

COMPARISON OF THE ELECTRICAL PROPERTIES OF
CONJUGATED AND PIGMENT POLYMER SYSTEMS

by

Fathey Al-Arrayed

Thesis

submitted to the University of Strathclyde

in accordance with regulations

governing the award of

Master of Science

in the

Department of Pure and Applied Chemistry



Department of Pure and Applied Chemistry,
Thomas Graham Building,
University of Strathclyde,
Glasgow.

December 1986.

To my sister Sana and Parents



Declaration:

The research presented in this thesis was carried out by me as part of my submission for the degree of Master of Science at the University of Strathclyde.

Signed Fathey Al-Arrayed . Date 1/12/86
Fathey Al-Arrayed December 1986

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Professor A.M. North for his valuable advice and encouragement throughout the duration of this work.

I would like to express my deep gratitude to Professor R.A. Pethrick for his helpful supervision and invaluable discussions during the execution of this work, and for his guidance and advice during the production of this thesis.

I would also like to thank all members of Professor Pethrick's research group for their encouragement and enthusiasm, in particular, Dr. M.B. Mahboubin Johns, Dr. David Haward and Dr. S. Doyle for their help and constructive criticism and the technical staff of the Physical Chemistry Department for their continuous cooperation in a friendly atmosphere.

My thanks also go to Bahrain University for the grants given during the period of this research.

I am deeply grateful to my parents, sisters and brothers for their support, kindness and encouragement.

I would like to thank Professor A.N. Bose for his care and patience during the organisation of this thesis and all the members of the Chemistry Department at Bahrain University for their encouragement and enthusiasm.

My thanks also go to Dr. M.N. Khan for his help and encouragement.

The author wishes to thank the SERC for the provision of the surface profile and electrical conductivity equipment.

Lastly, I would like to thank Mrs. Susan Hallam for her care and patience during the typing of this thesis.

SUMMARY

The work described in this thesis is concerned with an investigation of the electrical conductivity of polymers in which conductivity involves either a conjugated polymer backbone (polypyrrole para-toluene sulfonate) or carbon black filled polymers (polystyrene and polychloroprene).

The study presented on polypyrrole para-toluene sulfonate was carried out in order to establish the way in which variation of conditions used in the electrochemical preparation influence the conductivity of the films produced. It was found that the changes in the electrical conductivity of polypyrrole para-toluene sulfonate can be obtained by the variation in the voltage and concentration of electrolyte used in the synthesis of films. There is also a close correlation between the conductivity, rate of growth and the voltage used in the preparation of the films. It was found that the temperature dependence of the conductivity follows a typical $\sigma \propto \exp[-(T_0/T)^{1/4}]$ law. The experimental results are analyzed in the framework of Mott's model, for a variable range hopping process, and it was observed that the model predicts the right qualitative behaviour for the conductivity.

The study presented on the carbon black composites were carried out in an attempt to establish the influence of the matrix on the concentration conductivity relationship on composite systems. It was found that the addition of carbon black to polychloroprene can lead to the creation of filler-polymer interactions which influence the molecular relaxation processes as well as the conductivity of the carbon black composites.

Similar observations were made on polystyrene carbon black composites. The conductivity-frequency dependence indicates that the conductivity follows typically $\sigma(\omega) \propto \omega^S$ law and the carrier movement could be ascribed to a "hopping mechanism". The conductivity-frequency independence indicates that the conductivity does not follow a typical $\sigma(\omega) \propto \omega^S$ law. The conductivity decays with frequency and reaches a limiting value which does not decay further with frequency. This is indicative of the bulk conduction saturation.

TABLE OF CONTENTS

	<u>Page</u>
Acknowledgements	iv
Summary	v
 Chapter I. INTRODUCTION	 1
1.1 Literature Review: Electronic Conductivity of Polymers	2
1.2 Aims of the Thesis	19
 Chapter 2. LITERATURE REVIEW OF THE BAND MODELS AND CONDUCTION MECHANISMS OF AMORPHOUS SEMICONDUCTORS	 20
2.1 Introduction	21
2.2 A Review of Electrical Phenomena in Amorphous Materials	22
2.2.1 Band Structure in Solids	22
2.2.2 Conduction in Dielectric Materials	25
2.2.3 A Blocking Contact	26
2.2.4 Neutral Contact	27
2.3 Modern Ideas of Amorphous Materials	31
2.3.1 Band Models	31
2.3.2 Mott's Model	35
2.3.3 The Cohen-Fritzsche-Ovshinsky Model	36
2.3.4 The Davis-Mott Model	39
2.3.5 Phenomenology of Polaron and Bipolaron	39
2.3.6 Anderson Band	42
2.3.7 Gubanov Theory of Amorphous Conductors	44
2.3.8 Hopping Model	46
2.3.9 Hopping and Variable-Range Hopping	50
2.3.10 Hopping Conduction for Alternate Currents	52

2.4	Electronic Transport in Amorphous Semiconductors	56
2.4.1	Electrical Properties	56
2.4.1.1	D.C. Electrical Conductivity	56
2.4.1.2	A.C. Conductivity	60
2.5	Dielectric Relaxation	63
2.5.1	General Theory	63
2.5.2	Thermal Activation of Dipolar Relaxation	71
2.5.3	Dielectric Relaxation in Solid Polymers	73
2.5.3.1	Nomenclature	73
2.5.3.2	Origin of Dielectric Activity	73
2.5.3.3.	Relaxation in the Temperature of Frequency Domains	74
2.5.4	Interfacial Polarization	76
Chapter 3.	EXPERIMENTAL TECHNIQUES AND APPARATUS	77
3.1	Review of the Experimental Techniques	78
3.1.1	Direct - Current Methods	78
3.1.2	Alternate - Current Methods	83
3.2	Electrode Systems used for Measurement	84
3.3	Sample Cells	85
3.3.1	Conventional Dielectric Cell	85
3.3.2	Conventional Four Terminal Cell Configuration	85
3.3.3	Electrochemical Cell	88
3.4	Preparation and Purification of Chemicals	88
3.4.1	Purification	88
3.4.2	Preparation	90
3.5	Effects of Changing the Anions and Cations of Supporting Electrolytes, Electrolytes and Voltage on the Morphology of the Polypyrrole Films	99
3.6	Experimental Techniques	101

Part II: ELECTRICAL PROPERTIES OF POLYPYRROLE PARA-TOLUENE SULFONATE	170
4.6 D.C. Measurement Results	170
4.7 Dielectric Measurements Results	176
4.8 Results of Variation of Anions and Cations of Supporting Electrolytes, Electrolytes and Voltage on the Morphology of Doped Polypyrrole	179
4.9 Elemental Analysis Results	186
4.10 Cyclic Voltametry	187
4.11 Thickness Determination and Structural Properties	189
4.12 Discussion	196
4.12.1 Electrochemical Polymerization of Pyrrole	196
4.12.2 Conductivity and Electronic Conduction of Polypyrrole Para-Toluene Sulfonate	201
4.12.3 Conclusions	203
Appendices	205
References	214

3.6.1	Dielectric Measurements	101
3.6.2	D.C. Conductivity	103
3.6.3	A.C. Conductivity	103
3.6.4	The Current - Voltage Characteristics	104
3.6.5	Microanalysis of the Polymer Films	105
3.6.6	Cyclic Voltametry	105
3.6.7	Surface Thickness and Profile Measurements	105
3.7	Summary of Matrices used	106
Chapter 4. RESULTS AND DISCUSSION		107
Part I: ELECTRICAL CONDUCTIVITY AND DIELECTRIC STUDIES OF CARBON BLACK COMPOSITES OF POLYSTYRENE AND POLYCHLOROPRENE AND INFLUENCE OF FILLERS ON DIELECTRIC RELAXATION PROPERTIES OF POLYCHLOROPRENE		108
4.1	Electrical Conductivity of Carbon Black Filled Polystyrene	108
4.2	Electrical Conductivity of Carbon Black Filled Polychloroprene	120
4.3	Characterization of (α) Relaxation for Pure Polychloroprene and Carbon Black Composites	125
4.4	Powles Relationship and the Study of Change in the Dielectric Amplitudes of Carbon Black Filled Polychloroprene	160
4.5	Discussion	165
4.5.1	Influence of Carbon Black on the Dielectric Relaxation of Polychloroprene	165
4.5.2	Influence of Carbon Black on the Conductivity of Polychloroprene and Polystyrene	168
4.5.3	Electronic Conduction Mechanism on the Carbon Black Composites	169

I. INTRODUCTION

CHAPTER 1. INTRODUCTION

1.1 Literature Review: Electronic Conductivity of Polymers

Electrical conductivity of materials is a property which spans a very wide range as may be observed from the conductivity chart, figure (1.1). Some of the polymers like polyethylene, polytetrafluoroethylene and polystyrene are amongst the best insulators known. On the other hand the salts of 7,7,8,8, - tetracyanoquinodimethane (TCNQ) and combination of TCNQ and tetrathiafulvalene (TTF) have very high conductivities (1).

In most polymeric materials it is very difficult to observe any electronic conductivity at all and, even when conductivity is observed, is usually due to the movement of impurity ions. Therefore, in order to improve the quality of insulation in a polymer one should be very careful at the time of preparation and purification so as to avoid as much as possible the presence of ionic impurities, including catalyst residues, products of oxidation and dissociable end groups. In recent years high-conductivity polymers have been made. The credit, for generating interest in organic structures which conduct electronically, goes to the biologist Szent Györgyi (2) who speculated about the role of semiconduction in living systems. Although, semiconduction failed to explain complete electron transfer in living cells, nevertheless, chemists have been led by this work to conjecture that in certain organic compounds where the electrons are extensively delocalised in the molecules, there might be enhanced conductivity. Eley (3) for the first time demonstrated conduction on this premise. His work generated a considerable amount of interest in preparing such compounds and especially conducting polymers. These polymers, by virtue of their chemical structure, permit electronic conductivity and are classified under

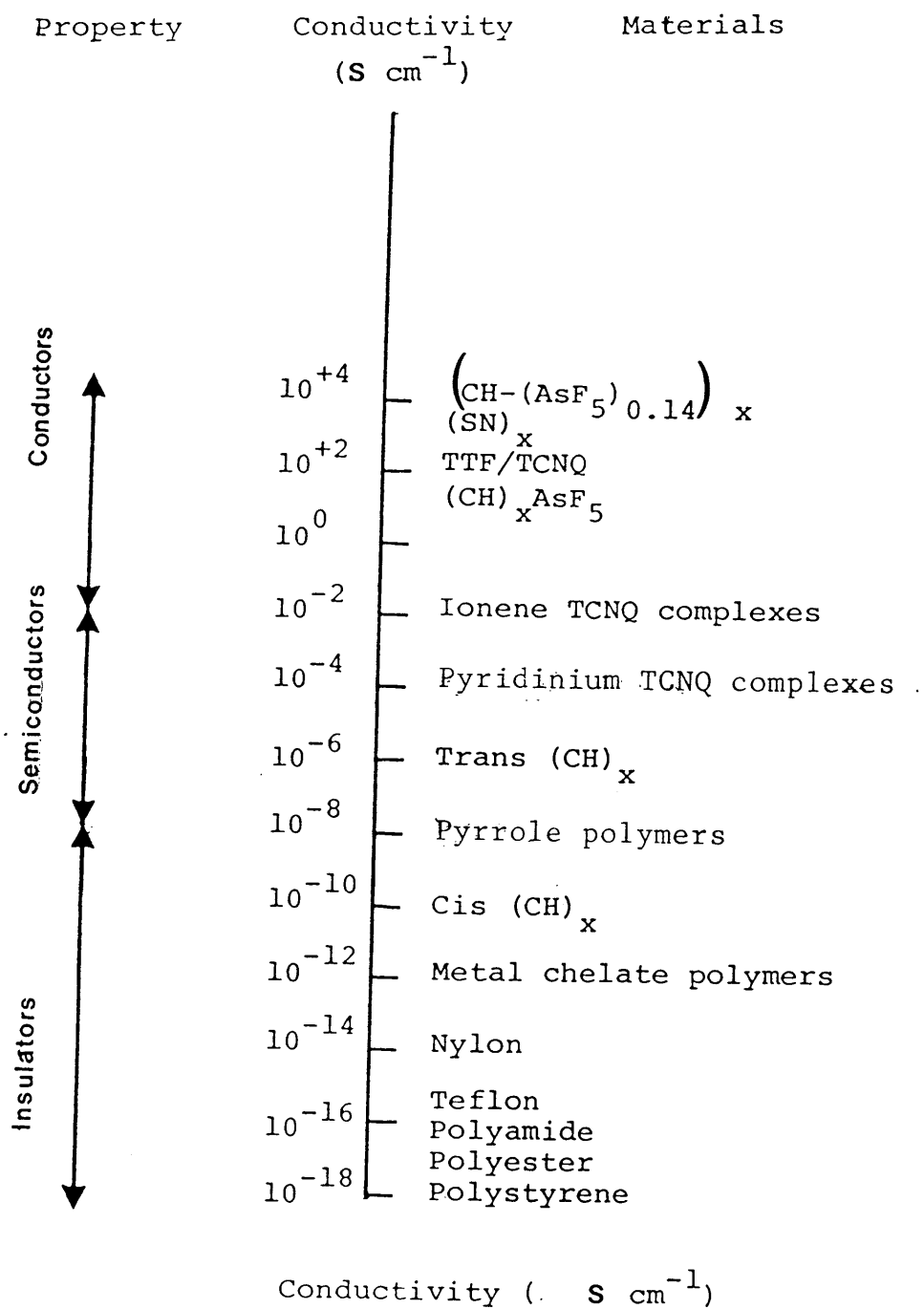


Fig.(1.1) The conductivity of polymers.

conducting polymers. There is another class of conducting polymers which are derived from the addition of metals or graphite particles to organic matrix. A brief review of the work done on conducting polymers is given below.

Wynne and Street (4) have reviewed the work done in this field in a recently published paper. There are several types of conducting polymers.

1. Intrinsically Conducting Polymers

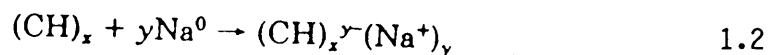
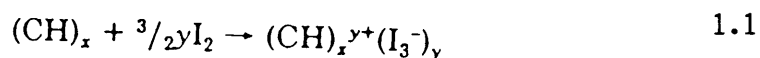
Walatka et al. (5) demonstrated for the first time that polymeric $(\text{SN})_x$ crystals have high conductivity. The conductivity of $(\text{SN})_x$ at room temperature along the chain direction is 1000 S cm^{-1} . Below 0.3K it becomes superconducting. Brominated $(\text{SN})_x$ (6,7) has conductivity 10 S cm^{-1} (8,9). Attempts to prepare similar polymer with open-shell electronic structure have not given any positive result (10).

2. Conducting Polymers Obtained by Electronic Modification of Insulating Polymers

The open shell electronic configuration can be achieved by oxidation or reduction of insulating polymers which contain an extended π -bonded system. There are two broad methods - direct chemical oxidation or reduction and electrochemical oxidation and reduction by which insulating polymers can be converted to metallic conductivity.

i) Direct Chemical Oxidation or Reduction: Polyacetylene, $(\text{CH})_x$, was the first insulating polymer to be converted to metallic conductivity by chemical oxidation or reduction. MacDiarmid (11,12)

has given an extensive list of oxidising and reducing agent for converting polyacetylene into a conductor. Two typical reactions are given below (13):



Wnek and co-workers have shown that copolymer films of acetylene and methylacetylene can be chemically oxidized with AsF_5 to give high conductivity (14).

Brominated $(\text{SN})_x$ (6,7) has been prepared by the oxidation of S_4N_4 with bromine vapor. Solid acetylene reacts with AsF_5 to give conducting polyacetylene.

Non-polyolefinic polymeric conducting materials have been prepared. Ivory (15) oxidised poly (p-phenylene) (PPP) using AsF_5 .

Conducting PPP has been prepared by the reduction of PPP using alkali metals. The actual conductivity of the final polymer is dependant on the degree of oxidation or reduction as in the case of polyacetylene. Conducting materials of oligomers of PPP have also been prepared (16).

Perhaps the most interesting of the polyphenylene derivatives are the sulfur linked phenylene polymer chains (17,18). Treatment of films of poly (p-phenylene sulfide (PPS) with AsF_5 leads to high conductivity.

ii) Electrochemical Oxidation or Reduction: Polyacetylene can be oxidised or reduced electrochemically (19,20). Flexible films of polypyrrole have been prepared by simultaneous electrochemical polymerization and oxidation of pyrrole (21,22).

3. Bridged-Stacked Phthalocyanines

A number of bridge-stacked phthalocyanines have been prepared as have their oxidised products have also been prepared (23).

Different kinds of oxidants have been used to prepare conducting oxo-bridge silicon, germanium and tin phthalocyanines (24).

Polymers with fluorine-bridged structure (24-26) have also been prepared. Fluorine-bridged polymers are thermally stable, they can be sublimed to form films, and they have potential optoelectronic properties.

4. Heterocyclic Aromatic Polymers

Part of the present work is on polypyrroles, therefore, a more detailed review is presented.

Chemical oxidation of aniline and pyrrole gives aniline blacks (27) and pyrrole blacks (28) respectively. By electrochemical polymerization of pyrrole, Dall'Olio (29) prepared high conductivity film of pyrrole. Recent improvements on Dall'Olio's technique have given more flexible films with higher conductivity (21,22). N-substituted pyrrole polymers have also been prepared electrochemically, but their conductivities were found to be much lower (30). Co-polymers can also be synthesized and they show intermediate activities (31). Finally in the last few years, there has been increasing interest in semi-conducting polymer films. Most of the work in this area has been concentrated in two main classes of polymer; namely polyacetylene and its derivatives (11,32) and polyheterocyclic systems (33-35). The interest in polyacetylene stems from the fact that it is the simplest structure which can exhibit a high electrical conductivity (σ) when doped with iodine (36). On the other hand, polyheterocyclic systems such as polypyrrole exhibit high electrical

conductivity and also high stability when exposed to ambient conditions (37). The drawbacks of these polymers are:

i) for polyacetylene, its poor stability at ambient conditions (38), and ii) for polypyrrole, its poor mechanical properties as indicated by its low elongation and its brittleness (39). These properties severely restrict the technological applications of these two classes of polymers. A number of attempts have been made to rectify these problems and this has caused the research to be extended into the study of composite systems. Part of the present work relates to the study of polypyrrole, therefore, a detailed review is being presented. Pyrrole monomer is very readily polymerized to give a black conducting powder (28). It can be polymerized by a large number of oxidizing agents and can even be observed taking place on the outside of bottles of pyrrole if the monomer is allowed to drip. The resulting conducting powders have been referred to as pyrrole black for many years. Oxidation of the powders with KMnO_4 has been shown to lead predominantly to the 2,5 dicarboxylic acid, and this has been interpreted as evidence that the polymerization leads to an $\alpha, \bar{\alpha}$ bonded polymer (28). The polymerization can take place electrochemically (29), as well as chemically. Chemically, pyrrole can be oxidatively polymerized both in solution and also in the vapor phase (40). Though chemical oxidation usually leads to powders, film can be obtained by allowing the oxidation to take place at a solid or liquid surface (40,41), however, these films are of poor quality. In some cases, there is no evidence that these chemically prepared films have much in common with what is now meant by polypyrrole, indeed, they are not even conducting (41). The pyrrole blacks like the analogous

acetylene blacks required to be doped to achieve high values of the conductivity. Thus, even through a chemical preparation of polypyrrole films remains a desirable goal, presently the electrochemical synthesis described below provides the only satisfactory route. Good quality films were first obtained by Kanazawa et al. (21,22) and Diaz et al. (37) using a modification of the electrochemical technique pioneered by Dall'Olio (29). Soon afterwards it was appreciated that their films consisted of polycationic chains of pyrrole, analogues to bromine treated $(SN)_x$ or oxidized $(CH)_x$ but with the charge counterbalanced by anions from the electrolyte solution (42).

Polypyrroles are prepared by these electrochemical methods:

i) by an aqueous technique in which an aqueous solution of pyrrole and copper sulfate are placed in a one compartment cell, equipped with two conducting electrodes. Copper is used as cathode and tin oxide coated glass slide as the anode (43). A bronze coloured to blue-black film of polypyrrole sulfate forms at the anode when $\sim 5V$ is applied across the two conducting electrodes using a d.c. power supply. Under these circumstances, the counter electrode reaction is the deposition of metallic copper on the cathode. During the preparation, the pH of the solution decreases consistently with the elimination of the α -protons. This aqueous technique can be used to introduce a variety of inorganic anions as well as some organic anions which are discussed in Chapter 3.

ii) The technique described by Diaz et al. (44) used non-aqueous acetonitrile solutions of silver-perchlorate as the electrolyte to grow films of polypyrrole. Acetonitrile can be replaced by isopropyl alcohol and acetone solutions of copper sulfate as the

electrolyte to grow films of polypyrrole.

Both the techniques were rejected because of the disadvantages discussed in detail in Chapter 3.

iii) A modification of this technique, convenient for film preparation in the dry-box, used carefully purified pyrrole and silver para-toluenesulfonate salt in acetonitrile and platinum as cathode and the anode was constructed from vapour deposited gold on a chrome plated glass substrate. The use of chrome ensures good adhesion of the gold to the electrode and avoids the problems of poor adhesion experienced when only gold is used by itself. The polymer was grown in a two electrode cell. The current-voltage control being obtained using a multi-range meter. Dry-box technique has been used extensively in the present work. A complete study of conducting polymers should include study of the electrochemical properties especially since one of the applications of polypyrrole may lie in their use as electrodes (44-48). Cyclic voltammograms (33,45,49-69) can also be used to identify the oxidation-reduction conditions for the preparation of polypyrrole and the role of the electrode potential on the growth of such films.

The electropolymerization of pyrrole to produce polypyrrole films and the electroactive behaviour of the polypyrrole films represent a unique combination of electrochemical processes (33). The electrochemical polymerization can be viewed as the organic counterpart to the known electrodeposition reactions of metals. The electroactive behaviour of the film is unique because it is an example of a redox polymer reaction which is accompanied by a change in the electrical properties of the film from an insulator

to an electric conductor (51,54).

As regards the electropolymerization reaction, continuous polymeric films are produced from the reaction when the nucleophilicity of the solution is low and the electrode potential is sufficiently positive to oxidize pyrrole. If the potential is reduced to a value intermediate between the potential required to oxidize the pyrrole monomer (51) ($E_{pA} = 1.2V$ VS. SSCE) and polypyrrole film ($E^0 = -0.2V$ VS. SSCE), the film will not continue to grow. Thus, film formation proceeds only when the monomer is oxidized. The oxidation potential of polymer and monomer are also changed by the presence of the substituent (52,56,58,67), electrolyte (68) and electrolyte salt (51,70). These parameters will also change the cyclic voltametry, especially in the case of polypyrroles (33,67) and these effects along with the thickness of the films (71) play a dominant role on changing their electrochemical properties.

Redox potential of pyrrole is 1.2V. In the present work, therefore, voltage range between 0.5V to 2.0V has been chosen to study the properties of films grown in oxidizing and reducing conditions, Cyclic voltamogram has been obtained by using the Solatron 1186 Electrochemical Interface for one of the films. For such a film, measurement has been made using a 0.1M silver para-toluene sulfonate in acetonitrile under the potential of -0.5V to 0.5V.

In the present work an attempt has been made to prepare films of polypyrroles and to study the conductivity of these films.

Survey of literature reveals that no systematic study has been made so far in this direction. This work focuses attention on the electrical properties of polypyrrole para-toluene sulfonate (22, 30-32, 39, 65, 72-82) because the mechanical properties (39) of

polypyrrole para-toluene sulfonate are significantly superior to other forms of polypyrroles which will be discussed in Chapter four. Conductivity measurements were carried out on the films using four probes contact method. The advantages and disadvantages of 4-terminal will be discussed in Chapter 3.

The film thickness and also the surface-edge profiles of the films were determined using Dektak II surface profile analyser.

5. Conducting Fiber Composites

One approach to the generation of conductivity in polymers is the introduction of conducting additives in the form of metal whiskers or carbon black particles. The additive which is used more than any other to produce conductivity in plastics and rubbers is carbon black. Carbon black can itself have different conductivities depending on the particle size and surface area. As a result of these variations, the conductivity of the composite materials can vary over several orders of magnitude.

Carbon black is usually added to the plastic in the form of fine particles of size typically $0.1\mu\text{m}$. Carbon black can also be added as fibers-typically $500\mu\text{m}$ in length and of cross section $1\mu\text{m}$ or, alternatively, as a matt of woven fibers. The addition of carbon black as fine particles should ideally lead to an homogenous composite and is preferred mechanism of achieving conductivity in a plastic. The nature of dispersion is critical for determining the conductivity of the composite as well as its mechanical and other physical properties.

Other additives which have been used to achieve conductivity are the fibrillar forms of fine metal wires and silver-coated glass

fibers. The electrical performance of conducting fiber composites are in some way analogous to the gelatin process. The fiber forms, an interpenetrating network, allow high charge mobility to be achieved in the fiber and also in inter-connections. If an inter-percolating network is formed, high conductivities can be achieved throughout the matrix.

5.1 Carbon Black Composites

Carbon black is, as mentioned above, used widely as an additive to achieve high conductivity in non-polar plastics such as polyethylene and polystyrene.

Measurements of polyethylene and polystyrene filled with carbon black show that there is conductivity variation with concentration levels of about $10^{-7} \text{ S cm}^{-1}$ order of magnitude (84-89). Similar effects have been reported for rubbers, such as polychloroprene, cis- polybutadiene and more rigid materials such as polyvinyl chloride (90).

Carbon black has generally been preferred for producing conductivity because:

- a) It is compatible with most polymers and mixes with and adheres well to the matrix.
- b) It does not change significantly the overall density of the polymer matrix.
- c) It is cheap and readily available.

The dependance of conductivity on concentration of a typical carbon black is shown in fig. (1.2) (83). The upper limit of conductivity which can be achieved is about 100 S cm^{-1} and is limited to the conductivity of the carbon black used in making the composite.

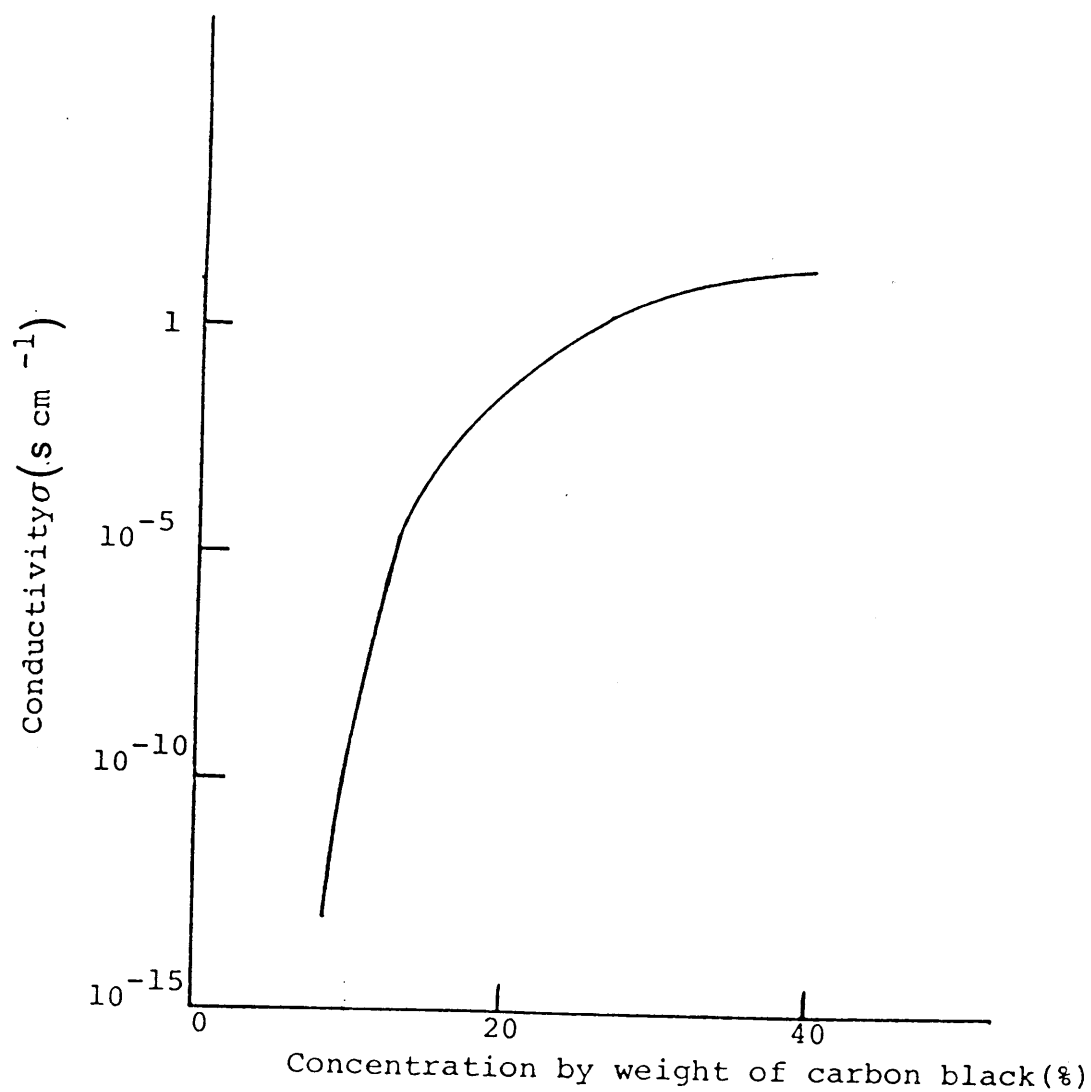


Fig.(1.2) The dependence of the conductivity of polyvinyl chloride composite on carbon black content.

Electron microscopy shows that the carbon black particles are essentially spherical and have a marked tendency to form themselves into continuous chain like structures. The chains form electrically conducting paths through the rubber or plastic structure. Both channel and furnace blacks are widely used as conductive fillers and have different conductivity values which depend upon the micro-structure.

5.2 Dielectric Studies of Pure Polychloroprene and the Influence of Conducting Filler Carbon Black on the Dielectric Relaxation of Polychloroprene

Polychloroprene was selected for the study of dielectric behaviour because its dielectric constant is moderately high and its dispersion region is situated in an easily accessible frequency region. On the other hand, carbon black is known to reinforce this elastomer only slightly (91), if at all, so that the interaction between polychloroprene and carbon black ought to be fairly small. Many investigators (92-101) have confirmed the existence of two kinds of dielectric absorption in polar polymer. In order to define completely the characteristics of the two dielectric absorptions it is necessary to investigate not only the temperature dependence of maximum loss frequency, but also temperature dependence of the shape and the magnitude of the dielectric absorption.

The effect of introducing fillers of different dielectric properties in the matrix might be expected to lead to a change in the effective local permittivity and hence to the motion of the molecular dipole. In order to examine the effect of change in dielectric permittivity on the relaxation, in the present work, Powles (102) relationship has been used,

$$\tau^* = [(2\epsilon_0 + \epsilon_\infty) / 3\epsilon_0] \tau$$

1.3

where (ϵ_0 , ϵ_∞) are zero and infinite frequency values of the permittivity time, and (τ) is the experimentally observed relaxation time, and (τ^*) is the time constant for the immediate molecular dipole relaxation. If the dielectric effect is dominant then the ratio (τ^*/τ) will remain independent of the system and will be approximately equal to unity.

5.3 Conduction in Carbon Black Composites

Over the last decade a number of papers have reported on the electrical properties of carbon black filled polymers (83, 84, 86, 91, 103-112). It has been recognised for a number of years that the inclusion of carbon black in insulating polymer matrix can alter its electrical conductivity. The nature of the carbon black can have a profound effect on the properties of the resultant material. Carbon black is produced commercially via a variety of different methods: channel black, furnace black etc. The carbon black produced by the various methods differ in terms of their surface areas, chemical functionality, porosity and crystalline size. Variations in the method of production leads to changes in the chemical functionality at the surface, rendering the carbon black acidic by incorporation of carboxylic or sulphuric acid functionalities or basic through generation of hydroxyl groups. The pH variation obtained using heterogeneous titration can be from pH 2-10 and is directly correlated with the chemical functionalities on the surface. Surface areas also can vary over large

range, typically from 150-600 m²/gram. In general, the particle size of carbon black can be of the order of 50Å but clusters can generate particles of 1000Å or more. For conduction to occur in a composite it is essential that carbon black particles should link together forming a string of connected elements. Electrical conduction results from excess electron migration between the carbon black particles.

Fundamental and practical interest is the very sharp transition from insulating to conducting behaviour, when the carbon black content is increased by a few percent (83, 86, 103, 113). The carbon black content at which the transition occurs at room temperature as well as the width of the transition depends on the origin of the carbon blacks, the extent and nature of the interaction between carbon black, polymer, and the method of sample preparation. When carbon black and polymers such as polychloroprene (PCP) and polystyrene (PS) are mixed together, an entirely new structure is formed (104), which has been studied in this work. The clustering of the carbon spheres is not simply an indication of poor mixing. Even under the best compounding conditions, some degree of clustering of the carbon black occurs. The tendency of carbon to cluster, called "structure" forming, depends on the type of carbon black used.

Previous studies on carbon black composites have suggested that different conduction mechanisms might operate. The earliest interpretations of the mechanism of electrical conduction involves conduction occurring through the carbon black particles dispersed in a resistive matrix. It is easily seen that in such a mechanism conductance depends on the length of the particle chains which can be built from the number of particles available per unit volume. This model requires that the conductance for a given carbon black should be proportional to specific

volume of the black in the polymer matrix. In the absence of a continuous string of carbon particles, attention must be given to the insulating gaps between the particles. The importance of the insulating gaps in the mechanism of conduction of carbon black dispersion in fluid media was first expressed by Veot (105) and later confirmed by Polley and Boonstra (106). It is known that when electron tunnelling occurs, the field emission current varies exponentially with the gap width (107). Thus, by assuming electron tunnelling to be the mechanism of current conduction - it is found that for each particle junction the resistance is an exponential function of the gap width. The electrical behaviour is divided into three regimes (108,109) the dielectric or tunnelling regime, the transition of percolation regime, and the conduction or metallic regime.

The electrical conductivities of these polymers are given in table 1.1.

Table 1.1

Electrical Conductivities of Various Conducting Polymers.

Conducting Polymers	Conductivity S cm ⁻¹ (Order of Magnitude)	Class of Polymer
		<u>Intrinsically conducting polymer</u>
Poly(sulfur nitride)(4)	1000	(Sulfur nitride)polymer
Brominated poly(sulfur nitride) (8,9)	3.4 x 10 ⁴	Poly(sulfur nitride) derivatives
		<u>Not intrinsically conducting polymer</u>
Oxidized polyacetylene with different degree of oxidation (11)	10 ⁻⁹ to 10 ³	Polyacetylene and derivatives
Co-polymer films of polyacetylene and methylacetylene oxidized by AsF ₅ (14)	50	Co-polymer films of acetylene monomer and derivatives
Oxidized poly(p-phenylene) PPP by AsF ₅ (15)	500	Phenylene polymers
Poly(p-phenylene sulfide) PPS treated with AsF ₅ (17,18)	1-10	Polyphenylene derivatives
Polypyrrole (21,22)	1-100	Pyrrole polymer
Oxo-bridged-stacked phthalocyanines (24)	10 ⁻³ to 1	Bridged-stacked phthalocyanine polymers
Fluorine-bridged structures PcAlF, PcGaF and PcCrF oxidized with iodone (24-26)	0.1-5	Bridged-stacked phthalocyanine polymers
Carbon black filled insulator polymers (33)	10 ⁻³ -1	Carbon black composites

1.2 Aims of the Thesis

The survey of literature reveals:-

- 1) that considerable work has been done on the preparation of films of polypyrroles and the study of their conductivity. It has also been observed that the electrical properties of these films depend on the conditions under which they are prepared. These films may be of potential industrial importance. Therefore, in the present work films of different thickness of polypyrrole para-toluene sulfonate have been prepared under various conditions. Their thicknesses have been measured accurately by using Dektak II surface profile analyser and conductivity determined by four probes contact method. An attempt has been made to explain the results on the basis of existing theories. For abnormal behaviour of some films which could not be explained on the basis of existing theories, a plausible explanation is given.
- 2) that no systematic work has been done on the electrical properties of pure and carbon black filled polystyrene and polychloroprene. Since these composites may be of potential industrial importance an attempt has been made in the present work to prepare these composites under various conditions and to study their electrical conductivity. Dielectric relaxation properties of polychloroprene and its composite have also been studied. An attempt has been made to explain the results on the basis of the existing theories.

2. LITERATURE REVIEW OF THE BAND
MODELS AND CONDUCTION MECHANISMS
OF AMORPHOUS SEMICONDUCTORS

CHAPTER 2. LITERATURE REVIEW OF THE BAND MODELS AND CONDUCTION MECHANISMS OF AMORPHOUS SEMICONDUCTORS

2.1. Introduction

The electrical properties of polymeric materials have been the subject of extensive study (1-5). Due to low production costs and their excellent electrical and mechanical properties, polymers have many industrial applications. Thin polymeric films can be used for the investigation of the electrical and optical properties and may be obtained by several means including thermal evaporation (4) and depositions by polymerization of monomers on surfaces bombarded with electrons or exposed to other radiations, e.g. a glow discharge (6) or ultra violet light. Radio-frequency sputtering (7) and dipping of a substrate into an appropriate solution can also produce thin layers of polymers (8).

The structure of the polymeric materials play an important role in controlling their electrical properties. Most polymers of practical significance are composed of fine mixture of small micrometer size crystalline regions, embedded in an amorphous matrix of similar composition (9).

