manufacture of alloys. It is added to the alloys of magnesium to improve their tensile strength and resistance to corrosion. A lead-lithium alloy is used for making bearings and shafts of electric cables.

Lithium compounds are employed to increase the fluidity of glass. Its carbonate is employed to increase the strength and resistance of glass. Lithium oxide is used in the manufacture of salts. But the salts of lithium are used in ceramics to prevent surface cracking of pottery. Its compounds have also been used in the synthesis of vitamin A and some other pharmaceuticals.

Its hydroxide is used in the manufacture of high quality lubricating greases which can withstand extreme variations of temperature.

1.5 OBJECTIVES OF THE PRESENT WORK

There is a widespread interest in polymer complexes in order to innovate advanced materials with improved properties. The interest has grown in the area

of electrical and other physico-chemical applications where the high resistivity, high dielectric breakdown strength, cost and other aspects have been of prime importance.

The aromatic polyimide polyvinylpyrrolidone (PVP) are very important of the moderate high temperature plastics and the complexes with Lithium Oxide (Li_2O) will be studied with the following objectives:

- i) The structural modifications of the PVP with different concentration of Lithium Oxide will be investigated using different techniques, e.g. XRD, IR, surface microscopy, DTA/TGA etc
- ii) Optical absorption measurements (UV-VIS) will be carried out to observe the excitation states.
- iii) The d.c. electrical properties of the sample such as current voltage (I-V) characteristics, variation of d.c. conductivity with temperature of the PVP and its complex with lithium oxide will be studied.
- iv) From the above investigations, an attempt will be made to understand the physical processes underlying in this material.

CHAPTER 2

THEORY AND LITERATURE SURVEY

2.1 X-RAY DIFFRACTION (XRD)

X-ray diffraction is a tool for the investigation of the fine structure of matter. This technique had its beginning with Von Laue's discovery in 1912 that crystals diffract x-rays, revealing the structure of a crystal. At first, x-ray diffraction was used only for the determination of crystal structure. Later on, however, other uses were developed and today the method is applied not only to structure determination, but to such diverse problems as chemical analysis and stress measurement, to the study of phase equilibria and the measurement of particle size, to the determination of the orientation of the crystal or the ensemble of orientations in a polycrystalline aggregate.

2.1.1 Qualitative Analysis

The powder pattern of a substance is characteristic of that substance and that forms a sort of fingerprint by which the substance may be identified. If there is a collection of diffraction patterns for a great many substances, one could identify an unknown by preparing its diffraction pattern and then locating the file of known patterns one which matched the pattern of the unknown exactly. The collection of known patterns has to be fairly large, if it is to be at all useful, and then pattern-by-pattern comparison in order to find a matching one becomes out of the question.

2.1.2 Procedure

After the pattern of the unknown is prepared, the plane spacing 'd' corresponding to each line on the pattern is calculated, or obtained from tables which give d as a function of 2θ for various characteristic wavelengths. Alternatively a scale may be constructed which gives d directly as a function of line position when laid on the film or diffractometer chart; the accuracy obtainable by such a scale, although not very high, is generally sufficient for identification purposes. If the diffraction pattern has been obtained on film, the relative intensities are usually estimated by eye, on a scale running from 100 for the strongest line down to 10 or 5 for the weakest. On a diffractometer recording the intensity is taken as the maximum intensity measured above background. After the experimental values of d and I/I₁ are tabulated, the unknown can be identified by the following procedure¹:

1. To locate the proper d_1 group in the numerical search manual.
2. To read down the second column of d values to find the closest match to d_2 . (In comparing experimental and tabulated d values it is always allowed for the possibility that either set of values may be in error by $\pm 0.01\text{\AA}$.)
3. Later the closest match has been found for d_1 , d_2 and d_3 to compare their relative intensities with the tabulated values.
4. When good agreement has been found for the lines listed in the search manual, locate the proper data card in the file, and compare the d and I/I₁ values of all the observed lines with those tabulated. When full agreement is obtained, identification is complete.

2.2 POLARIZING MICROSCOPY

The polarized-light microscopy provides a powerful tool to study the optical properties of transparent, translucent and opaque materials by using the polarized light. Polarized light technique, in recent years, has wide application in research and industrial technology.

The polarizing microscope is essentially an ordinary compound microscope, with the difference that it has a revolving, graduated circular stage, a polarizing device below the stage, called the polarizer (upper polar) and a similar device above the objective, called the analyser (lower polar).

Each polar transmits light wave vibrating in one direction only and for most purposes the polars are oriented so that their planes of vibration are mutually perpendicular or parallel.

The incident light passes through the polaroid disc, the polarizer, and is thus constrained to vibrate in one plane only. The polarizer can be rotated in its own plane and a second polaroid disc, the analyzer, is mounted in the body tube of the instrument. The analyser can be rotated or withdrawn from the field of view to enable a sample to be viewed in unpolarized light. When both the polarizer and analyser are in the "crossed position", and they will not permit light to reach the eye piece so long as the medium between them is entirely isotropic. This is because light emerging from the polarizer is completely extinguished by the analyser according to the principle of Malus in optics.

There is a compensator or tint plate, inserted in the body tube of the instrument. The tint plate made of gypsum plate (also called first-order red plate) is placed at an angle of 45° to the vibration planes of the polarizer and the analyser when they are in the crossed position.

The condensing lens system is situated between the rotating stage and the polarizer. Its primary function, as in the compound microscope, is to bring the incident light to a focus in the plane of the specimen.

The eye piece lens system, fitted to the microscope body is of the binocular type, having a X10 magnification. This together with the different objectives produces and overall magnification ranging from X25 - X1000.

The illumination of the microscope is provided with $6V$, $15W$ low-voltage halogen bulb. The bulb is contained in a well ventilated housing with a circular opening for the emission of light.

2.2.1 Modes of Observation in a Polarizing Microscope

Two modes of observations are available in a polarizing microscope: orthoscopic and conosopic.

a) Orthoscopic arrangement

A microscopic arrangement is said to be orthoscopic when a beam of parallel light rays are made to fall on the specimen crystal normally and all of them travel along the same crystallographic direction within the

crystal. In this type of observation there are three combinations of polarizer and analyser that enable three different sets of observations and measurements to be made.

In accordance with their behaviour between crossed polars, all non-opaque substances can be divided into two groups, namely, isotropic and anisotropic substances. The former remains dark, like the rest of the field of the microscope whatever be their orientations. On the other hand, anisotropic substances will appear coloured on rotation in most orientations and only in certain definite positions will become dark.

b) Conoscopic arrangement

The conoscopic arrangement requires, in addition to the polarizer and analyser, the insertion of an Amici-Bertrand lens and a substage condensing lens. The former converts the microscope into a low-power telescope focussed at infinity. The latter causes the object on the stage to be illuminated by a cone of light rather than by a bundle of near-parallel rays as it is with orthoscopic case. Important additional information may be obtained by passing a strongly convergent beam of light through the crystal when it is possible, by various means, to examine the optical characters in many directions at once at the same time. This is done by viewing between crossed polars, not the image of the crystal, but another optical image formed in the principal focus of the objective by the strongly convergent beams of light. This image is called the interference figure. Each point in the field corresponds to a given direction through the crystal. In effect, the Bertrand lens and the eye piece constitute a system used to examine the pattern in the back focal plane in the objective.

2.3 THERMAL ANALYSIS

2.3.1 Differential Thermal Analysis (DTA)

DTA technique is an important tool to study the structural and phase changes occurring both in solid and in liquid materials during heat treatment. These changes may be due to dehydration, transition from one crystalline structure to another, destruction of crystalline structure, oxidation, decomposition etc. The principle of DTA consists of measuring the heat changes associated with the physical or chemical changes take place when any substance is gradually heated¹.

2.3.2 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) involves the determination of weight loss from a samples as a function of time or temperature [$m = f(t \text{ or } T)$] while a sample is heated or cooled at a constant rate. This technique is effective for quantitative analysis of thermal reactions that are accompanied by mass changes due to release of volatile matter, evaporation, decomposition, gas absorption, desorption and dehydration.

The rate of decomposition varies with the heating rate. A maximum decomposition rate occurs at a higher temperature.

2.4 SPECTROSCOPIC ANALYSIS

2.4.1 Ultra-violet and Visible (UV-VIS) Spectroscopy

A display or graph of the intensity of ultraviolet-visible (UV-VIS) radiation emitted or absorbed by a material as a function of wavelength ranging from 100-400-800 nm is called UV-VIS spectrum and the absorption spectroscopy involving electromagnetic wavelengths in the range 100-400-800 nm is called UV-VIS spectroscopy⁹.

The intensity of the emitted light decreases exponentially as the thickness and concentration of the absorbing medium increase arithmetically. The statement can be expressed mathematically as:

$$\log_{10} \frac{I_0}{I_t} = \epsilon Cl$$

where, I_0 and I_t are the intensities of the incident and transmitted light respectively, l is the path length of the absorbing solutions in centimeters and c is the concentration in moles/litre. $\log_{10} I_0/I_t$ is called the absorbance or optical density, ϵ is known as the molar extinction coefficient and has units of 1000 cm^2/mole but the units are by convention, never expressed. The above equation is the fundamental equation of spectrophotometry, and is often spoken of as the Beer-Lambert law¹⁰.

In the visible and UV region, the outer-shell electrons are absorbed because they are loosely bound to the nuclear. This electron excitation is coupled with vibrations which can be observed in the IR and Raman spectra. The typical absorption spectrum in this region thus consists of several bands; there either

demonstrate a vibrational structure or appear as broadened humps due to unresolved vibrations¹¹. The identity of a synthetic product can be generally established by comparison of its spectrum with that of the natural product or another standard sample. 6 Most measurement of UV/VIS are made in solution and sometimes on the transparent film of the most important region where most investigations have been carried out, namely between 200 and 600 nm, there occurs electronic transitions of double bonds (e.g. carbonyl group at 280 nm). Whereas pure non-aromatic polymers does not show any specific absorption in the near UV and usually none in the visible region either, in the aromatic polymers (e.g. polystyrene), the basic unit becomes excited in the near UV. In many cases, absorbing groups are formed first by partial degradation or oxidation during the production or processing of the polymer. For example the conjugate double bonds in PVC which arise as a result of HCl elimination or carbonyl groups in polyolefine which are formed by thermo-or photo-oxidation.

2.4.2 Infrared (IR) Spectroscopy

Infrared spectroscopic study provides valuable information concerning the nature of different bonds and variation in the interaction among different elements. It is applicable to characterize both the organic and inorganic materials.

Band positions in infrared spectra are presented either as wave numbers or wavelengths. The wave number unit (cm^{-1}) is used most often since it is directly proportional to the energy of the vibration of molecules. Band intensities are expressed either as transmittance(T) or absorbance(A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm, to the base 10, of the reciprocal of the

transmittance, i.e., $A = \log_{10} (1/T)$. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms.

Two important techniques have been developed for the infrared examination of different materials. One of these is the thin-section technique, and the second method is the suspension technique or nujol technique.

The advantage of the potassium bromide technique over the other technique is that potassium bromide does not produce specific absorption bands in the region 2.5 - 15 μm . Moreover, the KBr tablets are stable.

2.5 D.C. CONDUCTIVITY

Electrical conduction is the transport of charge carriers through a medium under the influence of an electric field. The rate at which an element of charge dQ is transported over an area A in a time dt is given by the current, $I = dQ/dt = nqV_0A$, where n is the number density of charge carriers, q is the charge per carrier, and V_0 is the drift velocity of the charge carriers. If we assume that the drift velocity under an applied field is proportional to the applied field, i.e., $V_0 = \mu E$ and $i = nq\mu EA$, where $\mu(\text{m}^2\text{V}^{-1})$ is the drift mobility and $E(\text{V m}^{-1})$ is the applied field. The conductivity ($\text{Ohm}^{-1}\text{m}^{-1}$) defined by $\sigma = id/VA$, where d is the sample thickness in m , A is area in m^2 and V the applied voltage. Assuming the electric field E to be uniform across the medium, i.e., $E = V/d$,

$$\sigma = qn\mu \dots \dots \dots (2.1)$$

If there is more than one type of charge carrier the conductivity is

$$\sigma = \sum_i q_i n_i \mu_i \dots \dots \dots (2.2)$$

In any particular system the number and mobility of the charge carriers will depend upon the material and the experimental parameters of voltage, temperature and ambient atmosphere. If the material is crystalline or oriented, the conductivity will depend on the direction with respect to some molecular axis in which the measurement is made. These dependences can be expressed by writing:

$$n = n(T,V);$$

$$\mu = \mu(T,V,Z); \text{ and } \sigma = \sigma(T,V,Z)$$

where T represents temperature, V the applied potential, and Z the direction in which the measurement is being made.

Phenomenologically, the conductivity is obtained by measuring the current flowing through a piece of the material and using the sample dimensions to calculate σ from the equation:

$$\sigma = \frac{d}{AV} i \dots \dots \dots (2.3)$$

where d(m) is the sample thickness, A its area (m²), and V the potential across the material in volts.

The usual type of electrical measurement has involved measuring the current as a function of potential, temperature and in some cases ambient atmosphere. The conductivity and its changes with voltage, ambient atmosphere and temperature are then related to the physical processes thought to be occurring in the material. Frequently, it is found that the conductivity varies exponentially with

temperature T according to the equation

$$\sigma = \sigma_0 \exp(-E_r/kT) \dots \dots \dots (2.4)$$

where k is the Boltzmann constant and E_r the activation energy.

The resistivity is the reciprocal of conductivity. Therefore,

$$\rho = \frac{1}{\sigma} = \rho_0 \exp (E_r/kT)$$

The activation energy E_r can readily be evaluated from the slope of the linear $\ln \sigma$ vs. $1/T$ plot, which describes the nature and types of carrier involved in the conduction process.

2.5.1 Electrical conduction mechanism in solids

Electrical conduction in insulating solids may occur through the movement of either electrons or ions. There may be contribution to the conductivity from several different types of carriers, notably electrons and holes in electronic conduction and cation and anion pairs in ion conduction. In most of the insulating materials, it is very difficult to observe any electronic conductivity and whatever conductivity there is, it usually depends on the movement of adventitious ions. Therefore (a) ionic conductivity and (b) electronic conductivity are all improved in their own way in insulating solids. Again, the electronic conductivity may be of (i) band conduction and (ii) hopping (tunnelling) conduction within localized levels in the forbidden gap.

(a) Ionic conduction

In bulk material ionic conduction occurs due to the drift of defect under the influence of an applied electric field. The degrees of ionic impurities which may be totally ignored in the context of other properties may have a significant effect on conductivity. A theoretical expression may be derived, for the current density, flowing through a sample, on the basis of a simple model and is given by

$$j \propto \sinh (eaE/2kT) \dots\dots\dots (2.5)$$

where E is the electric field and "a" is the distance between neighbouring potential wells.

(b) Electronic conduction

(i) Band conduction

Electronic conduction in insulating solids may differ in several important ways from the more familiar kind in metals and inorganic semiconductors. That is not to say that they are separate subjects and indeed, the well-known band theory of atomic lattice has provided the essential basis of concepts for the discussion of conduction in solids, as in polymers.

In crystalline solid like silicon, where many atoms strongly interact, splittings of energy levels occur. Sets of energy levels form two continuous energy bands, called the valence band and the conduction band.

(ii) Hopping conduction

Disorder in a lattice affects both the energetic and spatial distribution of electronic states. For a random distribution of atoms the density of

electronic energy states tails into what is normally the forbidden zone and the electrons in these tails are localized. When the electrons are excited to higher energy, conduction via localized electron implies discrete jumps across an energy barrier from one site to the next as shown in fig. 2.1. An electron may either "hop" over or "tunnel" through the top of the barrier; the relative importance of these two mechanism depending on the shape of the barrier and the availability of the thermal energy. For variable range hopping the electrical conductivity is given by

$$\sigma = \sigma_0 \exp - (T_0/T)^{1/(d+1)} \dots \dots \dots (2.6)$$

where "d" is the dimensionality of transport (e.g. d = 3 for three-dimensional motion etc).

σ = conductivity,

σ_0 = initial value of conductivity,

T = absolute temperature and

T_0 = activation energy in terms of temperature.

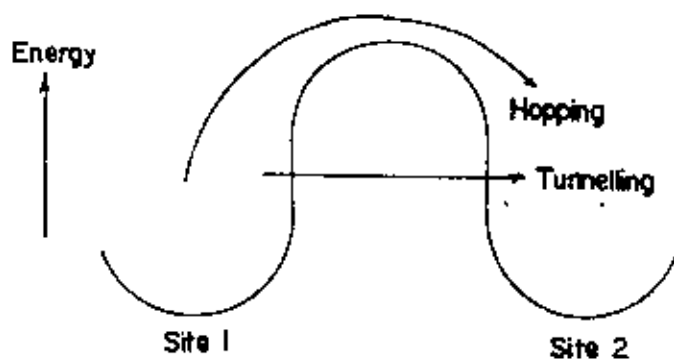


Fig. 2.1: Diagram of electron-transfer mechanisms between adjacent sites separated by a potential-energy barrier.

2.6 LITERATURE SURVEY

During the last few years studies have been done on the structural electrical, optical and mechanical properties of complex of polyvinylpyrrolidone with different polymers and other materials. Here, in this section, a survey on the reported works on PVP and their complex with other polymers are given.

L.L. Dubey et al¹² have studied the spontaneous current emission(SCE) from pure and iodine doped polyvinylpyrrolidone. They investigated the spontaneous emission of current from metal(1) polyvinylpyrrolidone/metal(2) and metal(1) polyvinylpyrrolidone + iodine/metal(2) system. The SCE variations were recorded in pure and iodine doped PVP samples from room temperature to just below the softening temperature of the polymer. The maximum value of SCE during the first run was found to be of the order of 10^{-7} to 10^{-6} amperes for pure and iodine doped samples. The SCE of pure and iodine doped PVP sample has found with two well resolved peaks in two distinct temperature region (i.e. $81 \pm 7^\circ\text{C}$ and $150 \pm 3^\circ\text{C}$). These peaks confirmed the transition of β and α . The active centers of PVP has found as carbonyl group of double bond and tertiary nitrogen atom ($>\text{N}-\text{C}=\text{O}$) and thus the charge transfer complexes are formed with the different concentrations of iodine in the polymers films and in pure PVP samples the SCE has been observed due to weak complex formation with the water molecules and the liberation of different types of charges. This process was highly influenced by the transitional charges of the polymer. In their investigation of PVP samples it was observed that the direction of SCE depends upon the choice of both the electrode materials (upper and lower) Radhakrishnan et al¹³ have observed that, if the electrode materials were of dissimilar metals, the magnitude of short circuit current was much higher in comparison to similar electrode materials.