The available theories for the crystalline, polycrystalline, and amorphous inorganic solids are usually used to describe the conduction processes of organic materials. In the following, a review of different band models and the conduction mechanism is given. The first part deals with the various models which have been suggested for the energy distribution of the density of states and is mainly concerned with the important question of the existence of localized states in tails of the valance and conduction band and of a mobility edge, separating extended from localized states. On the basis of these

models the different mechanisms for conduction in amorphous semiconductors have been briefly discussed. The next section is devoted to a derivation of some basic transport coefficients which have contributed considerably to our present knowledge about the conduction in amorphous semiconductors. In this part we shall treat in some detail dc and ac conductivity. Special attention has been paid to dielectric relaxation of amorphous polymer insulators and carbon black composites. Another theory has paid attention to variable range hopping in localized states near the Fermi level, a type of conduction which is unique for amorphous semiconductors. An important problem, which arises is the role played by lattice deformation in noncrystalline solids. If strong enough, the deformation may cause soliton-polaron formation and in stable defect states may cause bipolarons.

2.2 A Review of Electrical Phenomena in Amorphous Materials

2.2.1 Band Structure in Solids

It appears in the energy diagram 2.1a that the forbidden gap separating the conduction and valence bands has been shown with well-defined boundaries. A well-defined energy gap is a property of a crystalline solid, in which electrons move large distances before scattering occurs, but we are concerned with polycrystalline, or even amorphous insulators. In amorphous solids, because of the lack of long-range order, the electrons are scattered from atom to atom and this causes smearing of the conduction and valence-band edges, among other things, so that the energy gap is no longer well defined as shown in fig. 2.1b. However, Mott (10) and Jonscher (11) have shown that the basic features of the band structure, such as the width of the forbidden gap, are determined primarily by the short-range order within the

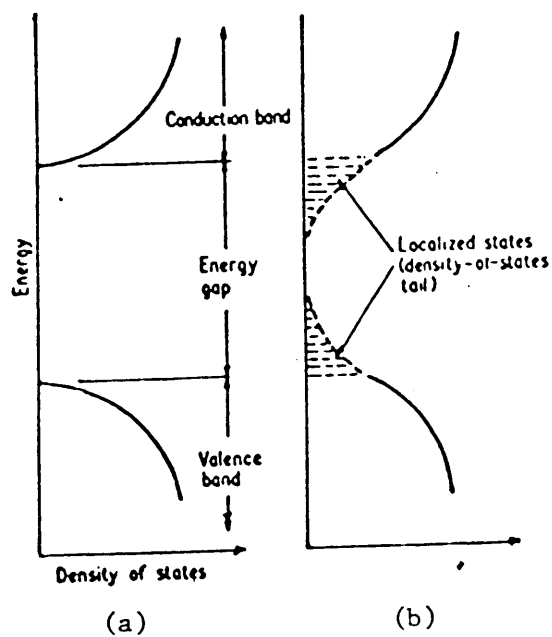


Fig. 2.1 Energy diagram of (a) Crystalline insulator and (b) amorphous insulator. Note that in the case of (a) the conduction and valence bands and energy gap are well-defined. In (b) there are no such well-defined regions, and the traps arising from the 'density-of-states' tail are an intrinsic property of an amorphous solid.

solids; so the general properties of the band structure of the crystalline state are carried over to the polycrystalline state. The disappearance of medium and long range order does influence the detailed shape of the band structure, however, in that it causes a considerable "blurring" of the edges of the conduction and valence bands, as well as giving rise to a distribution of deep localized levels (tail states) in the forbidden gap. In a crystalline solid, there exists a clear distinction between these "propagating" bands - conduction and valence bands - and the forbidden gap. In the former, charge carriers propagate freely except for collisions on thermal vibrations and other lattice imperfections which determine a mean free path which is greater than the lattice spacing. In the forbidden gap, the energy levels that may exist due to imperfections are strictly localized and an electron has to be excited from one of these levels into the conduction band before being able to move on. It has been suggested that when the localized levels are spaced so closely that their wave functions overlap this gives rise to the formation of the so-called impurity band, leading to "metallic" properties with zero activation energy (10). The spacing may not be as close as is necessary for the formation of an impurity band, but enough for phonon-assisted tunnelling between neighbouring centers, the so-called hopping conduction (12-14).

According to the band structure (15) of solid, an insulator is characterized by a full valence band separated from an empty conduction band by a forbidden energy gap of a few electron volts. Clearly, conduction cannot take place in either the filled or the empty band unless additional carriers are introduced. Carriers may be generated or modulated inside the insulator (bulk-limited processes), or injected from the metal electrode (injection-limited processes). Non-metallic

materials deposited on glass substrates by evaporation are usually amorphous, or at best polycrystalline, containing a large number of donor or acceptor centers and traps. For crystallite sizes of $100\text{\AA}$, trapping densities as high as 10^{18} cm^{-3} are possible because of grain boundary defects. In cadmium sulphide, trapping densities as high as 10^{21} cm^{-3} have been reported (16). Furthermore, vacuum-deposited films contain large stresses which induce further trapping centers. These traps are extrinsic to the insulator. As the band edges are diffused, there is a gradual transition from a quasi-continuous state (conduction and valence band), in which the carriers can move freely, to strictly localised states (density-of-states tail) or trap in which the carriers are immobilised (10). These traps are intrinsic property of amorphous insulators and probably exist in large quantities of order 10^{19} cm^{-3} . It is concluded that the vacuum deposited dielectrics can contain a large density of both impurity and trapping centers.

2.2.2 Conduction in Dielectric Materials

Simmons (17) has reviewed conduction through thin dielectric-films, generally less than 1 or $2\mu\text{m}$ thick, sandwiched between metal electrodes. It is found that the conductivity in thin insulating films is often due to extrinsic rather than intrinsic carriers. The current density is much higher than would be expected, and the activation energy associated with the conductivity is less than the insulator energy gap. This is because the electrical properties of thin film dielectrics are determined not by the intrinsic properties of the dielectric, but by other properties, such as the nature of the electrode dielectric contact. When the conduction process is electro-
nic, the conductivity is dominated by the dielectric properties and

the interaction of the metal electrodes with the dielectric at the interface and these are referred to as electrode-limited and bulk-limited conduction respectively. Simmons suggested the types of contact that can exist at a metal-dielectric interface fall into three categories: (i) ohmic contact, (ii) neutral contact; and (iii) blocking contact.

For an ohmic contact at a metal-dielectric interface it is necessary that the electrode work function (ψ_m) be smaller than the insulator work function (ψ_i); to satisfy the thermal equilibrium requirements, electrons are injected from the electrode into the conduction band of the insulator, thus giving rise to a space-charge region and hence a space-charge induced field in the insulator. This space-charge region is termed the accumulation region.

This type of contact, acts as a reservoir of charge which is capable of supplying electrons up to the insulator as required by bias conditions. The conduction process is limited by the rate of electron flow through the bulk of the insulator and the conduction process is bulk-limited.

2.2.3 A Blocking Contact

A blocking contact (Schottky barrier) occurs when ($\psi_m > \psi_i$); and in this case electrons flow from the insulator into the metal to establish the thermal equilibrium conditions. A space-charge region of positive charge, the depletion region, is thus created in the insulator and an equal negative charge resides on the metal electrode. The free electron density at the interface is much lower than in the bulk of the dielectric. Thus the rate of flow of electrons through the system will be limited by the rate at which they flow over the interfacial barrier and hence the conduction process is electrode limited.

2.2.4 Neutral Contact

When $\psi_m = \psi_i$; the vacuum and Fermi levels of the insulator and electrode line up naturally without the necessity of charge transfer between the electrode and insulator. Since no charge transfer occurs between the electrode and insulator, the conduction band is flat right up to the interface; that is, no band bending is present. This type of contact is known as a neutral contact and represents the transitional stage between an ohmic and a blocking contact.

According to Simmons (18) bulk conductivity measurements of Ta₂O₅ and SiO₂ films are shown to be consistent with the Schottky effect rather than the Poole-Frenkel effect. The Poole-Frenkel effect (field-assisted thermal ionization) is the lowering of a coulombic potential barrier when it interacts with an electric field, and is usually associated with the lowering of a trap barrier in the bulk of an insulator (19), (20) as shown in fig. 2.2.

The Poole-Frenkel effect is similar to the Schottky effect, which is the attenuation of a metal-insulator barrier arising from electrode image force interaction with the field at the metal-insulator interface. Denoting the barrier attenuation by ($\Delta\phi$), we have for the Poole-Frenkel effect (21)

$$\Delta\phi_{PF} = \left(\frac{e^3}{\pi E_0 K} \right)^{\frac{1}{2}} E^{\frac{1}{2}} = \beta_{PF} E^{\frac{1}{2}} \quad 2.1$$

$$\text{so that } \beta_{PF} = \left(\frac{e^3}{\pi E_0 K} \right)^{\frac{1}{2}}$$

and for the Schottky effect

$$\Delta\phi_S = \beta_S E^{\frac{1}{2}} = \frac{1}{2} \beta_{PF} E^{\frac{1}{2}} \quad 2.2$$

where ($\Delta\phi$) is the barrier attenuation, (e) is the unit of electronic charge, (ϵ_0) is the permittivity of free space, (K) is the high frequency dielectric constant of the insulator, and (E) is the electric field strength of the insulator. Both of these effects give the conductivity a field dependence of the form:

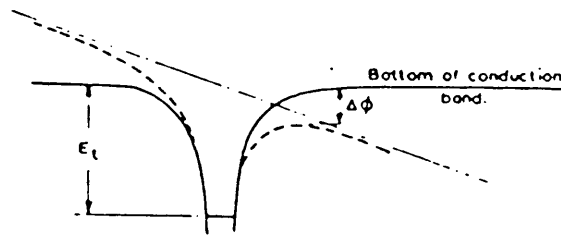


Fig. 2.2 Mechanism of Poole-Frenkel effect. The solid line represents the coulombic barrier without a field. The dashed line shows the effect of an electric field on the barrier. The slope of the dash-dot line is proportional to the applied field.

Poole-Frenkel

$$\sigma = \sigma_o \exp(\beta_{PF} E^{\frac{1}{2}}/kT) \quad 2.3$$

Richardson-Schottky

$$\sigma = \sigma_o \exp(\beta_S E^{\frac{1}{2}}/kT) \quad 2.4$$

where (σ_o) is the low field conductivity. Poole-Frenkel conductivity is observed only when the conduction process is bulk-limited, and the Richardson-Schottky when it is electrode-limited. Knowing that the conductivity is either bulk-limited or electrode limited, one can calculate a value for the high-frequency dielectric constant of the material by just equating the experimentally determined value for (β) to its appropriate theoretical equation

$$\left(e^3 / \pi \epsilon_o K \right)^{1/2} \quad \text{for bulk limited}$$

and $\left(e^3 / 4 \pi \epsilon_o K \right)^{1/2} \quad \text{for electrode limited conductivity.}$

Mead (19) has investigated a number of Ta-Ta₂O₅-Au diodes of different thickness over a range of temperatures in order to check the conduction mechanism. All specimens were prepared in vacuum of 10⁻⁷ torr and Schottky emission appears at first sight to meet requirements involved because the current is quite accurately logarithmic when plotted against ($V^{1/2}$) and the temperature dependence is of the right form. It has been pointed out by Mead (19) that, provided the dielectric is sufficiently thick, the current should be limited by the bulk properties of the dielectric rather than by conditions at the interfaces. However, he has proposed the following mechanism as the rate-limiting step in the current through tantalum oxide and other similar films.

- 1) At low applied voltage and high temperatures, current is carried by thermal excited electrons hopping from one isolated state to

next. This mechanism gives an ohmic characteristic, exponentially dependent on temperature (17).

2) At high fields and low temperatures, the rate limiting step in the current flow is field-ionization of trapped electrons into the conduction band. This process yields a current-voltage characteristics (independent of temperature).

3) At high fields and high temperatures, the rate-limiting step in the current flow is field-enhanced thermal excitation of trapped electrons into the conduction band. This process is known as the Poole-Frenkel effect.

O'Dwyer (22) suggested that the current voltage characteristic of insulating films is usually regarded as being due to quantum-mechanical tunnelling for very thin films and similar results were reported (23) for thin Al_2O_3 films in the form of the $\text{Al}-\text{Al}_2\text{O}_3-\text{Al}$ diode. He argued (22) that a straight line plot of $\log_{10} j$ vs $V^{1/2}$ for a reasonably thick dielectric film does not necessarily imply Schottky emission from the cathode; paradoxically the plot of $\log_{10} j$ vs $V^{1/2}$ is only approximately a straight line over the whole range of voltages when Schottky emission is the mechanism of electron injection into the dielectric. Stuart (24) investigated the current-voltage behaviour of evaporated silicon oxide films, several microns thick, and found that at low voltages, conduction is determined by contact barriers at the electrodes and at high voltages $\log_{10} j \sim V^{1/2}$ and conduction is by field enhanced thermal excitation of electrons from donor centers (Poole-Frenkel effect).

Pollack (25) investigated the mechanism of electron transfer between two metal electrodes, separated by a thin insulating film of $\text{Pb}-\text{Al}_2\text{O}_3-\text{Pb}$ and suggested that tunnelling and Schottky high-field

emission are the two mechanisms which can be employed to explain the current-voltage (I-V) and current-temperature (I-T) relationships usually observed in his investigation on aluminium oxide films which are of the order of $300\text{\AA}$ thick.

2.3 Modern Ideas of Amorphous Materials

Introduction

The general approach is to consider the electronic structure and transport in an impurity band in which conduction is quasi-metallic.

In a non-crystalline substance a minimum is expected in the density of states, a so-called 'pseudogap'.

A brief theoretical review is given for the depth of the minimum at which the one electron state becomes localised so that $\langle \sigma_E(0) \rangle$ vanishes.

Similarly in the second part the experimental evidence concerning the density of states in amorphous semiconductors and the range of energies in which they are localised is reviewed.

A modification suggested by Mott and Davis is also discussed.

Phenomenology of polaron and bipolaron is also discussed. Hopping and variable-range hopping is reviewed.

In the last section a comprehensive review of the Anderson band localised states and $\sigma(0)$ and some aspects of the quantum electron theory of amorphous conductors are reviewed.

2.3.1 Band Models

The electrical properties of a solid is intimately related to its allowed electron energy levels or "band structure". For electrons to move in a solid under an applied stimulus, such as an electric field there must be higher - vacant states into which they can move. For the consideration of their electrical properties solids can be divided into

three categories: metals, semiconductors and insulators. These band structure is shown schematically in fig 2.3. Electron movement is easy in metals as a band contains both full and empty states. Whereas in semiconductors and insulators there are forbidden bands (shaded areas in fig. 2.3 denotes forbidden bands). The probability of crossing the forbidden gap is proportional to $\exp(-E_g/2kT)$, where (E_g) is the width of the forbidden energy gap, (k) is Boltzmann's constant and (T) is the absolute temperature.

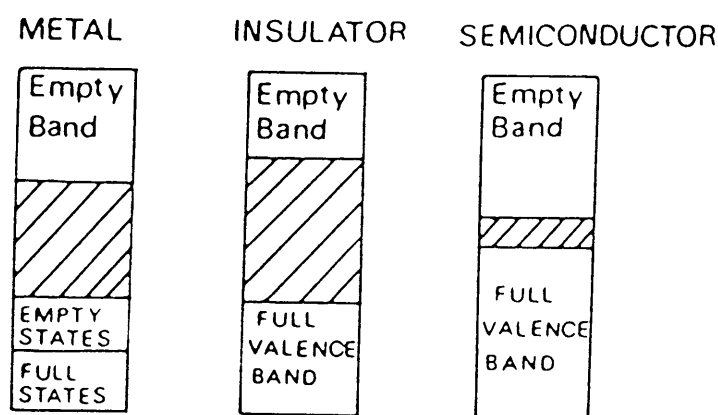


Fig 2.3 Simplified energy band diagrams for a metal, insulator and semiconductor. Shaded areas denote "forbidden" bands.

In the case of metals resistivity which increase linearly with temperature, whereas for semiconductors and insulators, the resistivity decreases exponentially with temperature. This classification has been explained on the basis of the band model and has been used (26,27) to describe conduction of electrons generated intrinsically in polymers. Detailed discussion of this model can be found in a number of text books on solid state physics (28-31).

Briefly, the conduction process is modelled in terms of the motion of an electron detached from its parent atom or molecule, and free to move in a periodically varying potential. The field within the solid can be described in terms of a modulated, travelling wave function.

Such a wave function has a series of real solutions for certain values of energy and these are termed energy bands. The ranges of energy for which there are no real solutions to the wave function are called "forbidden energies". In real solids we are concerned with the highest filled band termed the "valance band", and the lowest empty band called "conduction band". The difference in energy between the valance and conduction bands is called the "forbidden energy gap". The conducting properties of the solid are controlled by the width of the forbidden energy gap and the range of allowed energies in the conduction and valance bands. The width of the band depends upon the interatomic and intermolecular interaction in the systems. In strongly interacting systems the allowed bands are wide, in weakly interacting systems, such as molecular crystals, the bands are narrow. According to the model if there is no forbidden energy gap the material is metallic in nature, alternatively if the gap is large it is an insulator. Likewise if there is a filled band below a small forbidden energy gap the material is a semiconductor. Fig. 2.4 the diagram is useful to illustrate the energy distribution.

Case I.

The energy gap in insulators is many orders of magnitude larger than (kT) and hence generation of electrons from the valance band to the conduction band is very unlikely.

Case II.

The existance of states within the energy gap can provide sufficient probability for the electrons to gain the conduction state and hence the material will be semiconductive. Typically (E_2) will be of the order of (kT) or a little greater and (E_1) will be comparable with (E_2) .

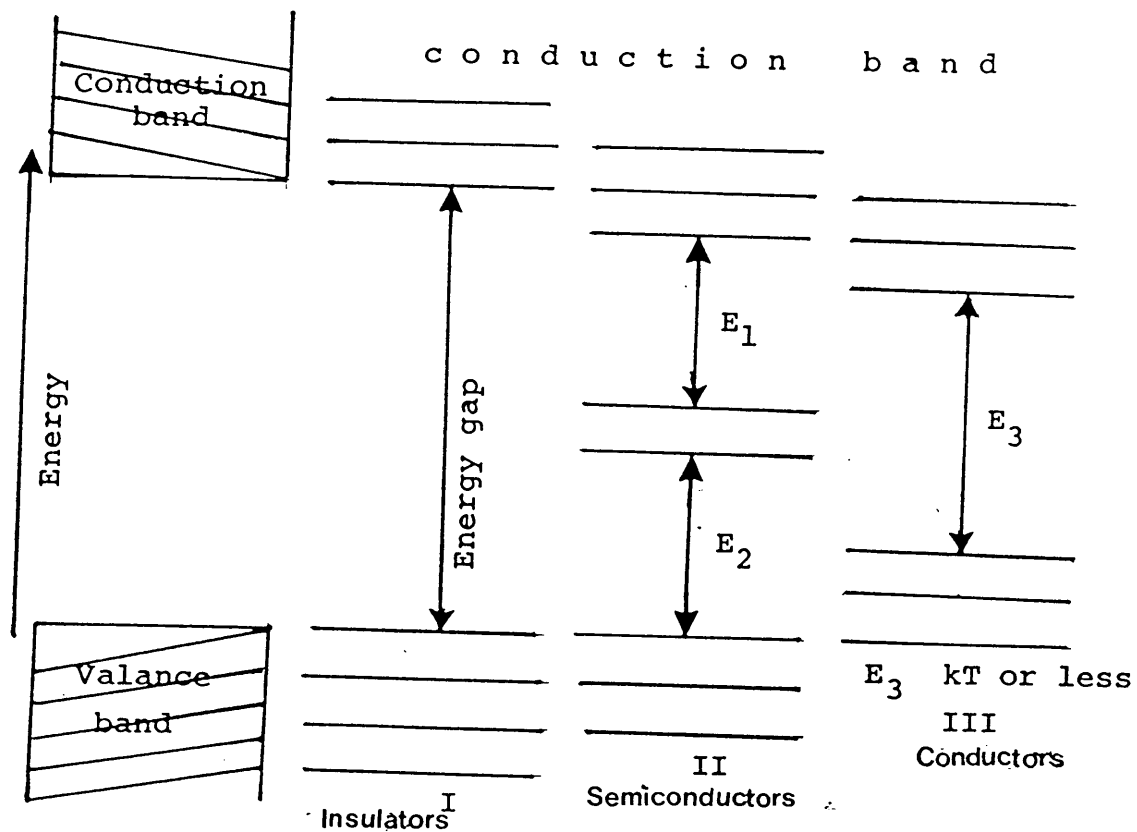


Figure 2.4

The inter-gap-states can be generated in an atomic solid either by the introduction of a defect or a dopant. The action of the semiconductor depends critically upon the type of dopant used.

Case III.

The narrowing of the energy gap to a value (E_3) which is comparable or less than (kT) allows the thermal generation of charge carriers: free electron and metallic conductivity is observed.

Covalent and ionic materials should have no conduction as they possess orbitals and shells which are completely filled and hence leave no free electron in conduction band (32-36). A low level of conductivity does however arise due to the existence of a small fraction of

electrons with energy in excess of the energy gap. The number of such electrons is statistically controlled by the Boltzmann distribution, where (E_g) is the forbidden energy gap

$$n_{(T)} = n_o \exp(-E_g/kT) \quad 2.5$$

The excitation of $n_{(T)}$ electrons to the conduction band will leave behind an equivalent number of holes in the valance band.

Conduction also occurs by means of electrons in the valance band moving to vacancies and results in a movement of positive holes in the direction of the field. Both electron and hole conduction are influenced by the magnitude of the forbidden energy gap width. When the energy or when inter-band states are created then conduction occurs as illustrated in case II and III above.

Several models were proposed for the band structure of amorphous semiconductors, which were the same to the extent that they all used the concept of localized states in the band tails. Opinions vary, however, as to the extent for this tailing which will be discussed shortly.

2.3.2 Mott's Model

According to Mott, if the distance between (37) atoms in a crystalline lattice is increased, an energy gap appears which in a divalent material will separate occupied from unoccupied states of an electron. In a non-crystalline substance a minimum is expected in the density of states (a pseudogap). Mott suggested that the density of states would behave in the following way:

- i) For non-crystalline structures the energy gap will be replaced

by a "pseudogap" or minimum in the density of states $N(E)$ as in fig.

2.5 but in a liquid or crystalline solid, thermal fluctuations of the density would take few states within the gap.

ii) States with energies (E) in the pseudogap may be localised.

Thus in Mott's model materials which are intrinsic semiconductors like the chalcogenide glasses valence and conduction bands would exist with a range of weakly localised states at the bottom, with the tail of strongly localised states due to structural defects which may give rise to 'd.c.' or 'a.c.' impurity conduction.

Actually, there are more states in the tail below the conduction band than above the valence band, so that the Fermi energy (E_F) lies near the valence than the conduction band for (P) type materials.

Stuke (38) gave this expression for the chalcogenide glasses regarding the conductivity,

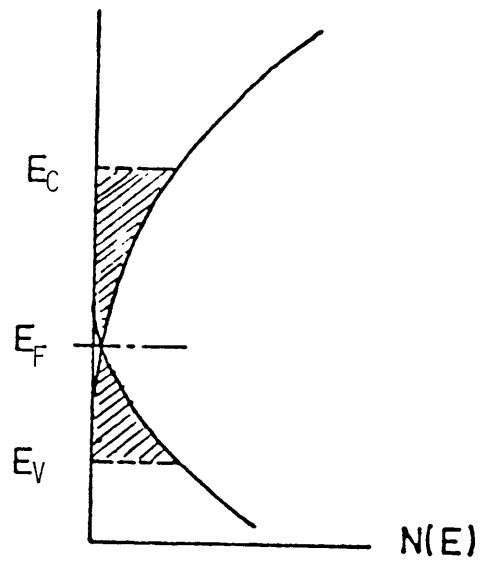
$$\sigma = \sigma_0 \exp \left(\frac{-E}{kT} \right) \quad 2.6$$

where (E) is constant over the wide range of (T) and

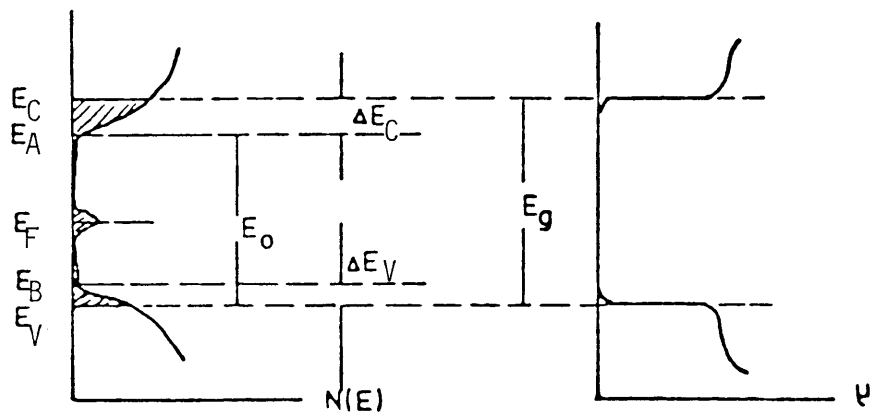
$$\sigma_0 \approx (10^5 \text{ ohm}^{-1} \text{ cm}^{-1}).$$

2.3.3 The Cohen-Fritzsche-Ovshinsky (CFO) model

The CFO model (39) shown in fig. 2.6b assumes that the tail states extend across the gap in a structureless distribution. This gradual decrease of the localized states destroys the sharpness of the conduction and valence band edges. The CFO model was specifically proposed for the multicomponent chalcogenide glasses used in the switching devices. The authors suggested that in the chalcogenide alloys, the disorder is sufficiently great that the tail of the conduction and



(a) Density of states in an amorphous semiconductor alloy according to Cohen, et al. (1969). Localised states are shown shaded.



(b) Suggested density of states $N(E)$ and mobility μ as function of energy in an amorphous semiconductor. Localised states are shown shaded.

Fig. 2.5

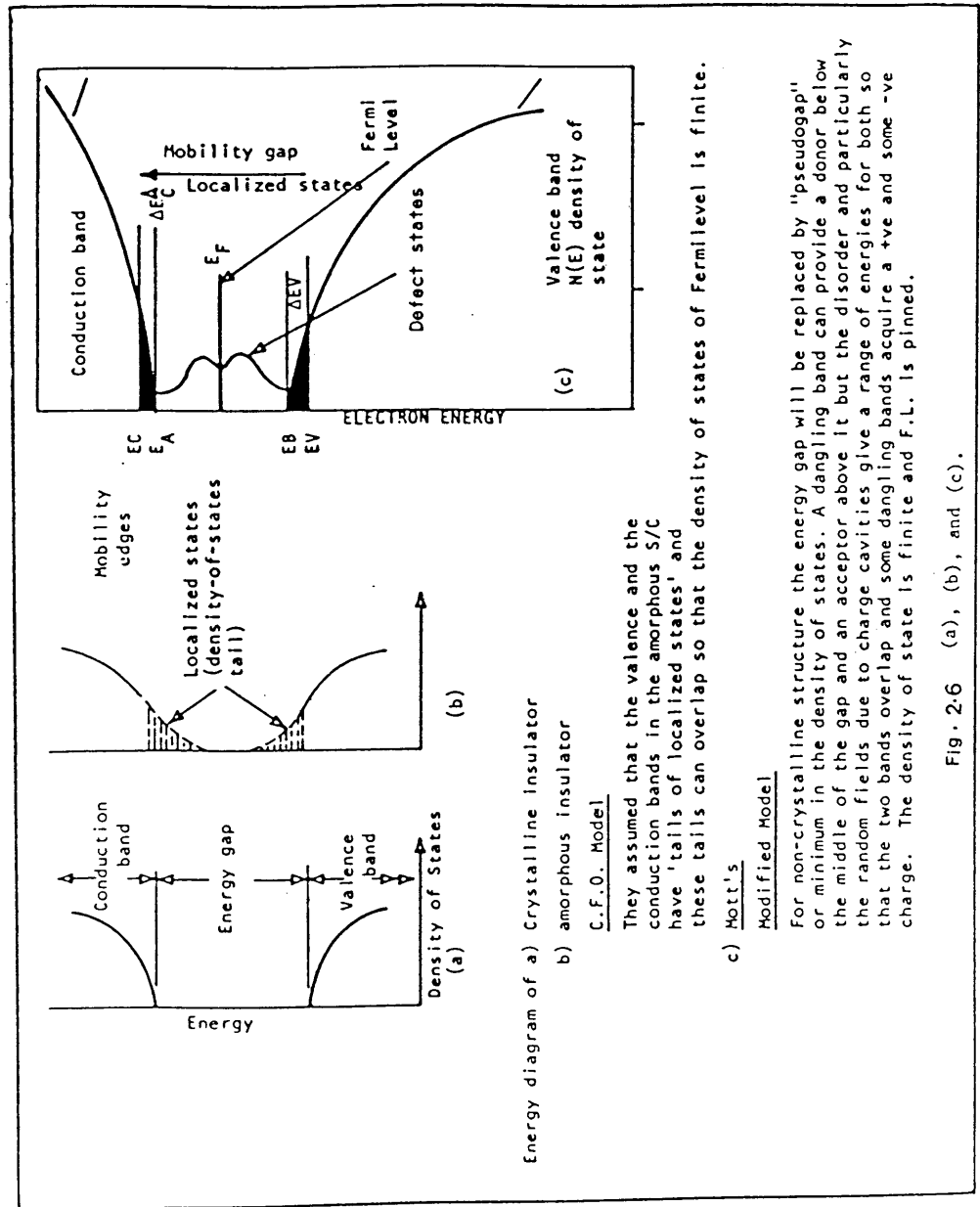


Fig. 2-6 (a), (b), and (c).

valance bands overlap, leading to an appreciable density of states in the middle of the gap. A consequence of the band overlapping is that there are states in the valance band, ordinarily filled that have higher energies than states in the conduction band that are ordinarily unfilled. A redistribution of the electrons may take place, forming filled states in the conduction band tail, which are negatively charged, and empty states in the valance band, which are positively charged. This model, therefore, ensures self-compensation, and pins the Fermi level close to the middle of the gap, a feature required by the electrical properties of these materials. One of the major objections to the CFO model was the high transparency of the amorphous chalcogenides below a well-defined absorption edge.

2.3.4 The Davis-Mott Model

According to their modification (30) fig. 2.6c, they have distinguished between the ranges (E_C) and (E_A) and (E_V) between (E_B) and (E_V) where the localized states lie in the bands and are due to lack of long range order and the hypothetical 'tails' are due to defects in the structure. The energies (E_C) and (E_V) separate the ranges of the energy where states are localized and non-localized (extended). The quantity ($E_C - E_V$) defines a mobility gap. The current carried by electrons or holes in extended states is given by

$$\sigma = \sigma_0 \exp [-(E_C - E_F)] / kT \quad 2.7$$

2.3.5. Phenomenology of Polaron and Bipolaron

The idea of a polaron is familiar in solid state physics (40) it consists of an electron (or hole) localized to a deformed region of the lattice. It is the coulomb interaction between the electron and the ions, which is responsible for the lattice distortion, and the breaking

of the translation symmetry results in a localized wavefunction occupied by the electron in question. We say that the electron is "self-trapped".

The situation is similar in linear conjugated polymers. In this case the lattice deformation consists of a tendency for the double bonds to become longer more like single bonds and vice versa. Two localized states are formed, one split off from the top of the valance band, and one from the bottom of the conduction band (31-43) fig. 2.7b. If the defect is formed by removal of an electron, then the lower state is singly occupied and we have a hole-polaron as shown in figure 2.7b.

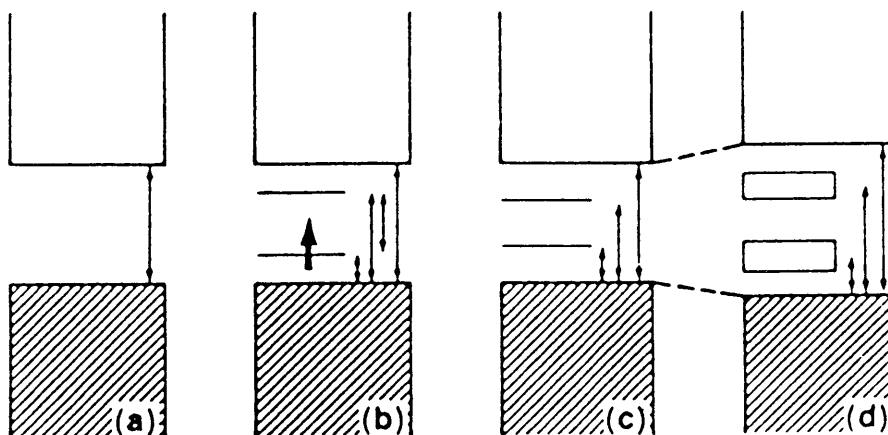


Fig. 2.7 Energy level diagram of a conjugated polymer at increasing levels of acceptor doping (oxidation): (a) Neutral polymer, showing full valence (π) and empty conduction (π^*) bands. (b) After removal of a single charge a polaron is formed with spin $S=1/2$. Three new optical absorptions appear. (c) When a second electron is removed a bipolaron is formed; $S=0$, and there are only two optical transitions below the interband. (d) At heavier doping levels the bipolaron levels broaden into bands, and the gap between valance and conduction bands widens.

Electron injection results in the single occupation of the upper level, while the lower state remains fully occupied. In either case, there is a net charge of one unit (positive or negative) on the chain, and the odd electron contributes spin $1/2$.

The energetics of polaron formation require consideration of the elastic energy which it costs to form the lattice distortion and the gain in electronic energy. Bredas (43) has described this gain, as the reduction in ionization energy (or increase in electron affinity) of the structure which has the double and single bonds reversed relative to the stable ground state configuration.

Restricting the remainder of the discussion to the case of acceptor doping (oxidation), which is relevant to the experimental situation in polypyrrole (44), further charge transfer from the polymer chain with one hole-polaron, may then proceed either by formation of other polarons, or by removing the single electron in the lower polaron level. The former process costs additional elastic energy, while the latter involves the Coulomb energy of two charges in the same region of space. In all of the materials of interest it is found to be favourable to form the doubly charged species: the lattice deformation increases slightly, further lowering the electronic energy, and the Coulomb energy is largely compensated by the effect of the nearby counterion (43). The doubly-charged spinless species which results is called a bipolaron fig. 2.7c.

From the above discussion it is clear that polarons and bipolarons are characterized by two experimentally measurable properties: changes in optical absorption which result from the new energy levels created in the band-gap, and appearance of additional susceptibility due to the spin of the polaron. Specifically, we expect the following features in the optical spectrum of polymers containing polarons fig. 2.7b: transitions from the valance band to each of the (1) lower and (2) upper polaronic levels, and (3) promotion of the electron from the lower level to the unoccupied upper level. When bipolarons are formed the

last of these transition is no longer possible because the lower state is unoccupied fig. 2.7c. The other two transitions are basically unaffected, though they may shift in energy. Finally at high doping levels, the depletion of states from the valance and conduction band edges lead to a suppression of the intensity of the interband transition, as well as a blue shift (45).

As doping of the neutral polymer proceeds, it is expected that the first species formed, at very low concentration, will be polarons, detectable because of their spin susceptibility and three features in the optical spectrum. At heavier doping levels, more and more bipolarons will be formed, the susceptibility should decrease and the middle of the three optical sub-bandgap transitions should disappear (46).

2.3.6 Anderson Band

In his model Anderson (47) has reviewed processes such as conduction in the "impurity band". These processes involve transport in a lattice which is in some sense random, and in them diffusion is expected to take place via quantum jumps between localized sites. In this model the essential randomness is introduced by requiring the energy to vary randomly from site to site.

Consider an (n) type compensated (48) semiconductor such that N_D (density of donors) $> N_A$ (density of acceptors). At some low temperature with all the acceptor sites ionised and $N_D - N_A$ of the donor sites occupied. At sufficiently low concentrations the overlap of the wave functions between different donor sites is small and the resonance energy between them less than the energy difference due to variation of local electric fields (caused by the essentially random arrangements of

charged acceptors sites). The electrons are then well localized and neighbouring sites non-degenerate. Miller and Abraham (49) discussed the conduction by hopping of electrons from occupied to unoccupied localized donor states. Thus the energy difference would be made up by the absorption or emission of a phonon. The conductivity in such a band will obviously go to zero with absolute temperature. If, however, ND is sufficiently large, then the wave functions on the donor sites may overlap such that the electron states lose their localized character. An impurity band is thus formed with the Fermi energy in the band. From the tight binding theory the width (J) of this band is shown to be

$$J = 2ZI \quad 2.8$$

where (Z) is the coordination number, and (I) is the overlap integral between nearest neighbours.

$$\text{and } I = I_0 \exp(-\alpha R) \quad 2.9$$

Here (α) is the rate at which the wavefunction on a single well falls off with distance ($\alpha = (2mW_0)^{1/2} / \hbar$). For hydrogen-like wavefunctions (I_0) can be evaluated (50)

$$I_0 = \left[\frac{3}{2}(1 + \alpha R) + \frac{1}{6}(\alpha R)^2 \right] e^2 \alpha \quad 2.10$$

Here (W_0) is the energy level for an electron in a single well, ($\hbar$) is fundamental unit of angular momentum (Plank's constant), ($\hbar$) divided by 2π , (R) is the lattice site, (e) is the unit of electronic charge, and (m) is the effective mass.

The wave function for a single well will fall off as

$$\psi = \frac{\text{constant}}{R_0} \exp(-R_0)$$

Another way of expressing the Anderson condition is to take for the initial state an electron localized in a large volume of radius (Δx).

Then if (E) is taken at the center of the band there will be no

diffusion if the condition is satisfied.

Some more recent work on Anderson localization Mott (1967), has concentrated on the quantity $\sigma(0)$. If there is no diffusion the conductivity too must vanish for all energies in the band.

The main objection that some people have expressed to Anderson localization is for the following reason. It is felt that starting with a given localized state at sufficient distance there must exist another state with just exactly the right energy to resonate with the wave function, which should not be localized but have a series of peaks and valleys.

2.3.7 Gubanov Theory of Amorphous Conductors

The most remarkable achievement of the quantum-mechanical theory of solids occurred in the development of semiconductor physics (51). Electron and hole conduction, the influence of impurities, the different effective masses of carriers, could be explained in a natural way by quantum mechanics.

Before taking the quantum-mechanical explanation of the electrical properties of metals and semiconductors we discuss the Pauli principle, according to which each allowed band has a limited number of electron vacancies, which in the simplest case, is equal to double the number of atoms in a crystal. Actually all electrons in a crystal are distributed over such levels filling the bands beginning with the lowest one. If one of the band is partly filled we have a metal with good electrical conductivity because the periodically distributed atoms do not impede electron motion in an external field, electrons are scattered mainly by the thermal motion of atoms, which causes the electrical resistivity of a metal to rise with temperature. If several bands are completely filled and the nearest band is separated by a gap,

conduction is prevented by the absence of free levels in the filled bands and we have an insulator or a semiconductor.

Conduction is possible only when electrons are transferred thermally from filled to a free band. Now the electrical conductivity increases with increase of temperature and with increase of impurity concentration, moreover, it may be of n-type (electrons) or p-type (hole conduction).

Actually the properties of semiconductors are very sensitive to the energy spectrum structure and existence of semiconductors and crystalline insulators depend on the presence of a forbidden gap.

The quantum-mechanical explanation of metals and semiconductors is based on the periodicity of the potential and presence of long-range order in the distribution of atoms.

Of course this contradicts the old established observation that the electrical conductivity does not change greatly on melting and that it retains its metallic nature.

The recent investigations of changes in the properties of semiconductors on melting showed that in some cases their electrical conductivity and other properties change very little and retain their semiconducting nature.

The question arises why semiconductors, which are so sensitive to changes in their band structure, do not change their properties. Upon the disappearance of the periodicity of the atomic distribution which is responsible for the presence of allowed and forbidden bands in the energy spectrum.

To prove it, it became rather essential to prove that in a liquid or in an amorphous substance, the following features are retained:

- 1) forbidden bands in the energy spectrum

- 2) allowed energy levels, forming continuous or quasi-continuous bands
- 3) electron behaviour is described, at least in the first approximation by certain waves propagated in the substance, i.e., the electrons are quasi-free as in crystals.

After proving these properties, one could develop the quantum electron theory of amorphous substances using the standard solid state theory as a model.

Calculations relating to a one dimensional model of an amorphous substance, i.e., assuming a chain of nonuniformly distributed atoms or cells are considerably more difficult than those relating to a one dimensional model of a crystal.

This problem has been solved in different ways. One method considers a chain of a finite, but sufficiently large number of cells and solves the system of equations for all the cells.

Another method uses the assumption of quasi-crystallinity of an amorphous substance, i.e., the distance between neighbouring atoms fluctuate at random.

2.3.8 Hopping Model

In order for conventional band models to be applied a number of conditions relating to the mobility must be considered. First, the mean free path (λ) of the charge carrier must be greater than the lattice spacing (a) second (λ) must be greater than the electron wavelength i.e. momentum relaxation (τ) must be greater than $(\hbar/kT)$ where ($\hbar$) is fundamental unit of angular momentum (Plank's constant, (h) divided by 2π), (τ) is the average time the charge carrier is free to move between collisions. A third condition, $\omega > \hbar / \tau$ is imposed by the uncertainty principle, where (ω) is the band width. If these

conditions are not met then the mobility of the charge carrier will be often below ($< 1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$) and cannot be described in conventional terms. In this case it is probable that the charge carrier spends more time in localized sites than in motion. Its movement then, must involve hopping or tunnelling between localized sites as shown in fig. 2.8. This hopping mechanism occurs when the interaction between these molecules is weak and the bands are narrow.

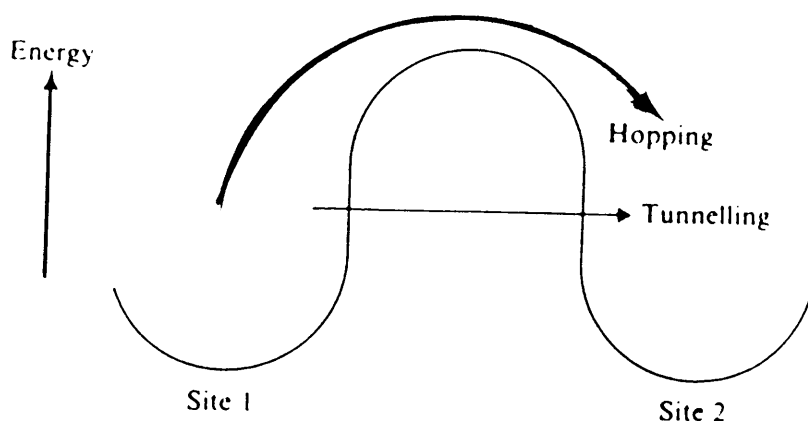


Fig. 2.8 Diagram of electron-transfer mechanisms between adjacent sites separated by a potential-energy barrier.

If the charge carrier spends a time on the lattice site which is greater than the period of vibration of the molecule or atom surrounding it, as should be the case for very low mobility solids, then the medium has time to relax around the charge carrier (52). This gives rise to the generation of a region of polarization around the charge carrier which is referred to as a polaron. The effect of this process is to reduce the mobility of the charge carrier and to increase its effective mass. Depending upon the coupling between the charge carrier (electron) and the lattice phonons, the effective mass may be increased to such an extent that the electron traps it within the region of the polarized dielectric. When this occurs the motion of the

charge carrier will involve a series of thermally activated hops (53). This situation is thought to occur in disordered materials such as transition metal oxides and in chalcogenide glasses, in which it is assumed that the long range order is extended throughout the system.

Pollak and Geballa (54) report the first observation of charge carrier hopping between two localized sites. In which they studied the a.c. properties of compensated silicon at very low temperature. As pointed out by Pollak it is difficult to distinguish the band-type from hopping type condition by using static-field methods. However, the frequency response of the conduction can be used to considerable effect in this connection. The real part of the conductivity in both cases can be written as

$$(\sigma)_{\omega} = \frac{ne}{\epsilon} \sum_i \langle v_i \rangle \Delta f_i (t=\infty) [1/(1 + \omega^2 \tau^2)] \quad 2.11$$

$$(\sigma)_{\omega} = \frac{ne}{\epsilon} \sum_i \langle x_i \rangle \Delta f_i (t=\infty) [\omega \tau^2 / (1 + \omega^2 \tau^2)] \quad 2.12$$

where $\langle x_i \rangle$ is the carrier coordinate in the field direction of the ith state, (Δf_i) is the deviation from equilibrium of the occupation probability (f_i), $\langle v_i \rangle$ is the velocity component in the ith state along the field (55). As can be seen by comparison of the last two expressions the conductivity in the band type conduction decreases as the frequency increases: where as that for hopping-type conduction will increase as frequency increases.

There have been many reports of disordered and amorphous or glassy materials exhibiting the same behaviour. Regions are observed in which $\sigma(\omega)$ changes linearly with frequency and other regions in which $\sigma(\omega)$ vary quadratically with frequency.

This subject was previously reviewed by Jonscher (56), it has been recognised by Pollak and Geballe (54) that the two localized site hopping is an idealized approximation and that there must be many site paths in which a carrier executes a series of hops before coming to a difficult hop where it may be blocked. The existence of a random distribution of hopping sites in a disordered solid must give rise to a wide distribution of hopping relaxation times which must follow an exponential dependence on distance between pairs of hopping sites (57). This review includes a list of papers which elaborate and refine the fundamental idea of the two site hopping model and predicting a wide variety of frequency dependences of conductivity from $\sigma(\omega) = \sigma_0$ = constant to $\sigma(\omega) \propto \omega^2$ through a range of powers with exponents between zero and one.

However, polymeric materials are by no means ordered even though they may possess short range order within a given polymer chain. The two site hopping model and its different modified forms can successfully be applied to describe a conduction in some polymeric materials while it fails to interpret the electric properties of some other polymers.

In 1974 Lewis (58) reported a generalized, but simple, localized hopping model, which can be readily applied to conduction in organic solids. It stresses the correspondence between the frequency dependence conductivity $\sigma(\omega)$ and the consequent current decay $j(t)$ following the application of a step-function field. According to this model the concept of a distribution of activation energies rather than of relaxation times (as it is always the case in dielectric measurements) is a more natural explanation of current characteristics for a wide variety of systems.

2.3.9 Hopping and Variable - Range Hopping

In this section we continue our discussions of conduction in a 'Fermi glass', that is a degenerate electron gas in a highly disordered medium, and consider what happens to the d.c. conductivity when the Fermi energy lie in the range of energies where states are localized. Then two mechanisms for conduction are possible.

i) Excitation of electrons to E_C , the contribution to the conductivity is

$$\sigma = \sigma_{\min} \exp \left(-\frac{\epsilon}{kT} \right) \quad 2.13$$

where $\sigma_{\min}$ is as before the value of σ_E at $E = E_C$, and

$$\epsilon = E_C - E_F$$

This form of conduction is normally predominant at high temperatures or when (ϵ) is small.

ii) Thermally activated hopping conduction by electrons in states near the Fermi energy: This is illustrated in fig. 2.9, the rate-determining process is the hopping of an electron from a state (A) below the Fermi energy to one above (B). The probability (P) per unit time that this occurs is the product of the following factors.

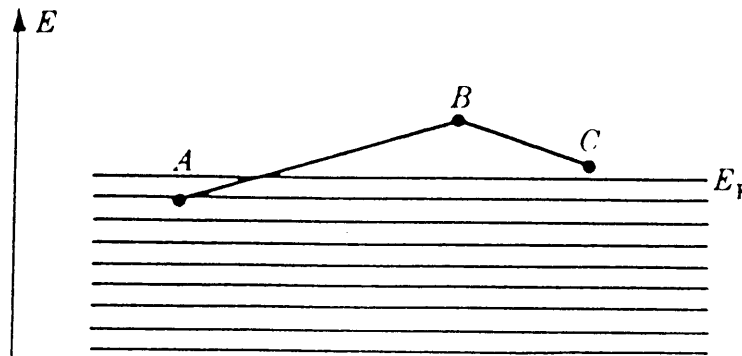


Fig. 2.9 The mechanism of hopping conduction. Two hops are shown, from A (an occupied state) to B and from B to C.

- a) The Boltzmann Factor $\exp(-W/kT)$, where (W) is the difference between the energies of the two states.
- b) A factor ν_{ph} depending on the phonon spectrum.
- c) A factor depending on the overlap of the wave functions.

As the temperature is further lowered, carriers will tend to hop larger distances in order to find sites which lie energetically closer than the nearest-neighbour site. This mechanism is called variable range hopping. Mott shows that the hopping probability in this case is

$$p = \nu_{ph} \exp\left(-\frac{A}{T^{1/4}}\right) \quad 2.14$$

where

$$A = 2.1 [\alpha^3 / kN(E_F)]^{1/4} \quad 2.15$$

Equation 2.5 leads to a temperature dependence for the conductivity of the form

$$\sigma = 1/6 e^2 R^2 \nu_{ph} N(E_F) \exp\left(-\frac{A}{T^{1/4}}\right) \quad 2.16$$

$$\text{or} \quad \sigma = \sigma_0(T) \exp\left(-\frac{A}{T^{1/4}}\right) \quad 2.17$$

$$\text{where} \quad R = 3^{1/4} / [2\pi\alpha N(E_F) k T]^{1/4} \quad 2.18$$

Equation 2.17 will have the form of section (d) in fig. 2.10.

The mechanism of conduction of polypyrrole can be explained by variable-range hopping (44), (59-74).

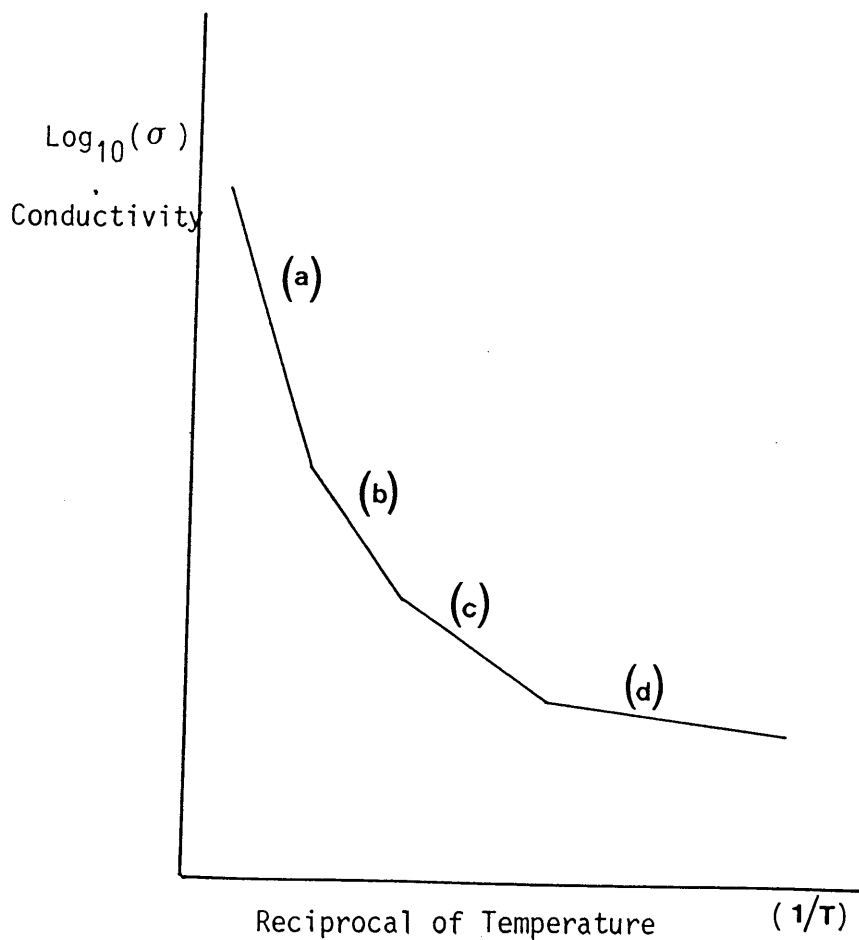


Fig. 2.10 Illustration of the activation energies associated with various conduction mechanisms

2.3.10 Hopping Conduction for Alternate Currents

Information about the nature of the conduction mechanism in a material can be obtained from a.c. conductivity. In these experiments the electrical conductivity is measured as a function of the frequency (ω) of an alternating electric field. The frequency range usually covered in the measurements extends from 10^2 to 10^8 Hz. In this work the frequency range covered in the measurements extends from 600 Hz to 10 kHz. A difference in behaviour of $\sigma(\omega)$ is expected when conduction

occurs by motion of charge carriers in the extended states or by hopping in localized states. The two types of conduction processes will now be examined when carriers are excited across the mobility edges into the range of extended states, the conductivity does not depend on frequency, at least in the frequency range up to 10^8 Hz. On the other hand, when conduction occurs by phonon-assisted hopping between localized states one expects the conductivity to increase with frequency. Austin (75) and Mott have derived a formula when hopping conduction takes place near E_f :

$$\sigma(\omega) = \frac{\pi}{3} e^2 kT [N(E_F)]^2 \alpha^{-5} \omega [\ln(\nu_{ph}/\omega)]^4 \quad 2.19$$

where ν_{ph} is a phonon frequency (typically of the order of 10^{13} s^{-1}) and (α) describes the decay of the localized state wave function ($1/\alpha$ is the effective range of the wave function).

Two important features can be drawn from this equation: (1) $\sigma(\omega)$ varies linearly with temperature; (2) because of the presence of the logarithmic term $[\ln(\nu_{ph}/\omega)]^4$, the shape of a plot $\ln \sigma(\omega)$ versus $\ln \omega$ is not constant, but decreases slightly with increasing frequency of the applied field.

The above equation can be approximated by an expression of the form

$$\sigma(\omega) \approx \text{const. } \omega^s \quad 2.20$$

where the exponent (s) is defined as $d(\ln \sigma)/d(\ln \omega)$

and is given by

$$s = 1 - \frac{4}{\ln(\nu_{ph}/\omega)} \quad 2.21$$

Taking $\nu_{ph} = 10^{13} \text{ s}^{-1}$ the exponent decreases from a value $s = 0.84$ at

$\omega = 10^2 \text{ s}^{-1}$ to $s = 0.65$ at $\omega = 10^8 \text{ s}^{-1}$. One often writes the frequency dependence of the a.c. conductivity in the form,

$$\sigma(\omega) = \text{const. } \omega^{0.8}$$

which means that the logarithmic term $[\ln(\nu_{\text{ph}}/\omega)]^4$ varies as $\omega^{-0.2}$, in principle only strictly valid for frequency values in the neighbourhood of 10^4 Hz .

Experimentally it has been found that the a.c. conductivity of many chalcogenide glasses follows over a large frequency range the relationship given by equation 2.20 with (s) (76) lying between 0.7 and 1.0. Values close to one are difficult to understand on the basis of this formula, since they only can be obtained for unreasonably high values of the phonon frequency (ν_{ph}).

If one makes a proper choice of the parameter (α^{-1}) (77) offers a straightforward way for evaluating the density of state at the Fermi level. For a number of chalcogenide glasses estimates in the range 10^{18} - $10^{20} \text{ eV}^{-1} \text{ cm}^{-3}$ were obtained. These values are considered to be much too high and are difficult to reconcile with those deduced from other experiments such as optical absorption or photo induced ESR, which give estimates lower by several orders of magnitude. As seen in thermopower, another approach to the evaluation of $N(E_F)$ is based on the temperature dependence of the d.c. conductivity for variable range hopping at the Fermi level. By utilizing (78), an estimate of $N(E_F)$ should be obtainable from the slope of a $\ln \sigma$ versus $T^{-1/4}$ plot. This procedure has been followed for amorphous Si and Ge but cannot be applied to most of the chalcogenide glasses because of the absence of any observable variable range hopping even at the lowest temperature of measurement. It must be remarked here that the use of the Austin-Mott

formula to describe the observed $\sigma(\omega) \propto \omega^S$ behaviour has been strongly criticized essentially on the grounds that a similar frequency dependence has been observed in a number of insulating noncrystalline solids, such as polymers, molten quartz, SiO_2 glasses, etc. Therefore, it is now generally accepted that there may exist many other sources of dielectric loss mechanisms, such as surface barriers, ionic dipoles, dipole layer, inhomogeneities, which could give rise to a ω^S behaviour. These observations certainly indicate that the interpretation of the results on the basis of the electronic model described by (78) and which implies phonon-assisted hopping in localized states at (E_F) is not necessarily the unique one.

According to the Davis-Mott model of the band structure a third channel for conduction is available when charge carriers are excited in to the localized states of the band tails. Because of the thermally activated nature of this transport process, one expects that $\sigma(\omega)$ will also increase as $\omega [\ln(v_{ph}/\omega)]^4$, i.e. approximately as $\omega^{0.8}$. A distinction between hopping near the mobility edges and nearby the Fermi energy can be found by looking at the temperature of $\sigma(\omega)$. The creation of charge carriers into the band tails requires an activation energy $E_A - E_F$ for electrons ($E_F - E_B$ for holes), yielding an exponentially increasing number of charge carriers with rising temperature. This term must be incorporated in the expression for $\sigma(\omega)$, which will therefore, have a temperature dependence of the form $\sigma(\omega, T) \propto kT \exp(-\Delta E/kT)$. Since the exponential term usually plays by far the predominant role, the a.c. conductivity should show in the case of hopping in the tails the same temperature dependence as the d.c. conductivity curve. For transport at (E_F) the number of carriers remain constant and $\sigma(\omega)$ varies linearly with temperature as can be seen from (77).

It is clear that the mechanism yielding the highest contribution to the conductivity at a given temperature will be observed experimentally. When changing the temperature one should be able to see the transition from one mechanism to another.

2.4 Electronic Transport in Amorphous Semiconductors

2.4.1 Electrical Properties

2.4.1.1 D.C. Electrical Conductivity

The essential features of the Davis and Mott model for the band structure of amorphous semiconductors are the existence of narrow tails of localized states at the extremities of the valance and conduction bands and furthermore of a band of localized levels near the middle of the gap. This leads to three basically different channels for conduction.

a) Extended State Conduction

Consider the case of electron conduction. In the nondegenerate case and under the assumption of a constant density of states and constant mobility like conductivity due to electrons excited beyond the mobility edge into the extended states is given by

$$\sigma = e N(E_C) kT \mu_C \exp [-(E_C - E_F) / kT] \quad 2.22$$

where $N(E_C)$ is the density of states in the conduction band, (e) is the electron charge, (k) is Boltzmann's constant and (μ_C) is the mobility. In order to get an idea of the order of magnitude of (μ_C) we shall follow Mott's treatment (79). Mott calculated the lowest value of the electrical conductivity before the start of an activated process, i.e. just at (E_C) . This quantity he called the "minimum conductivity". He

derived the expression

$$\sigma_{\min} = \text{const } e^2 / \hbar a \quad 2.23$$

where the constant lies in the range between 0.026 and 0.1, $\sigma_{\min}$ is usually of the order 200-300 S cm^{-1} . Taking constant = 0.026, one finds for the mobility

$$\mu_C = 0.078 e a^2 B / \hbar k T \quad 2.24$$

where (B) is the width of the band, ($\hbar$) is fundamental unit of angular momentum (Planck's constant, ($\hbar$) divided by 2π) and (a) is a interatomic distance. Taking $a = 2\text{\AA}$, $B = 5\text{eV}$ one finds at room temperature that $\mu_C \approx 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This value corresponds to a mean free path comparable or less than the interatomic distance. Cohen (80) derived a similar expression for the variation of (μ) with kT as an equation 2.15. Equation 2.22 may be written therefore, as equation 2.7 which is represented in fig. 2.10 by section (a) of the curve.

Optical absorption measurements made on amorphous semiconductors have shown that the band gap decreases with increasing temperature. The energy distance $E_C - E_F$ therefore will show a similar behaviour, and, under the assumption of a linear temperature dependence,

$$E_C - E_F = E(0) - \gamma T \quad 2.25$$

the expression for the conductivity becomes

$$\sigma = \sigma_0 \exp(\gamma/k) \exp [- E(0)/kT] \quad 2.26$$

Here $E(0)$ is the energy distance at $T = 0\text{K}$ and (γ) is the temperature coefficient, we can write this formula in the form

$$\sigma = C_0 \exp [- E(0)/kT] \quad 2.27$$

where

$$C_0 = e N(E_C) kT \mu_C \exp(\gamma/k) \quad 2.28$$

As seen before (μ_C) is proportional to $1/T$, so that the preexponential factor (C_0) is temperature independent. Mott (81) has made an estimate of the preexponential (σ). In general (σ_0) may lie between 10 and 10^3 S cm^{-1} in most amorphous semiconductors. An estimate of (γ) can be obtained from the temperature dependence of the optical gap. In chalcogenide glasses the temperature coefficient of the optical gap generally lies between 4×10^{-4} and $8 \times 10^{-4} \text{ eV deg}^{-1}$. As the Fermi level is situated near the middle of the gap, values of (γ) of approximately half this magnitude are expected and hence values of $\exp(\gamma/k)$ in the range 10 - 100 seem to be most probable.

b) Conduction in Band Tails

If the wave functions are localized, so that $\sigma(E) = 0$, conduction can only occur by thermally activated hopping. Every time an electron moves from one localized state to another it will exchange energy with a phonon. It may be expected that the mobility will have a thermally activated nature.

$$\mu_{\text{hop}} = \mu_0 \exp[-W(E)/kT] \quad 2.29$$

$W(E)$ is the hopping energy, and

$$\mu_0 = (1/6) v_{\text{ph}} eR^2/kT \quad 2.30$$

where (v_{ph}) is the phonon frequency and (R) the distance covered in one hop.

For a typical phonon frequency $v_{\text{ph}} = 10^{13} \text{ s}^{-1}$ and $W \approx kT$ (37) yields a mobility of the order $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature.

Comparison of this value with the one calculated for conduction in the extended states suggest, as postulated by Mott that the mobility may drop by a factor of at least 100 at the energy which separates the localized and nonlocalized states. The conductivity in this case is given by

$$\sigma_{\text{hop}} = \sigma_{0 \text{ hop}} \left(\frac{kT}{\Delta E} \right)^S C_1 \exp [-(E_A - E_F + W)/kT] \quad 2.31$$

where (W) is the activated energy for hopping, (E_A) is the energy at which the band tail in the conduction band starts (or E_B in the case of the valance band) where (C_1)

$$C_1 = 1 - \exp\left(-\frac{\Delta E}{kT}\right) [1 + (\Delta E/kT)]$$

Equation 2.31 is repeated by section (b) in fig. 2.10.

c) Conduction in Localized States at the Fermi Energy

If the Fermi energy lies in a band of localized states as predicted by the Davis-Mott model, the carriers can move between the states via a phonon-assisted tunnelling process. This is the transport analogous to impurity conduction observed in heavily doped and highly compensated semiconductors at low temperatures. An estimate for the temperature dependence of the hopping conductivity at (E_F) has been given by Mott (82). We shall follow here his original derivation. Let us consider an electron that is scattered by phonons from one localized state to another. The energy difference between the states is denoted by (W). The probability (p) that an electron will jump from one state to another is determined by the following factors:

- i) The probability of finding a phonon with an excitation energy equal to (W), given by a Boltzmann expression $\exp(-W/kT)$.

ii) An attempt frequency ν_{ph} , which can not be greater than the maximum phonon frequency (in the range 10^{12} - 10^{13} s⁻¹).

iii) The probability of electron transfer from one state to another.

This factor depends on the overlapping of the wave functions and should be given by $\exp(-2\alpha R)$. Here (R) is the jumping distance, which at high temperatures equals the interatomic spacing, and α is a quantity which is representative for the rate of fall-off of the wave function at a site. If overlapping of the wave function is important, the factor $\exp(-2\alpha R)$ becomes of the order of one.

The probability (P) that an electron jumps will then be expressed by

$$P = \nu_{ph} \exp(-2\alpha R - W/kT) \quad 2.32$$

This leads to the following expression for the conductivity

$$\sigma = (1/6)e^2 R^2 \nu_{ph} N(E_F) \exp(-2\alpha R) \exp(-W/kT) \quad 2.33$$

where $N(E_F)$ is the density of states at the Fermi level. This equation is indicated as section (C) in fig. 2.10.

As the temperature is lowered the number and energy of phonons decrease, and the more energetic phonon assisted hops will progressively become less favourable. Carriers will tend to hop to larger distances in order to find sites which lie energetically closer than the nearest neighbours. This mechanism is the so-called variable range hopping. The essential feature of the conduction due to variable range hopping (14) is discussed in section 2.3.9.

2.4.1.2 A.C. Conductivity

As we have seen in section 2.4.1.1, there are three mechanisms

of charge transport that can contribute to a direct current in amorphous semiconductors. They can all contribute to the a.c. conductivity as follows:

a) Transport by carriers excited to the extended states near (E_C) or (E_V). For these we might expect that $\sigma(\omega)$ would be given by a formula of the Drude type,

$$\sigma(\omega) = \frac{\sigma(0)}{1 + \omega^2 \tau^2} \quad 2.34$$

The time of relaxation (τ) will, however, be very short ($\sim 10^{-15}$ s) and a decrease in $\sigma(\omega)$ as ω^{-2} (i.e. free carrier intraband absorption) is not expected until a frequency $\sim 10^{15}$ Hz is reached.

It is sufficient to state here that in the electrical range of frequencies (up to, say, 10^7 Hz) no frequency dependence of the conductivity associated with carriers in extended states is expected.

b) Transport by carriers excited into the localized states at the edges of the valance or conduction band. No complete theoretical treatments of $\sigma(\omega)$ for hopping under conditions of non-degenerate statistics are known, but we might expect a similar dependence on frequency to that derived under degenerate conditions (see (c) below), and thus as $\omega [\ln(\nu_{ph}/\omega)]^4$. This varies approximately as ω^s where $s < 1$ when $\omega < \nu_{ph}$. In order to estimate the frequency at which such an increase is expected a comparison with the magnitude of the d.c. hopping conduction (2.4.1.1.) would be required. The temperature dependence of this component of the a.c. conductivity should be the same as that of the carrier concentration at the band edge, so that for the conduction band it should increase as $\exp [-(E_A - E_F)/kT]$.

(c) Hopping transport by electrons with energies near the Fermi level, provided $N(E_F)$ is finite. There have been several theoretical treatments of $\sigma(\omega)$ for this mode of conduction (see the review by Pollak 1976). $\sigma(\omega)$ should increase with frequency in a manner similar to that for process (b). However, the exponential dependence on the temperature will be absent, and $\sigma(\omega)$ should be proportional to $(T)^{-1}$ if (kT) is small compared with the energy range over which $N(E_F)$ may be taken as constant, and independent of $(T)^{-1}$ if (kT) is larger than the width of some well-defined defect band in which (E_F) lies. An analysis of observed results has been given by Davis and Mott (1970) using the formula given by Austin and Mott (1969) and reviewed in 2.3.10.

Fig. 2.11 illustrates schematically the frequency dependence of the conductivity expected for the three conduction mechanism outlined above.

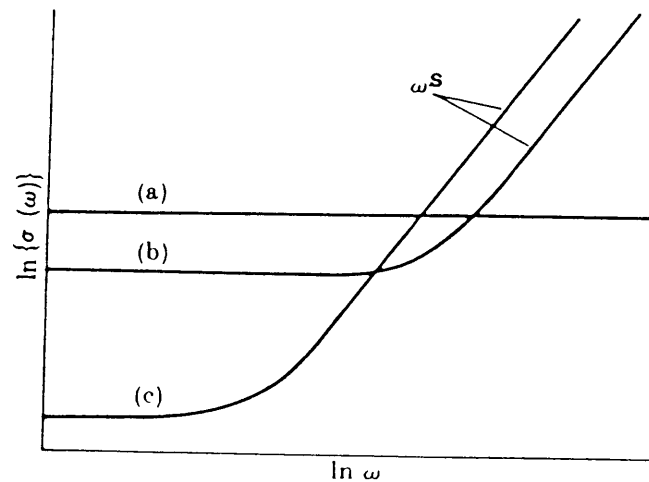


Fig. 2.11 Schematic illustration of the frequency dependence of conductivity for the three modes of conduction described in the text.

For the hopping processes (b) and (c), $\sigma(\omega)$ increases as ω^S . In practice the mechanism giving the highest conductivity at a particular temperature is observed; in the situation shown this would mean that

hopping at the band edge would not be observed at any frequency.

Conversely, if the onset of the ω^S behaviour for process (b) occurred at a lower frequency, then this would operate to the exclusion of process (c).

2.5 Dielectric Relaxation

2.5.1 General Theory

Orientation of molecular dipoles is relatively slow if comparison is made with electronic transitions or molecular vibrations which have frequencies generally above 10^{12} Hz (80), (84-88). It does not consist of a uniform switch in the arrangement of all molecules, it is more in the nature of a slight adjustment of their average orientations in the face of continued thermal agitation. Only when sufficient time is allowed after the application of an electric field for the orientation to attain equilibrium will the maximum polarisation, corresponding to the highest observable dielectric constant, be realised in a material. If sample time is allowed, then the observed dielectric constant is called the static dielectric constant (ϵ_s). On the other hand, if the polarisation is measured immediately after the field is applied, allowing no time for dipole orientation to take place, then the observed instantaneous dielectric constant, denoted (ϵ_∞) will be low and due to deformational effects alone. Somewhere in between these extremes of timescale there must therefore be a dispersion from a high to a low dielectric constant. In the above mentioned discussion the material under examination (the sample) is considered as a capacitance shunted by its conductance and the measured parameters are readily given by

$$\bar{\epsilon} = C_p/C_0 \quad 2.35$$

$$\bar{\epsilon} = \frac{G}{\omega C_0} = \frac{G}{2\pi f C_0} \quad 2.36$$

where (C_p) and (G) are capacitance and conductance of the sample at frequency (f) and (C_0) is the air capacitance. Linked by the relation

$$\bar{\epsilon}/\bar{\epsilon} = \tan \delta \quad 2.37$$

It is convenient to combine these two quantities into a complex dielectric constant or relative permittivity

$$\epsilon^* = \bar{\epsilon} - i\bar{\epsilon} \quad 2.38$$

The meaning of the real and imaginary parts may be readily appreciated by considering the material in a capacitor (capacitance C_0 when empty), as shown in fig. 2.12. The current (I) which flows in the external circuit after application of an alternating voltage given by the real part of $V = V_0 e^{i\omega t}$ may be calculated as follows:

$$I = \omega C_0 (\bar{\epsilon} + i\bar{\epsilon}) V \quad 2.39$$

This implies that we have a capacitive component of the current,

$$I_C = i \omega C_0 \bar{\epsilon} V \quad 2.40$$

which leads the voltage by 90° , and a resistive component,

$$I_R = \omega C_0 \bar{\epsilon} V \quad 2.41$$

which is in phase with the voltage, work can only be done by the latter component, and the physical meaning of the useful quantity $\tan \delta$, previously defined by equation 2.37, becomes apparently

$$\tan \delta = \frac{\bar{\epsilon}}{\bar{\epsilon}} = \frac{\text{energy dissipated per cycle}}{\text{energy stored per cycle}}$$

$(\bar{\epsilon})$ is called the dielectric loss factor and $\tan \delta$ is usually called the dielectric loss tangent or dissipation factor.

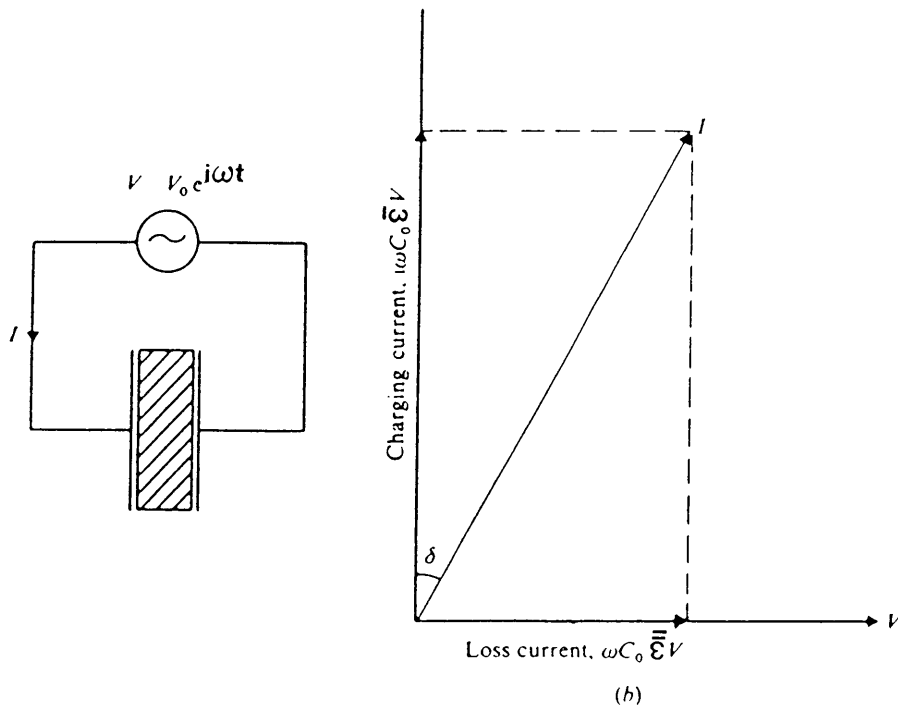


Fig. 2.12 A.C. losses in a dielectric: (a) circuit diagram, (b) Argand diagram of complex current-voltage relationship.

$(\bar{\epsilon})$ and $(\bar{\epsilon})$ are experimentally observable quantities which may be used to characterise the dielectric dispersion over a range of frequencies. In order to be able to interpret any such dispersion behaviour, it is first necessary to forge a link between their macroscopic, observable quantities and molecular properties, by postulating a reasonable model which describes the way the molecules respond to the applied field. The basic theory of dielectric relaxation behaviour, given by Debye (88), Fröhlich (89), Smyth (90), and Hill et al (91), begins with a macroscopic treatment of frequency dependence.