The β relaxation processes of PVP may possible at the lower temperature $80(\pm 5)^{\circ}\text{C}$, which may be due to disorientation of polar side groups in the presence of water traces. Bublevskii et al¹⁴ have observed a weak complex formation between carbonyl group of double bond of PVP and OH group of phenol. In the similar manner, there may be the possibility of a weak complex formation between dissociated OH^- ion of water and active carbonyl group.

According to Chaterjee et al¹⁵ the active groups of PVP were carbonyl or tertiary nitrogen atom which was also attached to the main chain of the polymer structures. On the other side, the hygroscopic nature of PVP was some what similar to protein like network structure, (C,N,H and O) also supports the mechanism of a weak complex formation with H_2O . A process of self ionization may be possible with a stereo change in the structure near T_g of PVP due to these active groups ($>\text{N}-\text{C}=\text{O}$).

P. K. Khare, et al¹⁶ have studied the polarization and depolarization properties in polymethyl methacrylate: PVP polyblend films. Thermally stimulated discharge current (TSDC) spectra of polymethyl methacrylate (PMMA) and PVP films and of their blend films of identical thickness have been studied as a function of polarizing field. TSDC of PMMA yielded current maximum around 90°C and 150°C . But for PVP the maxima occurred around 105°C and 155°C . TSDC thermograms of their polymer blends, however, exhibit single peak around 100°C which shift toward higher temperature on increasing the proportion of PVP. The occurrence of simple peak and enhancement of peak current for polymer blends have been explained on the basis of induced dipoles created because of the piling up of charge carriers at the phase boundary of heterogeneous structure of blend and increase in mobility of charge carriers due to plasticisation effect.

CHAPTER 3
EXPERIMENTAL DETAILS

CHAPTER 3 EXPERIMENTAL DETAILS

3.1 MATERIALS USED IN THIS WORK

Complex used in this work were prepared from polyvinylpyrrolidone (PVP) and lithium oxide (Li_2O). Water is the common solvent for both the component. Complex were prepared in different proportions. Details of the origin and the physical properties of PVP and Li_2O are given below:

(a) Polyvinylpyrrolidone (PVP)

PVP was obtained from GAF chemicals corporation, U.S.A and BASF of FRG, which was in the form of powder. In this work we used the commercial grade PVP supplied by BASF, Germany.

i)	Weight average molecular weight (M_w) :	35000-40000 g/mol
ii)	Melting temperature T_m :	225°C
iii)	Glass transition temperature T_g :	164°C
iv)	Density :	1.25 gm/c.c.

(b) Lithium Oxide (Li_2O)

Here, we used Li_2O of Junsci Chemical Co. Ltd., China.

(c) Solvents

In this work, for the preparation of the complex, distilled water is used as a solvent. Both PVP and Li_2O are dissolved in the distilled water.

3.2 PREPARATION OF THE DIFFERENT COMPLEXES OF PVP AND Li_2O

For different measurement five different complexes were prepared having different compositions of Li_2O and PVP. The samples were prepared in the following way.

At first, five different compositions were made with 0.5, 1, 2.5, 5 and 10% Li_2O by weight in PVP. The weight of the PVP and Li_2O was taken very accurately by an electronic digital microbalance (Model -A200S, Sartorius analytic, Germany). The mixtures were then put into separate test tubes. The mixtures of PVP and Li_2O were dissolved in 15 c.c. distilled water and were kept for about one hour to dissolve completely. When the solutes were uniformly dissolved in the solvent, the solutions were poured onto clean glass-slides. They were then kept for 24 hours under a fan to evaporate out the water leaving behind films on the glass slides. They were then put inside an oven at about 40°C for 24 hours to remove the traces of the solvent. To protect the samples from any kind of surface cracking they were taken out from the oven after cooled down to room temperature.

3.2.1 SAMPLES FOR DIFFERENT MEASUREMENTS

For the x-ray and electrical measurements, the films were peeled off from the glass slides and then were kept inside a desiccator to protect them from moisture.

For optical microphotographic studies, the raw sample (film) and the sample heated at 100°C were used.

For UV-VIS measurement, the thin films on to glass slides were used.

For DTA/TGA measurements, powder form samples were used.

For IR, free mounted film samples were used.

3.3 ELECTRODE DEPOSITION

These samples were stored in a dessicator for one week. Then silver dag (Ledinings silver D200, DEMETRON, Germany) was applied to each of the flat circular surface as shown in figure 3.1. The area of the electrode was about $6.13 \times 10^{-5} \text{ m}^2$. The silver dag coated areas on both the surfaces of a sample were equal. Here silver dag acts as conducting metallic coating. These coatings served as electrodes for electrical measurements.

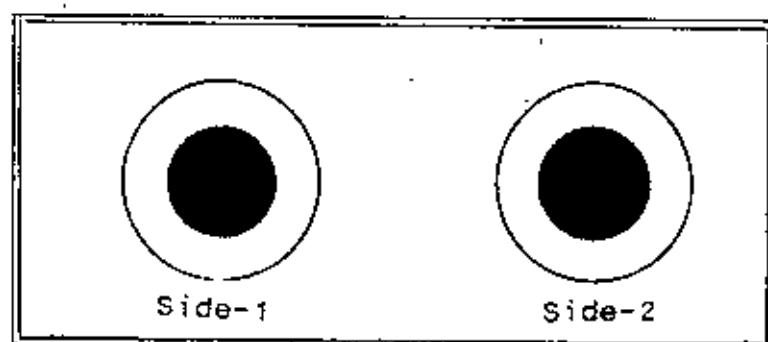


Figure 3.1 : The Specimen

3.4 X-RAY DIFFRACTION (XRD)

X-ray powder diffraction was carried out using a two circle diffractometer with Cu(K α) radiation at 30 mA/35KV. PVP and its complexes were taken as thin film on a glass substrate in an area of 1x1.5 cm² X-ray diffractometer (model JDX-8P) of JEOL LTD., Tokyo, Japan is used in this study. Target is CuK α and the wavelength of x-ray radiation is 1.5418 Å.

3.4.1 X-RAY INVESTIGATION OF THE SAMPLES

3.4.1.1 Working procedure for taking XRD pattern

The powder form of pure PVP and Li₂O and thin films of PVP with different concentration of Li₂O were taken for recording the diffractograms of different samples. The diffractograms of different types of samples were recorded using the above mentioned diffractometer in the Department of Metallurgy, Bangladesh University of Engineering and Technology, Dhaka. Seven XRD patterns were collected for samples; pure PVP, PVP complexes containing 0.5, 1, 2.5, 5 and 10% Li₂O by weight and pure Li₂O represented respectively by A,B, C, D, E, F and G.

3.4.3 Calculation of interplanar spacing, d_{hkl}

The Bragg equation for the first order diffraction is written as:

$$d_{hkl} = \frac{\lambda}{2\sin\theta}$$

where, d_{hkl} is the interplanar spacing

θ is the angle of diffraction

λ is the wavelength of the x-ray radiation used for diffraction (i.e., $\lambda = 1.5418$ Å).

3.5 POLARIZING MICROSCOPY

3.5.1 Polarizing Microscope

In this study, a Reichert Metavert reflected polarized light microscope of C. Reichert Optische Werke A. G., Austria is used. The eye piece lens system, fitted to the microscope body, is of the binocular type having a 10X magnification. This together with the different objectives produces an overall magnification ranging from 25X - 1000X. The illumination of the microscope is provided with a 6V, 15W low-voltage halogen bulb. The bulb is contained in a well ventilated housing with a circular opening for the emission of light. The photograph of the microscope is shown in fig. 3.2

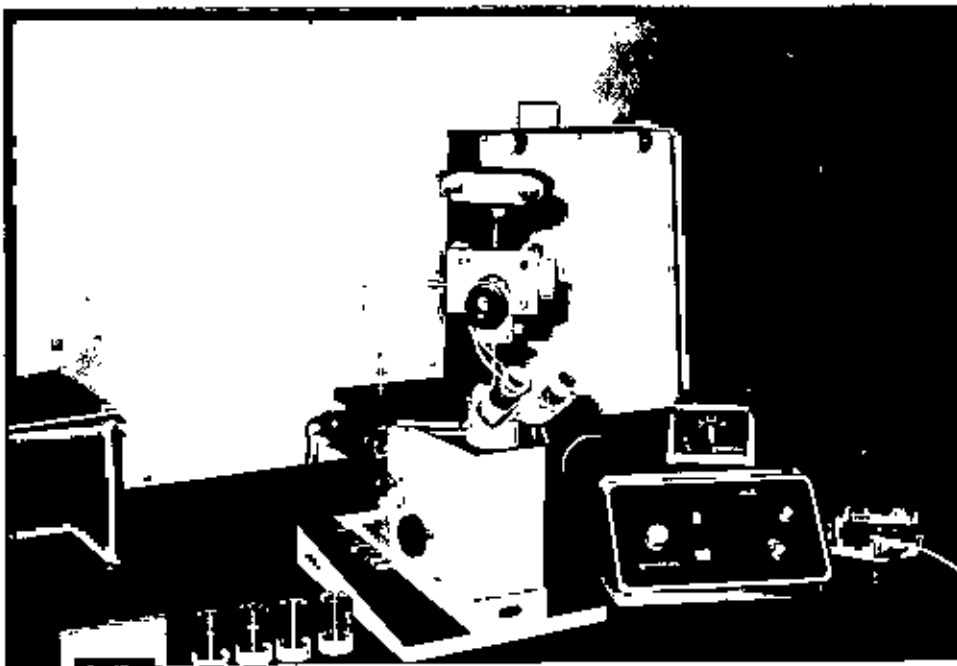


Fig. 3.2 : The Reichert Metavert reflected polarized light microscope.

3.5.2 PROCEDURE

The samples, as prepared and heat treated of 10°C, are placed on the stage of the microscope. In the surface microscopy the pellet is placed horizontally on the stage so that the reflected polarized light from the pellet surface can enter into the objective.

Fuji color film is used in this study. An automatic exposure time is programmed for the intensity of the reflected light. Exposure time is varied by using the various speed of films. Different areas are chosen to see the variation of the surface quality.

3.6 THERMAL ANALYSIS

3.6.1 Differential Thermal Analysis (DTA)

The technique of differential thermal analysis (DTA) is an important tool to study the structural changes occurring both in solid and liquid materials under heat treatment. These changes may be due to dehydration, transition from one crystalline variety to another, destruction of crystalline lattice, oxidation, decomposition etc. The principle of DTA consists of measuring the heat changes associated with the physical or chemical changes occurring when any substance is gradually heated.

3.6.2 Working principle of DTA

When a sample and a standard inert reference material (e.g., Aluminum oxide, Al_2O_3) are heated or cooled at a constant rate at the same environment, their temperature differences are measured as a function of time or temperature (as

shown by the curve in fig. 4.4 (Chap-4). The temperature of the reference material, which is thermally inactive, rises uniformly when heated. While the temperature of the sample stops rising then an endothermic reaction (e.g., fusion) occurs, because the heat supplied from outside is consumed by the reaction or varies differentially due to evolution of heat during phase transitions or chemical reactions. And when the reaction is over, the sample temperature is much different from that of the ambient, and then the rate of increase of the sample temperature changes rapidly to catch the rate of rise of reference material temperature. The temperature difference ΔT is detected, amplified and recorded. The exothermic and endothermic reactions are generally shown in the DTA trace as positive and negative deviations respectively from a base line. So, DTA gives a continuous thermal record of reactions occurring in a sample.

The temperature at the sample holder is measured by a thermocouple, the signal of which is compensated for the ambient temperature and fed to the temperature controller. This signal is compared with the program signal and the voltage applied to the furnace is adjusted. Thus the sample and reference materials are heated or cooled at a desired rate. The temperature in the sample holder is digitally displayed and is recorded on the recorder.

3.6.3 DTA apparatus

DTA apparatus consists of a thin wall refractory specimen holder made of centered alumina with two adjacent cubical compartments of exactly the same size 0.01 m in length, one for the reference (inert) material and the other for the test material. The specimen holder is placed in the cavity of the heating block, which is made of fine grained refractory cement. This block is heated with a uniform

heating rate using an electric furnace (9"x6"x9" deep). The input of current into the furnace is secured through the secondary of a variac transformer, which controls the current. Fine chromel-alumel wires (28 gauge) are used for thermocouples. A cold junction is used for thermocouples leads and the e.m.f. is recorded almost continuously, while the temperature of the inert material is measured at 3 minutes interval. It is essential to use perfectly dry materials as otherwise errors will be introduced in the analysis. Approximately 0.1 g anhydrous alumina is used in the reference cup and the sample weights varies over a range 0.05 g to 0.125 g, depending on their packed density. A heating rate of 10 K per minute (average) of the furnace is conveniently kept, and this gives satisfactory results in most cases. A block diagram of DTA apparatus is shown in figures 3.3 and 3.4

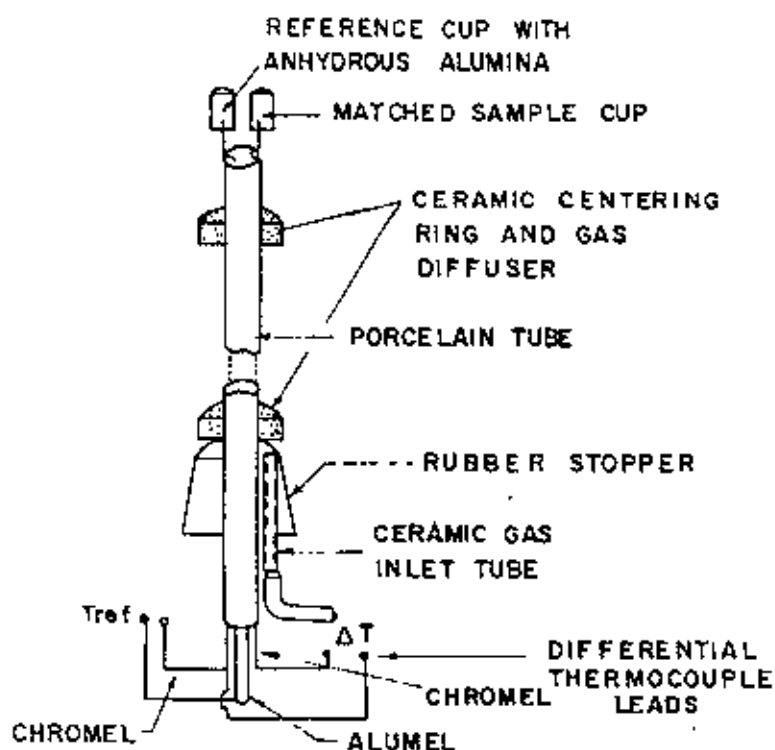


Fig 3.3 : DTA thermocouple assembly

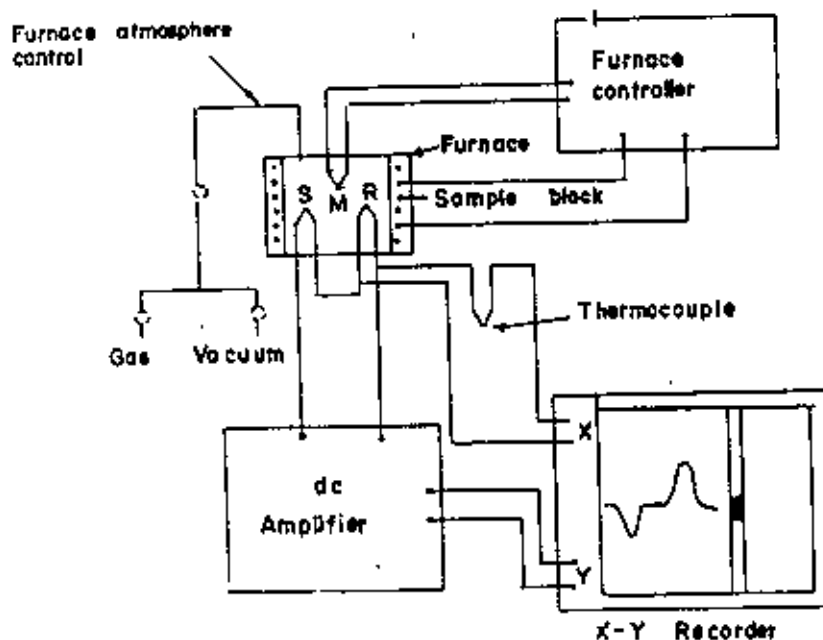


Fig 3.4: Block diagram of a differential thermal analysis equipment, (S) sample thermocouple, (R) reference thermocouple, (M) monitor thermocouple

The thermal analysis runs generally for 1 to 1.5 hours. Thermal analysis curves are obtained by plotting heating temperature and the difference between the temperatures of the test and the reference materials. From these traces the reaction temperature could be determined.

Melting and boiling points are indicated usually by a sharp endothermic peak. The temperatures of sublimation and decomposition were similarly given by exothermic peaks and in some cases, typical exothermic curves afforded useful information about the structural changes taking place in the material.

All experiments are run at atmospheric pressure in a continuous flow of purified inert gas. Gases are normally purged into the furnace chamber at the lower end

through a purification train in which oxygen and water are removed by heated copper wool and exhausted from the top into a condensate trap for collecting the condensable volatile products.

DTA AND TGA APPARATUS

All DTA and TGA scans were carried out from 30–900°C under argon gas flow at the heating rate of 10°C/min. DTA was performed using Shimadzu micro DTA system model DT-50. Mettler M3 balance TG 50 furnace and microprocessor TA-3000 system were used for TG analysis.