Consider the application at time $t = 0$ of a steady field (E_0) across a dielectric. The resulting electric displacement $D(t)$ at subsequent

times (t) will then comply with the equation

$$D(t) = \epsilon_0 \left[\epsilon_{\infty} + (\epsilon_s - \epsilon_{\infty}) \psi(t) \right] E_0 \quad 2.42$$

The first term on the right hand side, $\epsilon_0, \epsilon_{\infty}, E_0$, represents the instantaneous response of the materials to the field. The second term,

$\epsilon_0 (\epsilon_s - \epsilon_{\infty}) \psi(t) E_0$, represents the slower contribution from polarisation of the dipoles, with the factor $\psi(t)$ describing the time development of the underlying orientation process. By this definition $\psi(0) = 0$ and $\psi(\infty) = 1$. We further assume that the rates at which dipolar polarisation $D_p(t)$ progresses towards its equilibrium value $D_p(\infty) =$

$\epsilon_0 (\epsilon_s - \epsilon_{\infty}) E_0$ is proportional to its degree of departure from equilibrium, i.e.

$$D_p(t) = \frac{D_p(\infty) - D_p(t)}{\tau} \quad 2.43$$

Here (τ) is a characteristic time constant, usually called the dielectric relaxation time. By integration of equation 2.43:

$$D_p(t) = D_p(\infty) (1 - e^{-t/\tau}) \quad 2.44$$

$$\text{so that } \psi(t) = 1 - e^{-t/\tau} \quad 2.45$$

In general, for a series of field increments the electric displacement in the material

$$\tau \frac{dD(t)}{dt} + D(t) = \tau \epsilon_0 \epsilon_{\infty} \frac{dE(t)}{dt} + \epsilon_0 \epsilon_s E(t) \quad 2.46$$

For the particular case of an alternating field represented by the real part of $E(t) = E_0 e^{i\omega t}$, which produces an alternating displacement $D(t) = D_0 e^{i\omega(t-\delta)}$, the solution to equation 2.46 may be written

$$\epsilon^*(\omega) = \frac{D(t)}{\epsilon_0 E(t)} = \epsilon_0 + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau} \quad 2.47$$

which is called the Debye dispersion equation. Equation, real and imaginary parts of the two sides

$$\bar{\epsilon}(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \quad 2.48$$

$$\bar{\epsilon}''(\omega) = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \omega\tau \quad 2.49$$

The graphs of $(\bar{\epsilon})$ and $(\bar{\epsilon}'')$ against frequency of the applied field through the dispersion region are shown in fig. 2.13. The dielectric loss peak has a half-height width of 1.14 decades. The maximum loss value occurs when $\omega\tau = 1$, corresponding to a critical frequency $\omega_{\max} = 1/\tau$, and

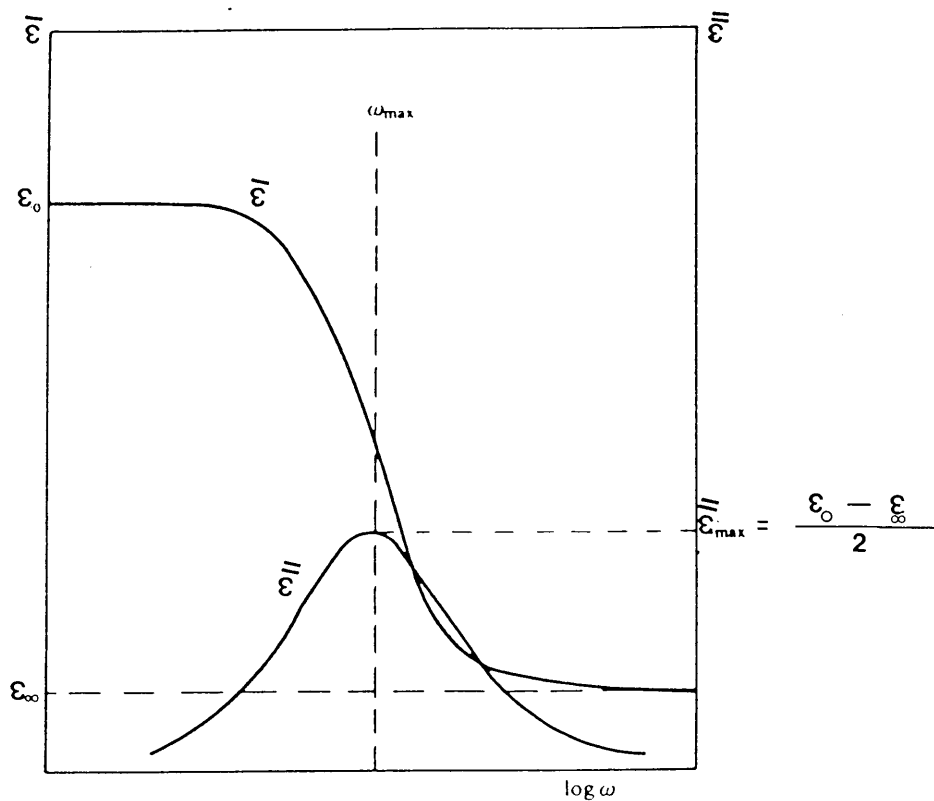


Fig. 2.13 Debye dielectric dispersion curves.

location of this peak provides the easiest way of obtaining the relaxation time from experimental results. The difference in dielectric constant measured at low and high frequencies is called the strength of the relaxation and it is related to the area under the absorption curve:

$$\Delta \epsilon = \epsilon_0 - \epsilon_\infty = \frac{2}{\pi} \int_{-\infty}^{+\infty} \bar{\epsilon}''(\omega) d(\ln \omega) \quad 2.50$$

This is a particular case of the Kramers-Krönig relaxation which expresses the general inter dependence of quantities like $(\bar{\epsilon}'')$ and $(\bar{\epsilon}')$ for any linear system.

The dependence of $(\bar{\epsilon}'')$ on $(\bar{\epsilon}')$ may be used to test how well the Debye model fits a real case. If we eliminate the parameter $(\omega\tau)$ between equations 2.48 and 2.49, we obtain

$$\left(\bar{\epsilon}' - \frac{\epsilon_s + \epsilon_\infty}{2} \right)^2 + \bar{\epsilon}''^2 = \left(\frac{\epsilon_s - \epsilon_\infty}{2} \right)^2 \quad 2.51$$

This is the equation of a circle, centre $[(\epsilon_s + \epsilon_\infty)/2.0]$, radius $(\epsilon_s - \epsilon_\infty)/2$, so that a plot of $(\bar{\epsilon}'')$ against $(\bar{\epsilon}')$ should give a semicircle, as shown in fig. 2.14(a). Experimental results for many polar liquids give excellent agreement with this theoretical curve, their relaxation times being of the order 10^{-11} s.

Relaxation observed in polymers, however, show broader dispersion curves and lower loss maxima than those predicted by the Debye model, and the $(\bar{\epsilon}'' - \bar{\epsilon}')$ curve falls inside the semicircle. This led Cole and Cole (92) to suggest the following semi-empirical equation for dielectric relaxations in polymers

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau)^\alpha} \quad 2.52$$

where (α) is a parameter, $0 < \alpha \leq 1$. The corresponding circular arc plot is shown in the fig. 2.14(b). Although the exact form of the distribution of relaxation times in the Cole-Cole equation is complicated and is not based on any special model, the parameter (α) is a convenient one for specifying the broadness of experimental relaxation peaks, and it has been used extensively for this purpose. Davidson and Cole (93) improved the fit with experiment by using a

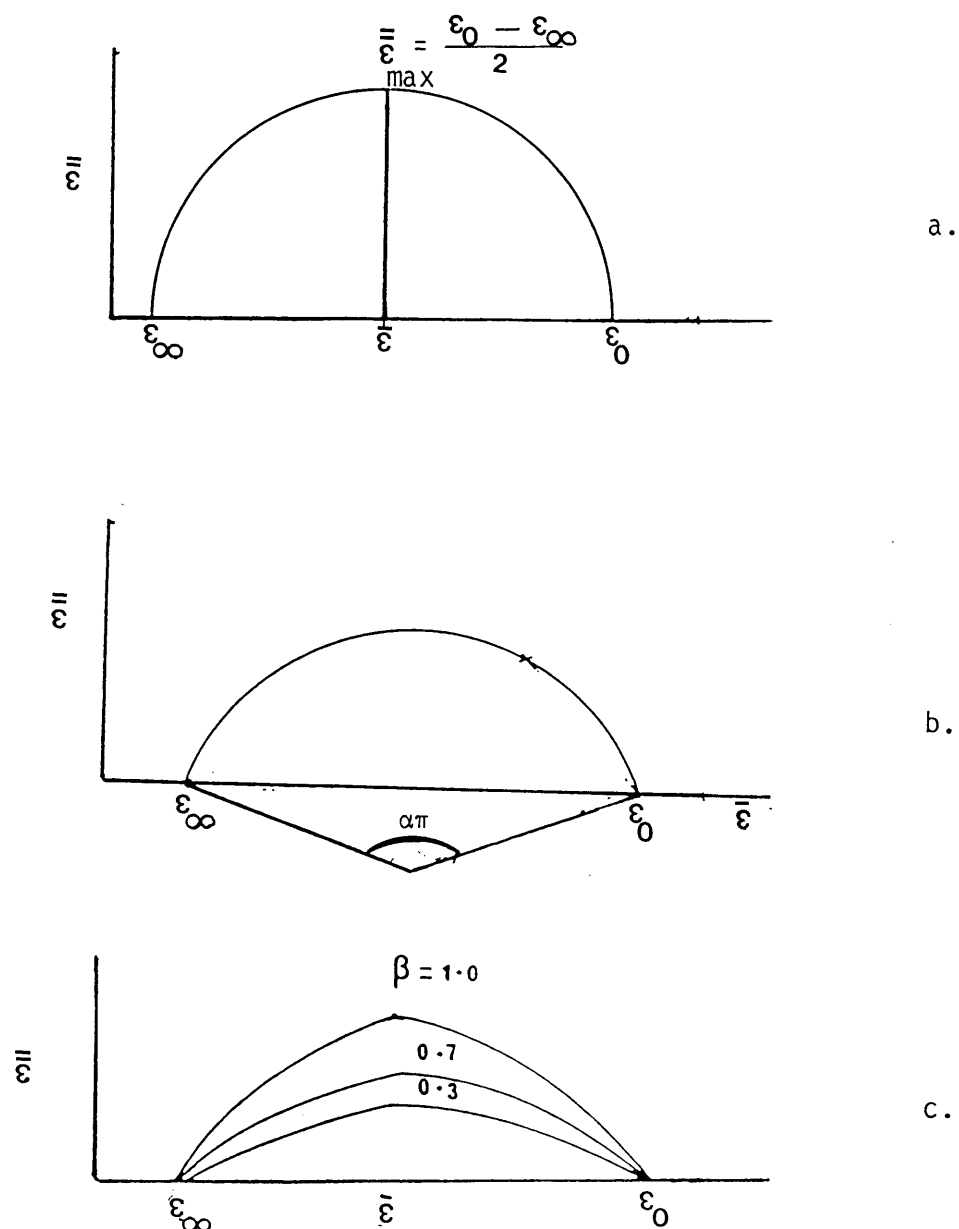


Fig. 2.14 Cole-Cole arc diagram.

slightly different semi-empirical equation:-

$$\epsilon^* = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{(1 + i\omega\tau)^{\beta}} \quad 2.53$$

where (β) is a parameter $0 < \beta \leq 1$. Equation 2.53 (93) corresponds to a skewed distribution of relaxation times about (τ) and hypothetical representation is shown in fig. 2.14(c), but it again has no particular theoretical foundation apart from the improved agreement with experiment for certain materials. For Debye semicircle $(\alpha, \beta=1)$, a combination of the equations have some time been used referred to as the Havriliak-Negami equations (94). The proposed equations of the form appears:

$$\frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \left(1 + (i\omega\tau)^{1-\alpha} \right)^{-\beta} \quad 2.54$$

to be a general representation of the three known dispersion i.e., Debye, circular arc and skewed semicircle. The complex dielectric constants calculated with the aid of this expression were found to be in excellent agreement with experimental results. In this equation 2.54 the (α) and (β) parameters indicate the presence of a distribution of possible processes of similar type and the existence of more than one type of relaxation, each of which is assumed to have an ideal distribution of relaxation times. Equation 2.54 fits most data and it is possible from an examination of the dependence of (α) and (β) on temperature to gain insight into the nature of the molecular processes giving to the observed dielectric processes.

More recently, it has been suggested that a departure from the assumed exponential from the approach to equilibrium may be responsible for the breadth of dipolar relaxation in polymers. A decay function of

the form

$$\psi(t) = e^{-(t/\tau)^\gamma} \quad 2.55$$

with $0 < \gamma \leq 1$, gives very good agreement in the case of many polymers, but the physical explanation for this kind of decay function has not yet been established (Williams et al (95) and Bailey et al (96).)

2.5.2 Thermal Activation of Dipolar Relaxation

In order to progress further in the interpretation of dipolar relaxation behaviour (83) one must study a molecular model in still more detail. In this thesis, two theories which are particularly relevant to polymers and provide a suitable basis for general discussion of the main features encountered have been discussed. Theory which has been central to the understanding of the temperature dependence of nearly all reaction rate processes: thermal activation over a potential energy barrier has been discussed.

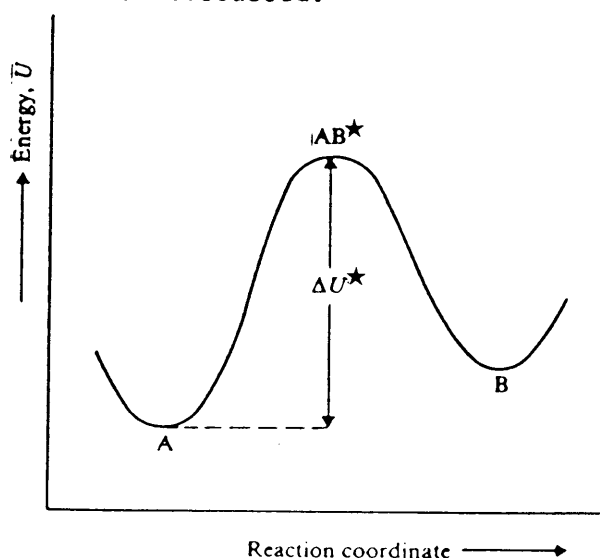


Fig. 2.15 Potential-energy diagram for a thermally activated process.

The model fig. 2.15 simply consists of two molecular states, (A) and (B), separated by a potential-energy barrier of height $\Delta U^\star$, and the reaction whose rate is calculated, is the change $A \rightarrow B$. (A) and (B) may be taken to represent two orientations of a dipolar group about a valance band linking the group to the rest of the molecule, the reaction coordinate being the angle of rotation about the bond. The reaction will follow the usual monomolecular rate equation:

$$-\frac{dc_A}{dt} = k_A C_A \quad 2.56$$

where (C_A) is the concentration of dipoles in state (A) and (k_A) is the rate constant. It is clear that molecules must acquire an extra amount of energy ($\Delta U^\star$) in order to surmount the energy barrier to passing from state (A) to state (B). Now it is well known from Boltzmann statistics that the probability that a given molecule possesses energy in excess of an amount ($\Delta U^\star$) is proportional to $e^{-\Delta U^\star/kT}$, so that we may expect the rate constant (k_A) to be given by

$$k_A = Ae^{-\Delta U^\star/kT} \quad 2.57$$

where (A) is a constant or a function which only varies slowly with temperature, and ($\Delta U^\star$) is called activation energy. The relaxation time (τ) may be roughly identified with $1/k_A$, so that we shall have

$$\ln \tau = \frac{\Delta U^\star}{kT} + \text{constant} \quad 2.58$$

This equation should give straight line when plotted $\ln \tau$ against $1/T$ whose slope is directly related to the activation energy.

2.5.3 Dielectric Relaxation in Solid Polymers

An enormous amount of work has now been carried out on the study of dielectric relaxation in solid polymers (96). The principle impetus for this has been derived from the use of such materials as insulators and dielectrics. The major objective of such studies has been to characterise the various loss and dispersion processes in the time (or frequency) and temperature domains, and to provide an explanation in terms of various polarization (usually dipole orientation processes).

2.5.3.1 Nomenclature

Considerable confusion exists in the literature with regard to the naming of the different relaxation or loss processes observed in polymers. This has arisen because of the custom of naming the process observed at higher temperatures or lowest frequencies as the " α -process" and then naming subsequent lower temperature (higher frequency) processes β, γ, δ etc. Of course this has depended, in a somewhat arbitrary way, on the initial temperature or frequency selected and on the dielectric activity of the processes observed. Bailey et al (96) prefers the system which designates the process associated with the main glass transition in amorphous polymer as the α -relaxation retaining a clear α -relaxation at appropriate temperatures and frequencies, and naming subsequent relaxations of amorphous polymer γ, δ etc.

2.5.3.2 Origin of Dielectric Activity

The dielectric activity of polymers is usually discussed in terms of partial segments between orientation polarization. This movement of non-polar segments between orientations of different energy may constitute a relaxation observable by dynamic mechanical or acoustic

techniques and not be observable as dielectric relaxation. Conversely, reorientation of dipolar segments through iso-energetic conformations may create dielectric polarization relaxation with no analogous mechanical relaxation.

The extent of reorientational freedom of the resultant dipole vector of the polymer chains determines the degree of polarization. The various component-group dipole moments, which together constitute the total resultant moment, may have differing degrees of freedom, and consequently achieve reorientational freedom at different temperatures so giving rise to the different transition or relaxation processes. It is important to note that this includes not only different chemical groupings but different degrees of co-operation in the movement of neighbouring identical groups or different amplitudes or degrees of orientational freedom of individual groups. Indeed the application of time-correlation functions to dielectric relaxation in polymers has yielded through the cross-correlation terms, insight into the extent of interaction between neighbouring group dipoles (96-98).

2.5.3.3 Relaxations in the Temperatures or Frequency Domains

Several distinct dielectric relaxation processes are usually present in a solid polymeric material. This multiplicity is seen most easily in a scan of dielectric loss at constant frequency as a function of temperature as shown in fig. 2.16. As the temperature is raised, molecular mobilities of various types become successively energised and available for dipolar orientation. By convention the dielectric relaxation processes are labelled α , β etc and so on, beginning at the high-temperature end. The same relaxation processes are generally responsible for dispersions in mechanical properties too, although a

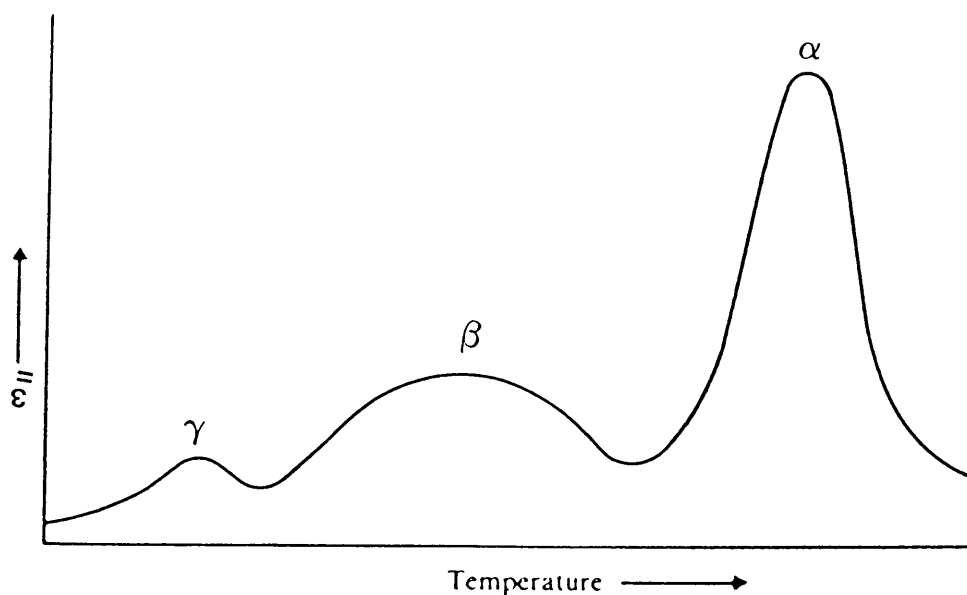


Fig. 2.16 A Schematic dielectric loss curve obtained by varying the temperature with the frequency of observation maintained constant.

particular molecular rearrangement process may produce a stronger dielectric than mechanical effect, or vice versa.

Some polymers are wholly amorphous and there is always a high-temperature α -relaxation associated with the micro-Brownian motion of the whole chain end, in addition, at least one low-temperature (β , γ etc) subsidiary relaxation. The relative strength of the α - and β -dielectric relaxations depends on how much orientation of the dipolar groups can occur through the limited mobility allowed by the β -process before the more difficult but more extensive mobility of the α -process comes into play; there is a partitioning of the total dipolar alignment amongst the molecular rearrangement processes.

Detailed examination of the relaxations requires isothermal scans of dielectric constant and loss as a function of frequency (f) so that

effective dipole movements and activation energies of relaxation times may be obtained.

The high-frequency β , γ etc subsidiary peaks in amorphous polymers are characteristically very broad with half-height width of several decades (compared with 1.14 decades for a single Debye relaxation process), although a good, linear Arrhenius plot is usually obtained suggesting a non-cooperative mechanism.

2.5.4 Interfacial Polarization

When a system contains internal boundaries to charge migration, as in heterogeneous polymers, polarization can arise due to charge build-up at the interfaces between regions of differing conductivity (σ) and dielectric constant $\bar{\epsilon}$. This phenomena is called interfacial, or Maxwell-Wagner-Sillars polarization, and have been reviewed by Van Beek (99).

The phenomenon was first considered theoretically by Maxwell (100) who treated the case of a layered system of which the phases differed in conductivity and dielectric constant. He showed that the equations for real permittivity and loss were very similar to the simple Debye equations. Wagner (101) produced similar equations for a system of small conducting spheres embedded in a continuum of lesser conductivity.

Sillars (102) extended the theory to spheroids, showing that the magnitude and frequency position of the observed loss were a function of the occlusion shape and volume fraction.

3. EXPERIMENTAL TECHNIQUES AND APPARATUS

CHAPTER 3. EXPERIMENTAL TECHNIQUES AND APPARATUS

3.1 Review of the Experimental Techniques

Measurement of Bulk Conductivity

The measurement of conductivity is the most fundamental of the routine measurements which are customarily made on solid polymers. Basically, any such measurement is made by passing an accurately known current through the sample and measuring a voltage drop between the points, at a known distance apart. A few of the specific techniques, are of sufficient importance to warrant extended discussion. A broad classification of methods can be based on the kind of current (direct or alternating) and the number of electrodes (two or four) (1-3).

3.1.1. Direct - Current Methods

Most measurements have been made with direct current and two electrodes. Although observations on organic and nonorganic semiconductors have been made more accurately with a four-electrode arrangement.

The Two - Electrode Method

In this method, voltage (V) is applied to the system and the resultant current (I) is measured in the external circuit as shown in fig. 3.1b, it gives a d.c. conductivity

$$\sigma = I l / va \qquad 3.1$$

where (a) is the cross-sectional area and (l) the length of the sample, but the value of (σ) thus obtained may not be characteristic of the material between the electrodes for two reasons.

- 1) A high resistance at the interface between the sample and the

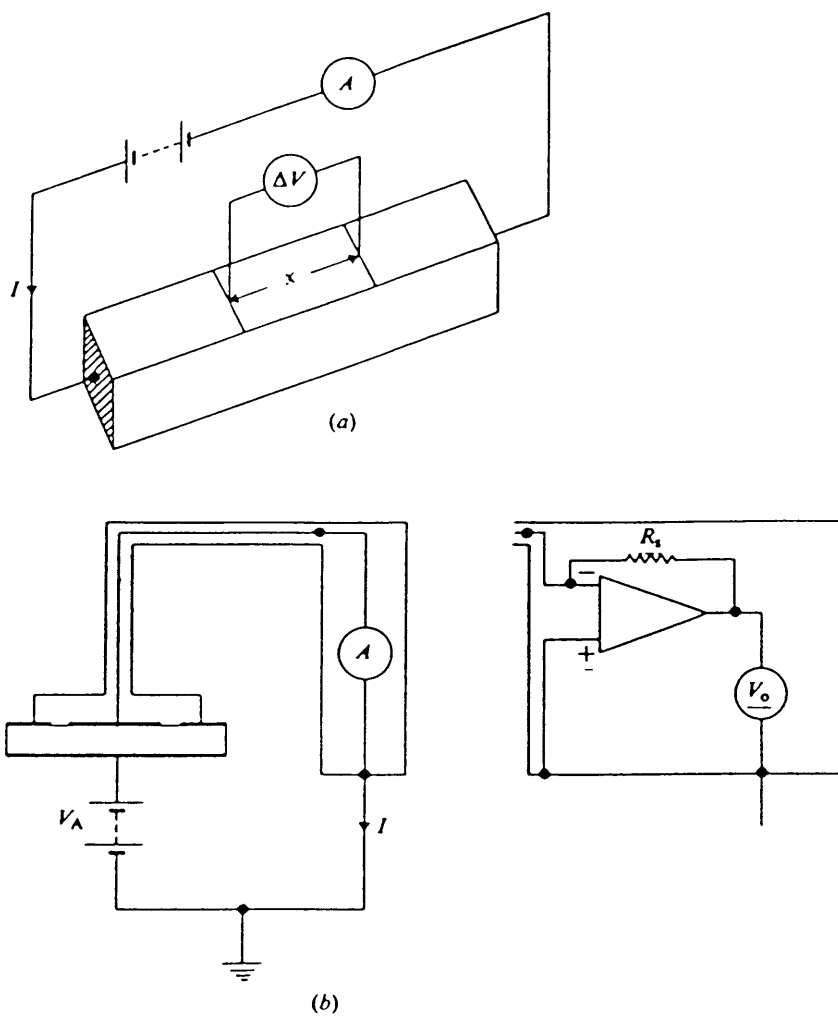


Fig. 3.1. Circuit diagrams for conductivity measurements:
 (a) 4-terminal method, (b) 2-terminal method with guarding.

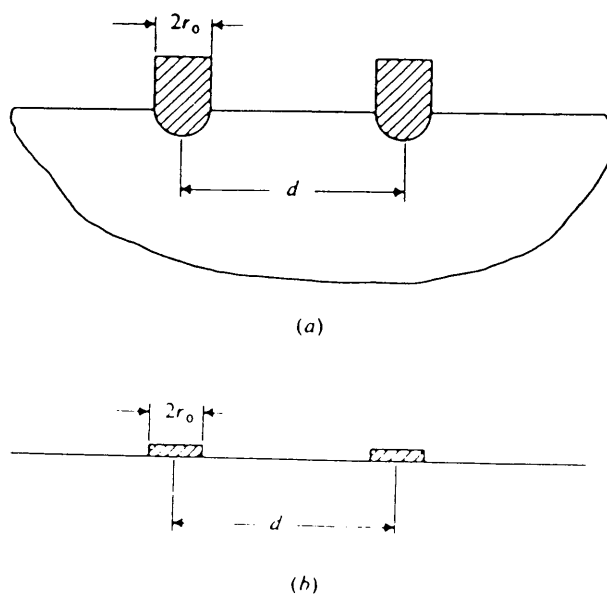


Fig. 3.2. Types of 2-terminal conductance probes: (a) hemispheres in a conductive solid, (b) disc electrodes on a conductive surface.

electrode will result in the voltage drop across the sample being less than the applied voltage (V). Consequently, (σ) will be lower than the true conductivity of the sample material. Either a poor mechanical contact or a rectifying junction at the electrode-sample interface will produce this effect.

2) Contacts can also affect the result if the electrodes inject holes or electrons into the sample, or, if in placing the electrode into the sample, some damage is done to the latter as shown in fig. 3.2.

The choice of apparatus to be used in making conductivity measurements depends on the conductance of the sample and the accuracy desired (3). When the conductance is low, a number of precautions must be taken in its measurement. These include,

- a) use of a guard ring to eliminate conduction in the surface layers, which is often much greater than in the bulk as shown in fig. 3.1b;
- b) placing the sample in an inert atmosphere or in a vacuum to prevent interactions and a consequent alteration either in the number or in the mobility of the carriers;
- c) shielding against radiofrequency fields as well as coupling with power line fields (the use of both shielded cable and a metal container with only one single earthing point around the sample and the grid resistor of the electrometer is essential);
- d) the removal of water vapor from the atmosphere around high value resistors.

Four - Electrode Methods

Difficulties arising from the electrode contact can be overcome, sometimes, by the use of four electrodes instead of two. Two probes

can make contact with one face of the sample having the form of a parallelepiped, two opposite faces of which meet two electrodes. A current is passed between the two electrodes, and the voltage drop between the probes is measured most accurately with a potentiometer, which prevents current from being drawn from the probes.

Instead of using two extended electrodes and two probes as described above, all four electrodes can function as probes. Figs. 3.3 and 3.1(a) show an arrangement of this type by Valdes (4). The distances between adjacent probes, S_1 , S_2 , and S_3 , were all about 1 mm. Where the size of the sample preferably a single crystal, permits, the four probes should be mounted clear of a boundary of the sample. If this is not possible, correction factors given by Valdes (4-7) should be introduced. A current (I) is passed between the two outermost probes, and the voltage (V) developed between the two inner probes is measured. With this arrangement, the conductivity of the outer contacts need only be sufficiently high to allow a measurable current to pass; the conductance of the inner contacts must be high in comparison with that of the current-measuring device.

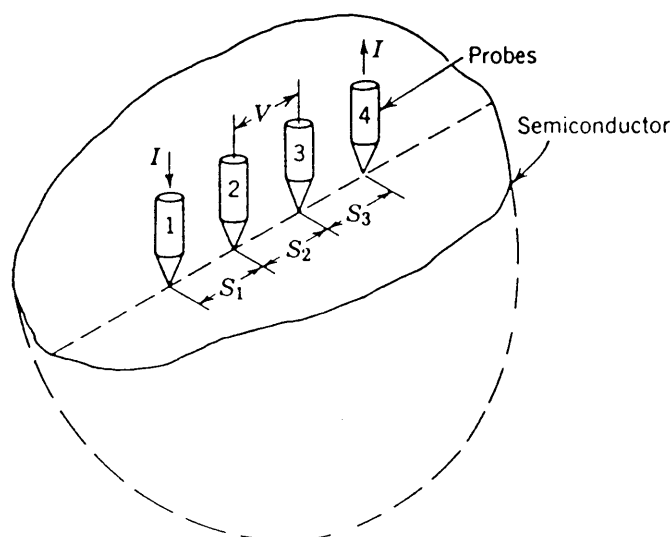


Fig. 3.3 Model for the four-probe conductivity measurements.
After Valdes (4).

When $S_1 = S_2 = S_3 = S$ are distances between the adjacent probes, when (S) is small compared to the smallest dimensions of the sample and when the probes are near a sample boundary (8); then

$$\sigma = I / (2 \pi V S) \quad 3.2$$

The form of the sample can affect the results. In general a measurement of V/I using four-point probe leads to an accurate value of conductivity only if the following requirements are met.

- a) The minority carriers injected by the points recombine in the immediate proximity of the points.
- c) The point area is small compared to the spacing between the points.
- d) The thickness of the semiconductor sample is large compared to the point spacing.
- e) The four points are not applied close to the semiconductor edge.
- f) The spacing between the points is equal.
- g) The sample diameter is large compared to the point spacing.

Other limitations of the four-probe method have been discussed by Kronick and Labes (9) in connection with organic semiconductors. They point out that, with samples of compressed powders, both the anisotropy of crystals and the presence of interparticle contact conductances make the results difficult to interpret. In addition, the presence of surface effects may raise problems that make it difficult if not impossible to understand the terms of the properties of the bulk crystal.

In order to eliminate contact resistance, in the present work four-terminal method has been used for conductance measurement for polypyrrole.

3.1.2 Alternating-Current Methods

We now consider that the potential (V) applied to a dielectric or near-dielectric is alternating, so $V = V_0 \sin \omega t$. The resultant current flow depends not only on the conductance of the sample but also on the capacitance. The essential feature of the alternating-current methods is discussed in Section 2.5.

Parallel Conductance and Parallel Capacitance

Parallel conductance and parallel capacitance refer to values measured, a sample which is regarded as equivalent to a resistance and a capacitance in parallel. This is an approximation frequently made for organic crystals.

Alternating-Current Conductivity σ_{ac}

Alternating-current conductivity (σ_{ac}) is the a.c. conductance of a sample of unit dimensions and refers to the active or conduction component of the current. Thus, for a capacitor showing some dielectric loss or for sample equivalent to a capacitor plus a resistor in parallel,

$$\sigma_{ac} = \omega \bar{\epsilon}'' \epsilon_0 \quad 3.3$$

where ($\bar{\epsilon}''$) is the imaginary parts of the permittivity $\bar{\epsilon}^* = \bar{\epsilon}' + i\bar{\epsilon}''$, (ω) is angular velocity, therefore, related to the frequency by $f = \omega/2\pi$. Because (σ_{ac}) depends on frequency, it is not a simple constant of a material. In computing dielectric loss, the d.c. conductivity can be

subtracted from the a.c. conductivity.

The choice of apparatus to be used in making a.c. conductivity and dielectric loss, depends on the resistance of the sample and the accuracy desired.

Bridge methods, of which the Wheatstone bridge is the basis, are discussed (10,11). These methods are inferior to the four-electrode methods, especially when a contact resistance is present. The Wheatstone bridge is most useful when (R) is between 10 and 10,000 ohms, but it can be used to measure values up to 10^{14} ohms. The null bridge circuit using resistors which are wire-wound increases the accuracy, but these can be obtained only up to 10^7 ohms.

In the present work bridge-method, a two terminal cell-configuration, and Farnell LFM2 sine-square oscillator with associated bridge network were used for dielectric loss and a.c. conductivity measurements have been used for carbon black composites and polychloroprene.

Alternating-current methods have the advantage of eliminating certain resistances at the contacts between particles, because such resistances, if large, are electrically shorted by the capacitance of the contacts.

3.2 Electrode Systems used for Measurement

In the present study (i) electrodes used for measurements of conductivity for polymers (polystyrene and polychloroprene) and carbon black composites were (a) a brass electrode system and (b) colloidal graphite suspension (Aquadag) was used to generate a strongly adhering electrode system. (ii) Evaporated gold electrodes were used for measurements of conductivity for polypyrrole.

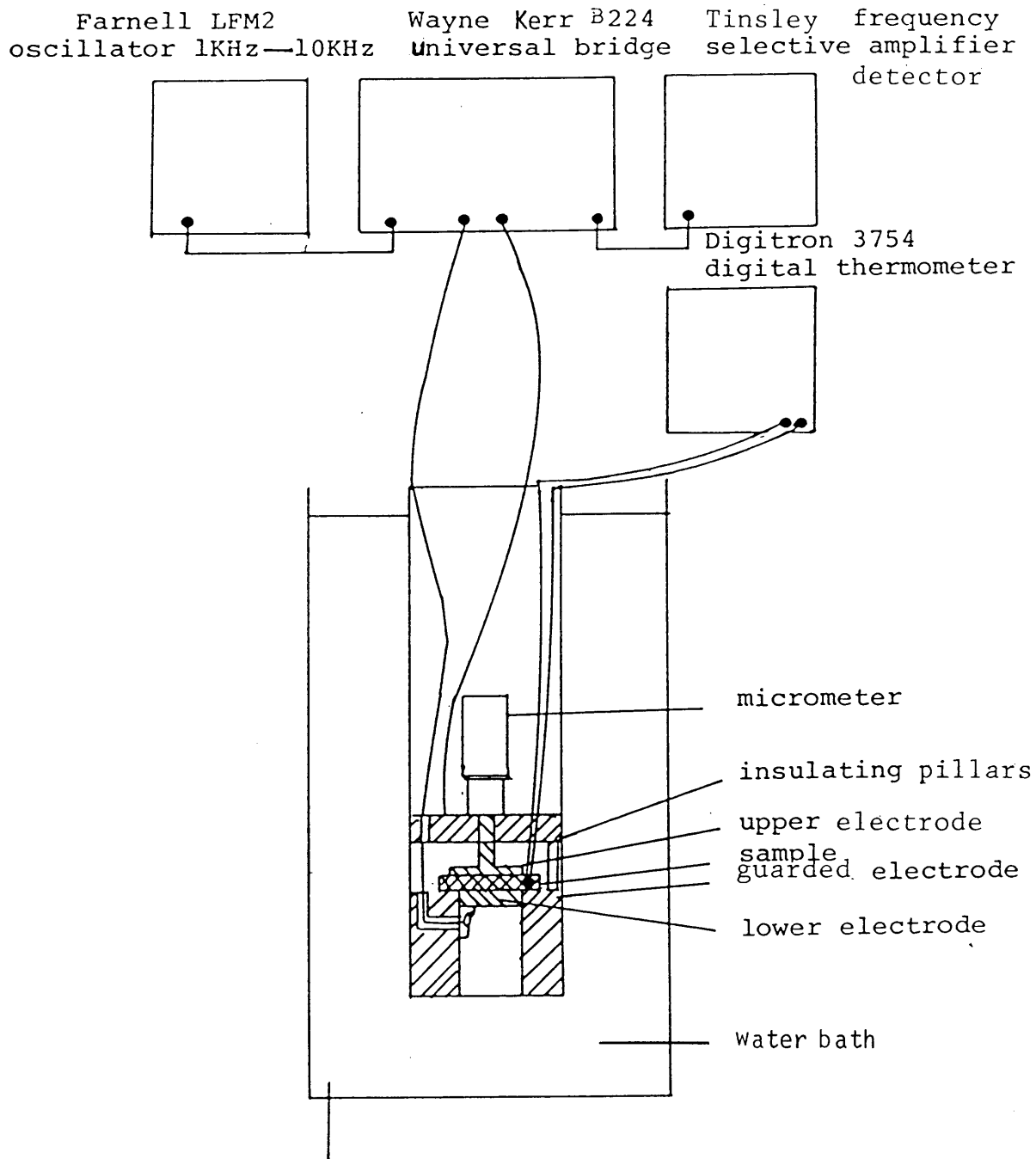
3.3 Sample Cells

3.3.1 Conventional Dielectric Cell

The first cell used in this study was a conventional dielectric cell fig. 3.4. The cell was designed in the laboratory. The cell was contained in a sealed copper canister and good contact between it and the cell ensured efficient thermal conduction from the thermostatic bath in which the cell was immersed. Two different cell electrode systems were used in this study, the brass electrode system and the colloidal graphite suspension (Aquadag) electrode system. They gave good contact between the sample and the electrode surface. The upper electrode was attached to a micrometer to provide reproducible measurements of sample thickness. The electrical connection was made by coaxial cable to the lid of the cell housing from which connection could be made to the measuring bridge. A thermocouple was fed into the cell via a hole drilled in the lid of the cell housing. The canister was sealed before each measurement. The rod which passed through the lid of the canister allowed the contact of the electrodes to the sample to be checked during measurements without disconnecting the cell from the bridge. This rod was always disconnected before measurements. All measurements using this cell were made in the frequency range of 600 Hz to 10 KHz.

3.3.2 Conventional Four Terminal Cell Configuration

The second cell used in this study was a four terminal cell configuration fig. 3.5. This cell was designed in the laboratory. Two wires were connected to each of the two brass electrodes and the other two wires were connected to the thermocouple. These wires were in turn



water bath (20°C—90°C, Gallenkamp thermometer 100)
ethanol bath (-70°C to +20°C cryocool 80II cold finger
and cryotrol controller)

Figure(3.4) Two-probes bridge measurement.

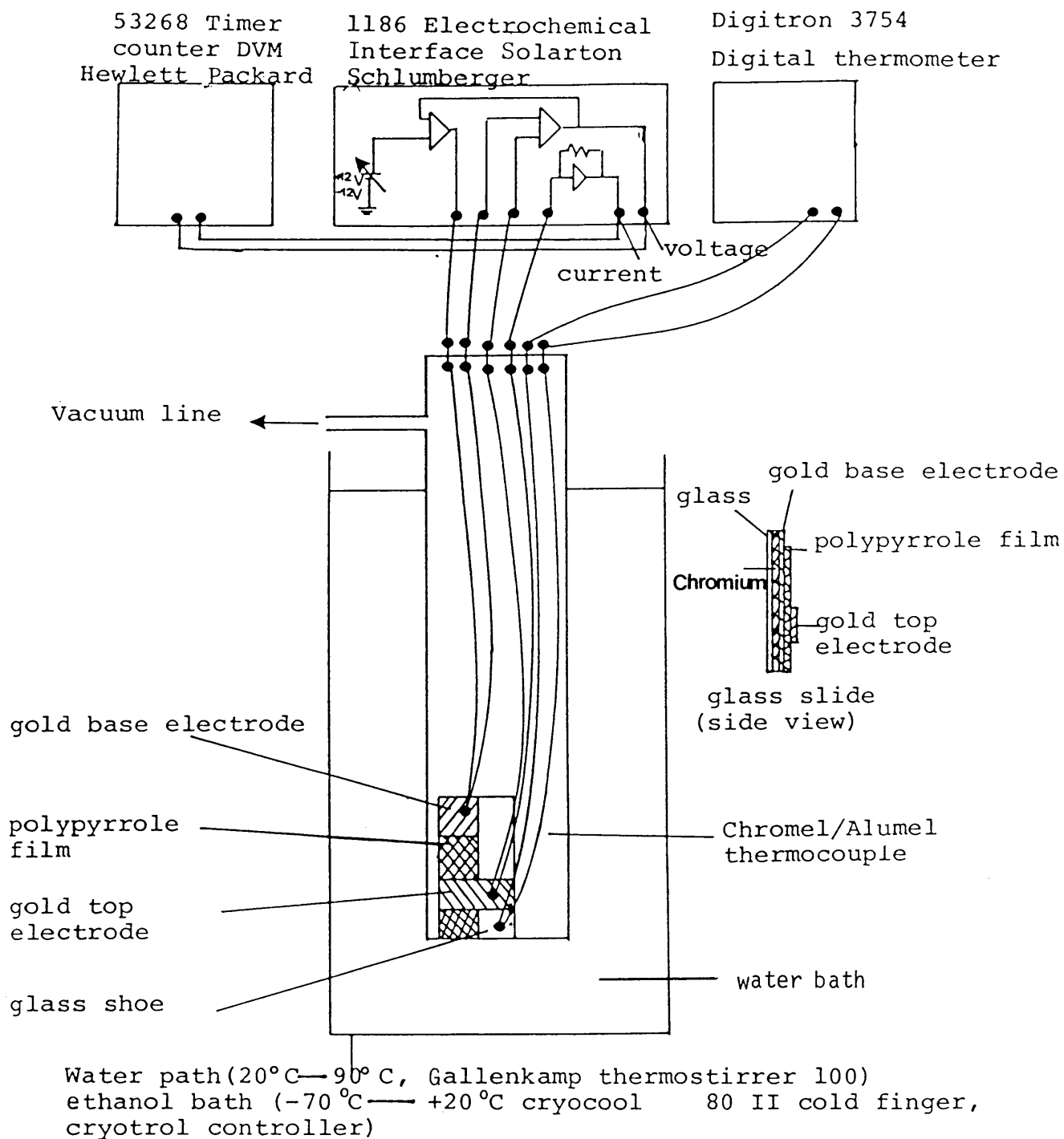


Figure (3.5) Four-probes conductivity measurement.

connected to terminals in the glass-lid of the cell allowing a vacuum to be maintained in the cell. An evaporated gold electrode was used in this study. The electrical connections were made by coaxial cables to the lid of the cell housing from which connections could be made to the DVM, 1186 Electrochemical Interface Solartron Schlumberger and Digitron 3754 digital thermometer. The lid was sealed before each measurement.

3.3.3 Electrochemical Cell

The apparatus used for the electrochemical synthesis of pyrrole consisted, as shown in fig. 3.6, of a 100 ml beaker supported on a cork base and housed in a large glass straight-sided vessel. Through the lid of this vessel passed electrical wires connecting the electrodes, suspended in the chemical system, to the circuitry. Two glass connectors were also positioned in the lid allowing the apparatus to be evacuated and purged with nitrogen gas as required.

Current and voltage measurements were recorded using a multi-range meter.

3.4 Preparation and Purification of Chemicals

3.4.1 Purification

Polystyrene (PS)

Polystyrene supplied by British Drug House Ltd., (BDH) had a molecular mass of 100,000 and was used without further purification.

Polychloroprene (PCP) (Chloroprene Rubber (CR))

Polychloroprene supplied by E. Dupont de Nemours Ltd., was purified by reprecipitation from Analar toluene in a large excess of methanol at about -20°C . The methanol was stirred constantly during

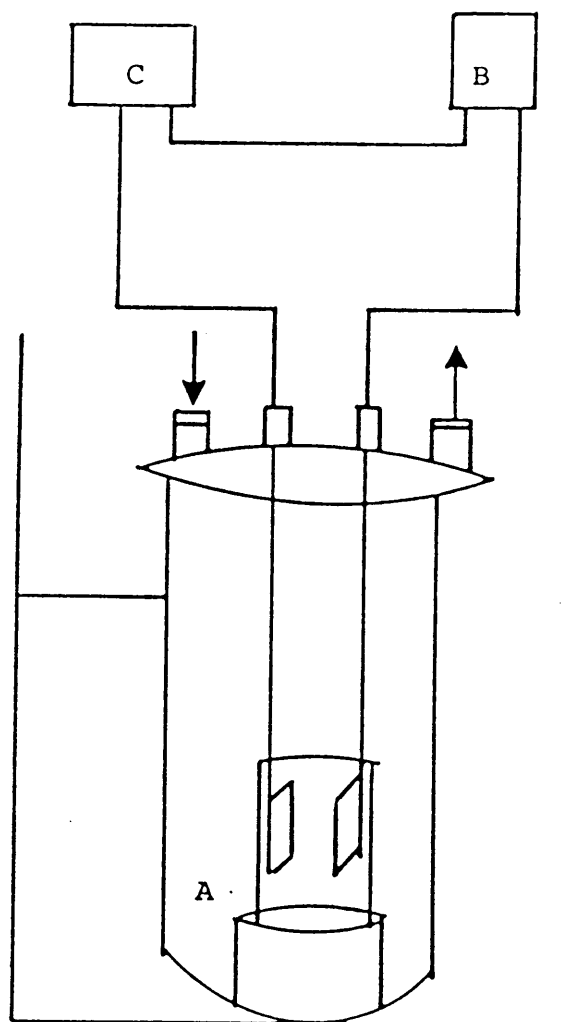


Fig.(3.6) Diagram of the electrochemical cell .

A Reaction vessel

B Power supply

C Avometer

A three electrode configuration using a SCE (standard calomel electrode) reference electrode and the 1186 Electrochemical Interface - Solarton Schlumberger was used for the growth of the silver para-toluene sulphonate films.

the precipitation process. This process was repeated to ensure a high purity of the sample and the polymer was finally dried under vacuum for 48 hours at room temperature.

Pyrrole (Py)

Pyrrole supplied by British Drug House Ltd., (BDH) was purified by redistillation several times at a pressure of 20 mm mercury at 32°C. Purified pyrrole was stored under a nitrogen atmosphere and in addition to storage conditions, it was necessary to encase the flask containing the monomer with aluminium foil to exclude completely from light. This additional precaution was necessary as it was found that pyrrole was highly susceptible to photopolymerization.

Pyrrole was analysed before and after purification by proton magnetic resonance ^1H -NMR and ^{13}C -NMR. The study of the spectra revealed (see Appendix A) a reduction in the intensity of impurity peaks. (Pyrrole is easily oxidized and is colourless when it is pure, and brown when it is exposed to air).

Carbon Black (CB)

Carbon black (Regal 300) supplied by Cabot Corp., was used without further purification.

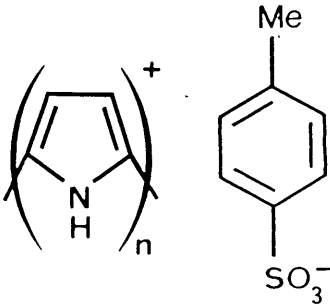
3.4.2 Preparation

Preparation of Carbon Black Filled Composite

(A) Preparation of Carbon Black Load Polystyrene Discs

The polymer (sample 1, table 3.1) was soluble in toluene, therefore, samples of this polymer prepared in the form of discs were generated by mixing the polymer and carbon black in solution. Carbon black Regal 300 and polystyrene were dissolved in a mixture of acetone

Table 3.1. Structures and the Physical Properties of the Different Samples used in this Study.

Sample	Structure	Colour	Conductivity $S\ cm^{-1}$
1	Carbon black (Regal 300) + polystyrene $\begin{array}{c} \text{---CH---CH}_2\text{---}_n \\ \\ \text{C}_6\text{H}_5 \end{array}$	black	$\approx 5 \times 10^{-6}$
2	Carbon black (pulverised Regal 300) + polychloroprene $\begin{array}{c} \text{Cl} \\ \\ \text{---CH}_2\text{---C=CH---CH}_2\text{---}_n \end{array}$	black	$\approx 1 \times 10^{-3}$
3	Polypyrrole para-toluene sulfonate prepared by special method of dry-box technique 	black	$\approx 1.27 \times 10^{-2}$ to 22.65×10^{-2}

and toluene and left for 24 hours in a laboratory shaker. The solvent was allowed to evaporate yielding a powder which was finally dried under vacuum at room temperature. The solid was then pressed into a circular form using a moulding pressure of 600 psi at 150°C. Discs of various thickness in the range of 0.11 to 0.35 cm were prepared. The thickness was determined using a micrometer. The precoat of the carbon black was found to be necessary because of the difficulty in obtaining good dispersion of the carbon black.

(B) Preparation of Carbon Black Load Polychloroprene Discs

The polymer (sample 2, table 3.1) was provided as a solution in toluene. Samples of these polymers, were prepared in the form of discs. A mixture of pulverised carbon black Regal 300 and polychloroprene were dissolved in toluene and acetone and poured dropwise into the moulder which was lined with polytetrafluoroethylene (PTFE), the mixture was finally left to dry in the moulder at room temperature and was covered with a watch glass to prevent formation of air bubbles. This method could be used up to 40% carbon black load polychloroprene, above 40% the discs were prepared as previously described and then the mixture was pressed into discs using a moulding pressure of 600 psi at room temperature. The thickness was determined using a micrometer.

Synthesis of Polymer Films (polypyrrole) Electrochemically

Polypyrroles were prepared by the following electrochemical methods:-

- (A) Aqueous technique
- (B) Non aqueous technique
- (C) Dry-box technique

(A) Aqueous Technique

Electrochemical preparation is probably the most simple method of preparing pyrrole. This technique is based on the original Dall'Olio (12) electrochemical synthesis. The main parameters of the four samples preparations are listed in table 3.2. They were mounted on the four probes measurement system. Measurements have been performed at room temperature.

Aqueous techniques were not used due to the following disadvantages:-

- i) Polypyrrole produced was black, insoluble and brittle. Colourless bubbles were evolved underneath the anode, preventing the formation of a good smooth film. In general the films obtained were non-uniform.
- ii) The bubbles formed between the electrode and the conducting film led to a bad contact between the film and the electrode.
- iii) The film formed had poor mechanical properties.
- iv) The excess of oxygen in the solution led to a decrease in the conductivity of the film.

(B) Non-Aqueous Technique

This technique is based on the Diaz et al., (13) who used acetonitrile instead of water to minimize the excess amount of oxygen in the electrolyte solutions which produced polypyrrole films. The main parameters of the three samples prepared are listed in table 3.3.

The non-aqueous technique was not used because the film had poor conductivities and non-uniform surfaces.

In both the techniques the tin oxide SnO_2 electrode was replaced with gold vapour deposited on a chrome plated glass substrate

Table 3. 2. Polypyrrole Sample Preparation Parameters and the Conductivity of the Films .

No.	Polymer Sample	Solvent	Monomer	Electrolyte	Electrodes	Voltage Applied	Sample Form	Conductivity $S\ cm^{-1}$
1.	Polypyrrole sulfate	water	0.05m pyrrole	0.05m $CuSO_4 \cdot 5H_2O$ as dilute H_2SO_4 as a buffer. pH decreased from 4 to 2.5	Cu as cathode and tin oxide coated glass slide as anode	5.0V	non uniform black film with crumbly surface	$\approx 1 \times 10^{-6}$
		"	0.1m pyrrole	$FeSO_4 \cdot 7H_2O$ + dilute H_2SO_4 as buffer. pH decreased from 3.8 to 2.0	"	"	"	"
		"	"	$Fe_2(SO_4)_3 \cdot 9H_2O$	"	"	Sandwich film consisting of black pyrrole, polypyrrole and black pyrrole in solution	-
2.	Polypyrrole perchlorate	0.06m MeCN in water	0.1m pyrrole	0.1m $AgClO_4$	Ag as cathode and tin oxide coated glass slide as anode	0.3 V	non uniform film	-
3.	Polypyrrole tetrafluoroborate	water	0.1m pyrrole	0.1m $NaBF_4$	Cu as cathode and SnO_2 coated glass slide as anode	5.0.V	matt black crumbly and wrinkled film	$\approx 5 \times 10^{-3}$
4.	Polypyrrole tetra-benzoborate	water	0.1m pyrrole	0.03m $NaB(C_6H_5)_4$	Cu as cathode and SnO_2 coated glass slide as anode	0.3 V	A black thin non uniform film	-

Table 3.3. Polypyrrole Sample Preparation Parameters and the Conductivity of the Films.

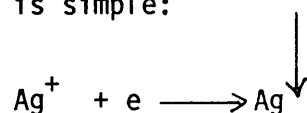
No.	Polymer Sample	Solvent	Electrolyte	Monomer	Electrodes	Voltage Applied	Sample Form	Conductivity $S\ cm^{-1}$
1.	Polypyrrole perchlorate	MeCN	0.001m hydroquinone+ 0.1m $NaClO_4$	0.1m pyrrole	Platinum as cathode and SnO_2 coated glass slide as anode	0.5V	non-uniform black film	$\approx 26.8 \times 10^{-3}$ to 23.8×10^{-3}
2.	Polypyrrole sulfate	isobutyl alcohol	0.1m $CuSO_4 \cdot 5H_2O$	0.1m pyrrole	Cu as cathode and SnO_2 coated glass slide as anode	0.3V	non-uniform black film with crumbly surface	-
		acetone	"	"	"	3.0V	non-uniform black film	-

electrode because analysis of the detached polypyrrole films produced using SnO_2 electrodes indicated that some of the electrode material was removed with the polymer. This was not the case when stabilised gold electrodes were used in the synthesis.

(C) Dry-box Technique

This method is useful in avoiding contamination of the film by oxygen or moisture. For film preparation in dry-box (14) repurified pyrrole and silver para-toluene sulfonate salt in acetonitrile were used. Platinum was used as a cathode and evaporated gold on a glass slide as anode.

The reaction vessel was purged with N_2 and evacuated. The silver ions play the same role as the copper ions in the aqueous preparation, providing a facile cathode reaction which does not interfere with the film forming reaction at the anode. Silver ions were used because the cathode reaction is simple:



This technique led to extremely smooth films of good stoichiometry and eliminated problems arising from accumulation of excess oxygen. However, these films, like all other polypyrrole films prepared so far, contained an excess of hydrogen. The origin of excess hydrogen was not well understood at the time this study was undertaken. Possible explanations will be put forward for its origin in the discussion part of the present work.

Despite their improved stoichiometries, these films had better electrical conductivities than previous films. Polypyrrole films doped with para-toluene sulfonate were used extensively in this investigation

for the following reasons, they formed very thick black uniform films, the composite electrode reaction was very simple and the films could be prepared reproducibly under anhydrous conditions.

These films prepared by dry-box technique were used in the extensive characterization experiments described in this work.

The main parameters for the first three sample preparations are listed in table 3.4 and for the fourth sample of polypyrrole para-toluene sulfonate, a special method was used. Details are given separately for this method. All the samples have been prepared using dry-box technique. Prepared samples were washed with acetonitrile. They were mounted on jig for four probes measurements.

The special method used for preparation of a series of films of polypyrrole para-toluene sulfonate will be described in detail.

The synthesis of polypyrrole para-toluene sulfonate (sample 3, table 3.1) was carried out by using 0.05m silver para-toluene sulfonate and 0.1m freshly redistilled pyrrole in 100% acetonitrile solution. Both the pyrrole and the solvent were thoroughly degassed and carefully dried before they were placed in the synthesis cell. This precaution was taken to avoid possible effects of water contamination of the film influencing the elemental analysis performed on the samples. The solutions were thoroughly degassed with nitrogen prior to polymerization and the reaction system was enclosed in a nitrogen atmosphere. In this synthesis a platinum foil served as the cathode and the anode was constructed from vapour deposited gold on a chrome plated glass substrate. The use of chrome ensured good adhesion of the gold to the glass and avoided the problems of poor adhesion and subsequent contamination observed with the SnO_2 electrodes. The polymer was grown at potentials ranging from between 0.5 and 2.0 volts relative to a standard calomel electrode.

Table 3.4 Polypyrrole Sample Preparation Parameters and the conductivity of the Films.

No.	Polymer Sample	Solvent	Electrolyte	Monomer	Electrodes	Voltage Applied	Sample Form	Conductivity $S\ cm^{-1}$	General Notes
1.	Polypyrrole para-toluene sulfonate	1:1: 98 water, ethylene glycol and acetonitrile	0.1m tetra-ethyl para-toluene sulfonate	0.2m pyrrole	Pt as cathode and Au as anode	1.3V	A black un-thick uniform film	≈ 1.27 to $1.32\ S$	The conductivity was observed to be independent of temperature in the range of 23.7 to -169.94°C, the frequency range was from 10^4 to 10 Hz. The colour of the solution changed from colourless to pale green and finally to yellow.
2.	Polypyrrole tetrafluoroborate	1:99 water and acetonitrile	0.1m silver para-toluene sulfonate	"	"	1.0V	"	-	-
		1:99 water and acetonitrile	0.1m silver tetrafluoroborate	0.2m pyrrole	Pt as cathode and Au as anode	1.0V	A black non uniform film with crumbly surface	-	The colour of the solution changed from colourless to green.
		"	0.1m tetra ethyl ammonium tetrafluoroborate	0.6m pyrrole	"	3.0V	A black matt uniform finish	-	-
3.	Polypyrrole perchlorate	1:99 water and acetonitrile	0.05m $AgClO_4$	0.06m pyrrole	Pt as cathode and Au as anode	0.5V	A film of uniform surface with matt black finish	-	-
4.	Series of films of polypyrrole para-toluene sulfonate. Special method was followed for these films. Details are given separately.								

The films formed over a four hour period and during this time the voltage remained constant, however, the current level varied. All the films formed had thick, black uniform surfaces. Polypyrrole films doped with para-toluene sulfonate were used extensively in this investigation. The thickness was determined using a Dektak II surface profile analyser.

3.5 Effects of Changing the Anions and Cations of the Supporting Electrolytes, Electrolytes and Voltage on the Morphology of the Polypyrrole Films.

Polypyrrole morphology is dependent on the conditions used in the preparation, the type of supporting electrolytes, purity of materials, electrode materials and voltage applied to the system. From the experiments described above it is clear that the most consistent films could be prepared using a dry-box method using purified pyrrole and silver para-toluene sulfonate as the support electrolyte in dried acetonitrile.

1) Effect of electrolytes on the morphology of the polypyrrole film.

In the following experiments the preparation conditions used in the synthesis were identical for the range of electrolytes studied. The method of preparation was as described above. The single compartment cell was filled with a platinum cathode and an anode of gold evaporated on a glass slide, and a 0.2m pyrrole and 0.1m silver tetrafluoroborate were taken in a mixture of water and propylene carbonate solution in a ratio of 1:99. A voltage of 0.25 V was applied to the cell and a current of 87.5 μ A was observed to flow in the cell. The film formed at the anode had a granular structure and a non-uniform black surface. When the electrolyte was replaced with a mixture of

water and acetonitrile solution in a ratio of 1:99, a current of 0.6mA was observed to flow. The film was shiny black and had a flaky surface. It was clear from these experiments that the structure of the films was dependent on the electrolyte used.

2) Effect of cations on the morphology of the polypyrrole film.

The single compartment cell was filled with a platinum cathode and an anode of gold evaporated on a glass solid and 0.1 m tetraethyl ammonium tetrafluoroborate and 0.06 m pyrrole in a mixture of water and acetonitrile solution in a ratio of 1:99. The voltage applied to the cell was 3 V and the current in the cell was 3 mA. The film formed on the electrode had a glassy finish and was uniform. When the support electrolyte was replaced with silver tetrafluoroborate the current generated was 0.6 mA and the film was shiny black and had a flaky surface. The cation of the electrolyte appeared to play a role on the morphology of film forms at the anode.

3) Effect of voltage on the morphology of the polypyrrole film.

The single compartment cell was filled with a platinum cathode and an anode of gold evaporated on a glass slide and 0.2 m pyrrole and 0.1 m silver tetrafluoroborate in a mixture of water and acetonitrile solution in a ratio of 1:99. Voltage of 1 V was applied to the cell and a current of 4 mA was observed to flow. Quite a thick crumbly surface was formed with the first layer being brown and the later layers appearing black. When a voltage of 0.25 V was applied across the two conducting electrodes a current of 0.6 mA was observed to flow with the formation of a shiny flaky film at the anode. The results of this study will be described later.

4) Effect of anions on the morphology of the polypyrrole film.

The single compartment cell was filled with a platinum cathode and an anode of gold evaporated on a glass slide and 0.05 M silver perchlorate and 0.06 M pyrrole in a mixture of water and acetonitrile solution in a ratio of 1:99. The voltage applied was 0.5 V and the current flow was 125 mA. The film had matt finish with a black and granular surface. When the electrolyte was replaced with silver para-toluene sulfonate, the current was found to be 2.6 mA. The film was quite thick and of uniform black surface. The electrical studies on these films will be discussed later.

It was clear from these observations that the morphology and hence, possibly the conductivity would be influenced by the conditions used in the generation of the doped films of polypyrrole.

3.6 Experimental Techniques

3.6.1 Dielectric Measurements

Dielectric measurements have been carried out for three systems:-

- 1) Polychloroprene (PCP)
- 2) Carbon black composites (carbon black filled polystyrene and polychloroprene) ((CB/PS) and (CB/PCP))
- 3) Polypyrrole para-toluene sulfonate (PPTS)

1) Polychloroprene (PCP)

The real and imaginary parts of the dielectric permittivity were measured for polychloroprene at 1 kHz, as a function of temperature using a Teradyne 357 automatic bridge and a two terminal electrode cell configuration. The temperature was recorded on a Digitron 3754 K digital thermometer attached to a thermocouple located close to the disc.

The cell was flushed with dry nitrogen prior to cooling the sample and contained a drying agent, silica gel, which was added as a precaution against the effects of condensation on the electrical measurements. The cell was cooled in liquid nitrogen then heated up. The conductance and capacitance were measured. All the samples in this study were coated with graphite (Acheson - Aquadag) to improve the contact between the electrodes and the samples.

2) Carbon black composites ((CB/PS) and (CB/PCP))

For carbon black composites (carbon black filled polystyrene and and polychloroprene) the real and imaginary parts of the dielectric permittivity were measured at 600 Hz to 10 KHz as a function of temperature using a Wayne-Kerr B224 universal transformer ratio arm bridge. A two terminal cell configuration and sine and square wave oscillator were used. A frequency selective detector amplifier was used to improve the null point. The temperature was recorded on Digitron 3754 K digital thermometer attached to a thermocouple located close to the disc. The cell was flushed with nitrogen prior to cooling the sample and contained a drying agent (silica gel) as an added precaution against the effects of condensation. All the samples in this study were coated with graphite (Acheson-Aquadag) to improve the contact between the electrodes and samples. All measurements were performed at a fixed temperature using either water bath at high temperatures, 20⁰C to 90⁰C or ethanol bath fitted with a crycool temperature controller for low temperatures (-70⁰C to + 20⁰C).

3) Polypyrrole para-toluene sulfonate (PPTS)

The real and imaginary parts of the dielectric permittivity were measured as a function of frequency at room temperature using a 1186

Electrochemical Interface Solartron Schlumberger, and a four terminal cell configuration.

3.6.2 D.C. Conductivity

Conductivity measurements were carried out on the films using a four point contacts method. In general, the polypyrrole films peeled off from the gold electrode and could be studied as detached films. The conductivity of the peeled film was determined by clamping these films between heavy copper electrodes. The thinner films could not be detached and were examined in situ. In this case the conductivity of the films were measured by the deposition through a mask from the vapour of a gold overlayer at right angles to the original electrode. Four point contacts were made to the upper and lower electrodes and the resistance of the sandwich was measured in the usual manner. Care had to be taken when performing this type of measurement to ensure that the resistance of the electrodes themselves were significantly lower than those of the polymer so as to ensure that the results obtained are reliable. The conductivity was determined from the value of the film resistance (R) using the equation

$$\sigma = \frac{1}{R} \cdot \frac{t}{A}$$

where (σ) is the conductivity, (R) is the resistance obtained from a current-voltage plot, (t) is the thickness of the film and (A) is the geometrical area of the active element.

3.6.3 A.C. Conductivity

Polystyrene and polychloroprene polymers and carbon black composites were used for these measurements. The a.c. conductivity was measured at 600 Hz to 10 kHz, firstly as a function of temperature and

then as a function of the amount of carbon black. The same apparatus and technique as described above were used for measuring the dielectric parameters. The conductivity was determined from the value of the disc conductance (G) using the equation

$$\sigma = \frac{Gt}{A} = \frac{1}{R} \cdot \frac{t}{\pi r^2} \quad 3.4$$

where (r) is the radius of the disc.

3.6.4 The Current-Voltage Characteristics

Polypyrrole para-toluene sulfonate films were used for these measurements using four-terminal method. Measurements were carried out by adjusting the voltage in the range -1 to +1 V and the results were recorded for both the voltage and current values for the film samples using the gold electrode system. The currents were measured as functions of temperature using the 1186 Electrochemical Interface Solarton Schlumberger. The voltages were measured as functions of temperature using Hewlett Packard 53268 Timer Counter DVM. The samples were mounted in a four terminal cell configuration. The temperature was recorded using a Digitron 3754 K digital thermometer attached to a thermocouple located close to the film. Measurements at a fixed temperature were performed using either a water bath at high temperature or a crycool temperature controller at low temperature. The range of -1 to +1 V was used to minimise the effects of the current passing through the cell generating heat in the sample. The rate at which work (W) is converted to heat is given by the equation,

$$W = i^2 R \quad 3.5$$

3.6.5 Microanalysis of the Polymer Films

Samples of polypyrrole for the thicker films could be detached from the gold electrodes and allowed elemental analysis to be performed. It was clear from the analysis that a small amount of gold was retained in the film and this led to an error in the elemental analysis. The amount of sample was, however, insufficient for an accurate analysis of sulphur to be performed and because of the problem of gold transfer, it was not possible to estimate the anion concentration accurately. The computation of the anion:monomer ratio were thus based on the carbon, hydrogen, sulphur and nitrogen analysis.

3.6.6 Cyclic Voltametry

Cyclic voltametry was carried out for the polypyrrole para-toluene sulfonate using the Solatron 1186 electrochemical interface on thin films of the polymer and were measured using a 0.1 M silver para-toluene sulphonate in acetonitrile. The electrochemical cell was also used to obtain cyclic voltamograms.

3.6.7 Surface Thickness and Profile Measurements

The film thickness and also the surface edge profiles of the polypyrrole para-toluene sulfonate films were determined, using a Dektak II surface profile analyser. The resolution of this instrument was approximately 80 Å vertically and 0.1 microns horizontally. The traces obtained were normalized for variations in the surface of the substrate and linearized. The electrode configuration used in these studies was a half plated microscope slide allowing examination of the contour of the glass parallel to that of the film and hence transverse measurements provided the film thickness and surface profile.

3.7 Summary of Matrices Used

The materials used in this study were the plastic polystyrene and the rubber polychloroprene which were filled with carbon black and the doped conjugated polymer polypyrrole para-toluene sulfonate. The structure and the physical properties of the different samples used in this study are illustrated in table 3.1.

Polymer 1 and 2 were soluble in a mixture of toluene and acetone, polymer 3 was insoluble in all normal solvents.

4. RESULTS AND DISCUSSION

CHAPTER 4. RESULTS AND DISCUSSION

Part I: Electrical Conductivity and Dielectric Studies of Carbon Black Composites of Polystyrene and Polychloroprene and Influence of Fillers on the Dielectric Relaxation Properties of Polychloroprene

4.1 Electrical Conductivity of Carbon Black Filled Polystyrene

A) Dependence of the conductance on the carbon black content

The dispersion of the carbon black (Regal 300) in the polymer matrix has a profound effect on the conductivity. At very low carbon black loading, the conductivity of the composite is low and characteristic of the polymer matrix, i.e. dielectric or tunnelling regime. Addition of carbon black increases the conductivity until a critical carbon black concentration is reached at which the conductivity of the composite changes many orders of magnitude for a small change in the amount of carbon black. Further addition of carbon black leads to only small increase in the conductivity. At high concentration a saturation value characteristic of the carbon black itself is obtained. The general features associated with changes in the carbon black loading are shown schematically in fig. 4.1

Variation of the carbon black content in the range 1% to 3% leads to the electrical conductivity decreasing from 2.51×10^{-11} to $6.31 \times 10^{-12} \text{ S cm}^{-1}$ and then swings up to $5.00 \times 10^{-7} \text{ S cm}^{-1}$. Above about 7% the electrical conductivity becomes almost concentration insensitive up to values of greater than 20% carbon black. Carbon black filled polystyrene has previously been shown to have

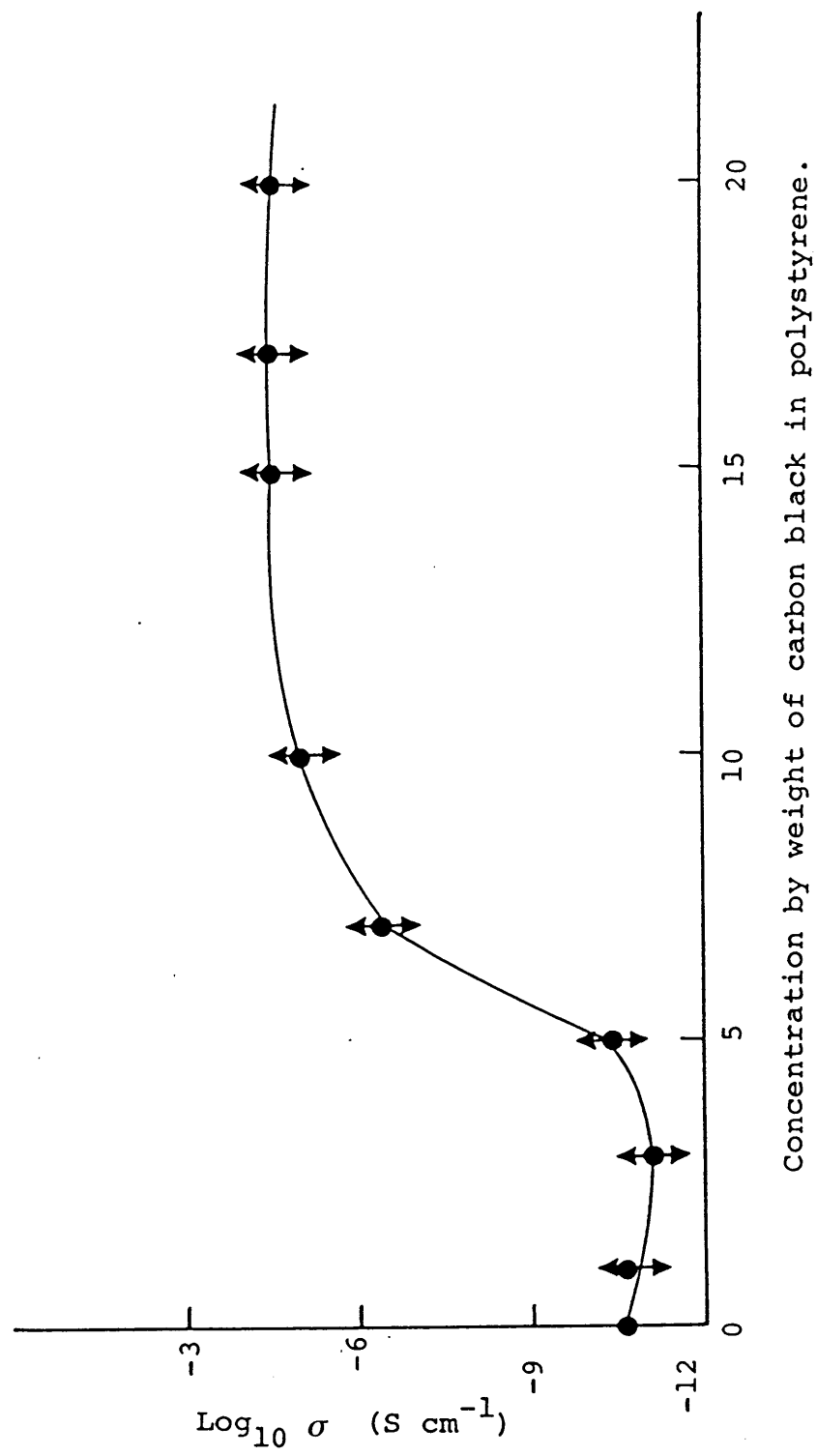


Figure (4.1) Log_{10} conductivity against concentration by weight of carbon black.

conductivities which level off at about $4.46 \times 10^{-5} \text{ S cm}^{-1}$ for an unspecified carbon black. The difference between the reported values in the literature (1) and these data are due to differences in the carbon black structure, porosity and specific area for a given concentration.

The dependence of the conductivity on carbon loading is widely documented (2). The critical concentration of carbon black, at which the conductivity changes most rapidly, is called the percolation threshold and depends on the structure of carbon black dispersion (2), and has been found to correspond to 5% of carbon black filled polystyrene in the present work. The percolation threshold for Regal 300 appears low indicating a high tendency of the carbon black particles to aggregate and form conducting paths in the polymer system. This hypothesis was confirmed by an optical examination of the discs, which showed the presence of extended aggregates of carbon black in a chain type of structure observable at an optical level.

In the generation of conductivity paths in the resin, optimal carbon black loading of 15-20% is usually necessary. It is clear that the coating procedure used initially to aid dispersion has in fact helped to prepare the aggregated chains necessary for conduction.

B) Dielectric constant ($\bar{\epsilon}$) dependence on carbon black content

The structure of carbon black in polymer matrix has a profound effect on the dielectric constant.