3.6.4 ^{or} Thermogravimetric Analysis(TGA)

About 10mg moisture free sample was taken initially in a platinum crucible. Thermogravimetric investigations were carried out here by determining the rate of loss in weight (%) as a function of temperature at constant heating rate.

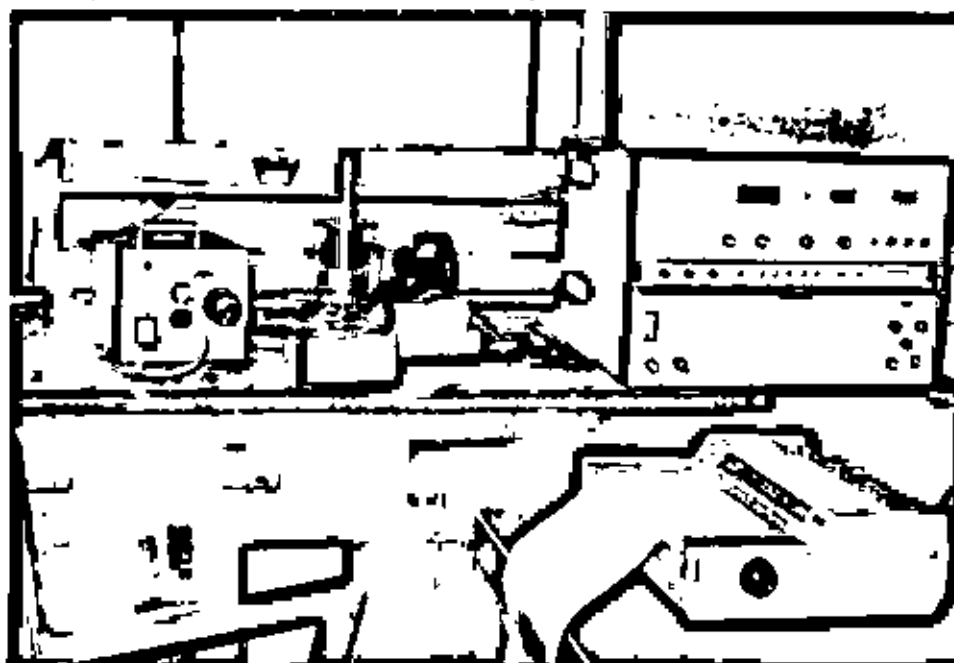


Fig. 3.5 : DTA & TGA apparatus

3.7 SPECTROSCOPY

3.7.1 ULTRAVIOLET-VISIBLE (UV-VIS) SPECTROSCOPY

The UV-VIS spectra of different samples were recorded at room temperature using an UV-Visible recording spectrometer UV-160A of Shimadzu Corporation, Japan. Films for UV-VIS measurements are deposited onto the glass-slides.

3.7.2 INFRARED (IR) SPECTROSCOPY

The IR spectra of different samples were recorded at room temperature using an infrared Spectrophotometer IR - 470 of Shimadzu Corporation, Japan. Thin films were used for IR measurements.

3.8 D.C. MEASUREMENT

3.8.1 INSTRUMENTS USED IN D.C. MEASUREMENTS

The following instruments were used for d.c. measurements.

(a) Keithley 614 Electrometer

A digital Keithley Electrometer (model 614, Keithley Instrument Inc, Cleveland, Ohio, U.S.A) was used for d.c. current measurement. It is a very sophisticated instrument and it has a versatile uses. It can measure a wide range of d.c voltages, currents, resistances, and electric charge. Resistance range of this model is from 1 ohm to 2×10^{11} ohms using the

constant current technique. This Electrometer can measure current as low as 10^{-14} amp. Voltage range is 10 μ V to 20V with an input impedance of greater than 5×10^{13} Ohms.

(b) D.C. Power Supply

A Hewlett regulated high voltage d.c power supply (Model 6181C) was used for d.c applied field measurement. This unit is capable of supplying d.c. voltages from 0 to 100 volts with a current range from 0 to 0.25 ampere. The input voltage of this unit is 220 volts a.c. Two analog meters are attached to measure voltage and current supplied by this unit.

(c) Keithley Microvolt Meter

A digital Keithley autoranging microvolt DMM (Model 197A) was used for the measurement of temperature inside the specimen where the sample is placed. This microvoltmeter gives reading in millivolt corresponding to the temperature sensed by the thermocouple.

(d) Oil Rotary Pump

An oil rotary pump was used to evacuate the specimen chamber. A pressure of about 10^{-2} torr can be attained using this pump.

(e) Specimen chamber

Specimen chamber is designed and fabricated in the local engineering workshop. A schematic diagram of the chamber along with its accessories is shown in the figure 3.6. This unit is basically consists of two main parts mainly, the iron tube and the sample holder.

An iron tube having inner diameter of 0.045 m. and length 0.24 m is used. The lower end of the tube is closed by welding a circular piece of iron sheet. At the tube one flat iron sheet (0.092 x 0.09 m²) with a circular hole (diameter 0.045 m) at its center is welded. Another iron sheet (same as above) with a hole of the same dimension is welded to an iron tube of diameter 0.045 m and of length 0.24 m. A rubber gasket is placed in between the two iron sheets. This prevents the air leakage when it is evacuated.

The upper portion can be fixed to the lower portion by screws. The top opening is closed tightly with a teflon stopper. Two copper leads (electrodes) which hold the specimen holder and a chromel-alumel (Cr-Al) thermocouple are inserted through this teflon stopper. A thick layer of mica sheet is placed on to the inside and bottom of the iron tube for electrical insulation. The distance between the leads is about 0.014 m. There is a sub tube welded to the main iron tube which acts as a outlet of the chamber. A rotary vacuum pump is connected to the chamber through the sub tube with the help of rubber tube. By this pump it can be obtained a pressure of about 10^{-2} torr. Required temperature in the chamber can be maintained by a heating tape which is wrapped outside the iron tube and its temperature is controlled by a variable transformer. Sample holder is a spring system which is shown in the figure 3.7.

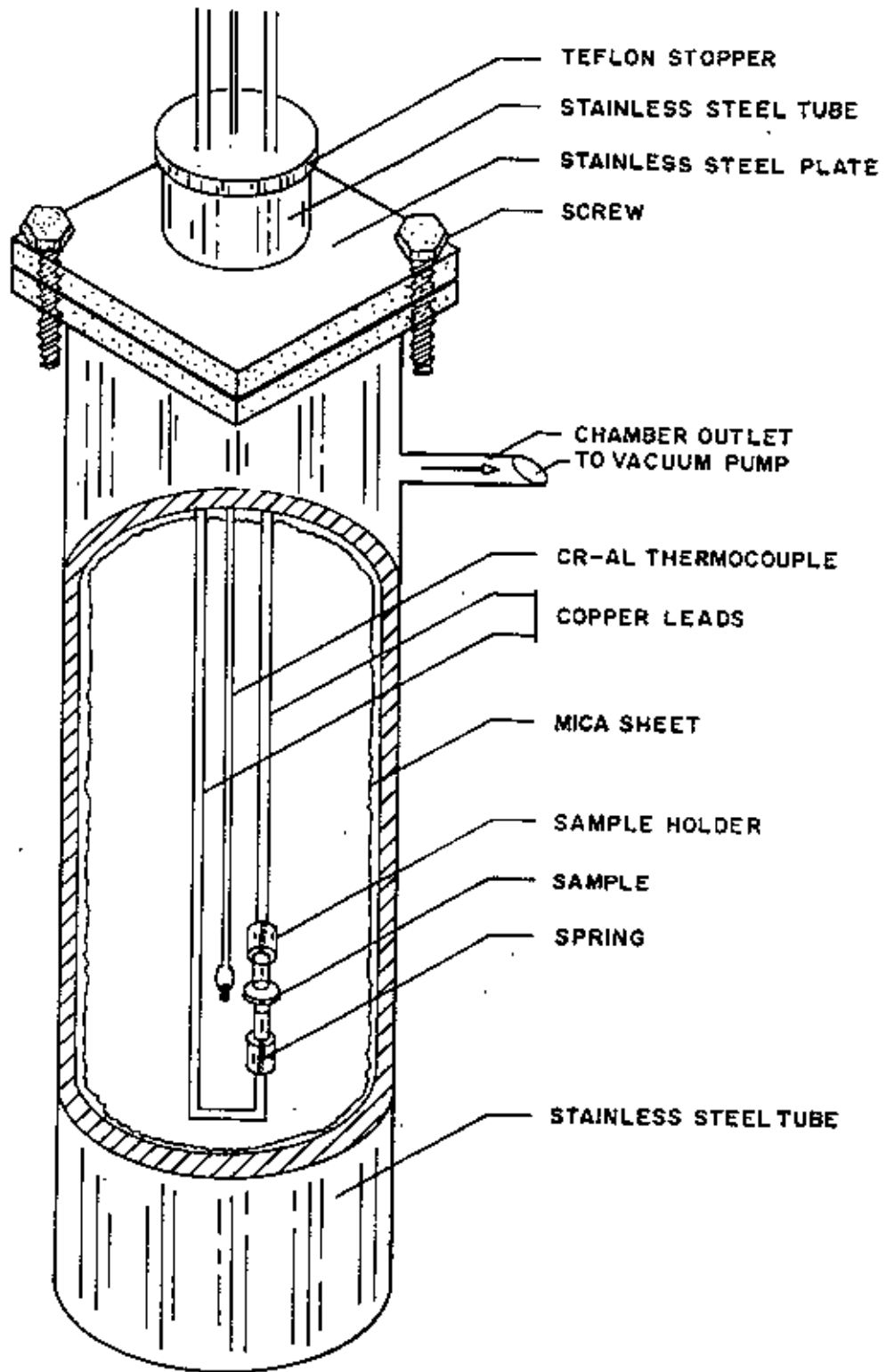


Fig. 3.6 : The schematic diagram of the specimen chamber

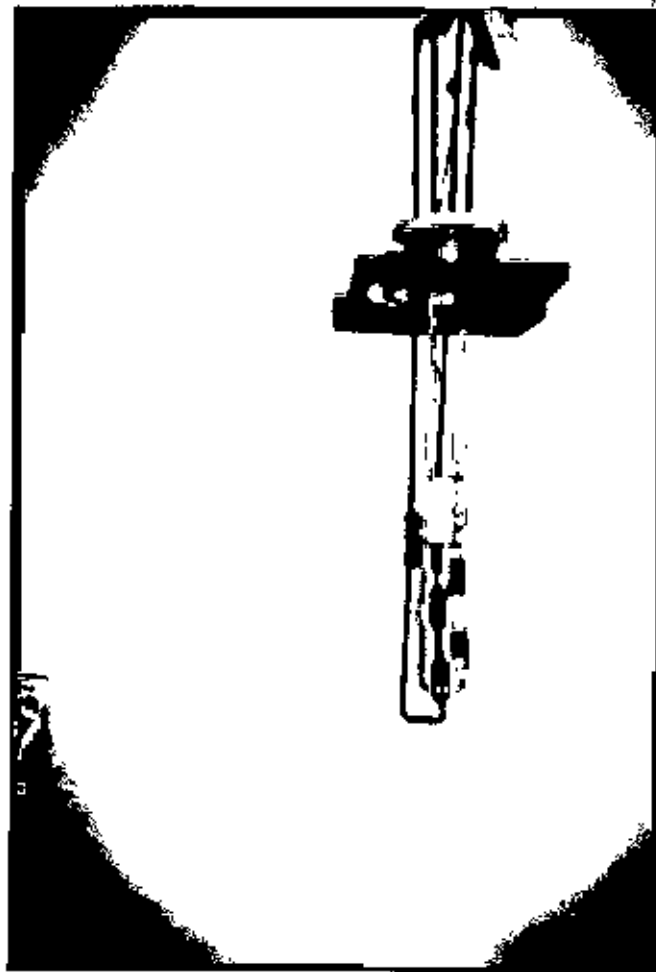


Fig 3.7 : Photograph of sample holder

(f) Heating tape

A heating tape (ISOPAD LTD BOREHAMWOOD, HERTS, ENGLAND) was used to heat the specimen chamber. It is about 1.75 m long and 0.03 m width tape. It can be wrapped around the specimen chamber easily.

3.8.2 EXPERIMENTAL PROCEDURE

The silver coated sample was placed in between the electrodes inside the chamber. The chamber was evacuated using a rotary vacuum pump to about 10^{-2} torr. Then a 614 Keithley electrometer and stabilized d.c. power supply were connected in series with the specimen as shown in fig. below:

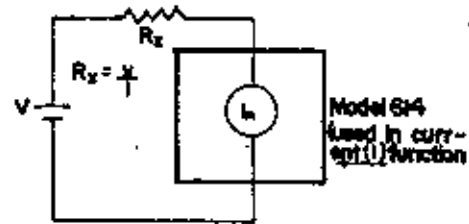
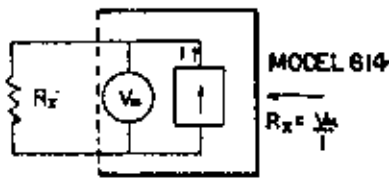


Figure 3.8 (a) Constant current method employed by the model 614

(b) Technique for measuring resistance $> 10^{11}$ Ohm

To record the d.c. current through the sample, an electrometer was set to current mode. The meter was warmed up for one hour. At first nano ampere unit and 2K range were chosen in the electrometer. Two types of d.c. measurement were taken in this experiment.

(i) Direct method

A Keithley 614 electrometer was set in the current mode for recording the current through the sample at different applied voltage, at constant temperature (room temperature). In this case the voltage was varied from 0 to 80 volts. The current was recorded every 2.5 volt interval upto 20 volts and then after 20 volts the current was recorded every 5 volts interval. Here twenty sets of data were recorded. The electrometer was set in the resistance mode for the direct measurement of resistance at different temperature. For temperature rising, the specimen chamber was heated by a heating tape which can be easily wrapped around the specimen

chamber. The resistance was measured at every 0.2 millivolt increase of thermocouple reading from room temperature to 375K depending on different samples.

(ii) I-V method

After the completion of 1st cycle the samples show very low current. Then it was impossible to measure the conductivity in the direct method because in that case the voltage across the specimen was unknown. The current was recorded through sample at different temperature at constant 50 volt.

The Keithley electrometer is connected parallel to measure the voltage drop across the resistance R. A constant current d.c. power supply is used to supply desired voltage. Firstly, the voltage drop across the resistance is recorded by varying the total voltage with the aid of the T.P.S. From these set of readings the voltage drop across the specimen is then found out by subtracting the voltage across resistance from the total voltage and finally the current across the specimen is calculated by using the following relation:

$$I_s = \frac{V_R}{R} \dots\dots\dots (1)$$

where, V_R = voltage across the resistance (R)

R = resistance in series with the specimen

I_s = current through the specimen

From these sets of data the various curves are drawn.

Precautions

Silver dag coating on the surface of the sample was done very carefully such that two coated areas become equal. Electrometer used in this experiment is very sensitive device. Precautionary steps were taken to prevent flow of any large current through the electrometer. Copper leads should be arranged in such a way that they never come into contact. A cylindrical shaped mica sheet was set inside the chamber. Grounding of the metal chamber is essential. So it was done carefully.

3.8.3 Working formula

According to Ohm's law, conductance G is defined as,

$$G = 1/R = I/V$$

In this experiment V is the applied voltage and I is the corresponding current through the sample. I - V curves give the slope which is as

$$I = V^n$$

$$\text{Log } I = n \log V$$

$$n = \log I / \log V$$

where n is the power factor. When $n=1$ then it follows the Ohm's law.

Conductivity σ of the specimen was calculated from the measured conductance G of the sample, from the thickness of the specimen and the area of electrodes by using the following relation

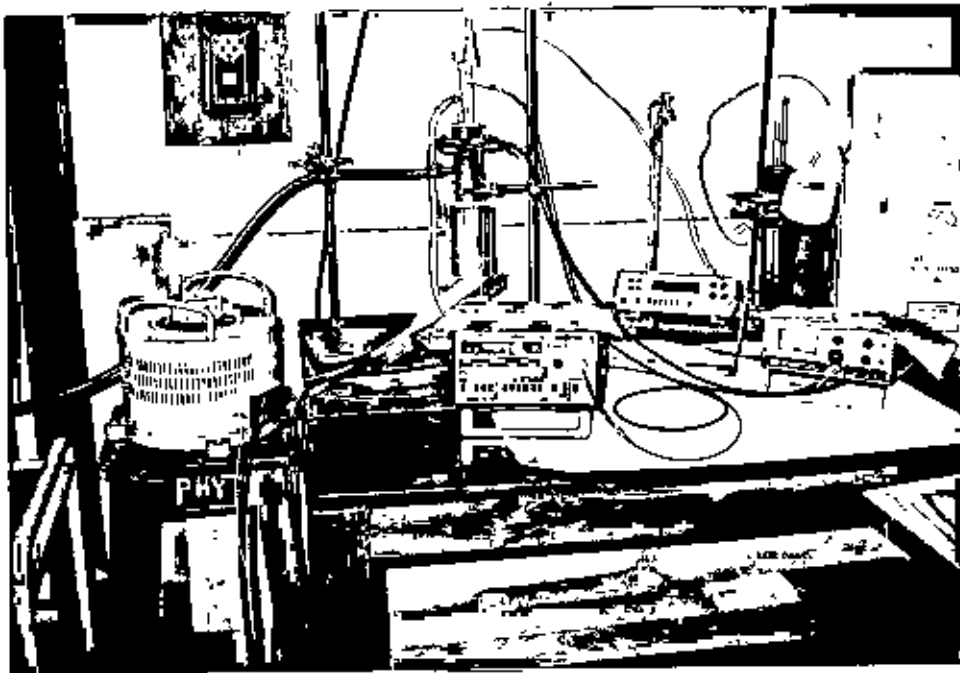
$$\sigma = G d / A$$

where σ =conductivity (Ohm-m)⁻¹

G =conductance of the specimen in Ohm^{-1}

d = thickness of the specimen in m

A = Area of the electrode in m^2



Experimental Setup

CHAPTER 4

RESULTS AND DISCUSSION

4.1 STRUCTURAL ANALYSIS

4.1.1 X-RAY DIFFRACTOMETRIC (XRD) ANALYSIS

The XRD patterns of samples A,B,C,D,E,F, and G are presented in figure 4.1. These are represented by diffractograms A,B,C,D,E,F, and G . There is a hump in the diffractograms of all the samples around $2\theta = 10^\circ$ which may be due to induced back ground scattering. The 2θ and d_{hkl} values for all samples are depicted in a Table in the appendix.