The general features associated with changes in the carbon black loading are shown schematically in fig. 4.2. At very low carbon black loading, the dielectric constant of the composite is low $\bar{\epsilon} = 3.6$. The addition of carbon black increases ($\bar{\epsilon}$) of the composite to 121.5. This

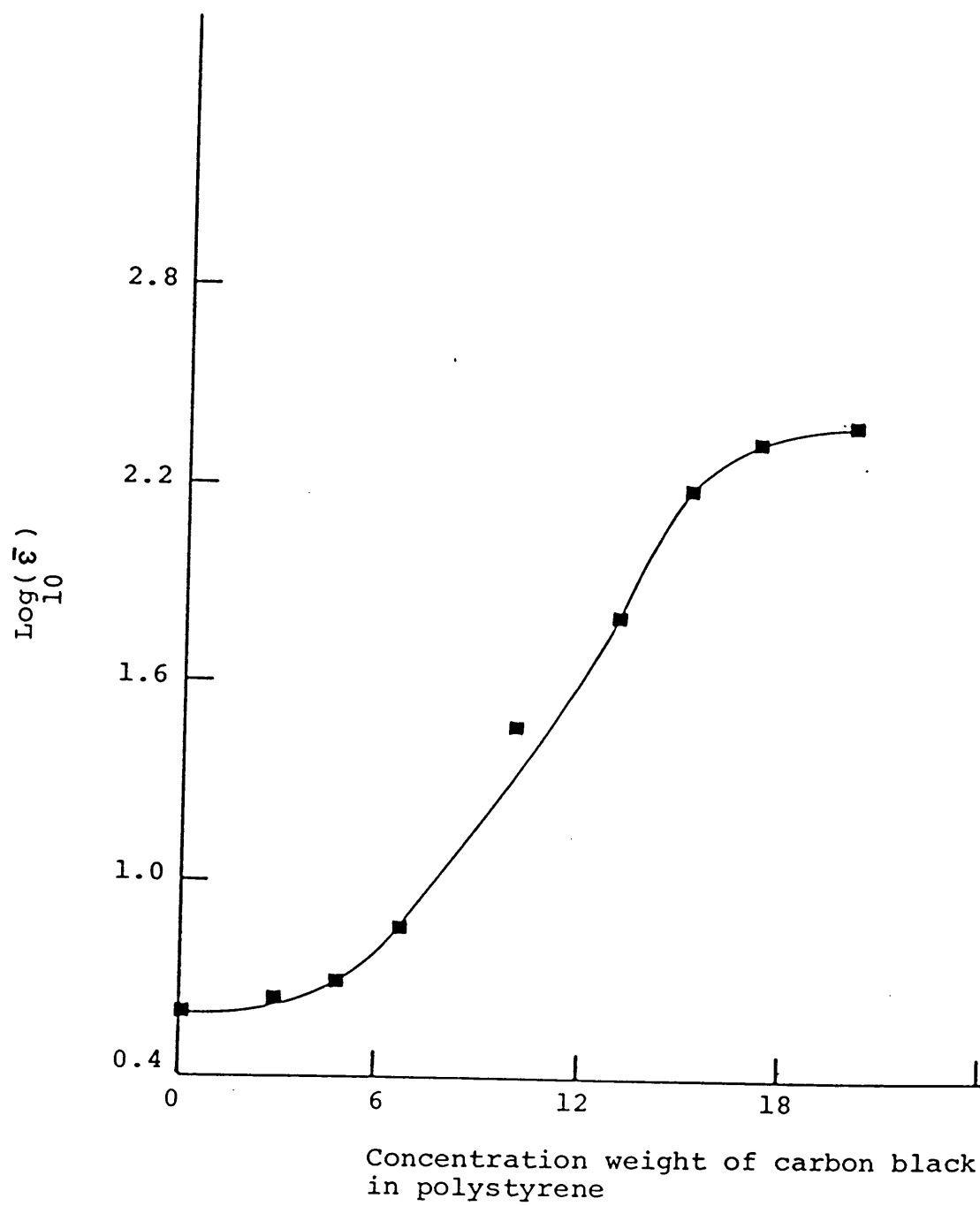


Figure (4.2) Dielectric constant against concentration by weight of carbon black.

could either arise from the effect of increasing in the dipole moment but is more probably the effect of chained carbon black increases the magnitude of the Maxwell Wagner Sillars loss for this system. Dipole relaxations rarely add an increment of more than 2-5 to the dielectric constant and, therefore, would be unable to account for an increase of approximately 120. It is therefore, more likely that the increment is associated with the effects of aggregation and chaining of the carbon black particles; the Maxwell Wagner Sillars process. Theoretical analysis would indicate that the dielectric loss will be higher in (A), fig. 4.3, than in (B), the increment ($\bar{\epsilon}_{\text{sample}} - \bar{\epsilon}_{\text{unfilled}}$) to the permittivity being proportional to the volume fraction of the carbon black chain, where (A) is the situation corresponding to chained particles of carbon black dispersed in the polymer matrix and (B) is the situation corresponding to carbon black particles dispersed in the polymer matrix. This increase in the increment may be ascribed to the occurrence of chained aggregates of carbon black particles as shown in fig. 4.3. These ideas are consistent with the optical structures

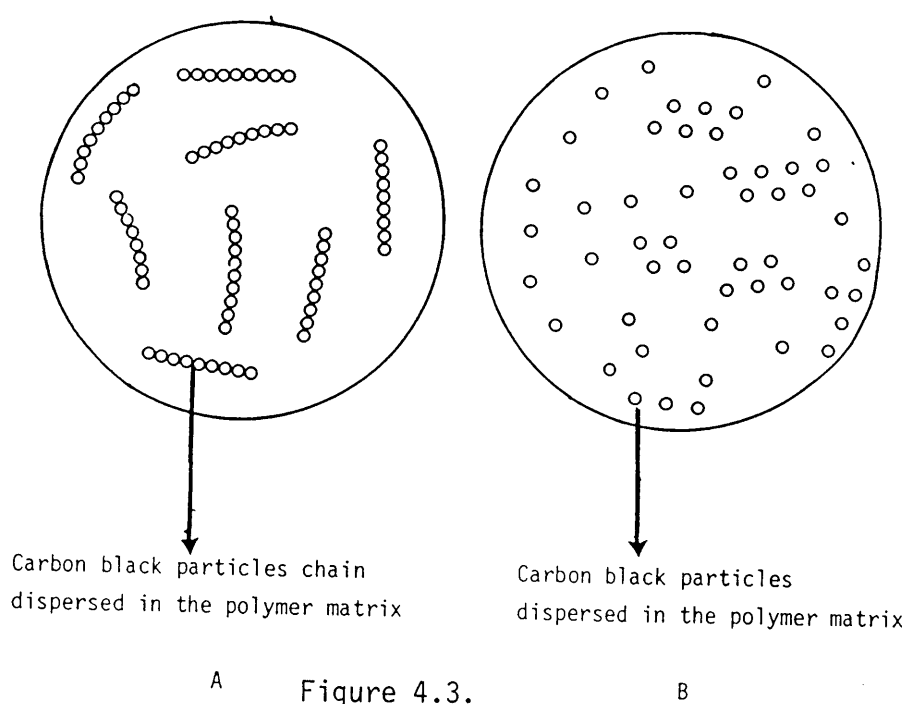


Figure 4.3.

observed in the lightly loaded discs. In the 5% and greater extensive chaining was observed consistent with a preponderance of type A structures in the system.

C) Temperature dependence of the A.C. frequency

At lower carbon black loading, dependence of conductivities on the temperature is shown in fig. 4.4. The activation energy equation (2.6) depends on the percentage of carbon black in polystyrene. For 15% carbon black in polystyrene, it is 0.03 ± 0.015 ev which is essentially the value of the carbon black itself (3). The temperature dependence of conductivity is predominantly determined by the number of electrons that can contribute to the conductance. In certain samples, for example 5%, 7% and 13% loading discs, the electrical conductivity decreases with temperature due to expansion of the polystyrene in the regions between the carbon black particles. Expansion of the polymer will decrease the probability of the electron migration between carbon black particles, and hence reduce the number of effective chains contributing to the conductivity of the disc. The decrease in the conductivity, therefore, reflects a compensation of the greater probability of electron tunnelling as a consequence of expansion the polymer matrix with a decrease in tunnelling because of the increased distance between the carbon black particles. At very high loading, the data shows that the temperature dependence of the conductivity is very weak (4). This is indicative of the matrix tunnelling having a negligible effect on the electrical conduction of the matrix.

D) Frequency dependence of the conductivity of carbon black polystyrene composite

The electrical conductivities are independent of frequency in the

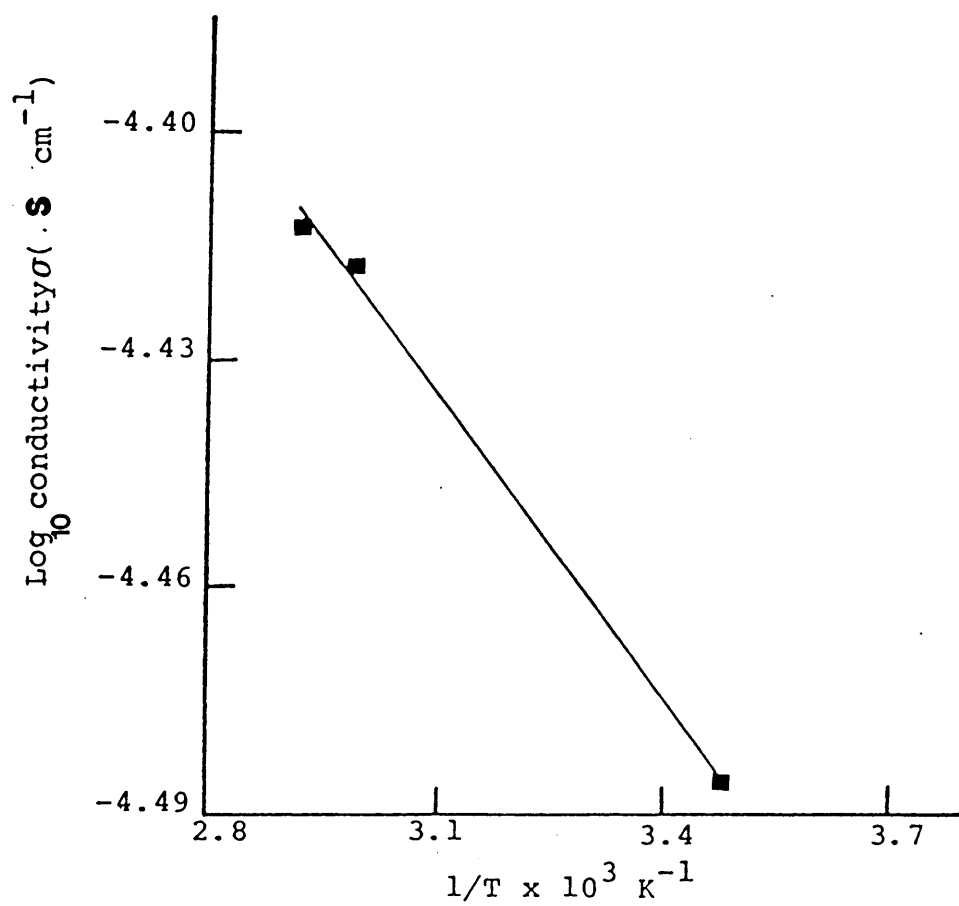


Fig. (4.4) Temperature dependence of conductivity of sample 15% carbon black in polystyrene measured at 10 kHz

range 600 Hz to 10 kHz. For 7% and above loading of carbon black-polystyrene composite, conductivity remains constant and is not affected by frequency. At lower loading from 1% to 6% the conductivity increases with frequency as shown in fig. 4.5. The observation of a rapidly increasing conductivity with increasing frequency is typical of that observed for charge carrier migration in amorphous materials (5,6). This is typical of the behaviour observed in this study.

In charge carrier migration it has been observed that despite large differences in composition and structure, charge conduction in amorphous solids can be described by a simple law (7,8). The problem of charge carrier hopping between localized sites in amorphous solids has been considered theoretically by Mott (8), Pike (9) and Lewis (10). It has been pointed out that if energy states exist in the band gap then the coefficient (s) in equation (2.20) will not remain constant, but will fall below unity and $\sigma(\omega)$ will become independent of (ω) (11,12). In this study the coefficient (s) fig. 4.6 does not remain constant but rises above unity. The value of (s) decreases to (0) for high values of (ω) indicative of a change in the conduction mechanism in the system. Figures 4.7 and 4.8 are the plot of conductivity divided by angular frequency against angular frequency. Fig. 4.7 shows that the factor σ/ω increases with frequency and the coefficient (s) has a value about 1.2 which indicates that mechanisms other than a simple hopping model are operative. But in fig. 4.8 the factor σ/ω decays with frequency and reaching a limiting value which does not decay further with frequency, this is indicative of the bulk conduction saturation having been achieved.

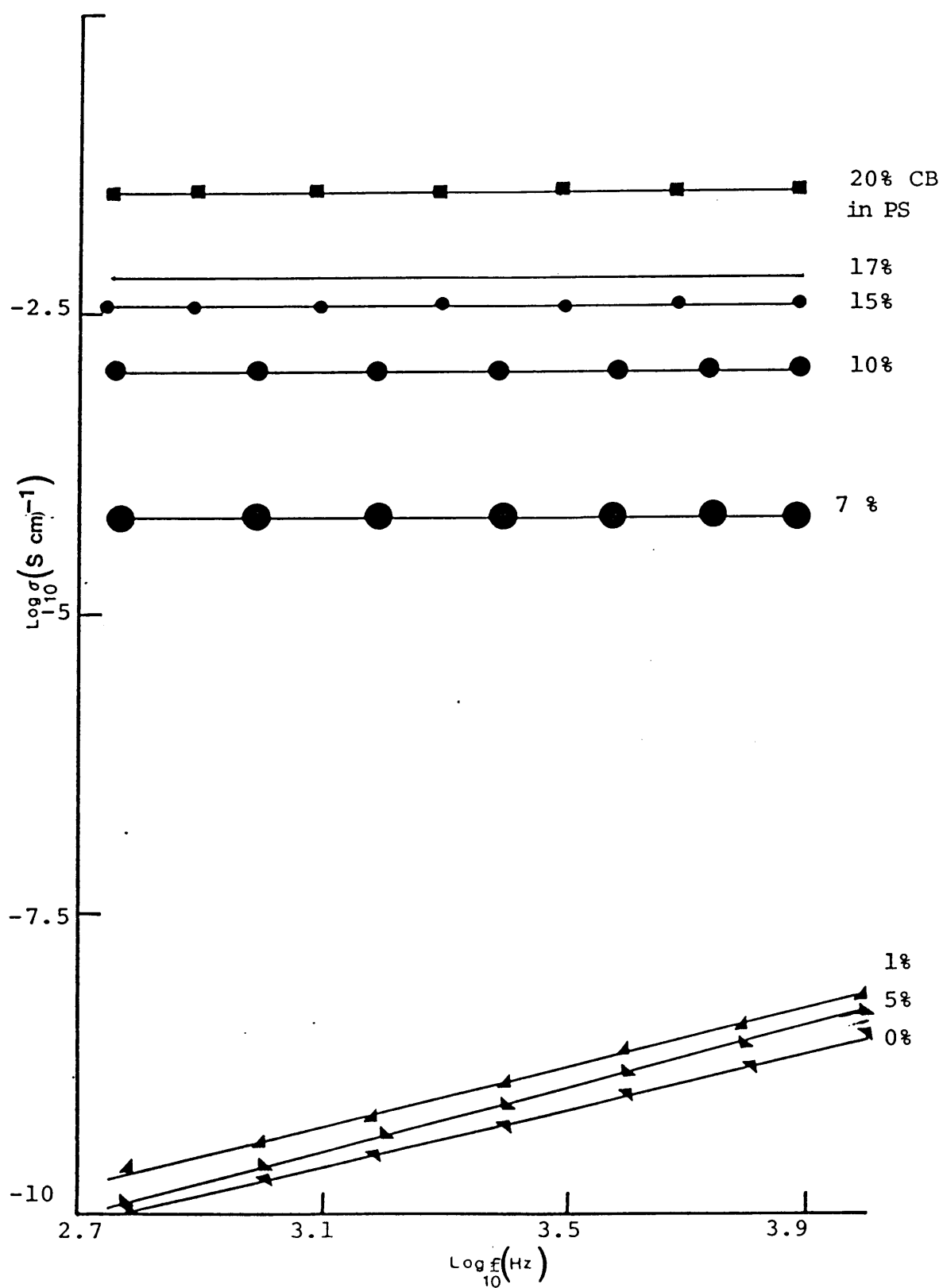


Figure (4.5) Frequency dependence of conductivity of carbon black in polystyrene composite.

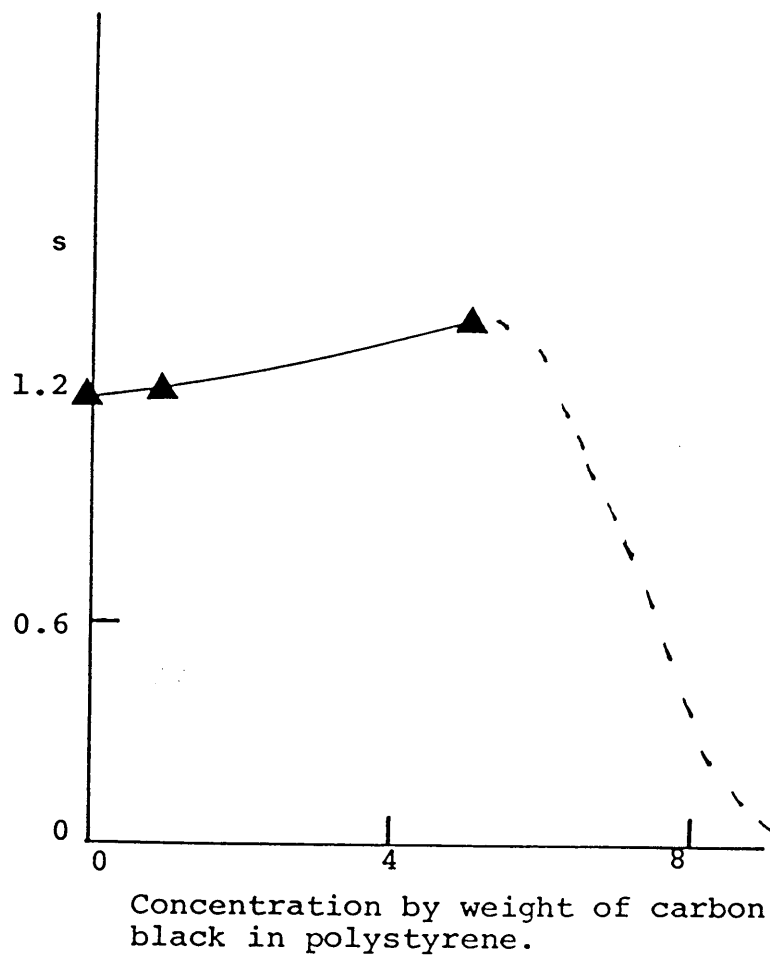


Figure (4.6) Variation of the coefficient s ,
 $\sigma(\omega) = \omega^s$, with carbon
black in polystyrene composite.

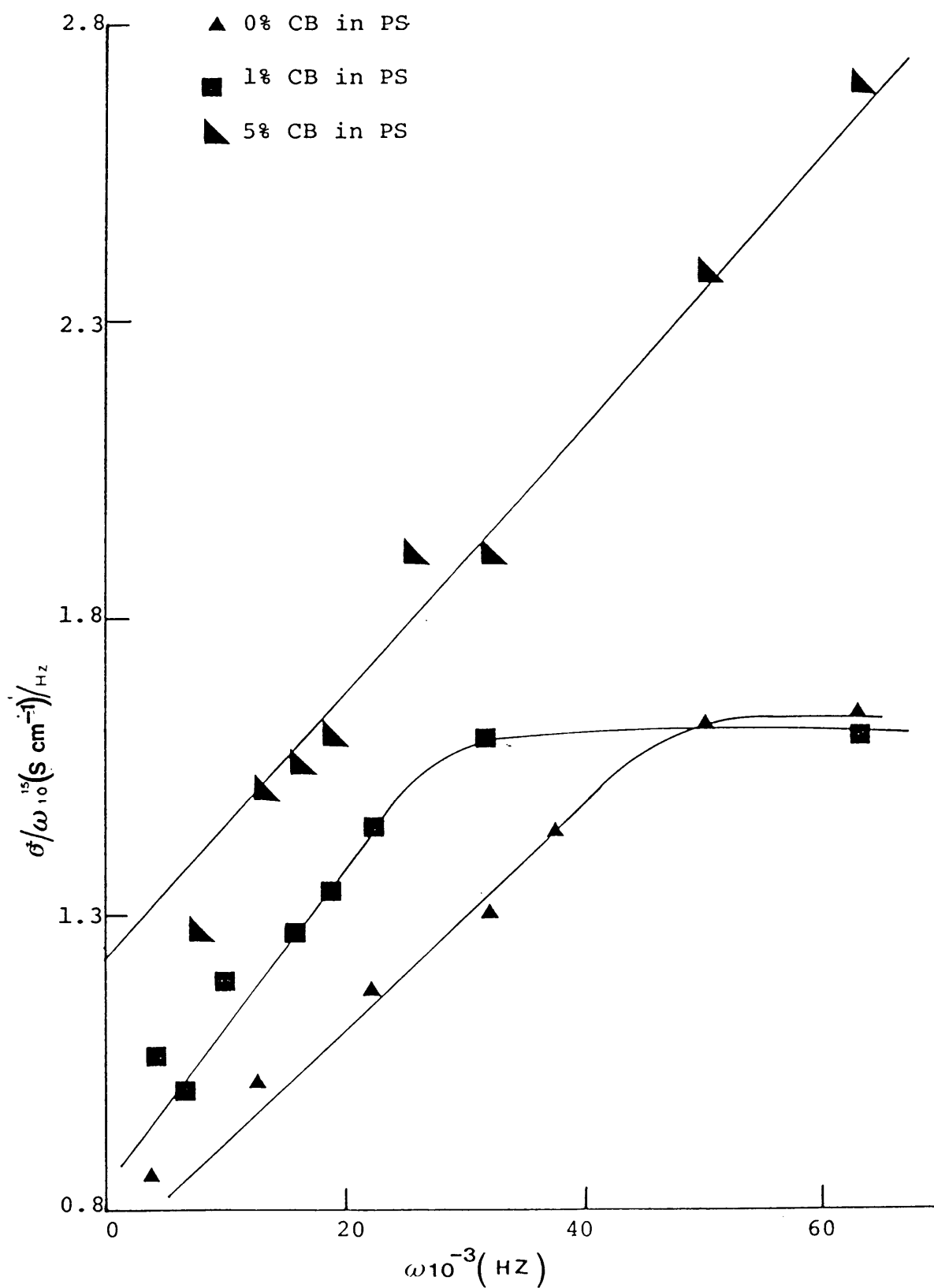


Figure (4.7) Variation of the a.c. conductivity with frequency as a function of carbon black in polystyrene.

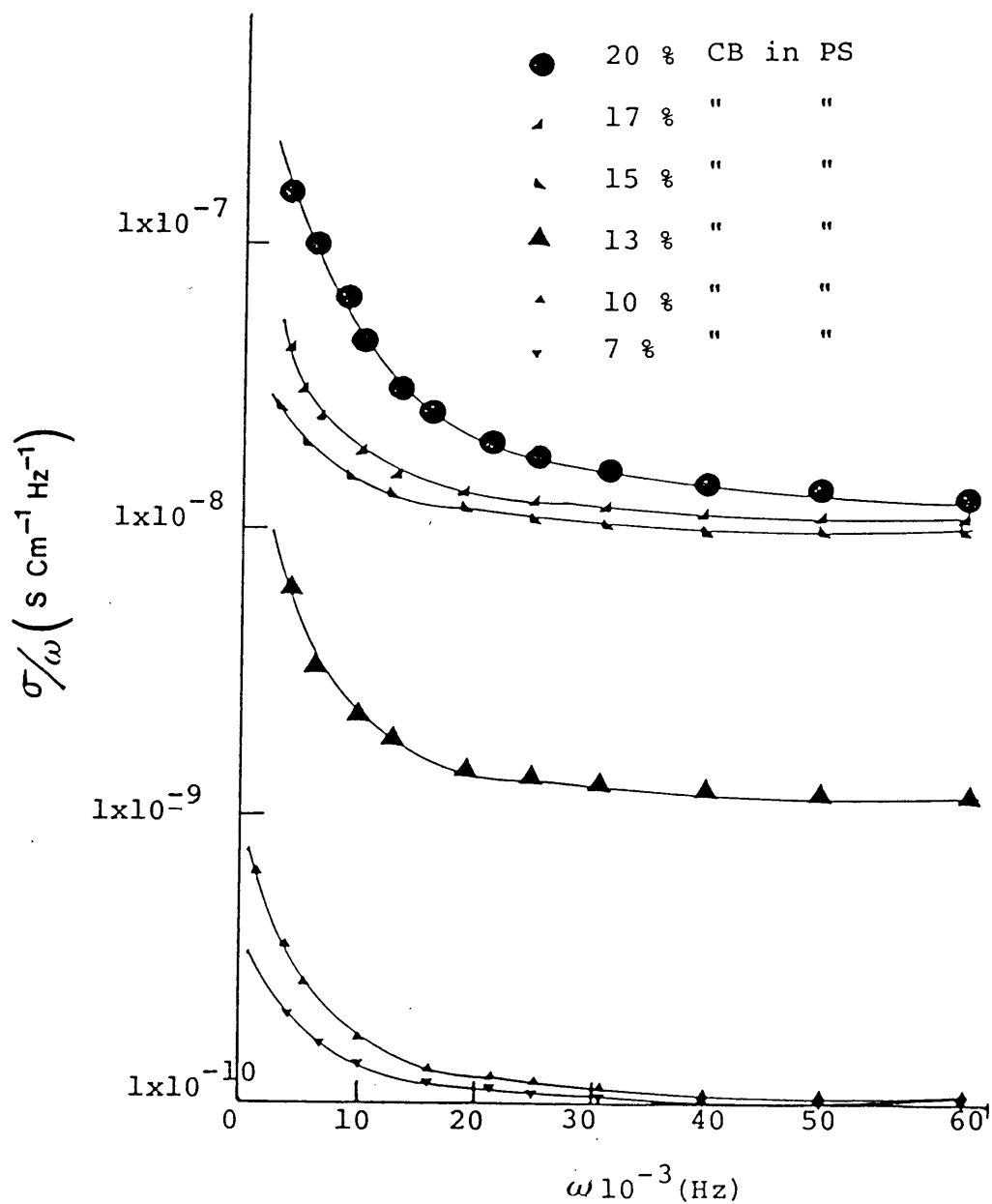
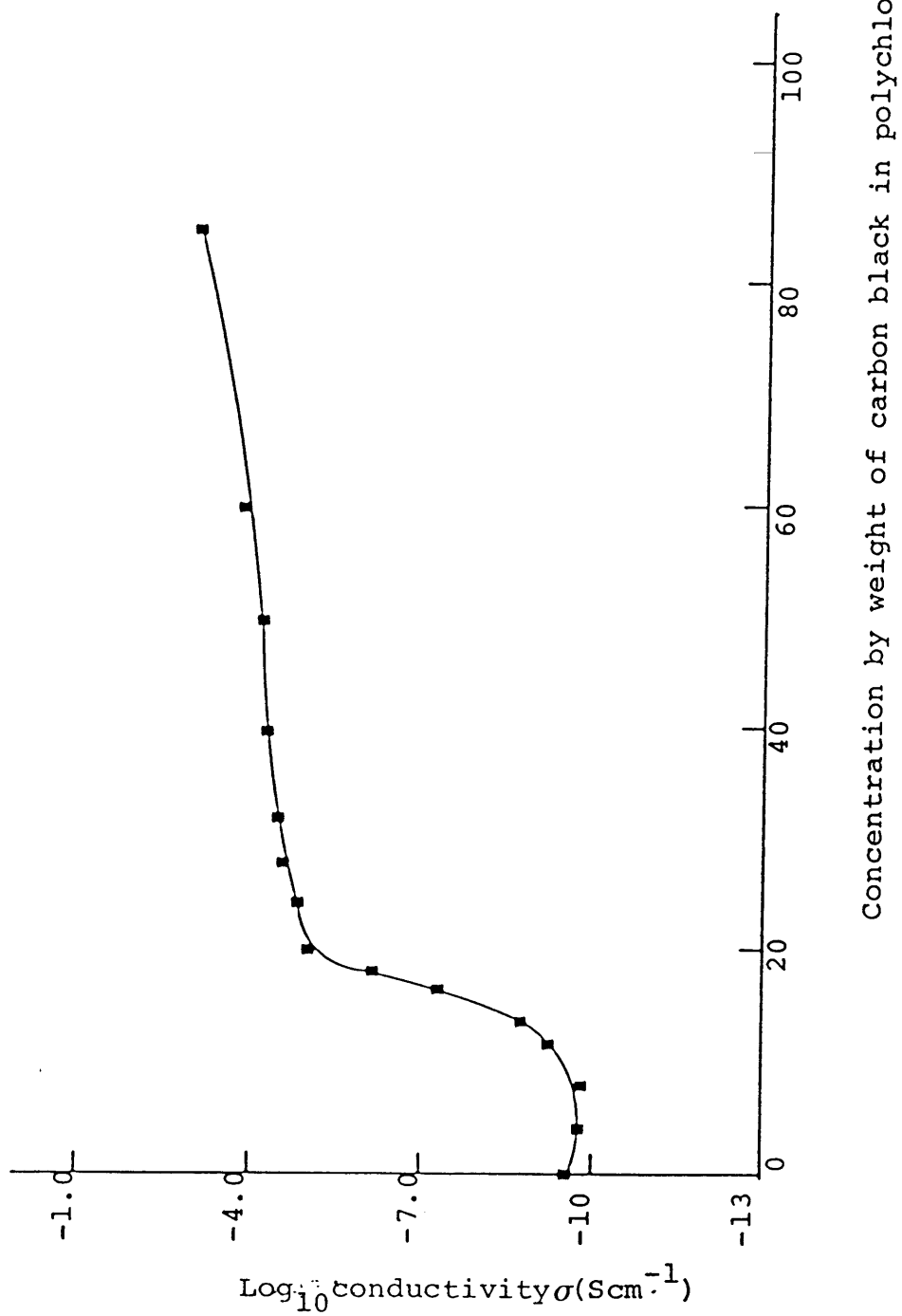


Figure (4.8) Variation of the a.c. conductivity with frequency as a function of carbon black in polystyrene

4.2 Electrical Conductivity of Carbon Black Filled Polychloroprene

A) Dependence of the conductance on the carbon black content

The variation of electrical conductivity at room temperature with different carbon black (pulverised Regal 300) contents is shown in fig. 4.9. Change of the carbon black content in the range 4% to 8% leads to the decrease of electrical conductivity from 1.47×10^{-10} to $2.04 \times 10^{-10} \text{ S cm}^{-1}$ and then swings up to $1.04 \times 10^{-5} \text{ S cm}^{-1}$. Above about 20% the electrical conductivity becomes almost concentration insensitive up to a value of greater than 20% carbon black. Carbon black filled polychloroprene has previously been shown to have a conductivity level off at about $4.89 \times 10^{-4} \text{ S cm}^{-1}$ for an unspecified carbon black. The difference between the reported values in the literature (13,14) and these data are due to difference in structure, porosity and specific area for a given concentration of carbon black. The critical concentration of carbon at which the conductivity changes most rapidly is 14%. This is in contrast to the value of 5% observed in the case of polystyrene. In the polychloroprene the carbon black appears to be dispersed more easily and as a result it is more difficult for aggregated chain structures to be formed. The differences in the ability of the matrix to disperse the carbon black is probably a reflection of the differences in the characteristics of the matrix. Polystyrene has a high glass transition temperature and as a result its coating will be maintained and hence, the aggregate structure is generated in the matrix. The rather more polar polychloroprene is able to stabilise better individual carbon black particles and this will itself enhance the dispersion of the individual carbon black



Figure(4.9) Log. conductance against concentration
by weight of carbon black in polychloroprene.

particles. The initial change in the conductivity of the matrix on the addition of the carbon black is consistent with the idea that the impurities which add to the conductivity of the pure polymer are absorbed onto the surface of the carbon black and immobilised. This process leads in turn to a reduction of the conductivity of the matrix and a resultant curve of the form figures 4.1 and 4.9. The conductivity of the composite at 85% carbon black loading is $7.9 \times 10^{-4} \text{ S cm}^{-1}$ and is in the range of semiconductors which are normally taken to be in the range 10^{-10} to $10^{+2} \text{ S cm}^{-1}$, which is quite reasonable for a mixture of rubber and carbon black where the electrical properties vary from near insulators to near semiconductors (Appendix B).

B) Dielectric constant dependence on carbon black content

The general features of the dependence of dielectric constant ($\bar{\epsilon}$) on carbon black loading are shown schematically in fig. 4.10. It is found that addition of carbon black increases the dielectric constant from 3.4 to 396.8. This change is once more consistent with the idea of the carbon chained structures leading to a high value of the dielectric permittivity through a large Maxwell Wagner Sillars loss contribution.

C) Temperature dependence of the A.C. frequency

At lower carbon black loading the conductivity of the composites is strongly temperature dependent as shown in fig. 4.11. The activation energy equation (2.6) depends on the percentage of carbon black in polychloroprene. For example, 0%, 1%, 8%, 12% and 17% the activation energies are 0.70 eV, 0.50 eV, 0.60 eV, 0.82 eV and 0.35 eV respectively. In certain of the samples for example 4%, 15%, 16%, 18%

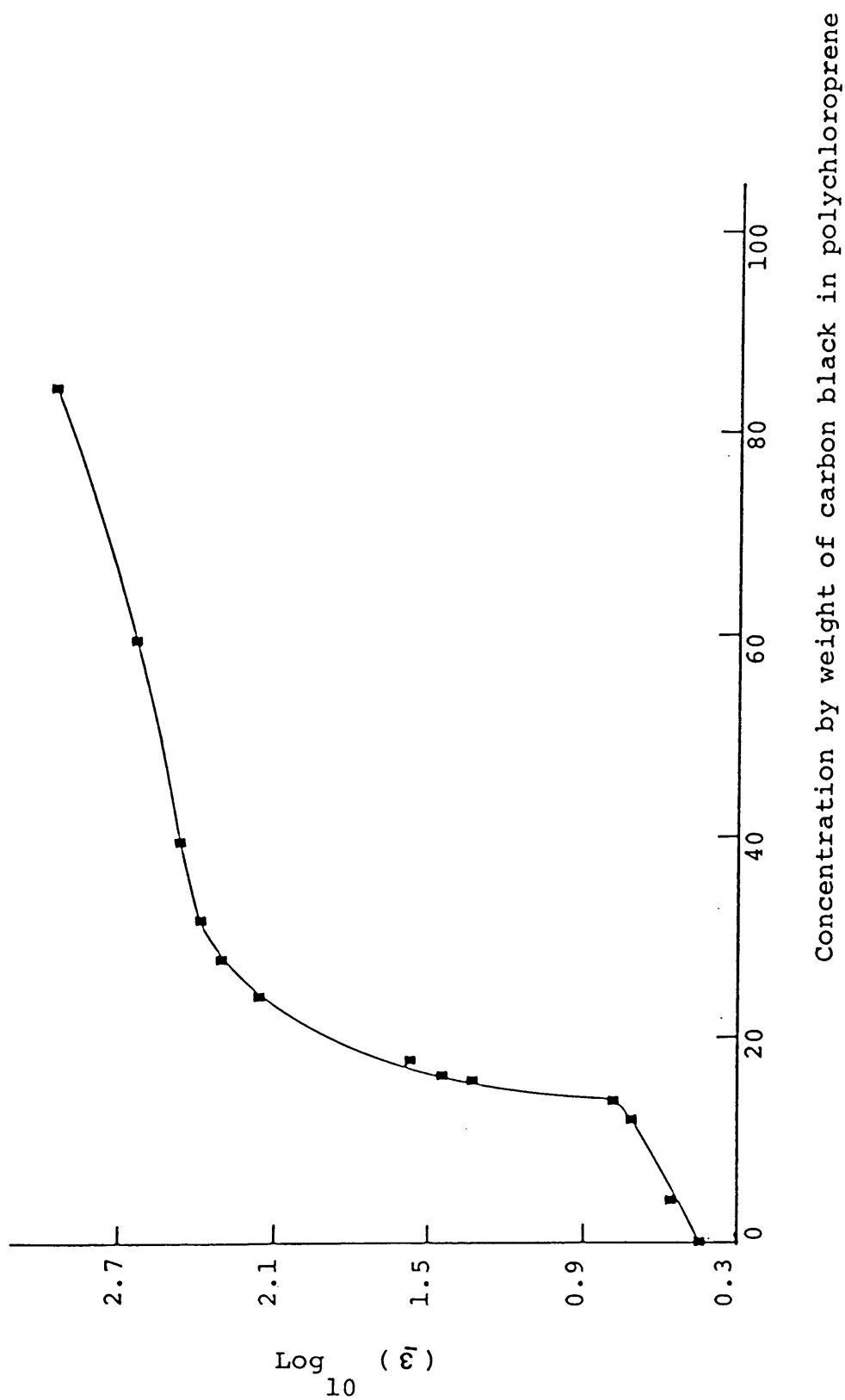


Figure (4.10) Log_{10} dielectric constant against concentration by weight of carbon black in polychloroprene.

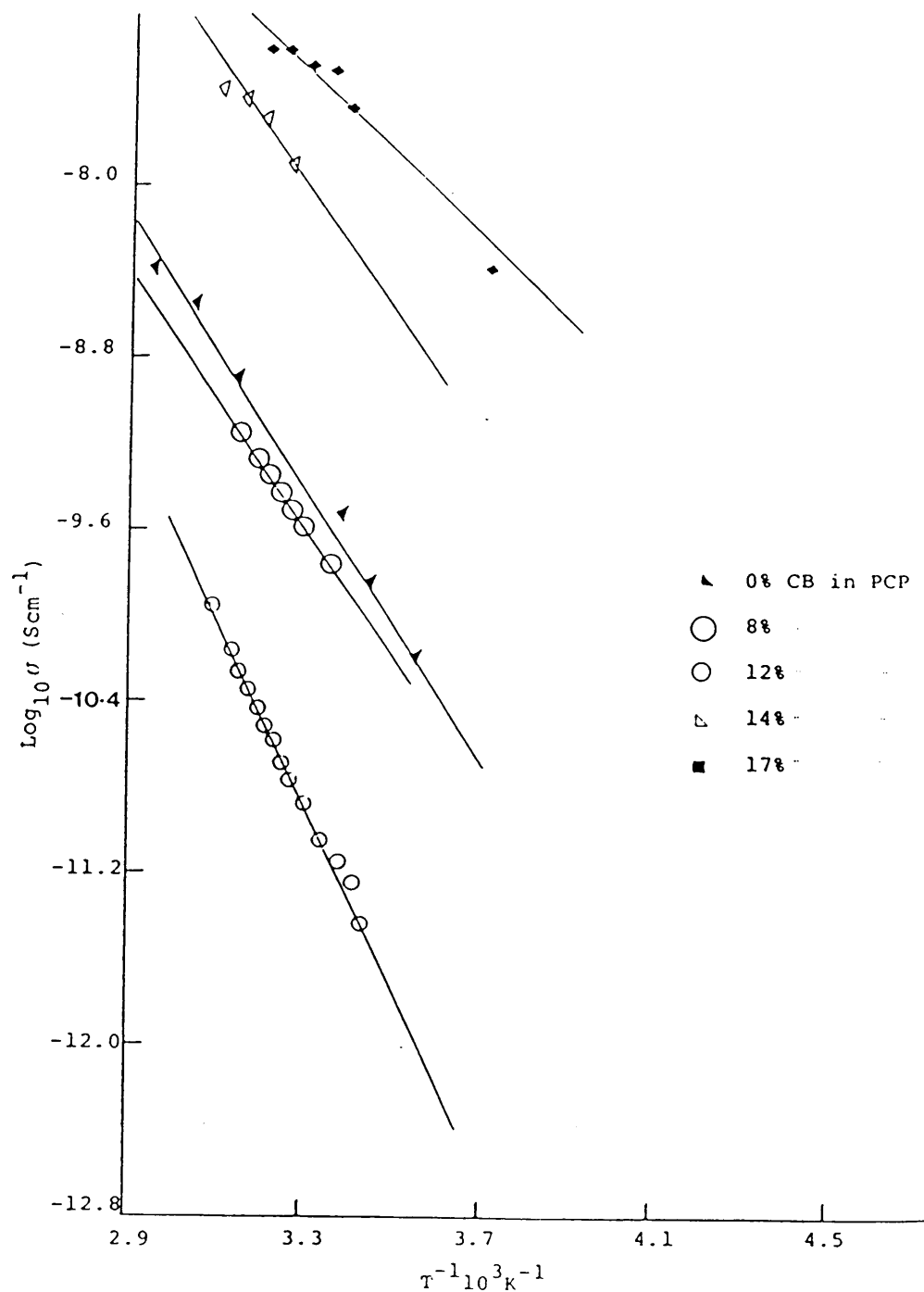


Figure (4.11) Temperature dependence on the conductivity of carbon black in polychloroprene composite.

loading discs, the electrical conductivity decreases with temperature due to expansion of the polychloroprene in the regions between the carbon black particles. Expansion of the polymer decreases the probability of electron migration between carbon black particles. At very high loading the data shows that the temperature dependence of the conductivity is very weak. The apparent scatter and non systematic changes in the data near to the critical loading for the generation of an interpercolating net work are consistent with the idea that the formation of chained structures is a delicate process which can be influenced by a number of subtle factors. The general trends are assumed correct although individual data points are probably highly scattered.

D) Frequency dependence of the conductivity of carbon black polychloroprene composite

The electrical conductivities are independent of frequency in the range 600 Hz to 10 kHz. For 15% and above loading of carbon black polychloroprene composite, conductivity remains constant and is not affected by frequency. At lower loadings of 1 to 14% conductivity increases with frequency as shown in fig. 4.12. This behaviour is similar to that observed for polystyrene and a similar explanation is believed to apply for the polychloroprene/carbon black matrix.

4.3 Characterization of (α) Relaxation for Pure Polychloroprene and Carbon Black Composites

1) Characterization of (α) relaxation of pure polychloroprene

In the case of polychloroprene, dipole relaxation behaviour in addition to the effects of pure electronic conduction can be observed

All the percentages are CB in PCP.

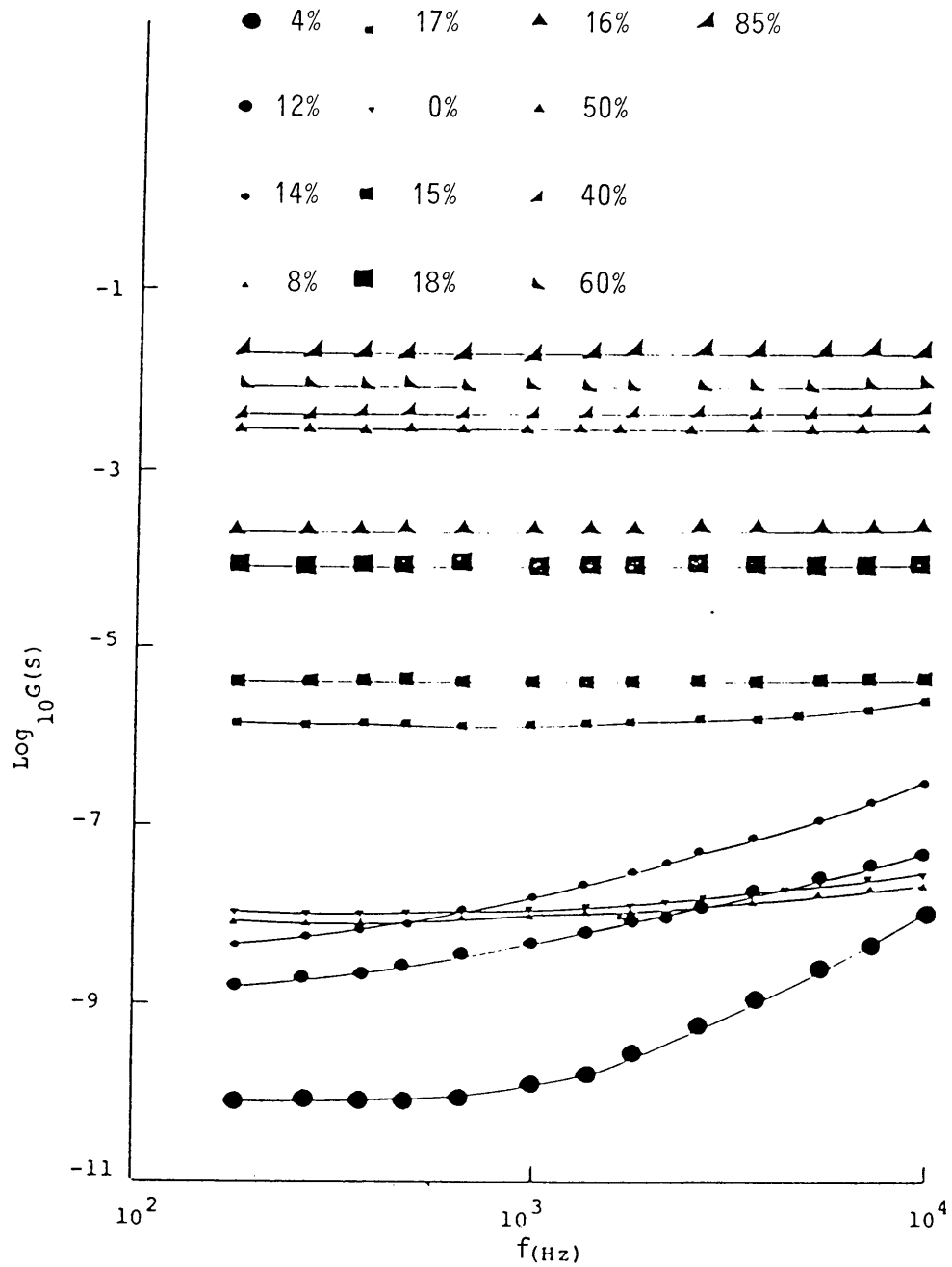


Figure (4.12) Frequency dependence on the conductivity of carbon black in polychloroprene composite.

in the dielectric spectrum. The absorption peak which appears at the highest temperature is usually called the high temperature absorption, the primary dispersion, or the (α) absorption. For the sake of simplicity the process will be called the α absorption.

The real parts of the complex permittivity ($\bar{\epsilon}$) are illustrated in figures 4.13 and 4.14 and was found to increase with temperature and decreasing frequency. The rate of increase of ($\bar{\epsilon}$) with decreasing frequency was slow at high frequencies, and increased at low frequencies. The imaginary part of the complex permittivity ($\bar{\epsilon}''$), calculated from the measured conductance value at each frequency, was found to increase with decreasing frequency as shown in figures 4.15 and 4.16. The rate of increase of ($\bar{\epsilon}''$) with decreasing frequency was small at high frequencies and increased markedly at low frequencies. These results show that a clear dipole relaxation process is observed at -21°C and 1 kHz (13-16), further increase in temperature results in a shifts in $\bar{\epsilon}_{\text{max}}$ towards high frequencies, also ($\bar{\epsilon}$) increases with temperature. The dielectric results for polychloroprene are shown in figures 4.17, 4.18, 4.19 and 4.20 respectively. The loss curve 4.17 and 4.18 rises rather steeply, and the sample possesses a definite d.c. conductivity and a loss maxima at -21°C . The dielectric constant, fig. 4.19 rises steeply with temperature due to increasing cooperative motion of dipole bond of C—Cl with temperature associated with an increasing degree of molecular motion in the polar polymer with temperature. The conductivity, fig. 4.20, rises rather steeply with temperature and the sample possesses a definite d.c. conductivity with activation energy 1.26 eV and the maxima peak appears at -21°C , is indicative of a definite a.c. conductivity with activation energy 1.74 eV. An analysis was conducted using the Havriliak and Negami circular arc law (17) to discuss the

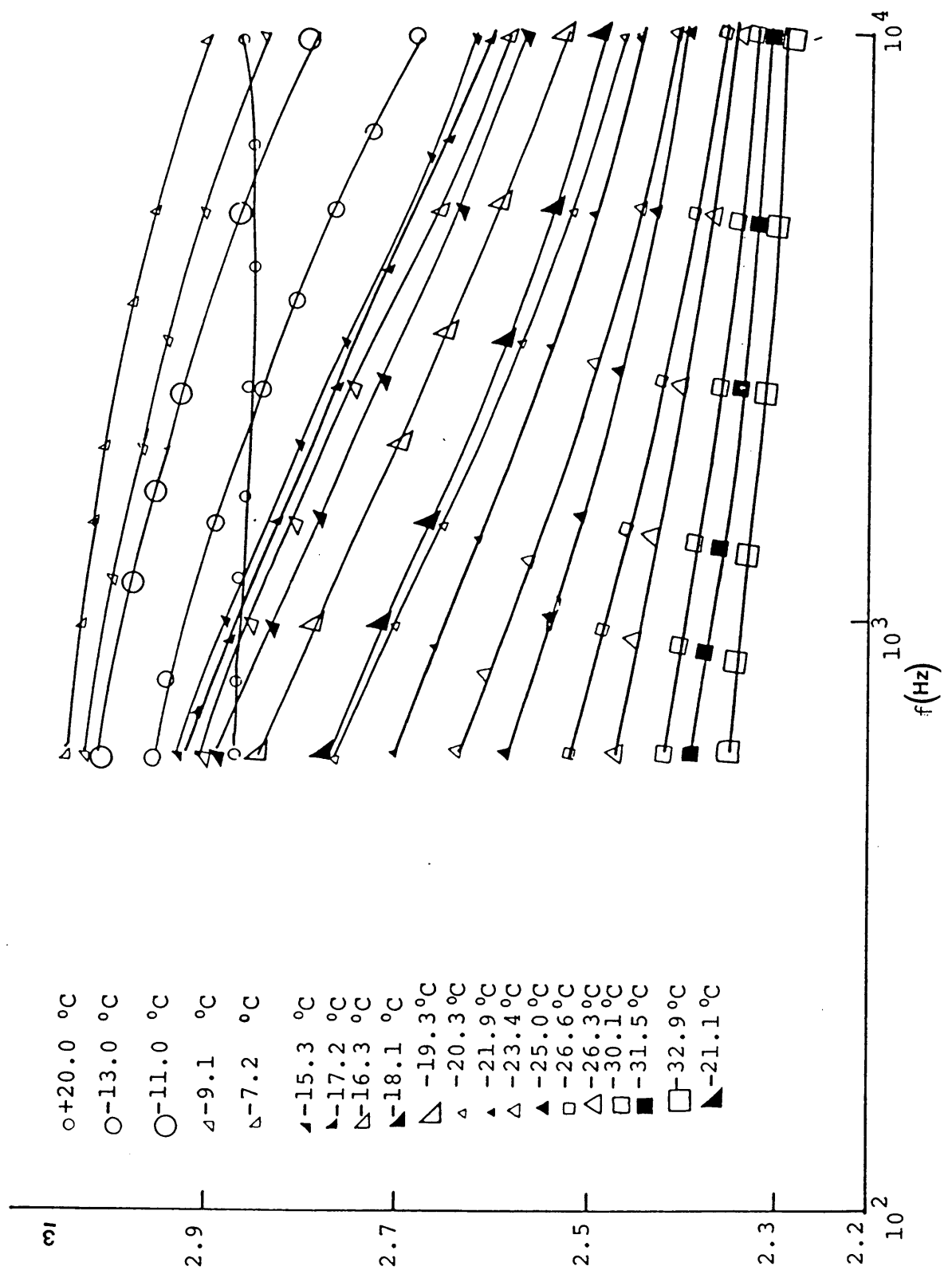


Figure (4.13) The frequency of ϵ'' at various fixed temperature for polychloroprene.

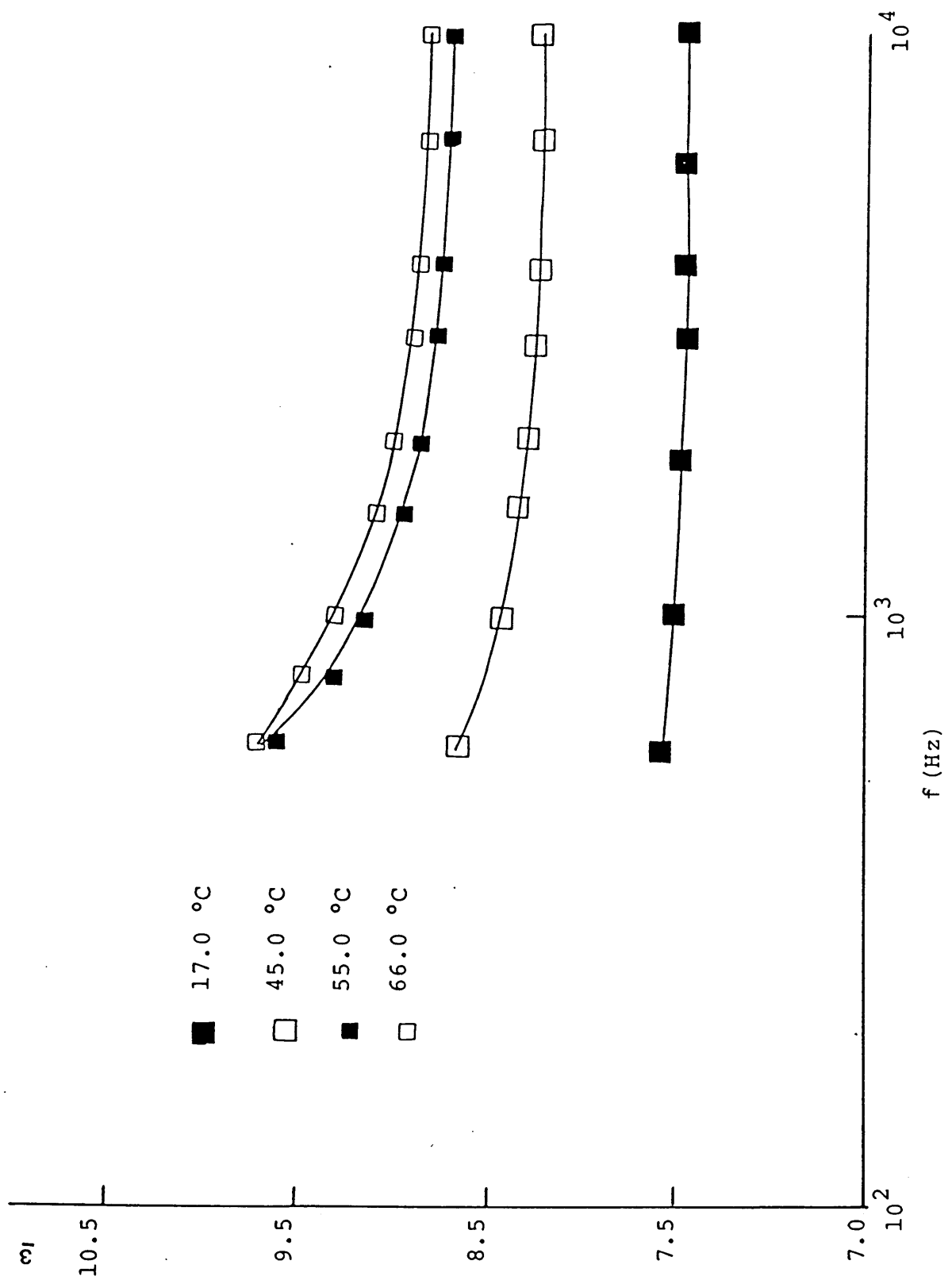
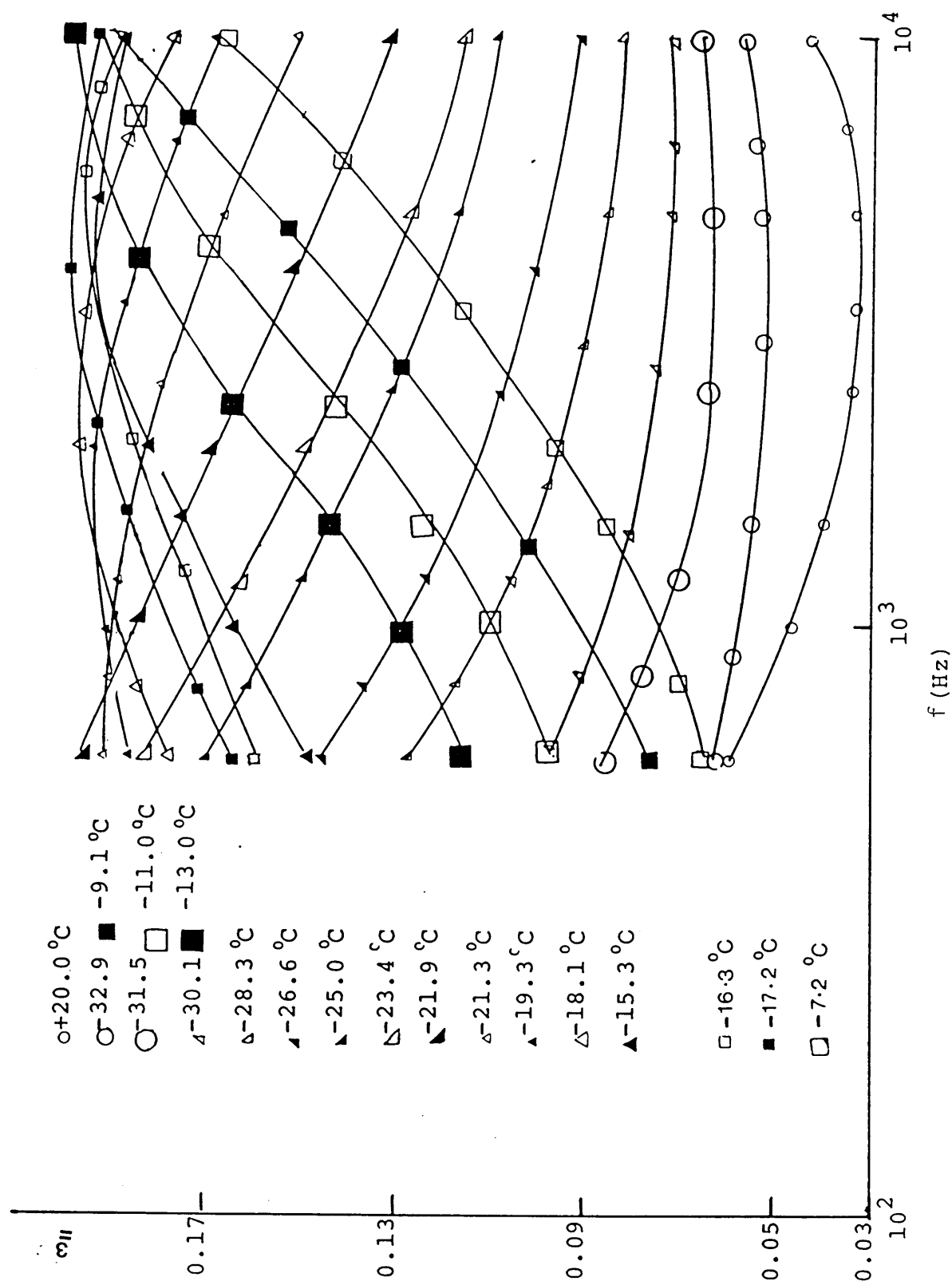
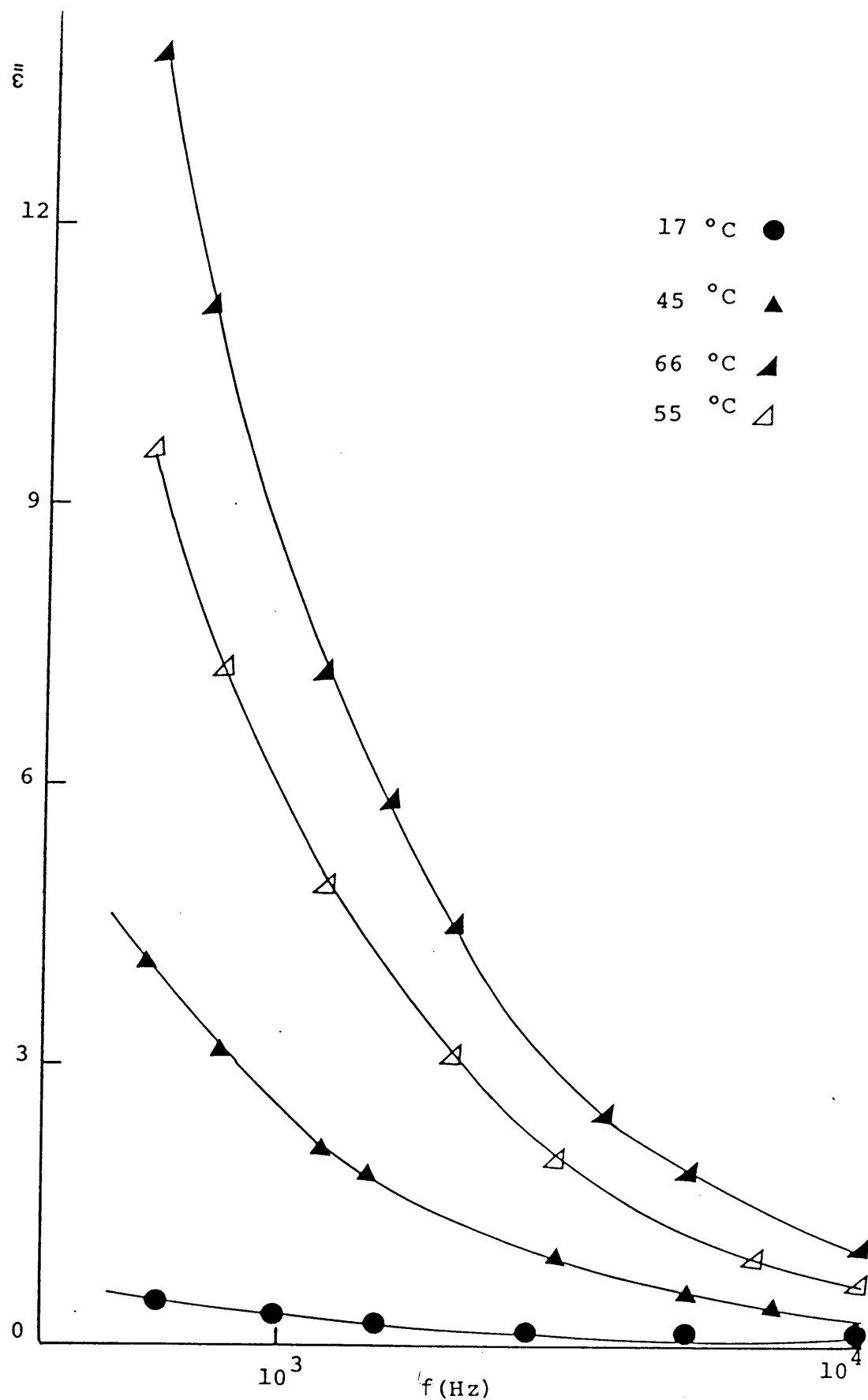


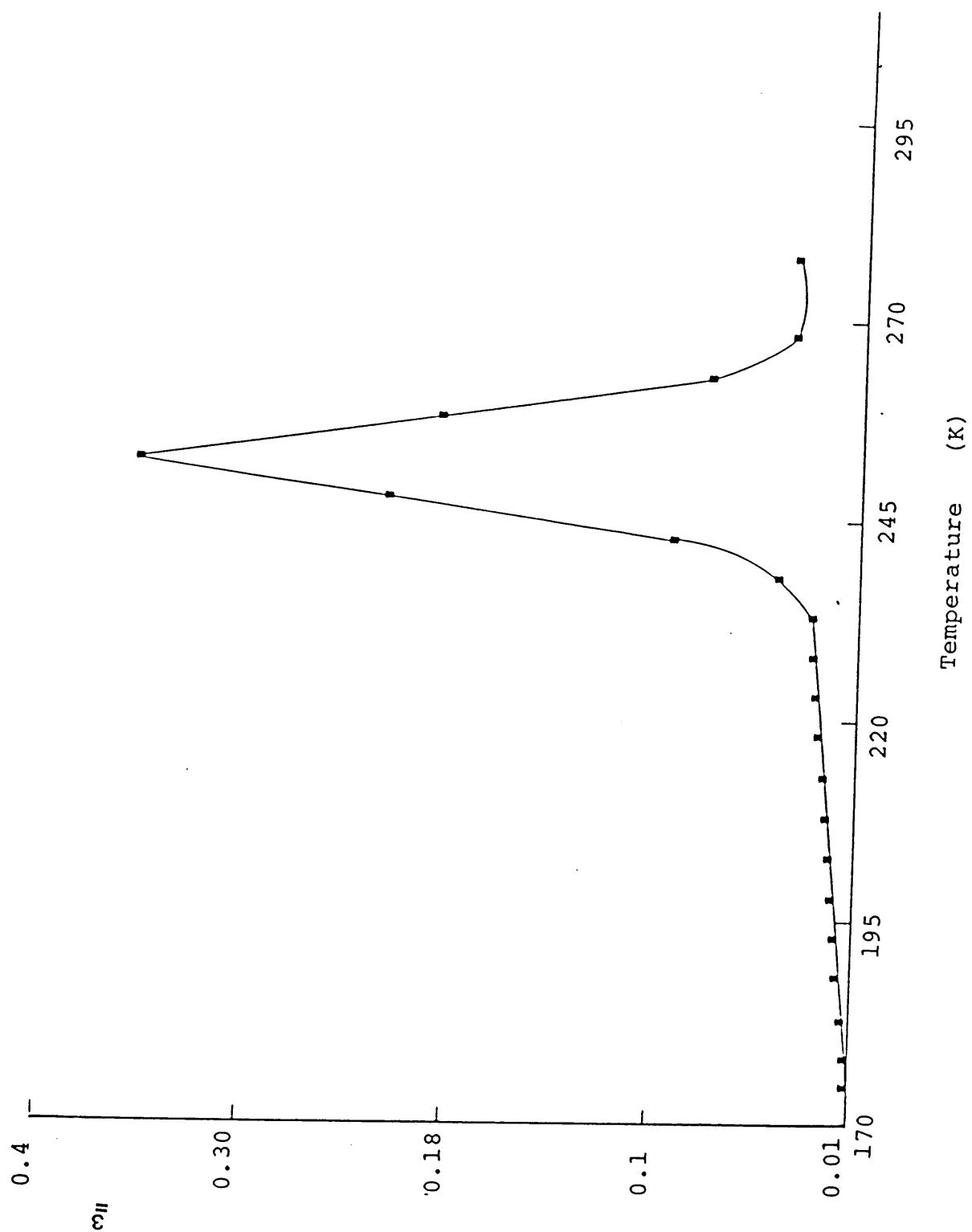
Figure (4.14) The frequency dependence of ϵ'' at various fixed temperature for polychloroprene.



Figure(4.15) The frequency dependence of ϵ'' at various fixed temperature for polychloroprene.



Figure(4.16) The frequency dependence of $\bar{\epsilon}''$ at various fixed temperature for polychloroprene.



Figure(4.17) Variation of the dielectric loss at 1 kHz
versus temperature for pure polychloroprene.

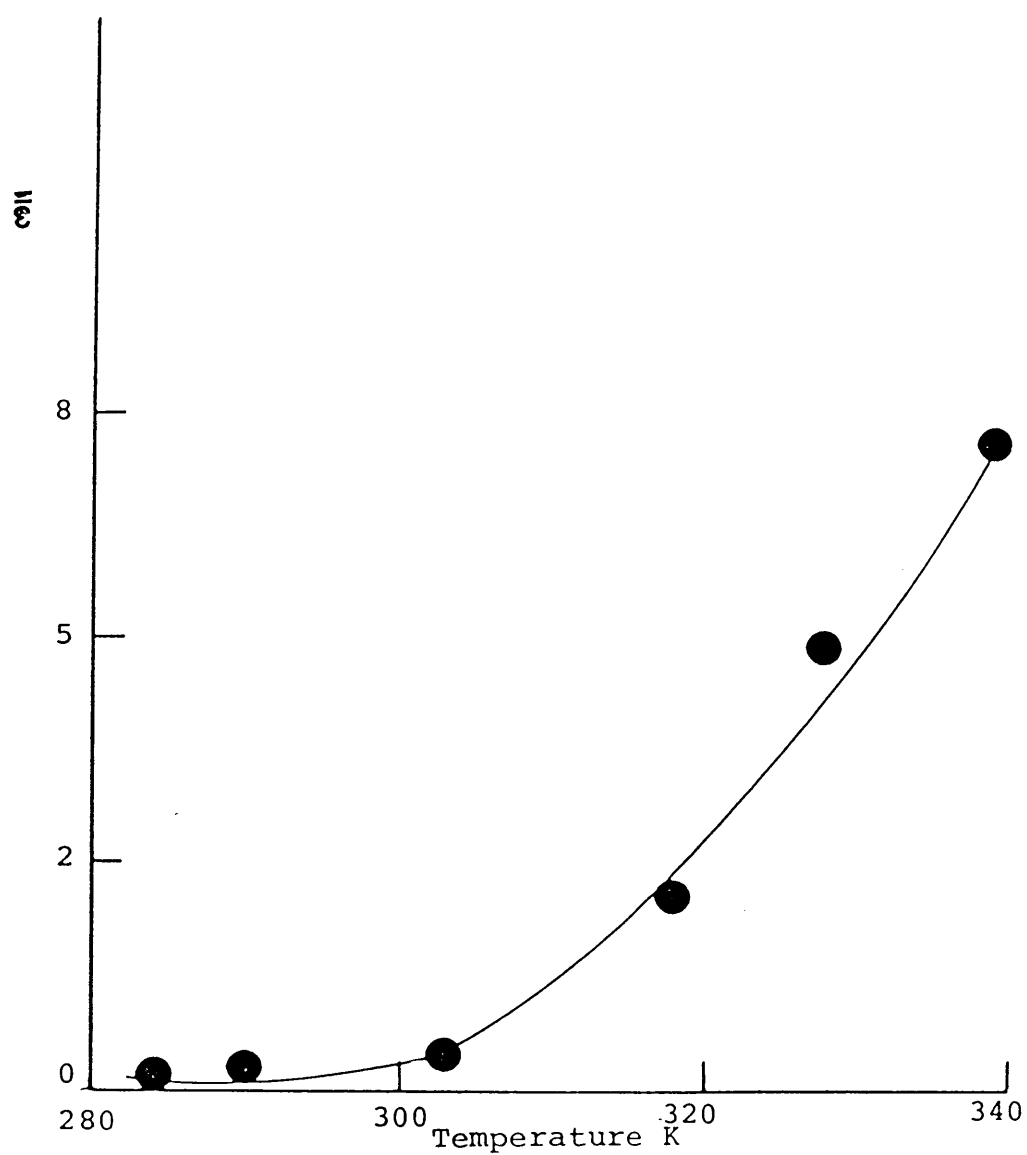


Figure (4.18) Variation of the dielectric loss at 1 kHz versus temperature for pure polychloroprene.

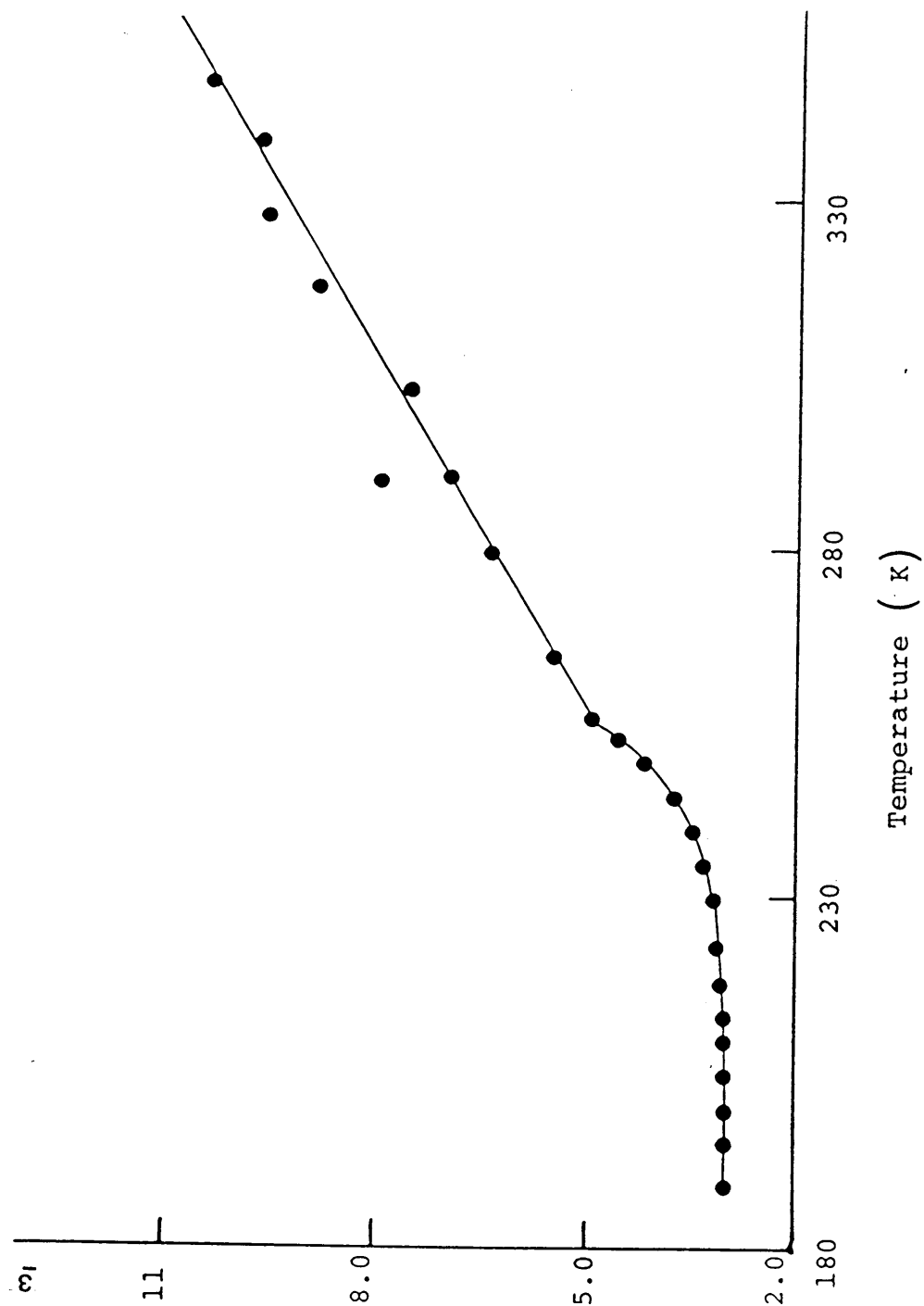


Figure (4.19) Variation of the dielectric constant ϵ_1 at 1 kHz versus temperature for polychloroprene.