The diffractogram of the sample A (pure PVP), the pattern A, shows a wide hump at $2\theta = 20.5^\circ$, the d_{hkl} value calculated corresponding to this 2θ value is 4.42Å. In fact this diffraction pattern is a feature of a amorphous polymer.

The XRD pattern of sample G(Li₂O), diffractogram G, shows the presence of characteristic reflections together with other reflections. The other reflections may arise from LiOH, Li etc.

The XRD patterns of sample B(PVP with 0.5% Li₂O),diffractogram B, show the same feature as that of the pure PVP, except the appearance of a very small peak at about $2\theta = 20.5^\circ$. It is obvious that it is not possible to detect any major change in the structure of PVP due to the presence of small amount of Li₂O.

The XRD pattern of samples C(PVP with 1% Li₂O), D (PVP with 2.5% Li₂O), E(PVP with 5% Li₂O) and F(PVP with 10% Li₂O) show the presence of different reflections at $2\theta = 21^\circ, 23.4^\circ, 30^\circ, 31.4^\circ, 34.8^\circ, 35.6^\circ, 36.6^\circ, 39^\circ$ etc. with progressively increasing in intensity of reflections on going from lower to higher

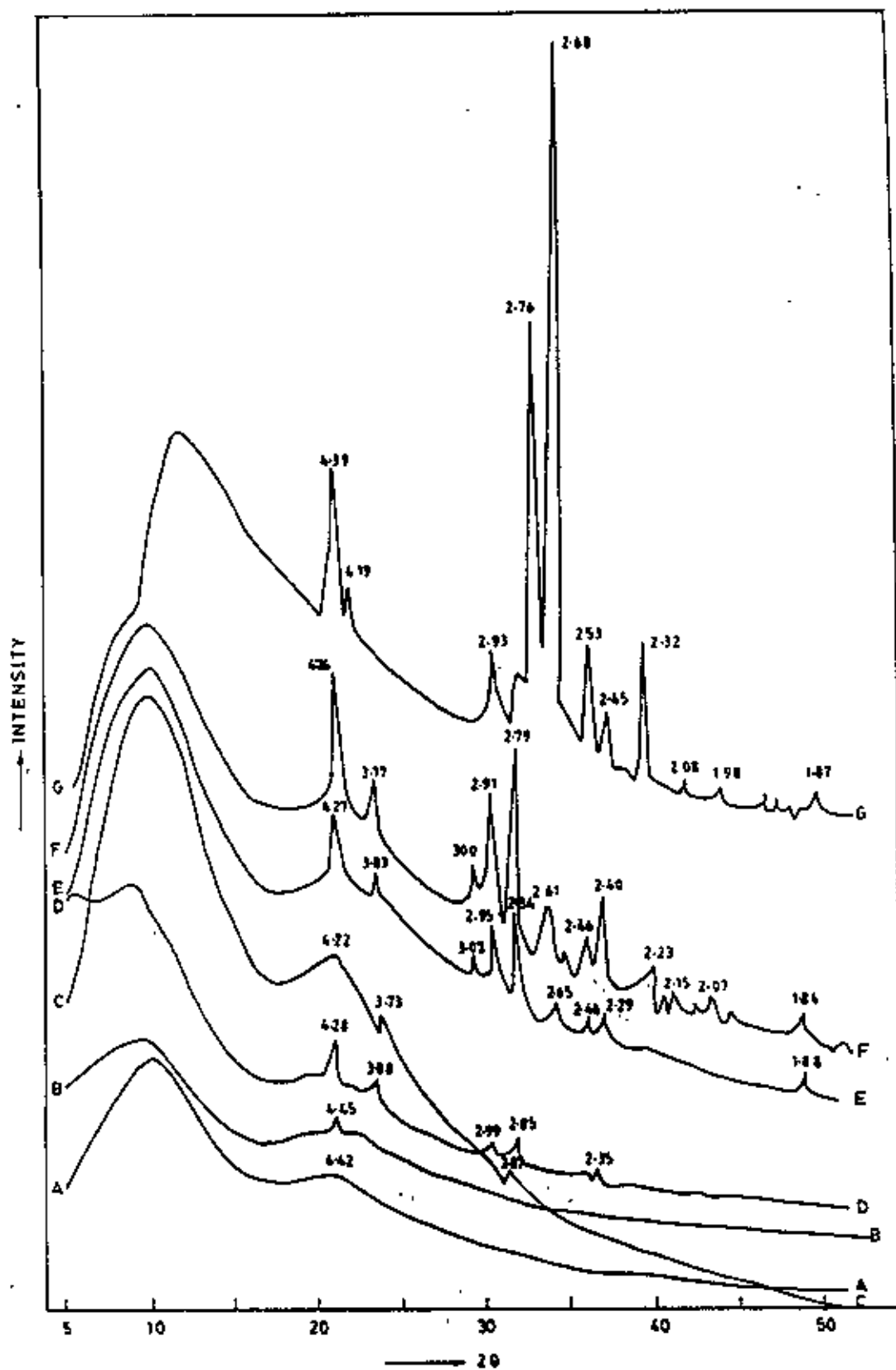


Fig 4.1 : X-ray diffractograms A, B, C, D, E, F and G respectively for PVP, PVP with 0.5,1, 2.5,5 and 10% Li_2O and Li_2O .

concentration of Li_2O . If all the XRD patterns are compared, it is seen that there are absence of some reflection of Li_2O and appearance of some new reflections in the complexes. These prove the incorporation of Li_2O and other forms of Lithium (Li , LiOH etc). Owing to this incorporation, it can be said that some definite modification takes place as is seen from the XRD patterns of different complexes.

4.1.2 INFRARED (IR) SPECTROSCOPIC ANALYSIS

The IR spectra of the thin films of PVP (pure) and PVP complexes containing 0.5, 1, 2.5, 5, and 10% Li_2O were recorded at room temperature and are presented in fig. 4.2. These reveal the structural modification of PVP due to the incorporation of different amount of Li_2O . The IR spectra of PVP and PVP complexes containing .5, 1, 2.5, 5, and 10% Li_2O are represented by spectra a, b, c, d, e and f respectively. Spectra 'a', in fig. 4.2, is for the pure PVP thin film. The absorption band indicated by P ($3200\text{--}3500\text{ cm}^{-1}$) corresponds to NH and OH stretching vibration (OH may be due to absorbed water); band Q(2900 cm^{-1}) may arise from OH stretching vibration; band R($1600\text{--}1700\text{ cm}^{-1}$) indicate N-C=O (aromatic) group; band S($1400\text{--}1450\text{ cm}^{-1}$) is for amide III vibration, CN stretching; band T(1295 cm^{-1}) may be assigned to secondary amide vibration and band U (1020 cm^{-1}) may be due to oxygen bonded to carbon.

It is seen that with the increase of Li_2O concentration in PVP the band S and T decreases. Further, it is observed that the band at U is absent in the IR spectra of samples containing 0.5 and 1% Li_2O . The complication arises may be due to (i) the probable plasticization effect owing to absorption of water in the materials (ii) transformation of Li_2O to LiOH . But it may be seen that there ~~are~~ some modifications take place in the materials. This fact is also seen from the other measurements. Except these, no major structural change could be assessed from the IR spectra.

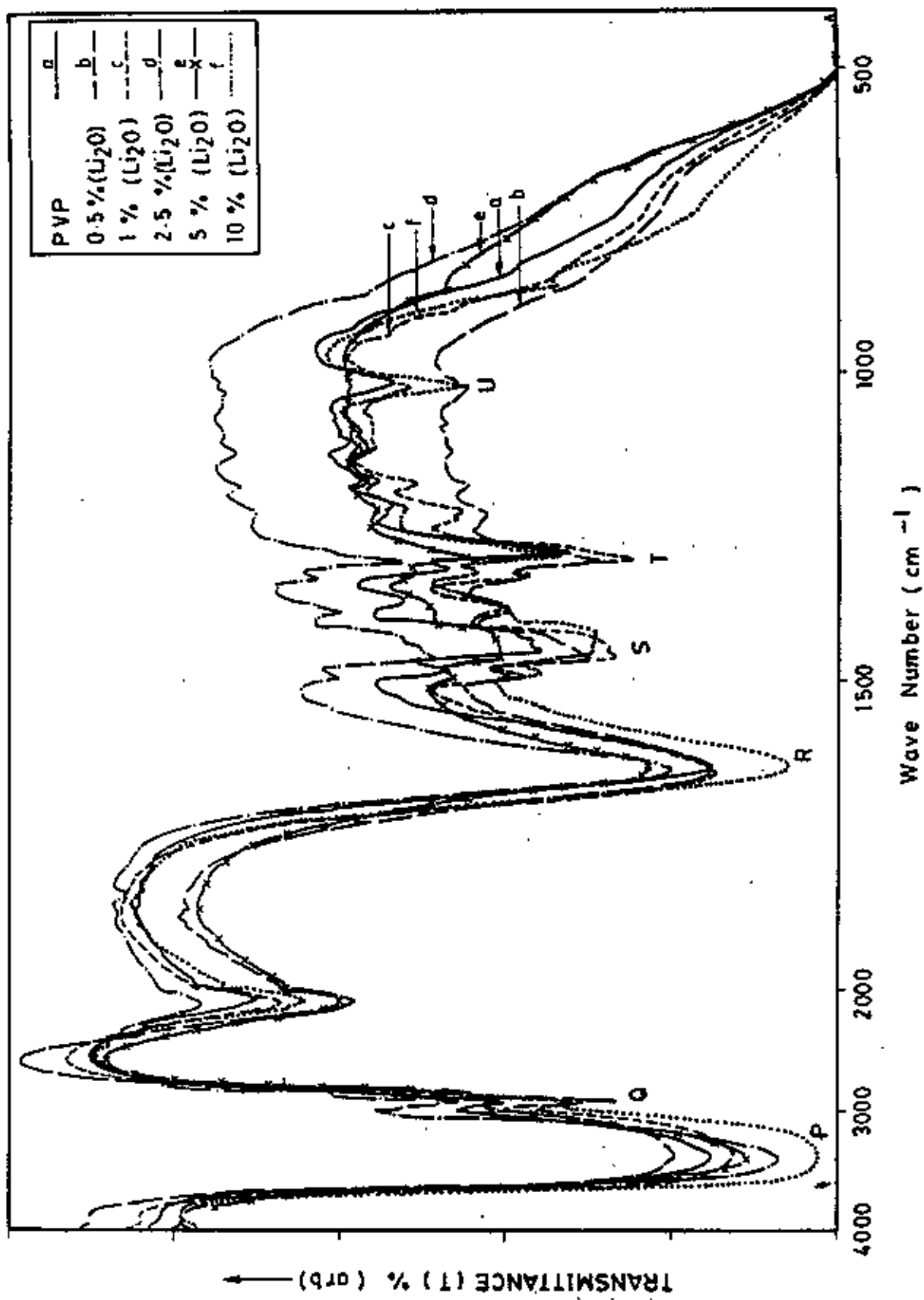
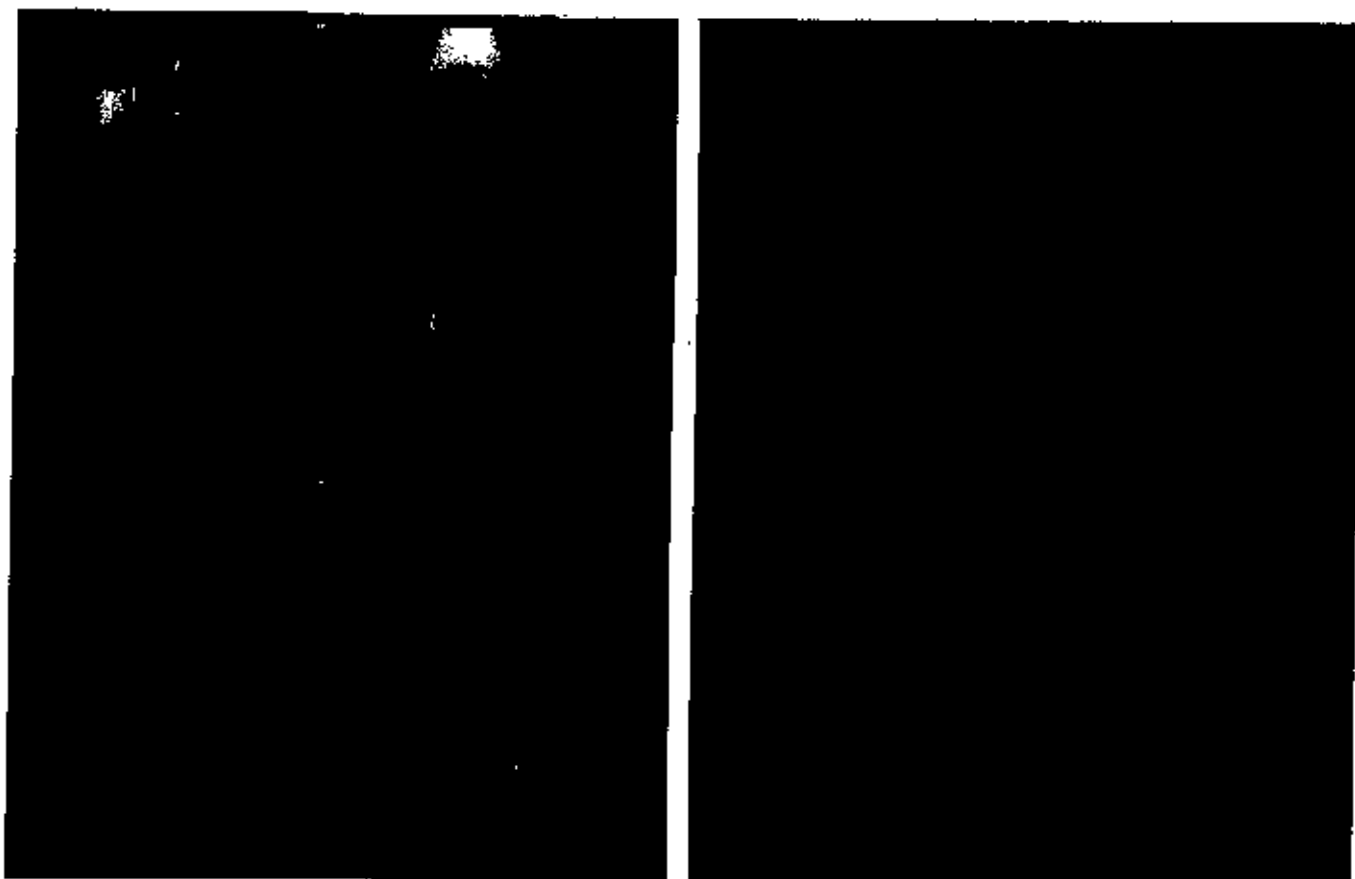


Fig 4.2 : IR Spectra of PVP, Li_2O and PVP with different concentration of Li_2O

4.1.3 SURFACE MICROSCOPIC ANALYSIS

The microphotographs of PVP, PVP containing 0.5, 1, 2.5, 5 and 10% Li_2O are presented in pages 59 to 62 for (a) as prepared and (b) heat treated at 100°C samples.

It is seen that with Li_2O concentration, segregation in the structure increases and on heat treatment the clustering becomes more homogeneous. This shows a definite change in the structure owing to heat treatment. It is observed that the surfaces of all the samples are optically isotropic.



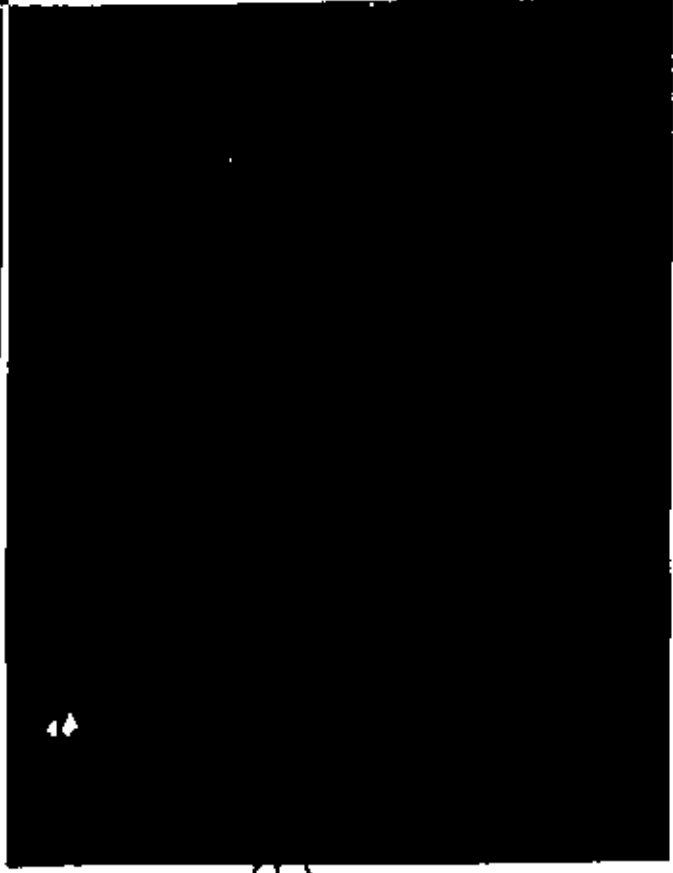
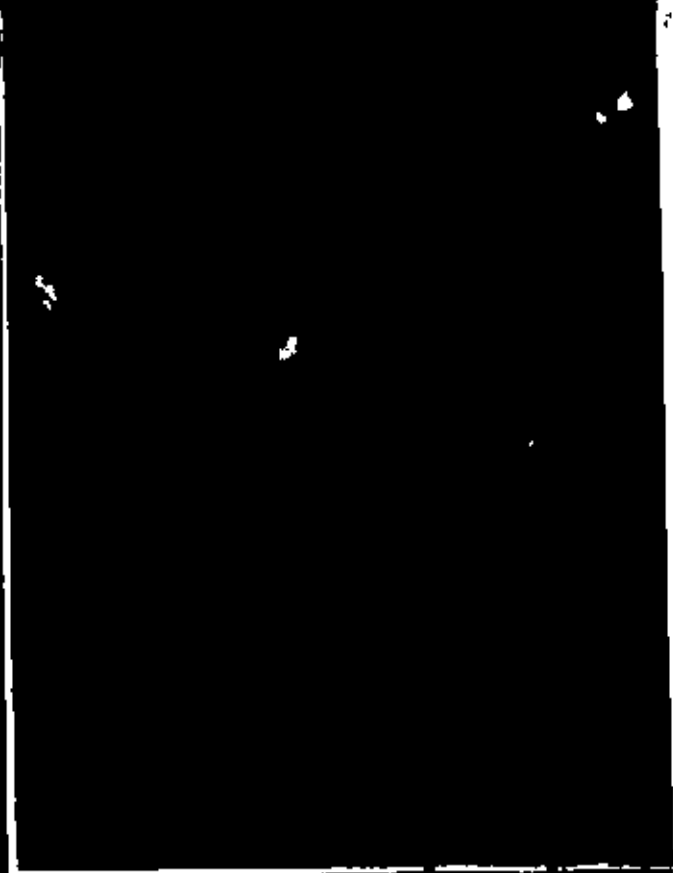
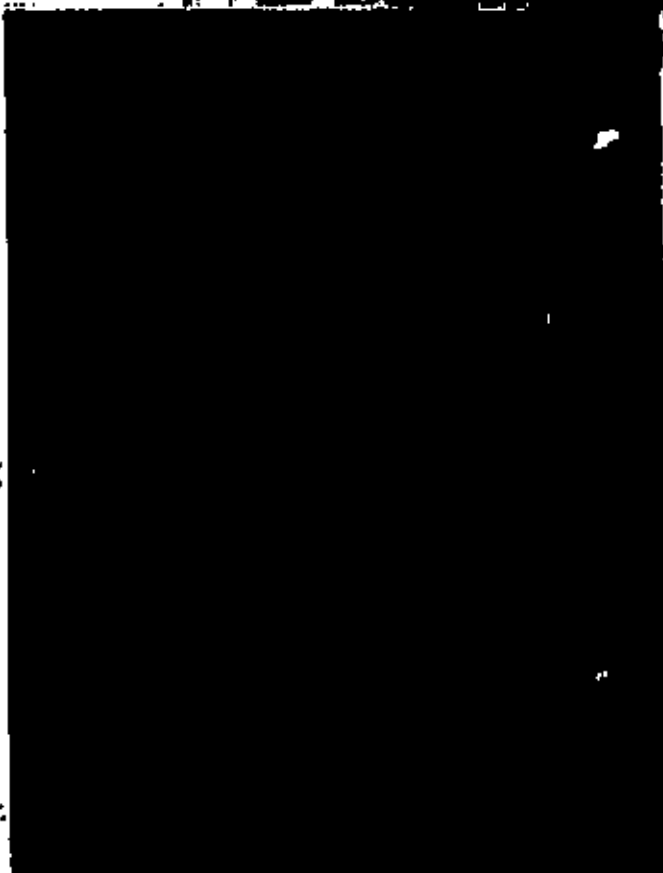
(a)

(b)

Microphotographs of (a) as prepared PVP (b) heat treated at 100°C. X 250 magnification

5%

10%

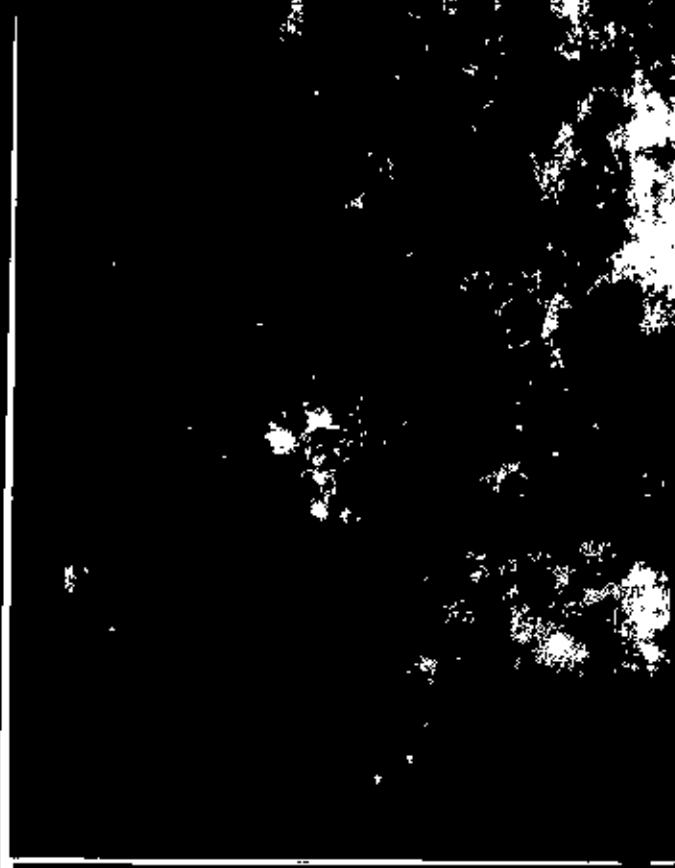


(a)

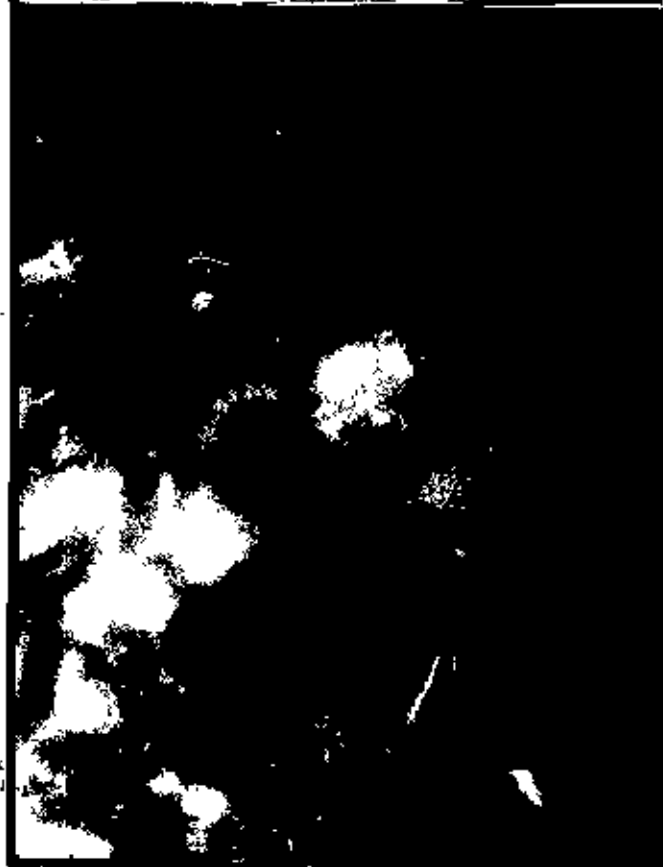
(b)

Microphotographs of (a) as prepared PVP complexes with .5 and 1.0% Li_2O and (b) heat treated at 100°C . X250 magnification.

257



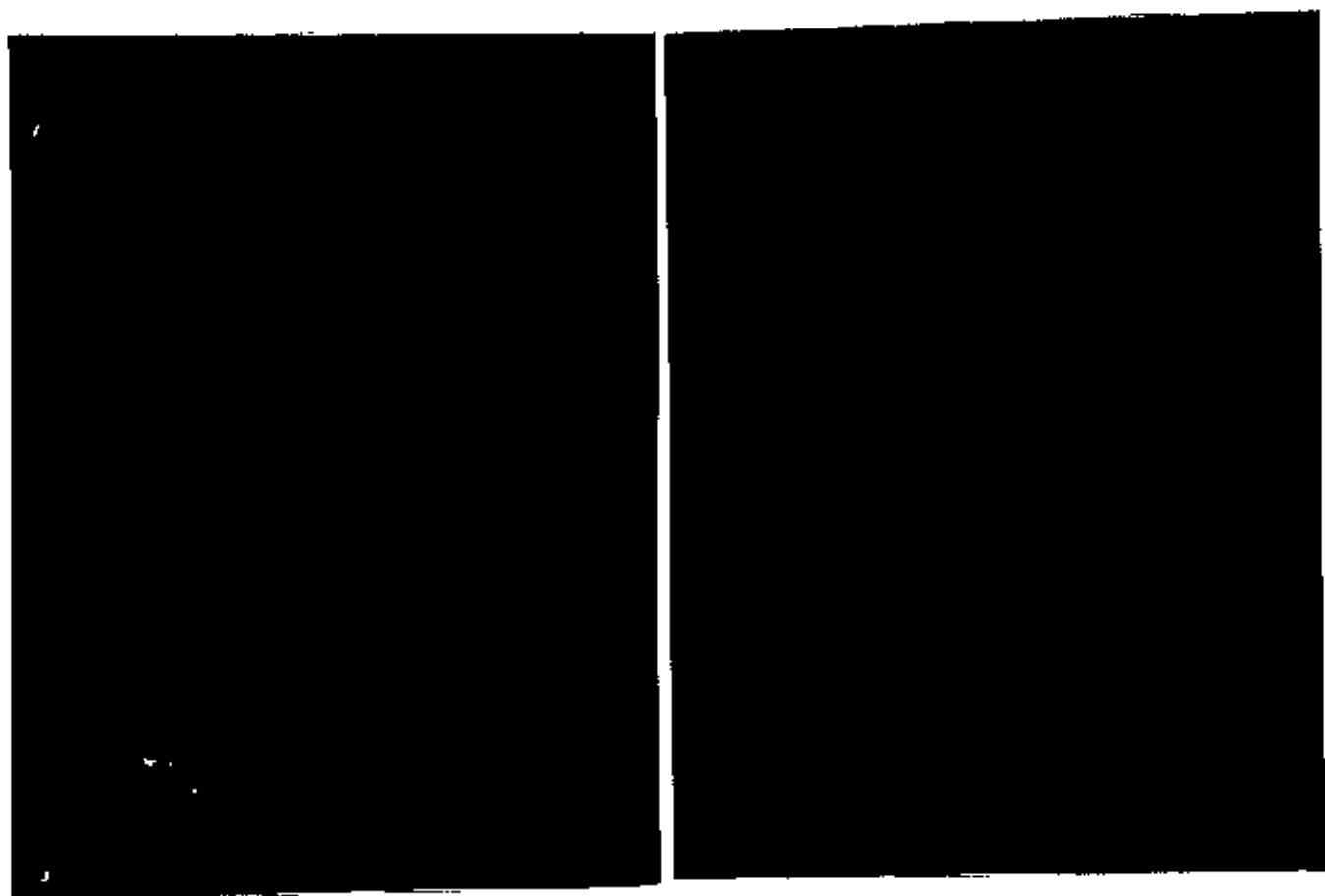
51.



(a)

(b)

Microphotographs of (a) as prepared PVP complexes with 2.5 and 5.0% Li_2O and (b) heat treated at 100°C . *x250 magnification.*



(a)

(b)

Microphotographs of (a) as prepared PVP complex with 10% Li_2O and (b) heat treated at 100°C . *X250 magnification.*

4.1.4 DIFFERENTIAL THERMAL ANALYSIS (DTA) AND THERMOGRAVIMETRIC ANALYSIS (TGA)

The DTA and TGA traces of the samples PVP, PVP complexes containing 0.5, 1, 2.5, 5 and 10% Li_2O and Lithium oxide are shown in figures 4.3 to 4.9 respectively. It is observed that an endothermic broad peak is appeared in the region $90-95^\circ\text{C}$.

This endotherm may be due to the release of absorbed moisture. There are several exothermic peaks above 400°C in all the samples. In the present study different investigations are performed upto 100°C, that is why the high temperature exotherms are not discussed here.

In figures 4.3 to 4.9, it is observed from the TGA traces that the first step of the weight loss occurs in the temperature region of the first DTA endotherm and the 2nd step of the weight loss corresponds to the DTA exotherms appeared above 400°C. It is clear from the TGA traces that there are evaluation of different gases from the samples in two steps; one is below 100°C and another above 400°C.

66588

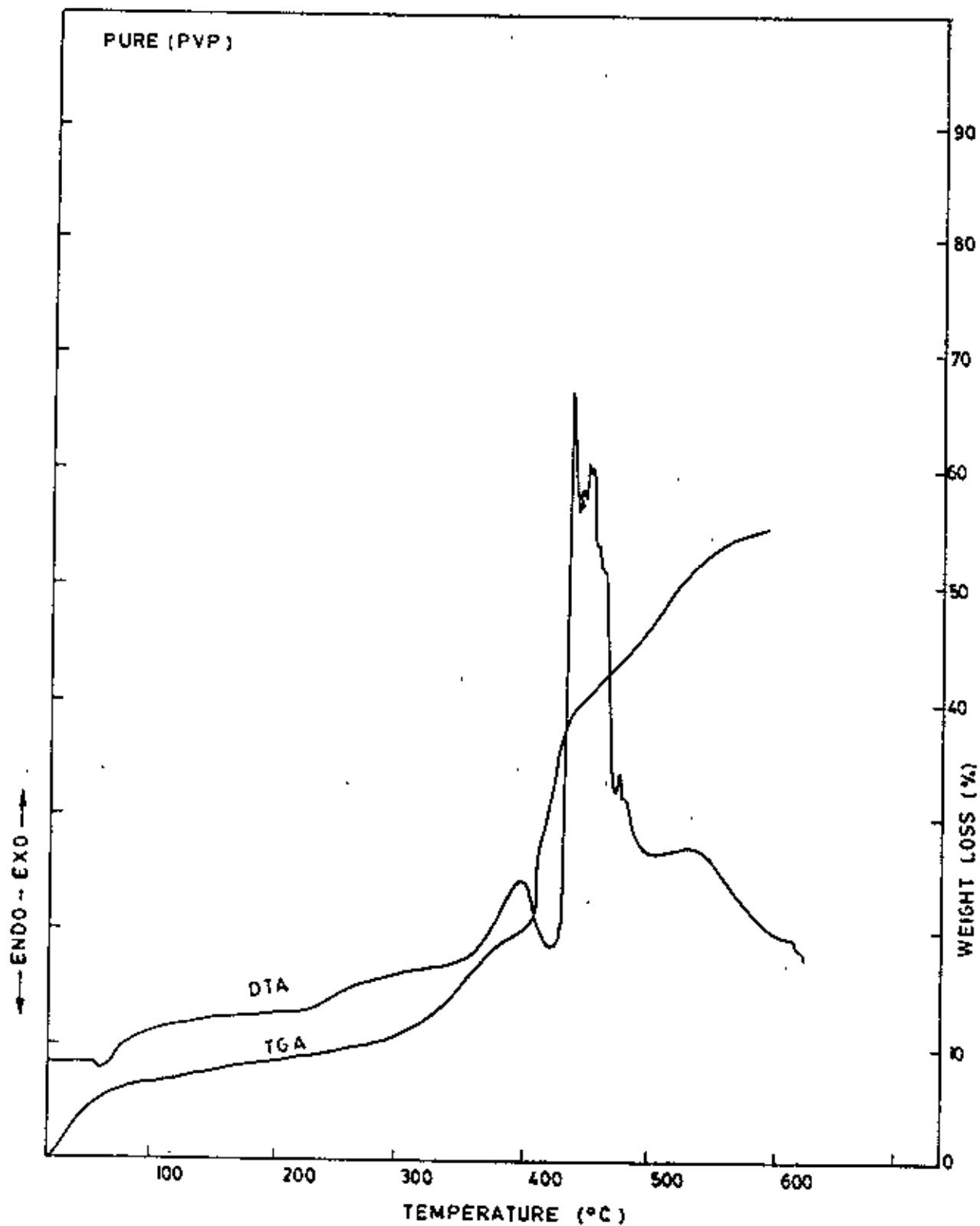


Fig 4.3 : DTA and TGA traces of pure PVP.
Temperature rate : 10°/min

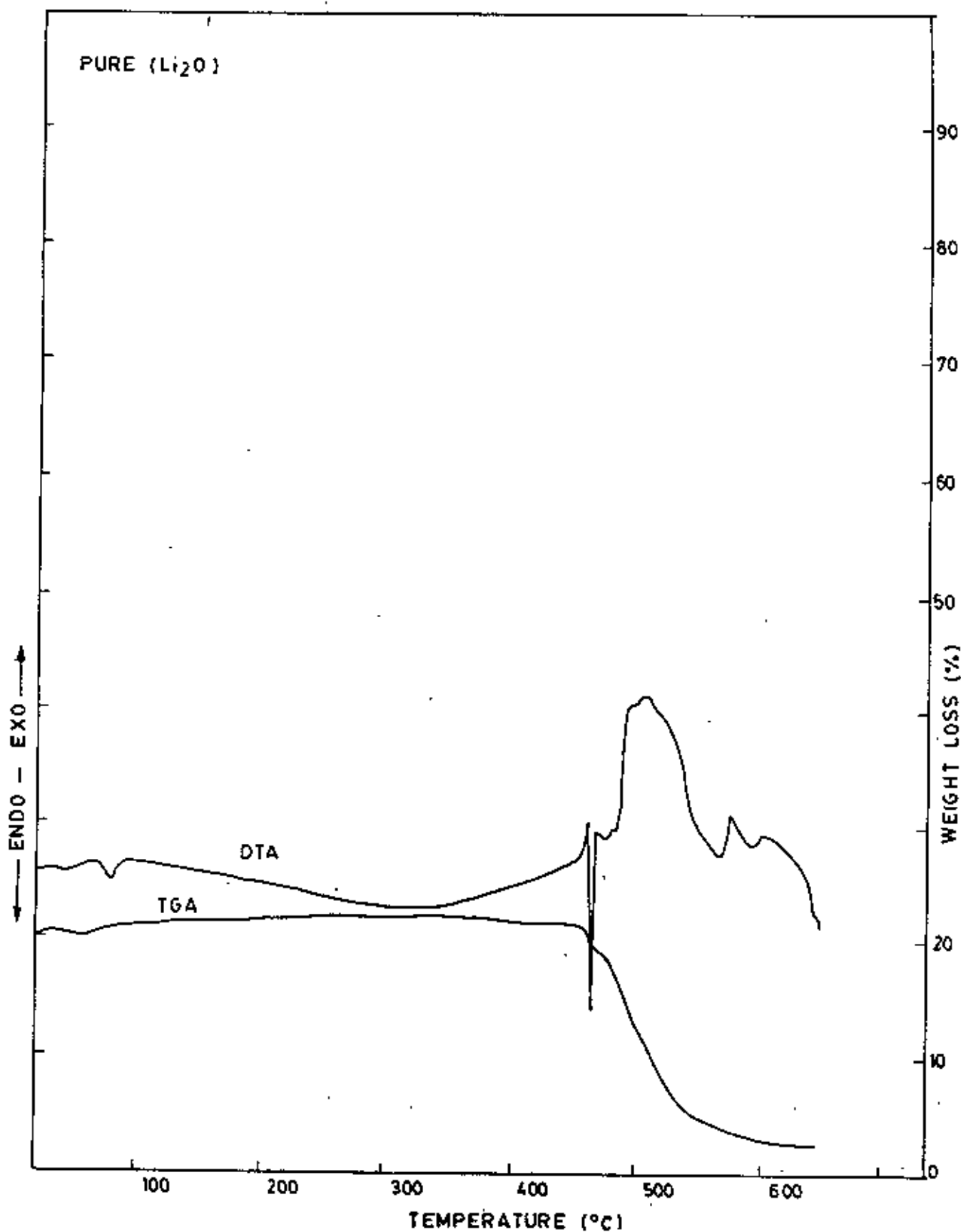


Fig 4.4 : DTA and TGA traces of pure Li₂O.
Temperature rate : 10°/min

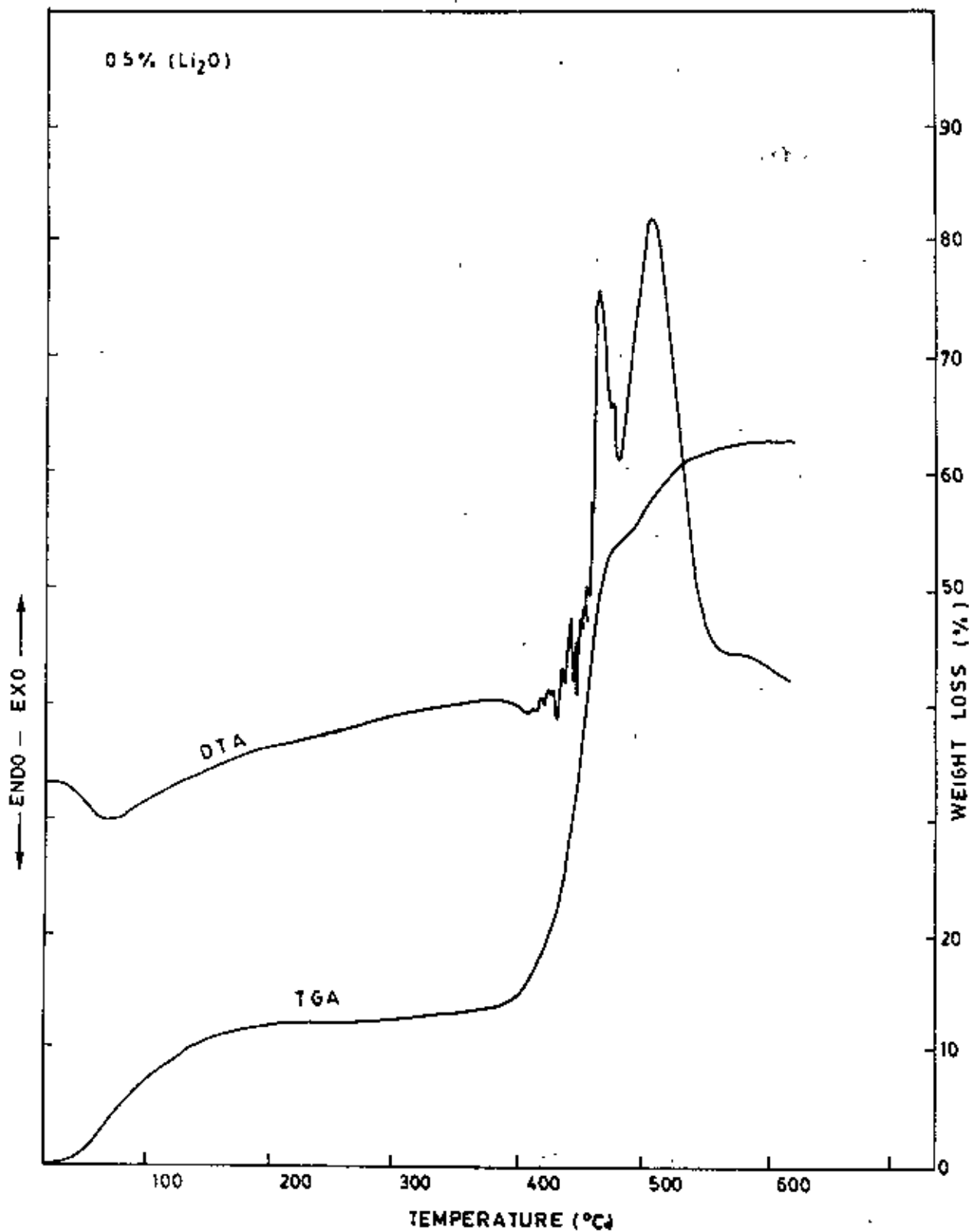


Fig 4.5: DTA and TGA traces of PVP with 0.5% Li₂O.
Temperature rate : 10°/min

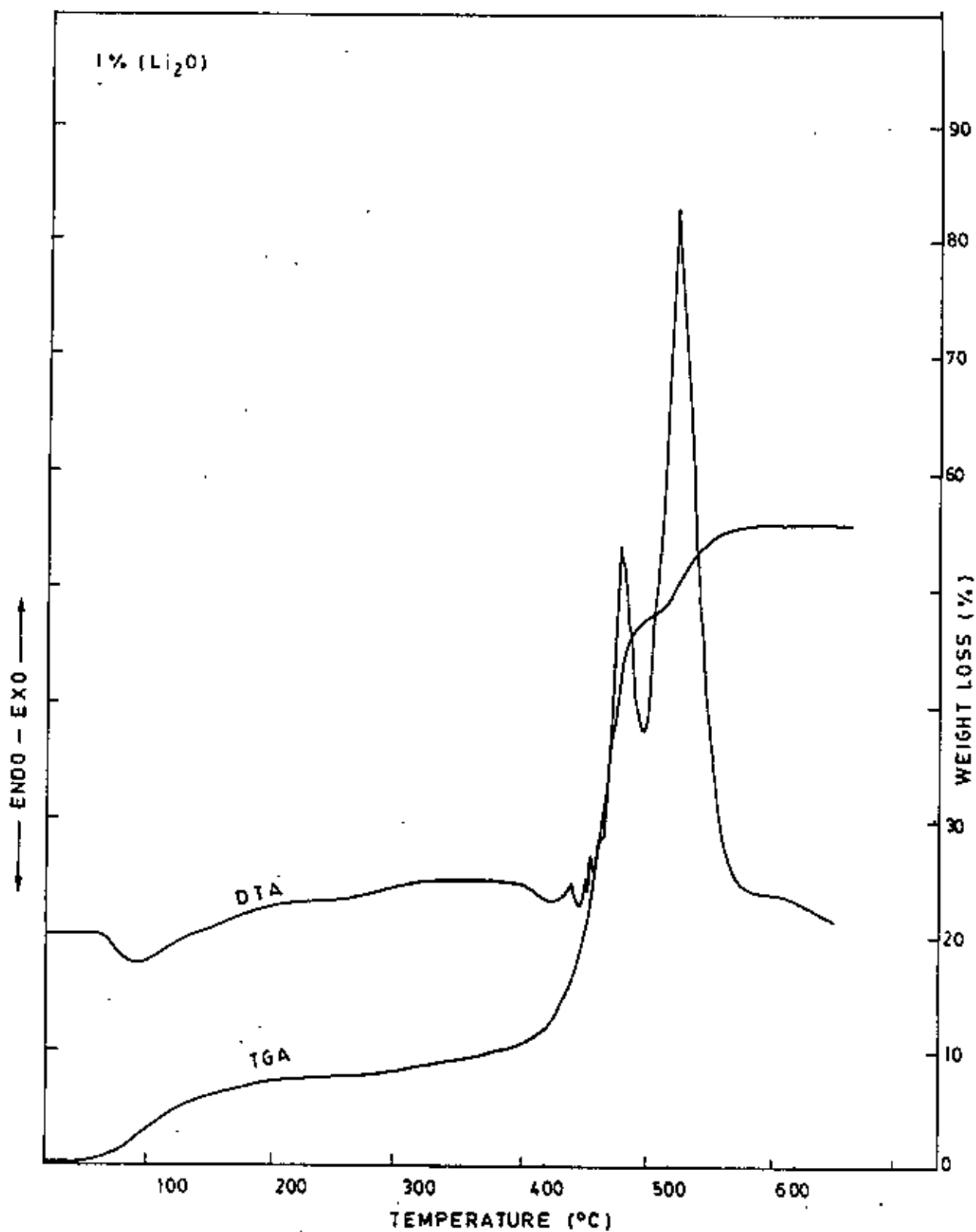


Fig 4.6 : DTA and TGA traces of PVP with 1% Li₂O.
Temperature rate : 10°/min

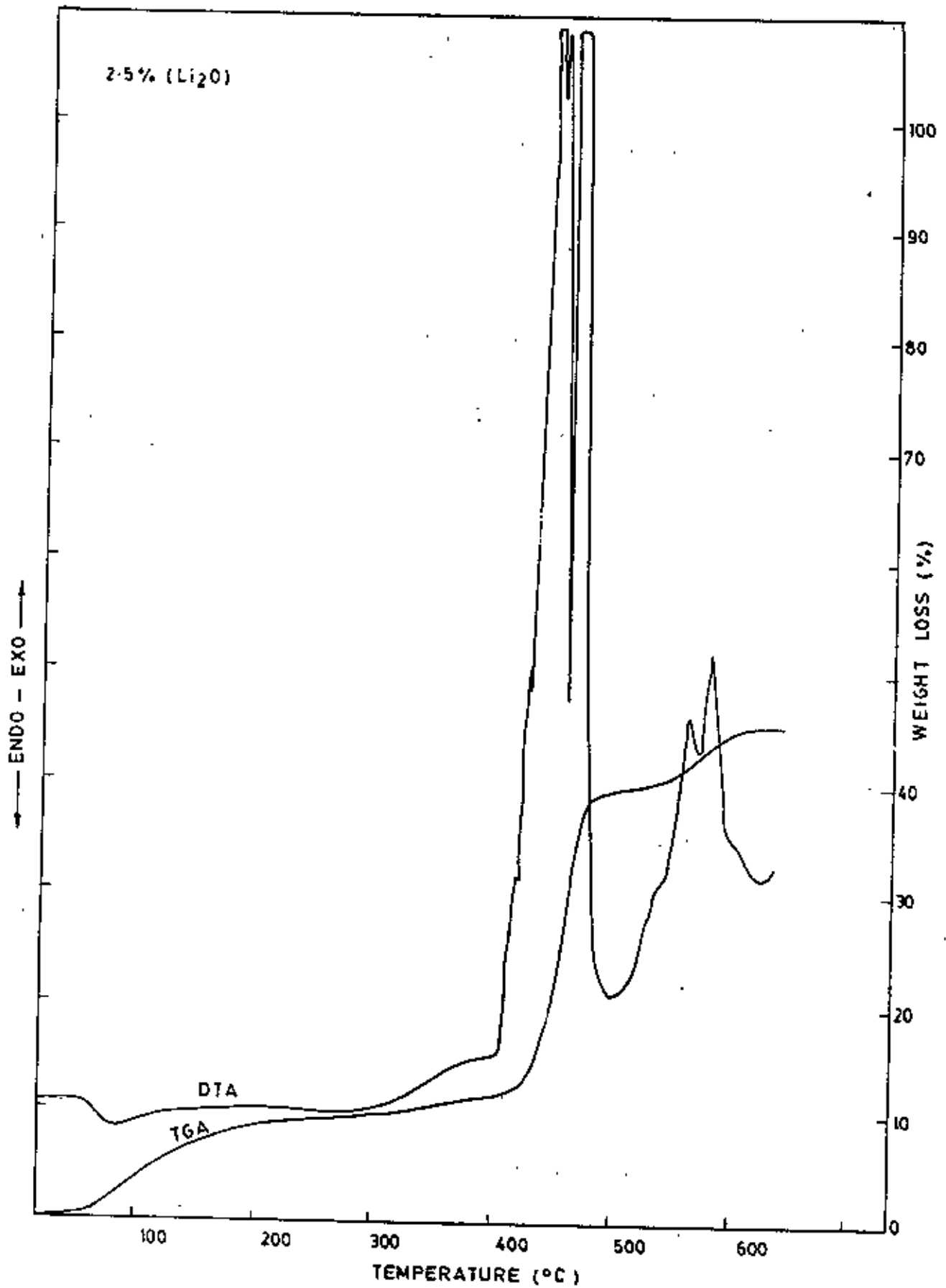


Fig 4.7 : DTA and TGA traces of PVP with 2.5% Li₂O.
Temperature rate : 10°/min

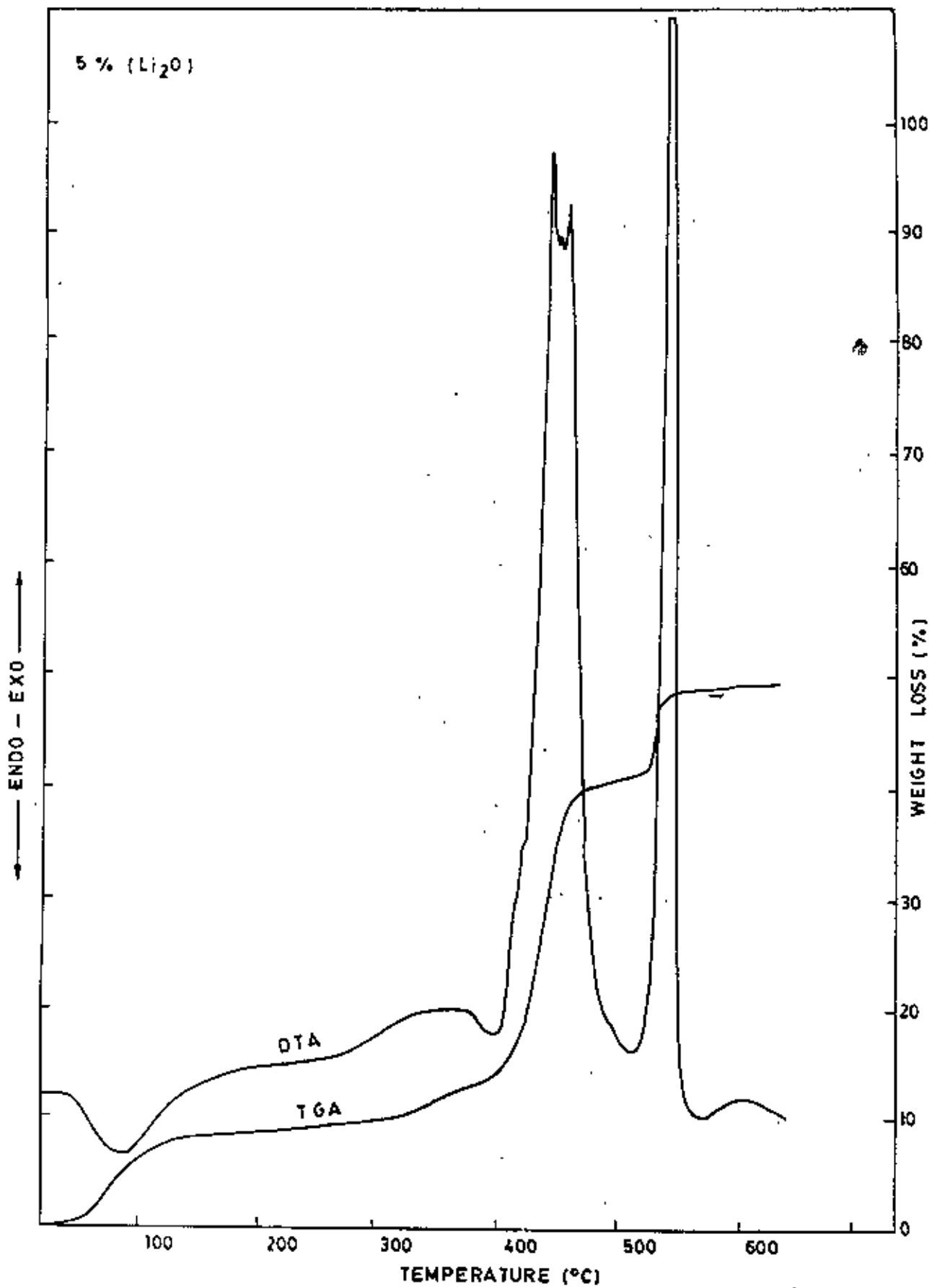


Fig 4.8 : DTA and TGA traces of PVP with 5% Li₂O.
Temperature rate : 10°/min

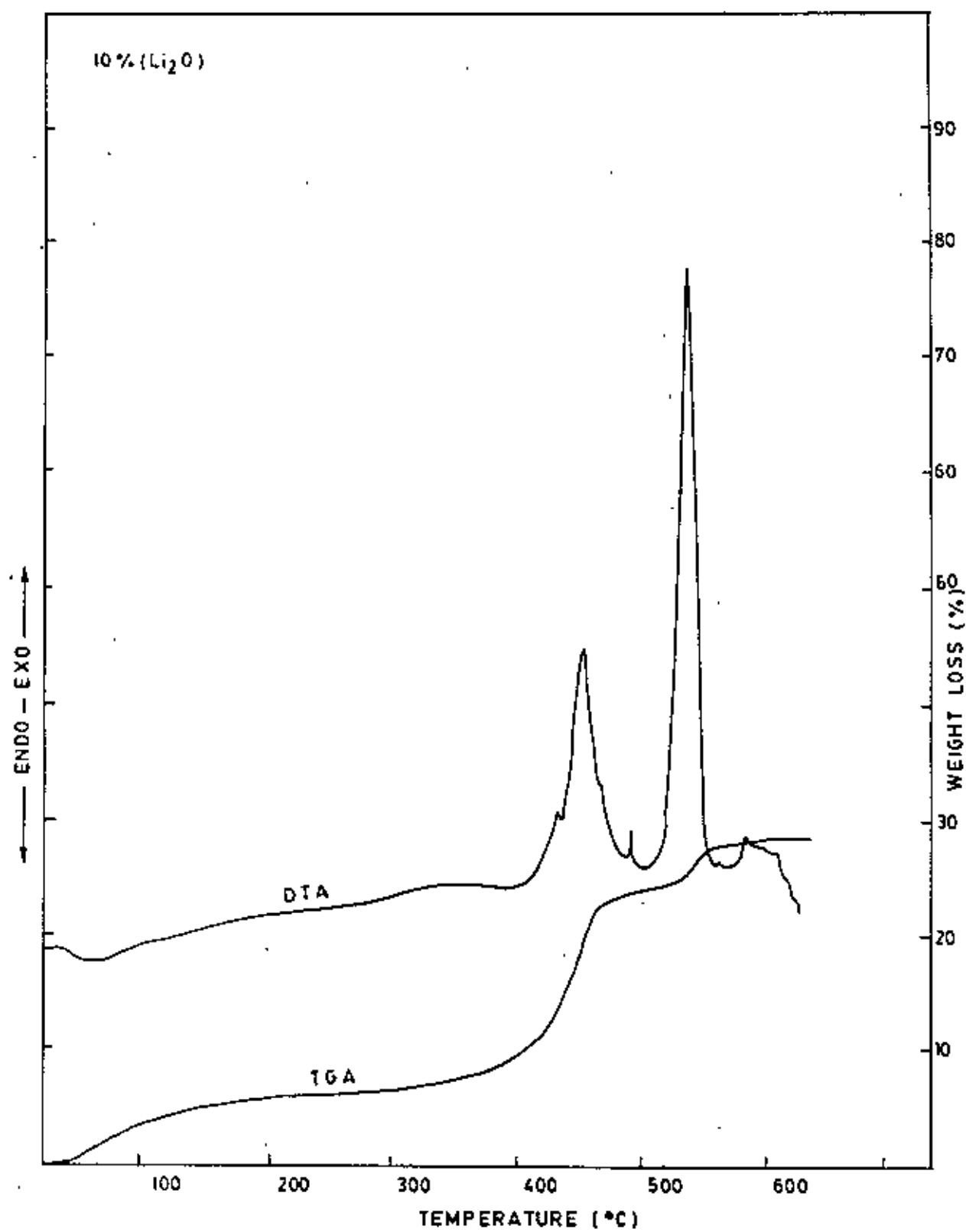


Fig 4.9 : DTA and TGA traces of PVP with 10% Li₂O.
Temperature rate : 10°/min

4.2 OPTICAL ABSORPTION STUDIES

The absorption coefficient against photon energy for the samples PVP and PVP complexes containing .5, 1, 2.5, 5 and 10% Li_2O are presented in figure 4.10. The optical band gap calculated from the maximum absorption edge are recorded in Table 1. It is seen that the energy band gap decreases with the increase of Li_2O . It is also observed that there is tailing near the band edges. This may be due to the presence of defect states within the band gap.

Table 1 : Optical Band gaps calculated from
UV-VIS spectra.

Samples	Energy (eV)
PVP	3.85
0.5%(Li_2O)	3.85
1%(Li_2O)	3.86
2.5%(Li_2O)	3.84
5%(Li_2O)	3.79
10%(Li_2O)	3.59

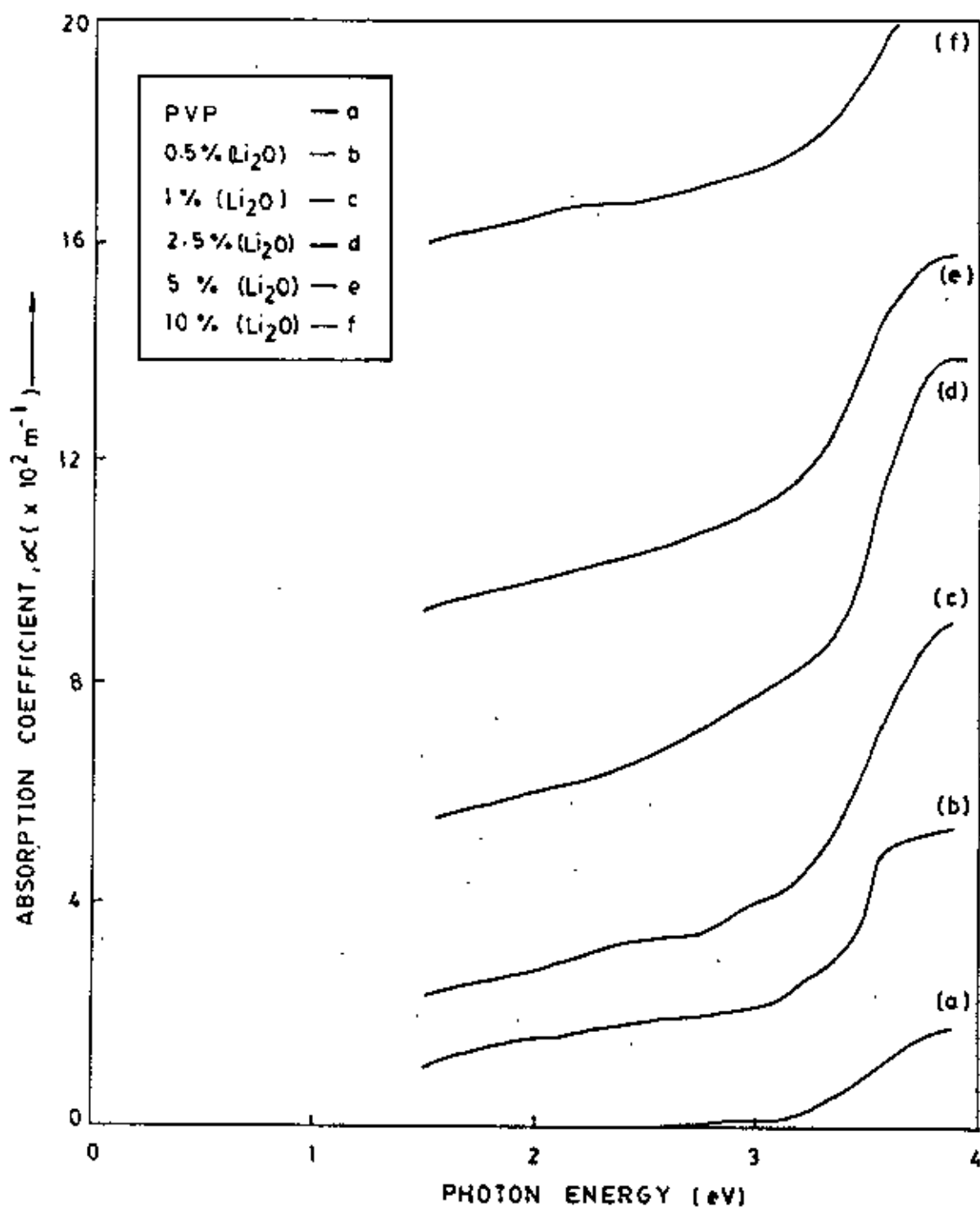


Fig. 4.10: Absorption co-efficient vs photon energy with different concentration of lithium oxide (Li_2O)

4.3 D.C. ELECTRICAL STUDIES

It is a general practice to metalize surfaces of a specimen to perform different electrical measurements. But, this metalization influences the observed results owing to the development of contact potential, contact electrification etc. The electrical measurement using metal contacts help to understand different mechanism of conduction in materials. Therefore, it is very important to know the contact behaviour of metals to the material concern. In this purpose, at the beginning, the I-V characteristics are investigated and the observed results are discussed below. Then the variation of conductivity with temperature for all the samples are discussed here.

4.3.1 CURRENT- VOLTAGE (I-V) CHARACTERISTICS

The I-V characteristic curves recorded at room temperature for the samples PVP and PVP complexes having 0.5, 1, 2.5, 5, and 10% Li_2O are presented in figures 4.11 and 4.12 for as prepared samples and samples heat treated at 100°C respectively. It is observed in both class of samples that there are two regions of voltage dependence. At the low voltage region, little fluctuation in the current data can be noticed. Whereas in the high voltage region, current is quite stable. These I-V curves can be fitted to a relation of the form $I = V^n$, where n is the power factor. The 'n' calculated from the I-V characteristics are depicted in Table 2.

Table 2 : Values of power factor n for different samples

Samples	As prepared		Heat treated at 100°C	
	0-20 volt	20-80 volt	0-10 volt	10-80 volt
PVP	0.985	0.919	0.824	0.948
0.5%(Li ₂ O)	1.056	1.031	0.807	0.862
1%(Li ₂ O)	1.267	1.035	0.966	0.991
2.5%(Li ₂ O)	1.025	1.044	0.921	0.938
5%(Li ₂ O)	1.004	1.041	0.628	0.880
10%(Li ₂ O)	1.244	1.115	0.919	0.991

These show that the n value lies within unity. This means that the contact is Ohmic. Thus, this contact would be appropriate to investigate the electrical properties without any influence on the observed data.

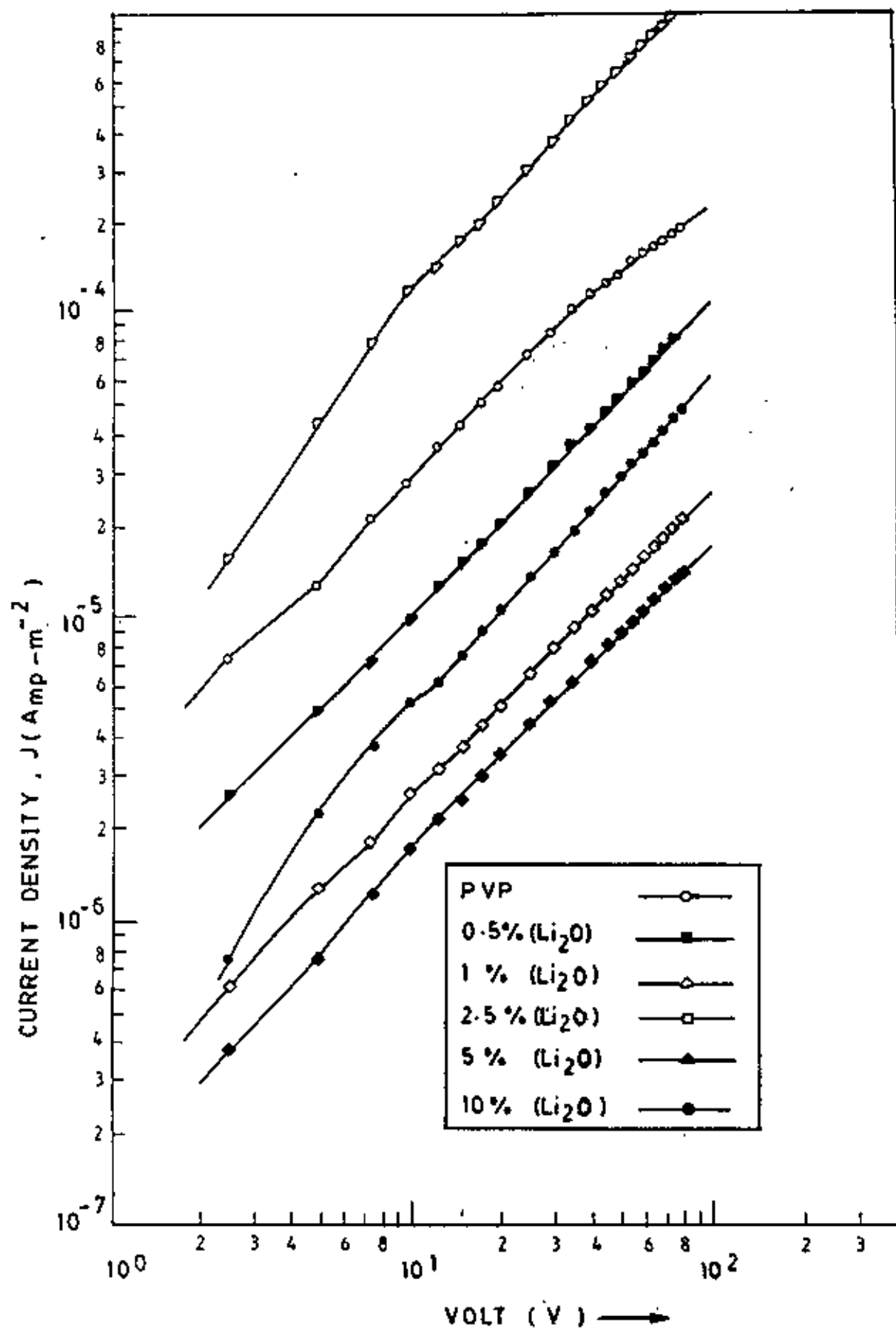


Fig. 4.11: Variation of current density with applied d.c. voltage for different as prepared samples.

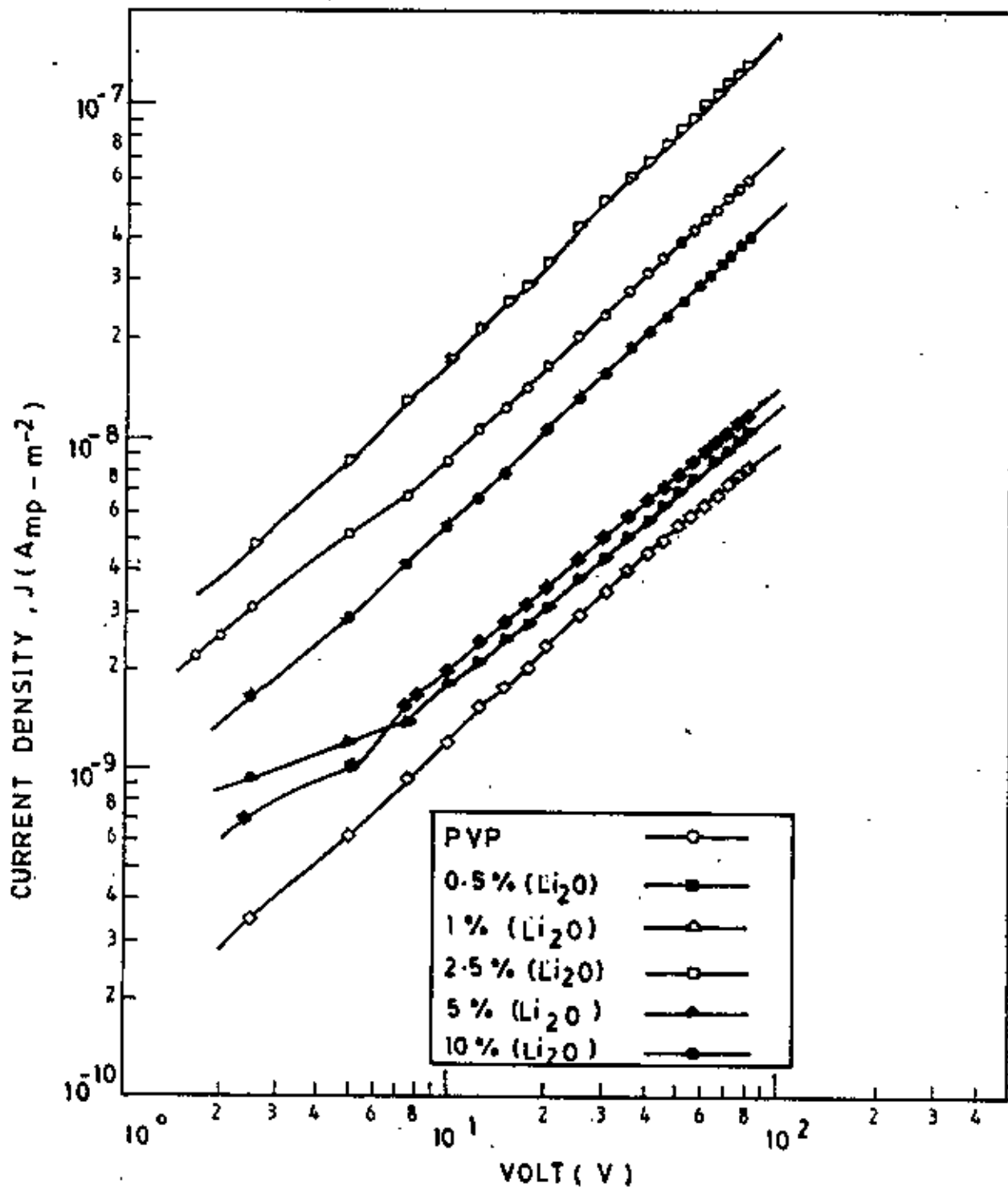


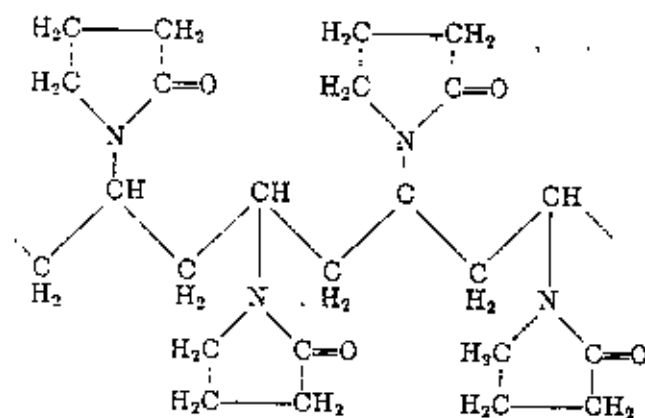
Fig. 4.12: Variation of current density with applied d.c. voltage for different samples heat treated at 100°C.

4.3.2 D.C. CONDUCTIVITY

The dependence of d.c. electrical conductivity on temperature for as prepared PVP and PVP complexes having 0.5, 1, 2.5, 5, and 10% Li_2O and heat treated (100°C) PVP and its complexes are presented in figures 4.13 and 4.14 respectively.

In figure 4.13, for as prepared samples, it is seen that there is an increase in the electrical conductivity in the low temperature region and then decreases with temperature.

It is interesting to note that the turning point i.e. the temperature at which the d.c. conductivity starts decreasing shifts toward higher temperature from 45 to 75°C with the increase of Li_2O concentration except one sample (1% Li_2O). This point may be understood from the following discussion. PVP is believed to have somewhat coiled chainlike molecules. It contains $-\overset{\text{O}}{\parallel}\text{C}-\text{N}<$ groups which can attract and hold water and other molecules. The somewhat clumped, long macromolecules in solution may be regarded as made up of recurring units of the following type:



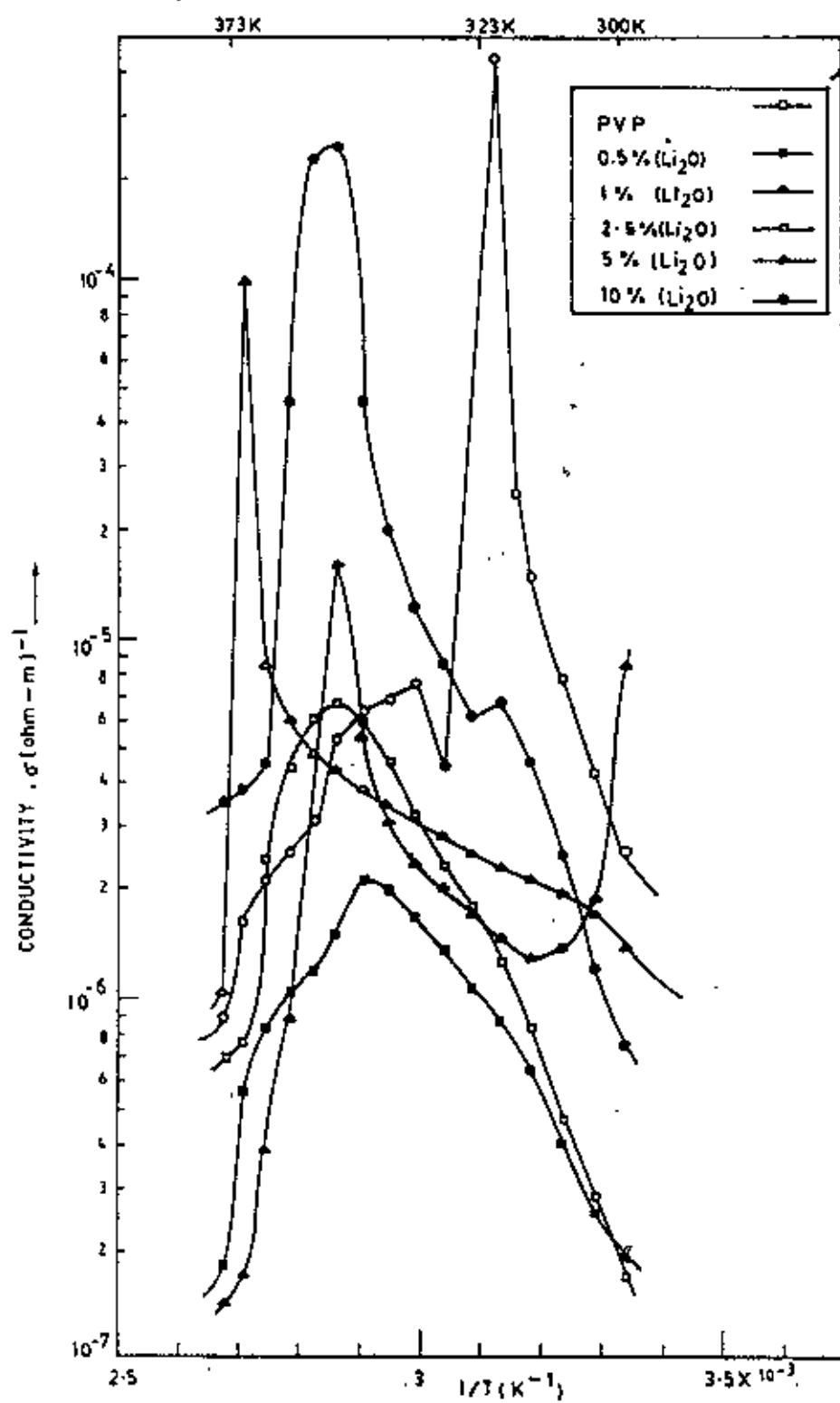


Fig. 4.13: Variation of d.σ conductivity as a function of temperature for as prepared samples.

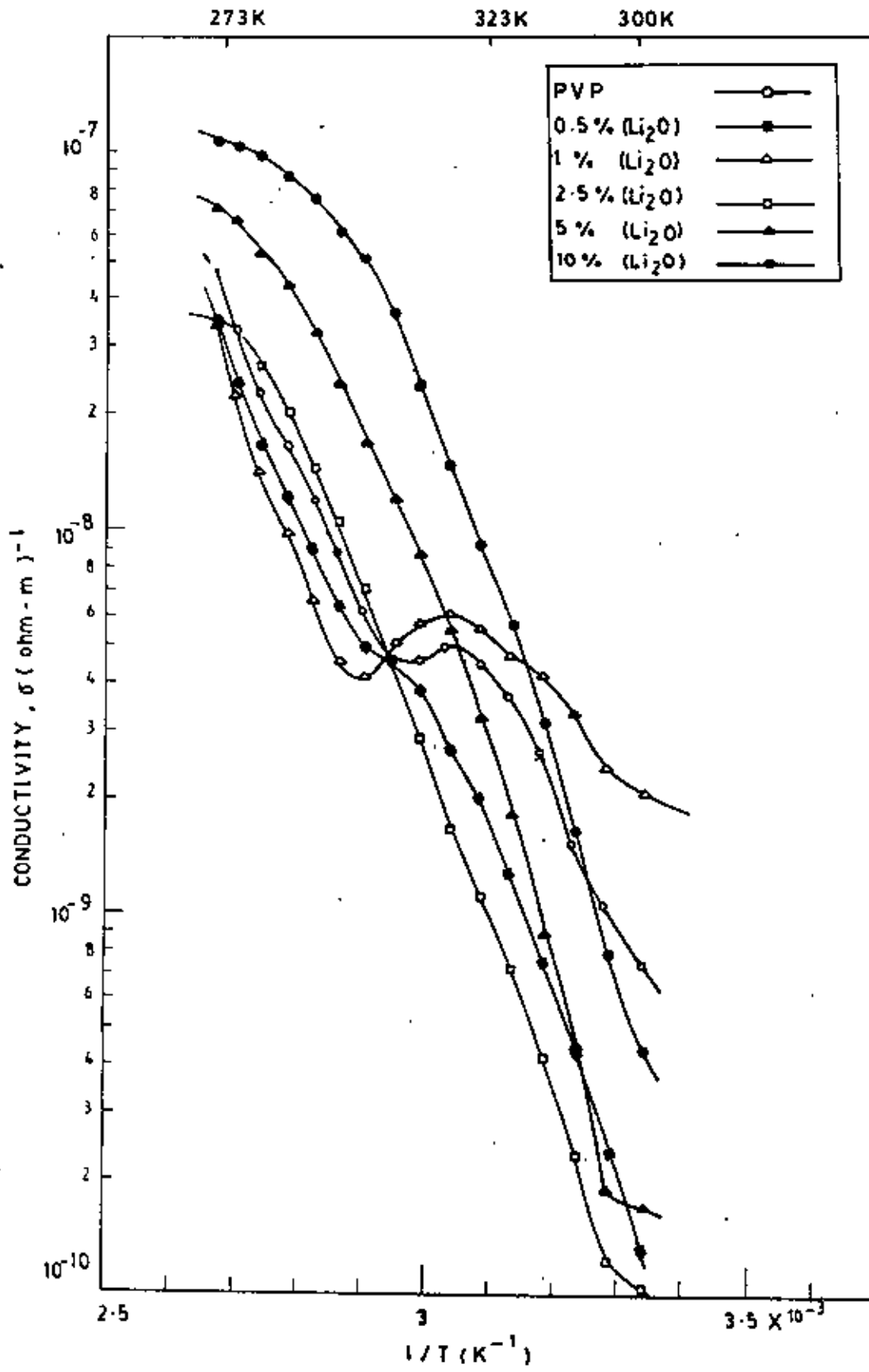


Fig. 4.14: Variation of conductivity as a function of temperature for samples
 ○ heat treated 100°C.
 ▲₀

In water solution, clusters of water molecules are held to the polymer chain molecules, especially in the vicinity of the polar nitrogen and carbonyl oxygen atoms. It is also probable that PVP samples contain some branched chains; there may also be uncertain number of end groups. On the otherhand, when Li_2O is dissolved in water, it transforms to LiOH . Thus, when PVP and Li_2O dissolve in water, the LiOH and water molecules have a sort of competition to take the spaces in the vicinity of the polar groups. As Li is somewhat heavier and more electropositive; this compound interacts more than water molecules. When the sample is dried, most of the water leaves the sample. There may be only LiOH and Li_2O left in the sample. However, the presence of trace amount of water may not be ignored. Thus, it can be said that the incorporation of Li compounds in PVP network prevents the presence of water. As a result, with the increase of Li_2O concentration, the water content in PVP decreases thereby increasing the turning temperature. The activation energies calculated from the initial rise part of the conductivity-temperature curves are recorded in Table 3.

Table 3: Activation energies in (eV) calculated from the conductivity-temperature curves (Fig. 4.13 and 4.14).

Samples	As prepared	Heat treated at 100°C
	Energy (eV)	Energy (eV)
PVP	0.963	0.625
0.5%(Li_2O)	0.668	0.869
1%(Li_2O)	0.226	0.297
2.5%(Li_2O)	0.861	0.917
5%(Li_2O)	0.320	1.164
10%(Li_2O)	0.975	0.994

In figure 4.14, for heat treated samples at 100°C, it is seen that a transition appears in samples PVP and PVP complexes containing 0.5 and 1% Li₂O in the temperature region 70-80°C. Whereas this is not present in the other samples i.e. PVP containing 2.5, 5 and 10% Li₂O. After heat treatment, a major transformation occurs as evidenced from the optical microphotographes and electrical measurements. The probable modification may be due to the increased interaction of Li₂O with the PVP structure after heat treatment. As Li₂O increases, the chance for water molecules to be held in the PVP structure decreases. Further, it is important to notice that after heat treatment, the samples turn to be semiconducting with low conductivity. At same time, the effect of water on the electrical properties decreases markedly. The activation energies are calculated from the curves and are tabulated in Table 3.

From the high values of the activation energies, it may be inferred that the conductivity may be due to motion of protonic ions. It is interesting to note that there is a decrease of conductivity of the order 10³ due to heat-treatment at 100°C (Table 4).

Table 4 : Conductivity variation with different concentration of Li₂O at room temperature (30°C)

Samples	Conductivity (ohm-m) ⁻¹	
	As prepared	Heat treated at 100°C
PVP	2.55 x 10 ⁻⁶	7.42 x 10 ⁻¹⁰
0.5%(Li ₂ O)	1.89 x 10 ⁻⁷	1.30 x 10 ⁻¹⁰
1%(Li ₂ O)	1.39 x 10 ⁻⁶	2.05 x 10 ⁻⁹
2.5%(Li ₂ O)	1.7 x 10 ⁻⁷	1.01 x 10 ⁻¹⁰
5%(Li ₂ O)	8.48 x 10 ⁻⁶	1.73 x 10 ⁻¹⁰
10%(Li ₂ O)	7.57 x 10 ⁻⁷	4.35 x 10 ⁻¹⁰

In the as prepared samples, the room temperature conductivity is observed to increase with Li_2O concentration. This fact can be substantiated by the decrease of band gap with Li_2O concentration (Table 1).

In the heat treated samples, the room temperature conductivity is decreased a little with the Li_2O concentration. Moreover, if conductivity variation with temperature data are observed carefully, it is interesting to mention that after heat treatment, the materials under study become semiconducting in nature. But the conductivity is decreased by order of about 10^3 . The fact can be corroborated with the structural modification about at 90°C (endotherm) as observed in the DTA and weight loss in the TGA.

CHAPTER 5
CONCLUSIONS

5.1 CONCLUSIONS

Polyvinylpyrrolidone (PVP), a polar and nontoxic polymer, and its complexes containing different amount of Li_2O have been prepared and structural and electrical properties have been investigated. The results have been discussed in the previous chapters. The findings and suggestions for the future work are described here.

The incorporation of Li_2O in the PVP structure is seen from the XRD and IR investigations. The optical microphotographs show segregation in the as prepared sample and the samples become homogeneous on heat treatment. Optical absorption measurement shows that the maximum optical absorption edge decreases with Li_2O concentration in the PVP. It is also observed that there are lots of defect states in the band gap. From the DTA study, it is seen that the first reaction occurs at about 90-95°C (endotherm) and at this temperature first step of weight loss takes place which is evident by TGA.

The I-V characteristics with silver paste contact give Ohmic contact within the measurement limitations. The variation of d.c. conductivity with temperature reveals that the conductivity may be due to the motion of ions. It is also observed that the conductivity is decreased by about 10^3 order of magnitude on heat treatment at 100°C. Further, it is seen that the samples become semiconducting on heat treatment. The influence of water on the electrical properties is decreased with the Li_2O concentration and on heat treatment.

5.2 SUGGESTION FOR FUTURE WORK

It has been found that PVP and its complexes with Li_2O have very interesting properties. These materials require proper investigation for better and particular application. This thesis initiates the work and further investigation on these material is very necessary. The DTA and TGA reveal that major changes occur at above 400°C . This result dictates detail investigation of high temperature treated complexes.

For better understanding and proper application, structural studies are necessary using DSC. The study of the mechanical properties is also necessary to understand the structure and the charge motion in the material. It is important to carry out the dielectric studies at different temperatures and frequencies. At the same time, thermally stimulated polarization current (TSPC) and thermally stimulated depolarization current (TSDC) studies are also necessary to know the relaxation behaviour of the materials.

REFERENCES

1. M.O.W. Richardson, "Polymer Engineering Composites", Applied Science Publishers Ltd., 1977.
2. S.G. Burnay, "New materials and their applications", (Published under the Institute of Physics imprint by IOP Publishing Ltd., Bristol, England), 1987
3. A. A. Berlin, "Principle of Polymer of Composites" (Printed in GDR) 1987.
4. "Kirk-othmer Encyclopedia of Chemical Technology", (A wiley-interscience publication) V-13, p-1238, 1984.
5. V. R. Gowariker, "Polymer Science" (Published by Wiley Eastern Ltd.), 1993.
6. S. Z. Haider, "Introduction to Modern inorganic Chemistry" (Students Publication, Dhaka), 1973.
7. B. D. Cullity, "Elements of X-ray diffraction" 2nd ed; Addison-wesley Publishing Inc., Phillipines, 1978
8. Chatelier, H. Le., Bull. Soc. France mineral, [10] 204, 1884
9. Sybil P. Parker, "Mcgraw-Hill Dictionary of Physics", 1986

10. P. R. Singh, "Molecular spectroscopy Principles and Chemical Applications", (S. Chand & Company Ltd.), 1985
11. "Characterization of plastics by Physical methods" (Hanser Publishers), 1986
12. L.L. Dubey, B.L.Sharma and A. P. Srivastava, "Electrical and Optical behaviour of solids", Edited by : R. Nath, Mithal Publications, Delhi 110035, India, 1989, P-149-159
13. S. Radhakrishna and S.Haridoss, Ind. J. Phys. 53 (1979), 103.
14. I. M. Bublevskii, S.I. Belykh, A.B. Bavydov, L.M. Lipovich, M. A. Mekhuzula and YE A Sminova : Polymer Sci. USSR, Vol. 22, (1980)
15. S. K.Chaterjee and K. R. Sethi : J. Polym. Chem. Vol. 21, (1983), 1050
16. P. K. Khare, M. S. Gaur and A. P. Srivastava, "Indian J. of Pure and appl. Phys", Vol. 31, (1993), 102-105

APPENDIX

APPENDIX

Table I : 2θ and d_{hkl} values calculated from the X-ray diffraction patterns for PVP, PVP containing 0.5, 1, 2.5, 5 10% Li_2O , Li_2O and standered Li_2O .

Samples	2θ in degree	d_{hkl} in Å
Standered Li_2O	33.64	2.66
	39.06	2.30
	56.42	1.63
	67.34	1.39
	83.91	1.15
Li_2O	20.2	4.39
	21.2	4.19
	30	2.93
	32.4	2.76
	33.4	2.68
	35.4	2.53
	36.6	2.45
	38.8	2.32
	43.4	2.08
	45.8	1.98
	48.6	1.87
PVP	20.06	4.42
0.5% Li_2O	19.93	4.45
1% Li_2O	21.04	4.22
	23.84	3.73
	31.06	2.87
2.5% Li_2O	20.72	4.28
	22.91	3.88
	29.87	2.99
	31.36	2.85
	38.23	2.35

Samples	2θ in degree	d_{hkl} in Å
5% Li_2O	20.8	4.27
	23.2	3.83
	29	3.07
	30.2	2.95
	31.4	2.84
	33.8	2.65
	36.5	2.46
	39.2	2.29
	48.4	1.88
10% Li_2O	21.42	4.14
	23.56	3.77
	29.68	3
	30.7	2.91
	32.03	2.79
	34.27	2.61
	36.41	2.46
	37.33	2.40
	40.39	2.23
	41.82	2.15
	43.65	2.07
49.47	1.84	