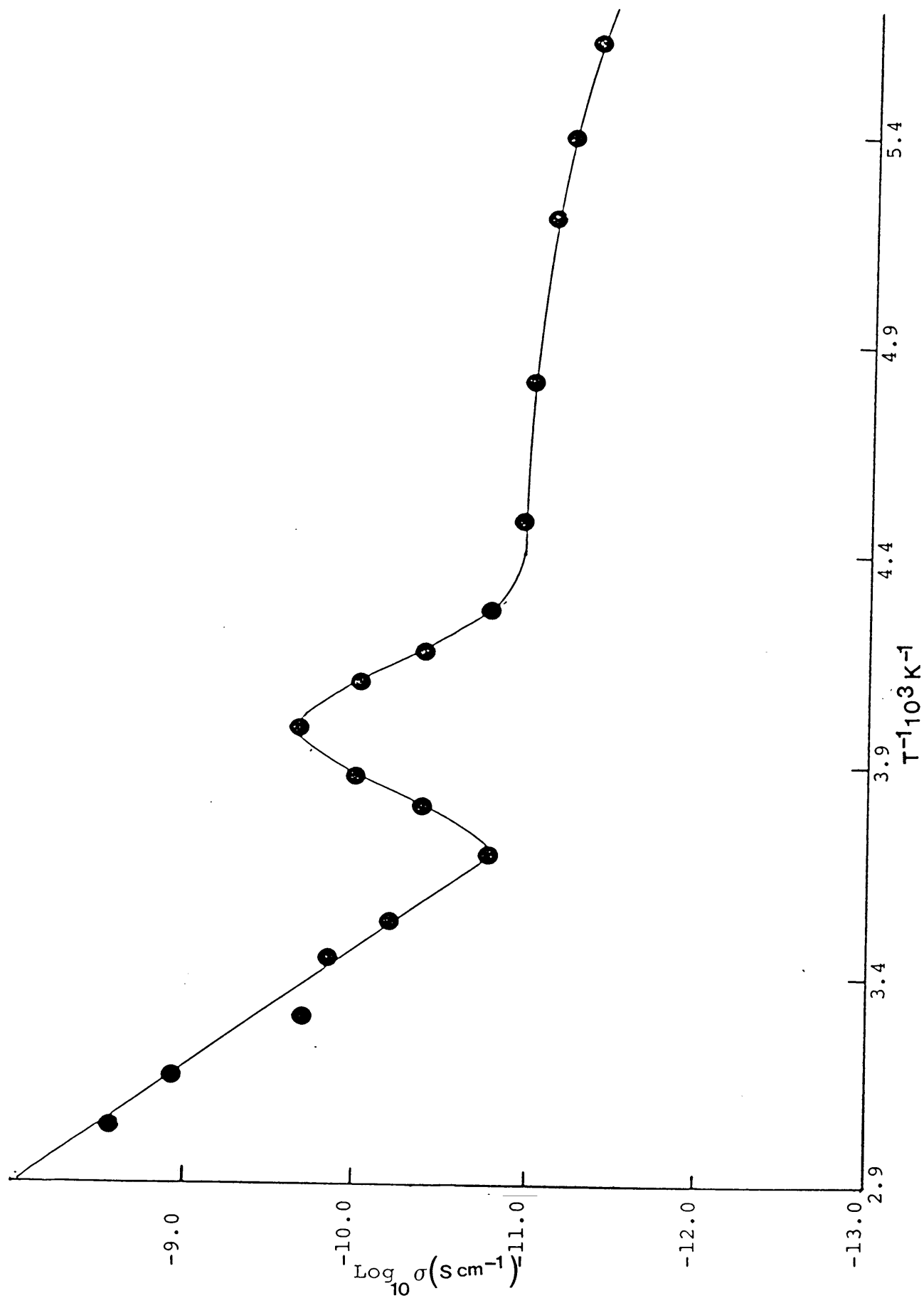


Figure (4.20) Variation of conductivity at 1 kHz versus temperature for polychloroprene.

data obtained. As is well known, the law consists of plotting the values of $(\bar{\epsilon})$ against the corresponding values of $(\bar{\epsilon})$, $(\epsilon_0 - \epsilon_\infty)$ corresponding to the length of the chord of the circular arc, where (ϵ_0) is the dielectric constant for lower frequency and $(\bar{\epsilon})$ is the dielectric constant for the higher frequency. The value of $(\epsilon_0 - \epsilon_\infty)$ represents the magnitude of the dielectric absorption, $(\alpha\pi)$ corresponds to the angle between the radii of the arc drawn to the points (ϵ_0) and (ϵ_∞) from the center of the circle and (α) is the parameter representing the degree of the broadness of a dielectric absorption curve. The generalized relaxation time (τ_0) is given by $\tau_0 = 1/2 \pi f_{\max}$ where $(f_{\max})$ is the frequency corresponding to the loss maximum. The results of the Havriliak and Negami plot for the absorption are shown in fig. 4.21 and the value of (α) , $(\epsilon_0 - \epsilon_\infty)$ and (β) at each temperature are obtained from each circular arc, i.e. the magnitude of the absorption $(\epsilon_0 - \epsilon_\infty)$. (α) representing the broadness and (β) representing the degree of skew of the dielectric absorption are determined using Havriliak and Negami analysis at each temperature. The plots of $(\epsilon_0 - \epsilon_\infty)$ and (α) against temperature are shown in fig. 4.22. The shape of the absorption curve does not change with temperature which leads to the conclusion that the (α) and (β) parameters do not vary with temperature, and hence, the breadth of the relaxation does not change with temperature also. This is consistent with the idea that the dominant process involves molecular motion of the to C—Cl bond, and further that the nature of the process does not change the temperature. Detailed analysis of dielectrics relaxation spectra have indicated that in many systems the reorientation of the dipole involves cooperative motions of between six and eight bonds. The observation that the breadth of the process does not change with temperature implies that the relaxation mechanism is

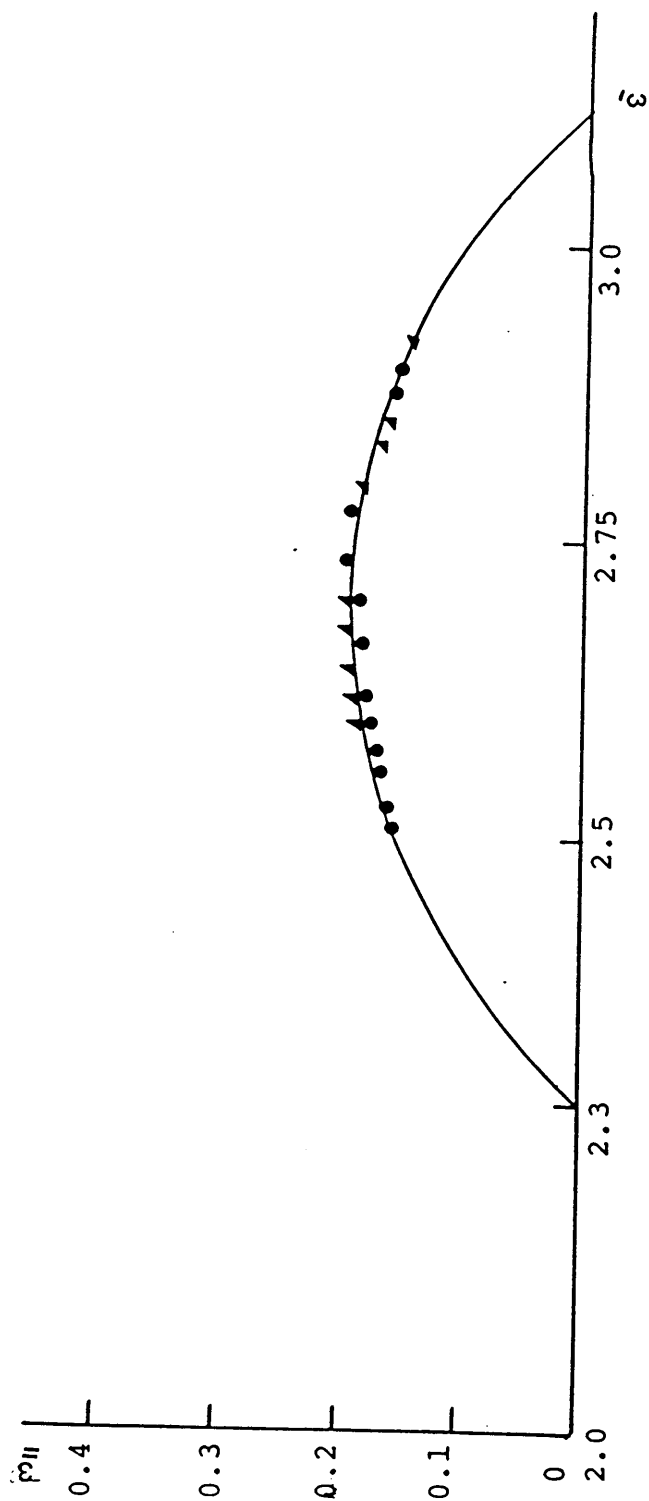


Figure (4.21) Argand diagram of real and imaginary permittivity for pure polychloroprene.

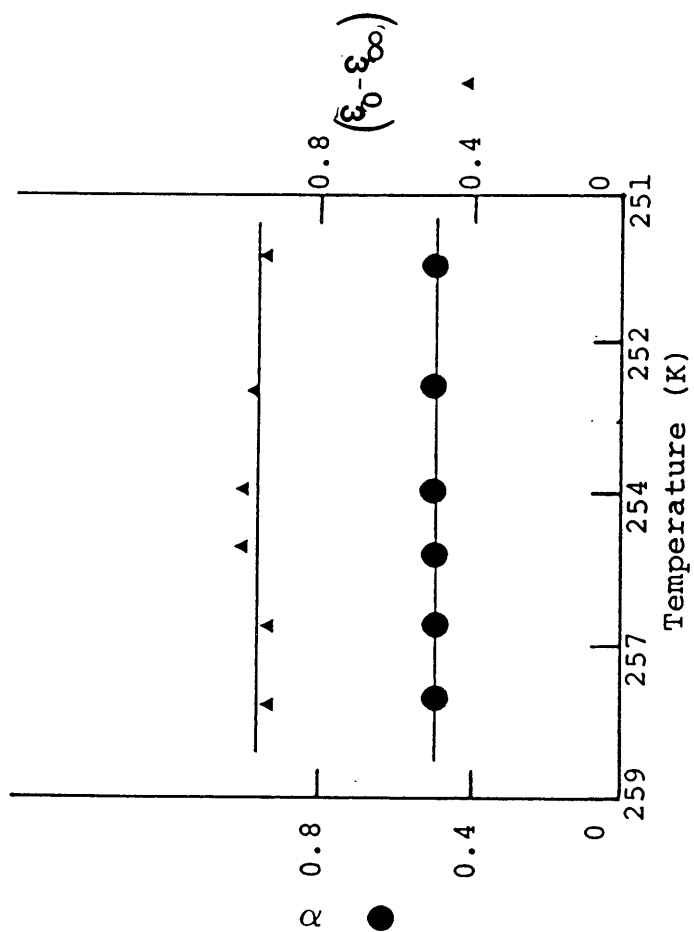


Figure (4.22) The temperature independence of α and $(\epsilon_0 - \epsilon_\infty)$ for polychloroprene.

not changing significantly with variation in temperature. The so called "transition map" for polychloroprene fig. 4.23 is obtained by plotting the logarithm of the frequency of the relaxation process versus the reciprocal of the temperature.

The experimental data on dielectric loss is normally represented by the plot of $\log_{10} \bar{\epsilon}$ versus $\log_{10} f$, with temperature as a variable parameter, together with the normalised plots of $\log_{10} \bar{\epsilon} / \bar{\epsilon}_{\max}$ versus $\log_{10} \omega / \omega_{\max}$ where $\bar{\epsilon}_{\max}$ and $\omega_{\max}$ represent the values at the loss peak (Appendix C) and are shown in fig. 4.24. The loss peak is symmetrical and has a full width at half height of $\lambda = 2.4$ decades. Loss peaks of the Debye type are sometimes, but by no means always, observed in the dielectric relaxation of liquids (18), but they are never seen in solid polymers. In polymers the observed loss peaks are always broader usually not less than two decades and sometimes considerably more and are invariably asymmetric in the $\log_{10} \omega$ plot, being steeper on the low frequency side than on the high frequency side of the peak. The dependence of dielectric loss on temperature may provide valuable insight into the nature of the physical mechanism governing the loss processes in polymer. The results show that the loss peak is broader than two decades. Applying this method of plotting, fig. 4.25, the logarithm of the frequency shift, required to achieve normalization of the experimental data corresponding to different temperatures, against the reciprocal of the corresponding temperature yields activation energy plots. The resulting activation energy has been calculated. The activation energy (13) for the absorption of polychloroprene is 160 kJ/mole (1.66 eV) and corresponds to the dipole relaxation of the chlorine-carbon dipole. Table 4.1 summarizes the results of dielectric technique data for pure polychloroprene.

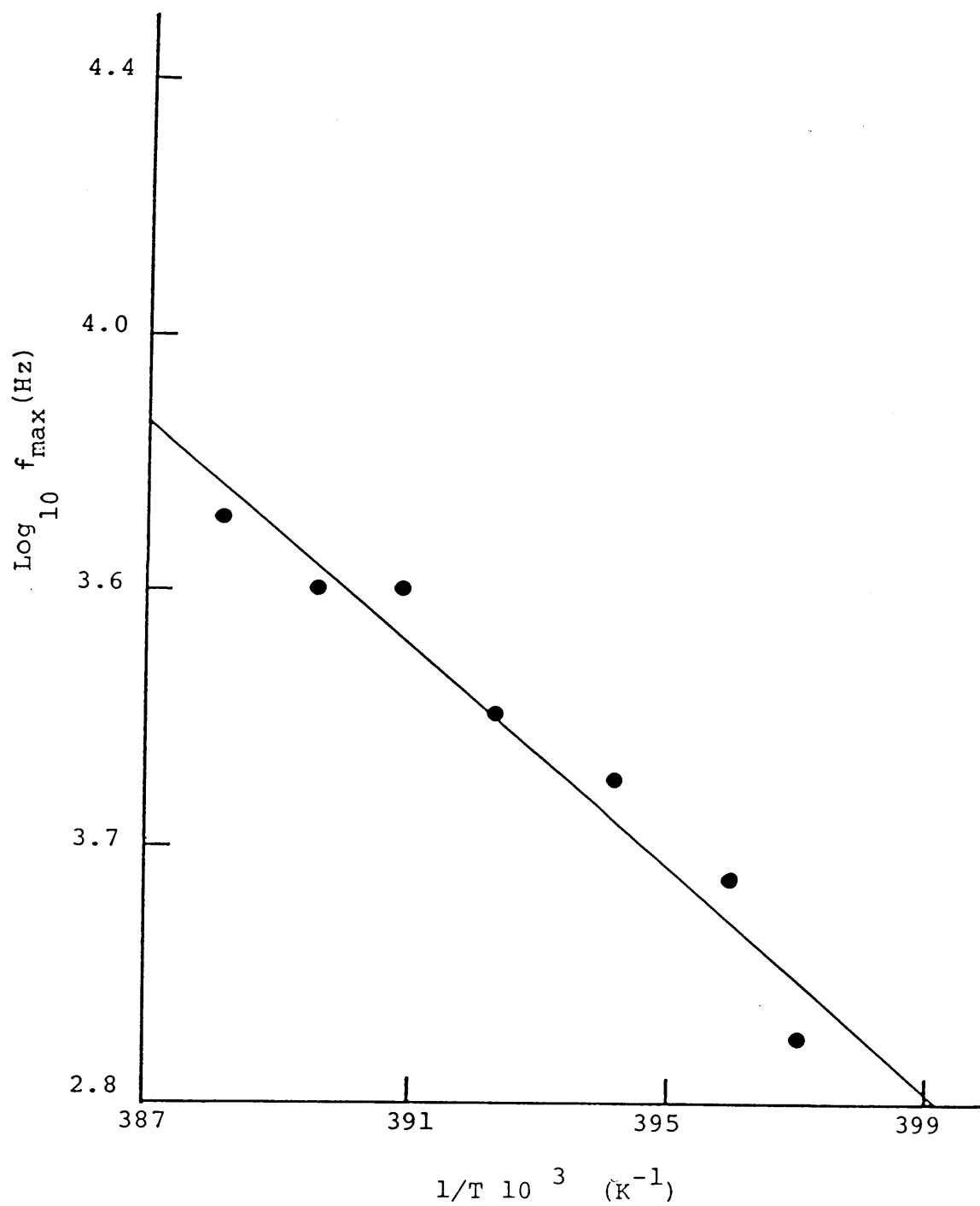
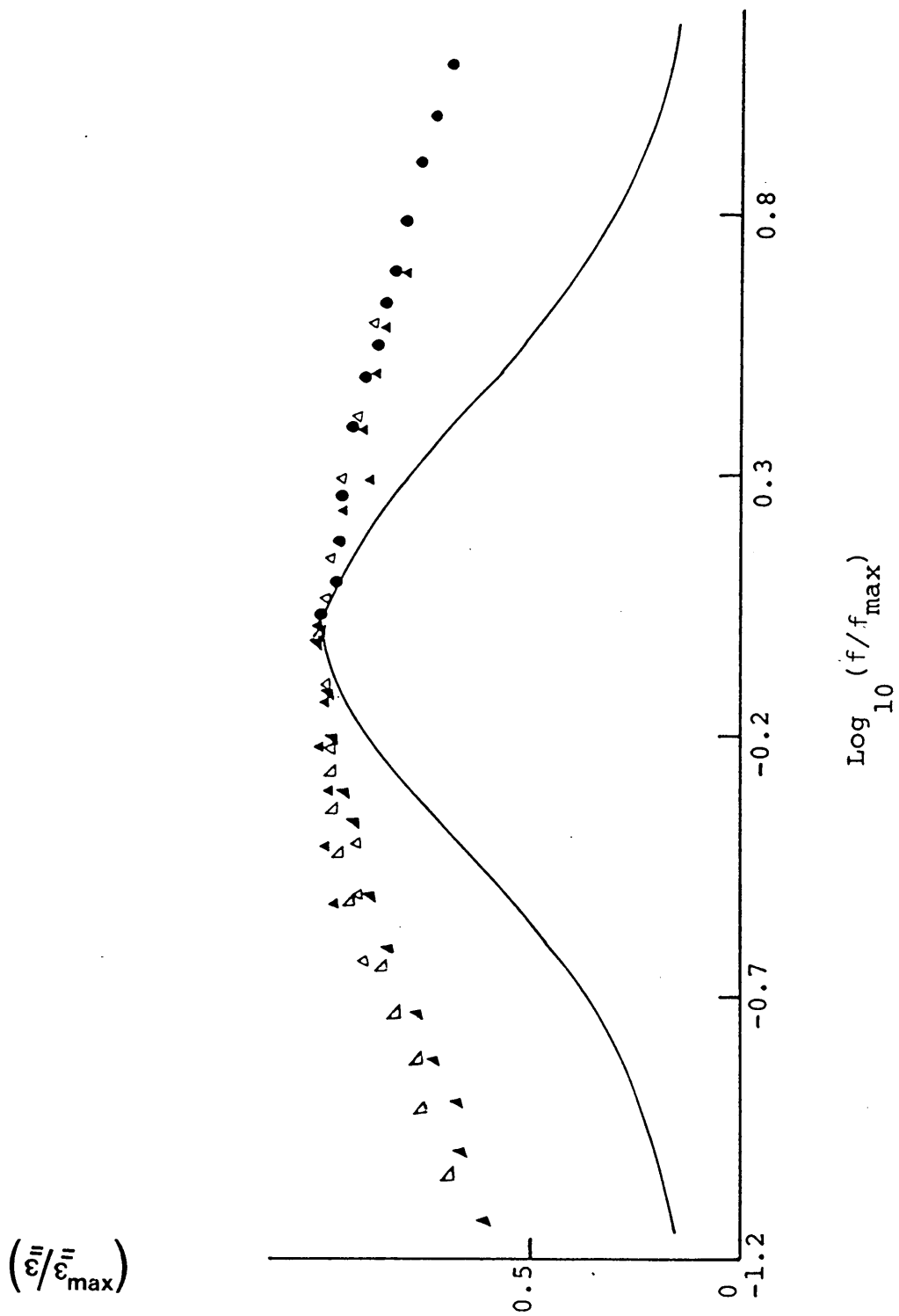


Figure (4.23) The transition map for pure polychloroprene.



Figure(4.24) Normalised loss plots for high temperature relaxation for pure polychloroprene.

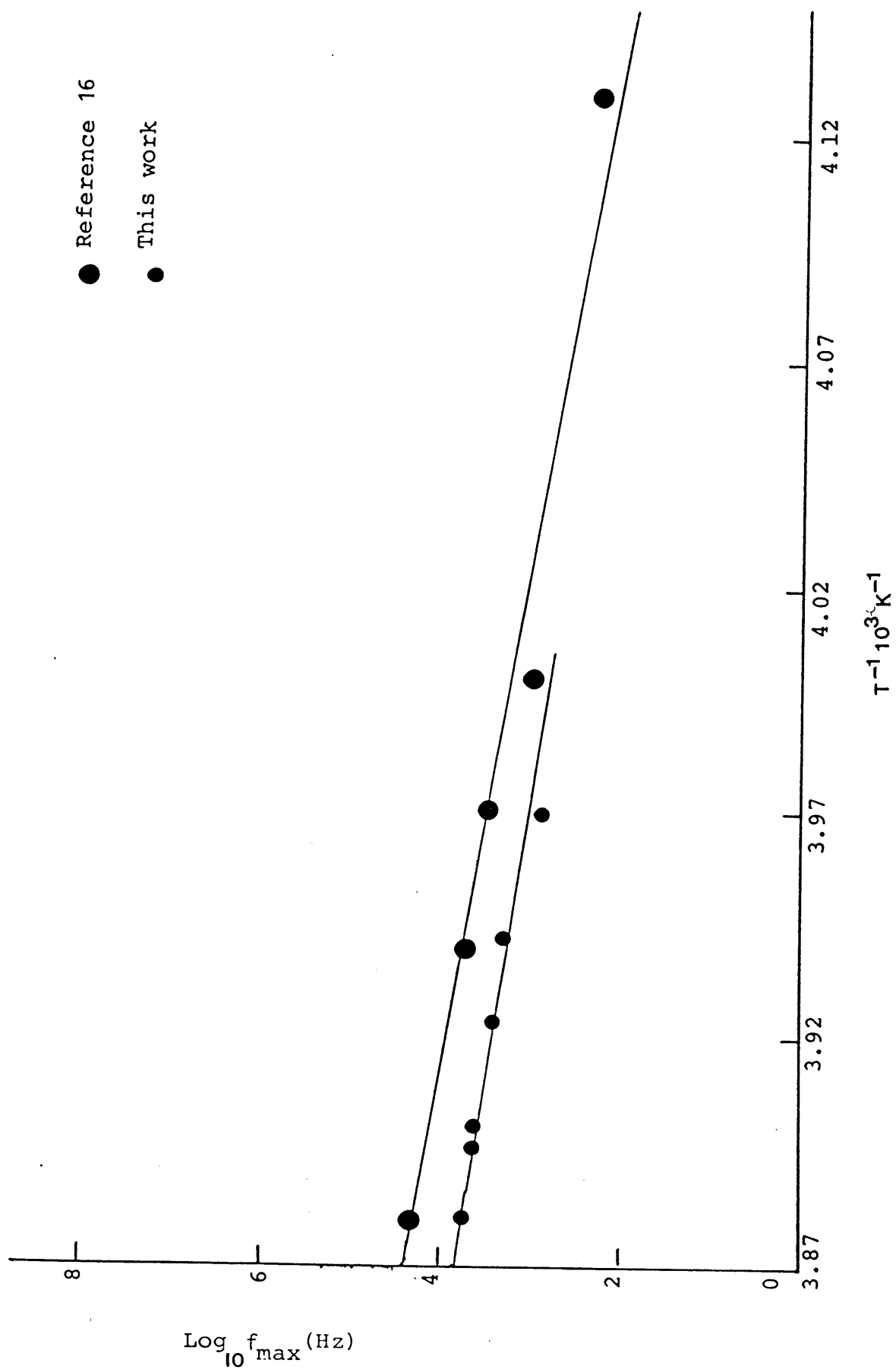


Figure (4.25) Activation energy plot for pure polychloroprene.

Table 4.1 Summary of the Results of the Dielectric Technique for
Pure Polychloroprene

Material	Data	Reference
Polychloroprene	$\Delta E = 160 \text{ kJ/mole (1.66 eV)}$ $\bar{\epsilon} = 2.33, \bar{\epsilon} = 0.058 \text{ S Hz}^{-1} \text{ F}^{-1}$ at -32.9°C and 3 kHz $\bar{\epsilon} = 9.8, \bar{\epsilon} = 8.5 \text{ S Hz}^{-1} \text{ F}^{-1}$ at 3 kHz and 60°C $\Delta E = 164 \text{ kJ/mole (1.69 eV)}$ $\bar{\epsilon} = 3.6, \bar{\epsilon} = 0.40 \text{ S Hz}^{-1} \text{ F}^{-1}$ at -32°C and 3 kHz	This work 13
Polychloroprene gum	$\bar{\epsilon} = 7, \bar{\epsilon} = 1.1 \text{ S Hz}^{-1} \text{ F}^{-1}$ at 3 kHz and 60°C	14
Polychloroprene tread	$\bar{\epsilon} = 17, \bar{\epsilon} = 3.8 \text{ S Hz}^{-1} \text{ F}^{-1}$ at 3 kHz and 60°C	

2) Characterization of (α) Relaxation of Carbon Black Composites

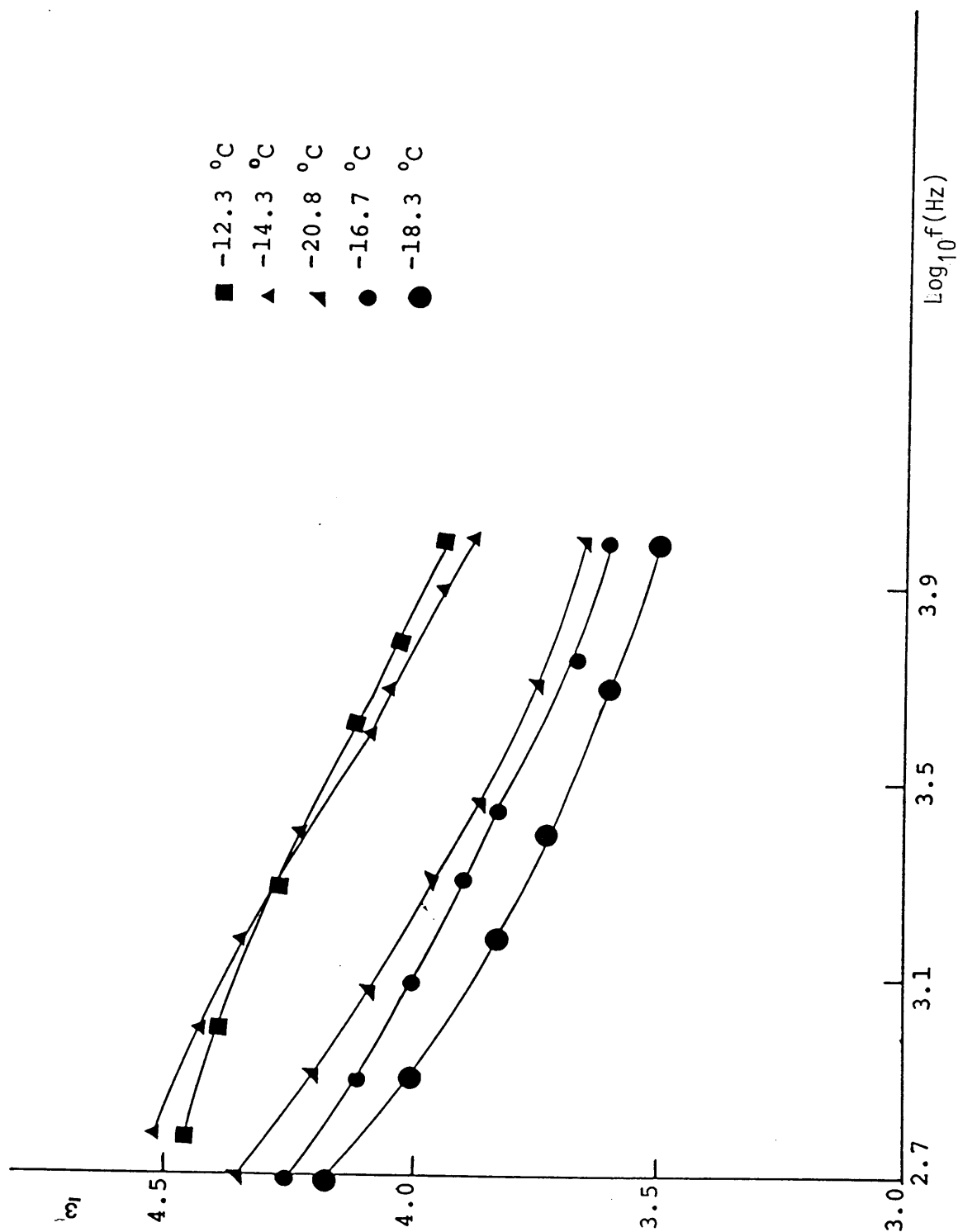
A) Characterization of (α) relaxation for 4% carbon black in
polychloroprene

In the case of 4% carbon black loaded polychloroprene, the whole

range of behaviour of the dielectric absorption can be observed. The (α) absorption appears at high temperature. The real part of the complex permittivity ($\bar{\epsilon}$) is illustrated in figure 4.26 and was found like pure polychloroprene, to increase with temperature and decreasing frequency. The imaginary part of the complex permittivity ($\bar{\epsilon}''$), was found to increase with decreasing frequency as shown in figure 4.27. An analysis was conducted using the Havriliak and Negami circular arc equation (2.54) to discuss the data obtained. The results show that the loss peak was broader than the ideal Debye and spreads over two decades. The loss peak was symmetrical but the (λ) value was only half that of the ideal Debye (Havriliak and Negami graph was depressed to half the value of ideal Debye), as shown in figure 4.28. The experimental data on dielectric loss is normally represented by the normalization plot of $\log_{10} \bar{\epsilon}'' / \bar{\epsilon}''_{\max}$ versus $\log_{10} \omega / \omega_{\max}$ as shown in figure 4.29. The loss peak has a full width at half height of $\lambda = 2.4$ decades. By plotting the logarithm of the frequency shift required to achieve normalization of the experimental data at different temperatures against the reciprocal of the corresponding temperature, as shown in figure 4.30, results in an activation energy for the relaxation of 156 kJ/mole (1.62 eV).

B) Characterization of (α) relaxation for 8% carbon black loaded polychloroprene

In the case of 8% carbon black loaded polychloroprene, the complete spectrum of the dielectric absorption could be observed. The (α) absorption appears at high temperature. The real part of the complex permittivity ($\bar{\epsilon}$) is illustrated in figure 4.31 and was found to increase with temperature and decreasing frequency. The imaginary



Figure(4.26) The frequency dependence on $\bar{\epsilon}'$ at various fixed temperature for 4% carbon black in polychloroprene.

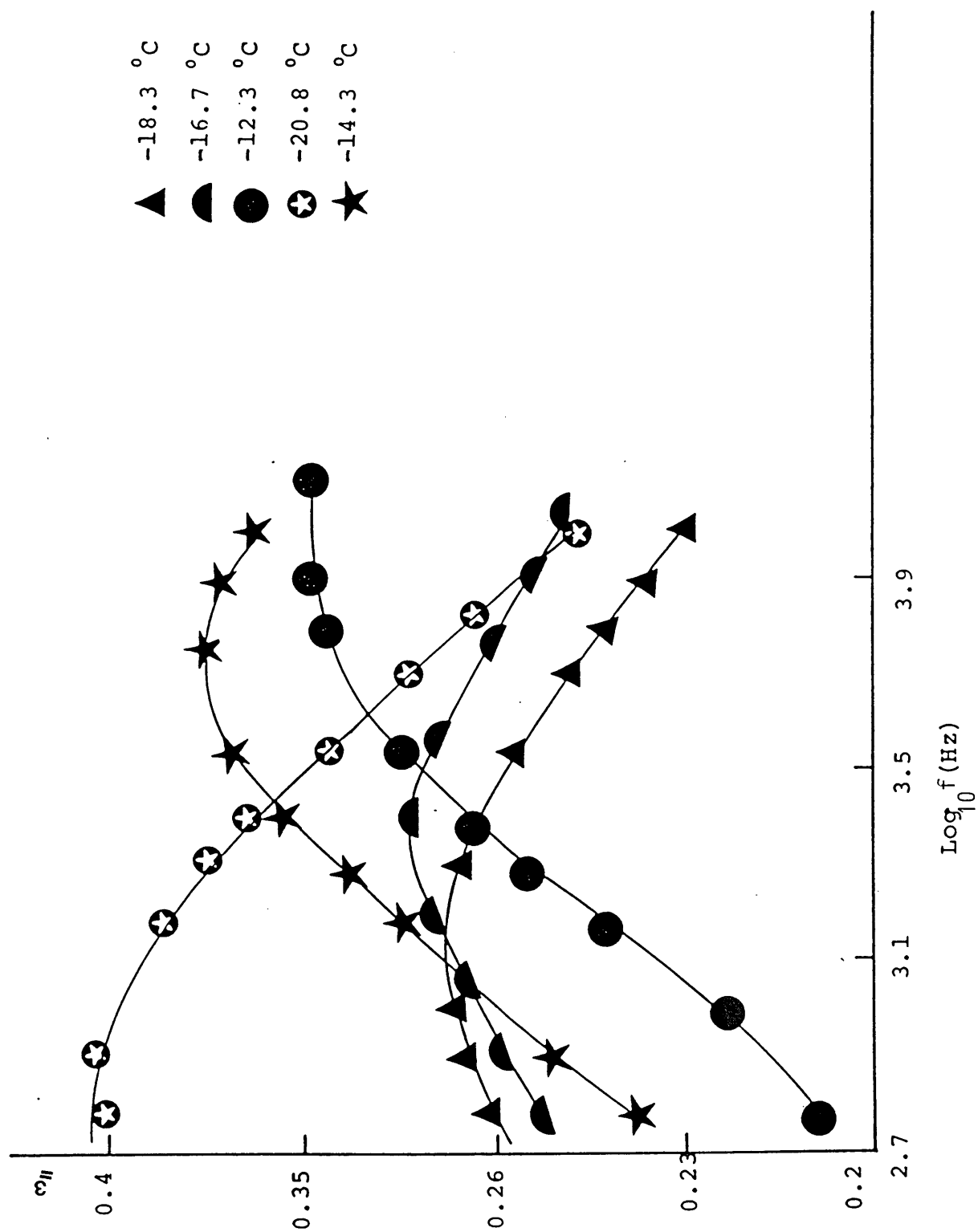


Figure (4.27) The frequency dependence of ϵ'' at various fixed temperature for 4% carbon black in polychloroprene.

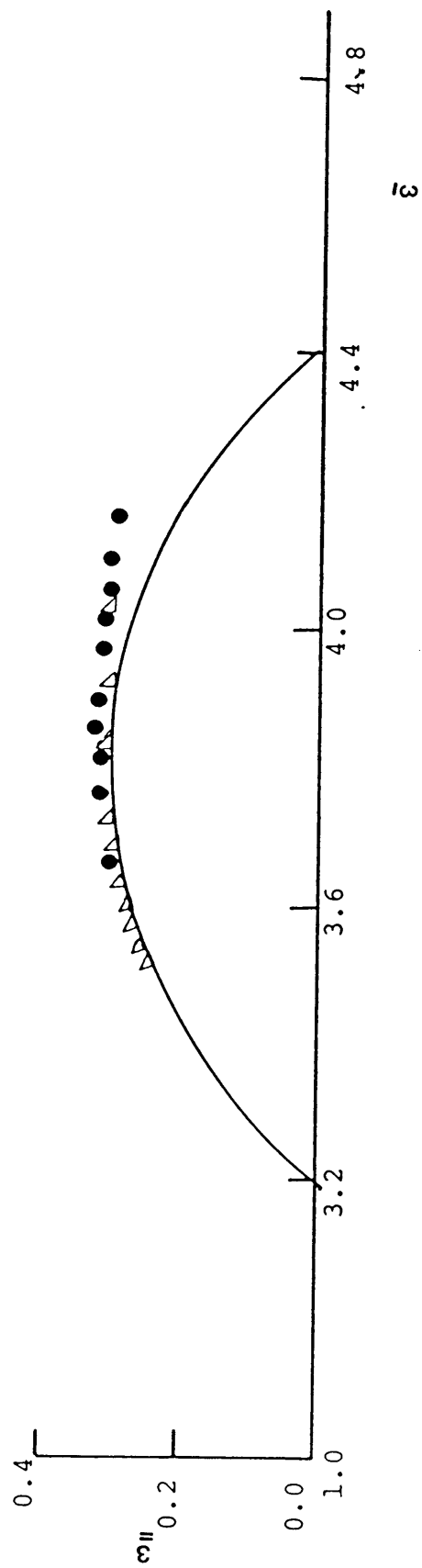
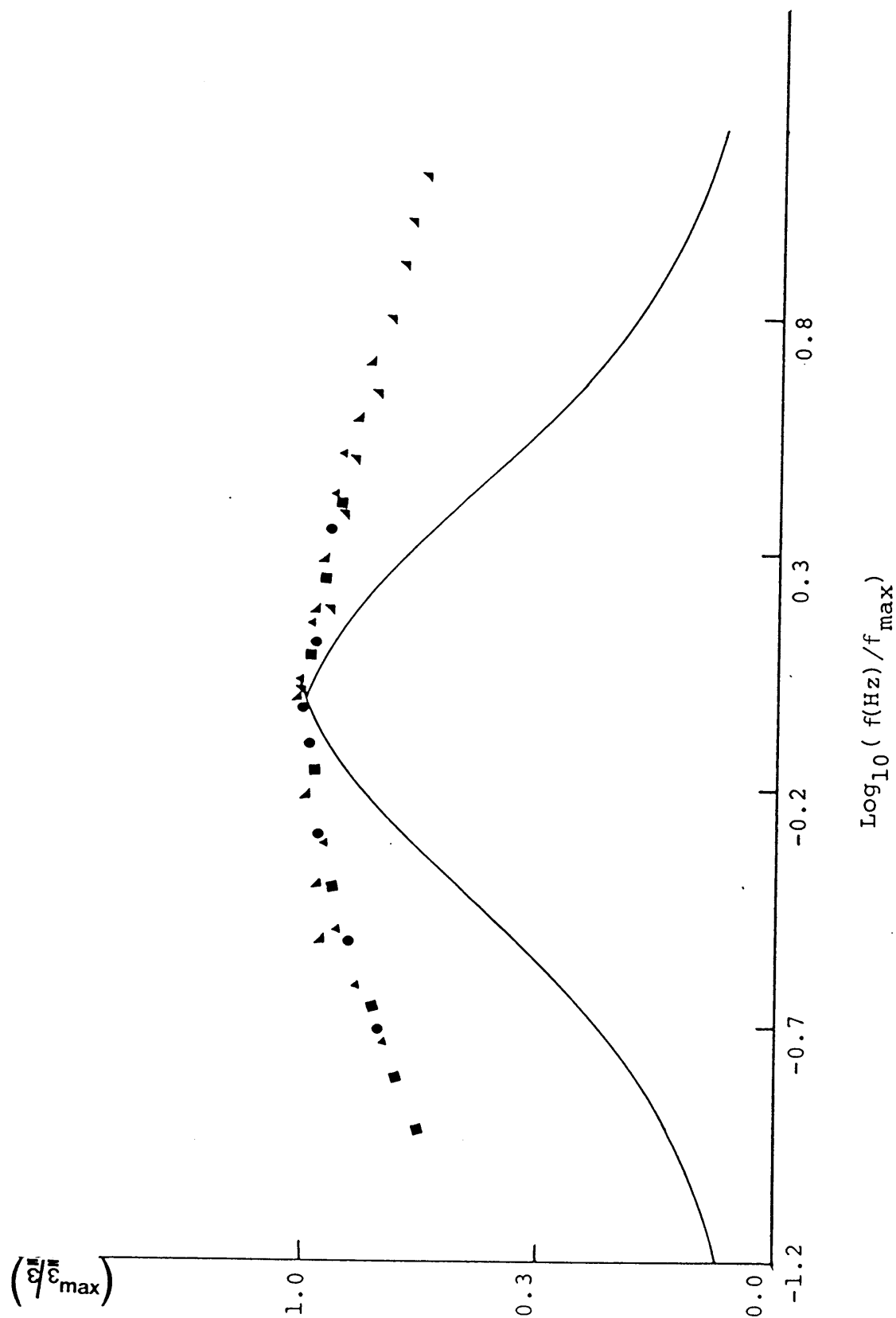


Figure (4.28) Argand diagram of real and imaginary permittivity for 48 carbon black in polychloroprene.



Figure(4.29) Variation of the logarithm of the normalized dielectric loss with normalized frequency for 4% carbon black in polychloroprene.

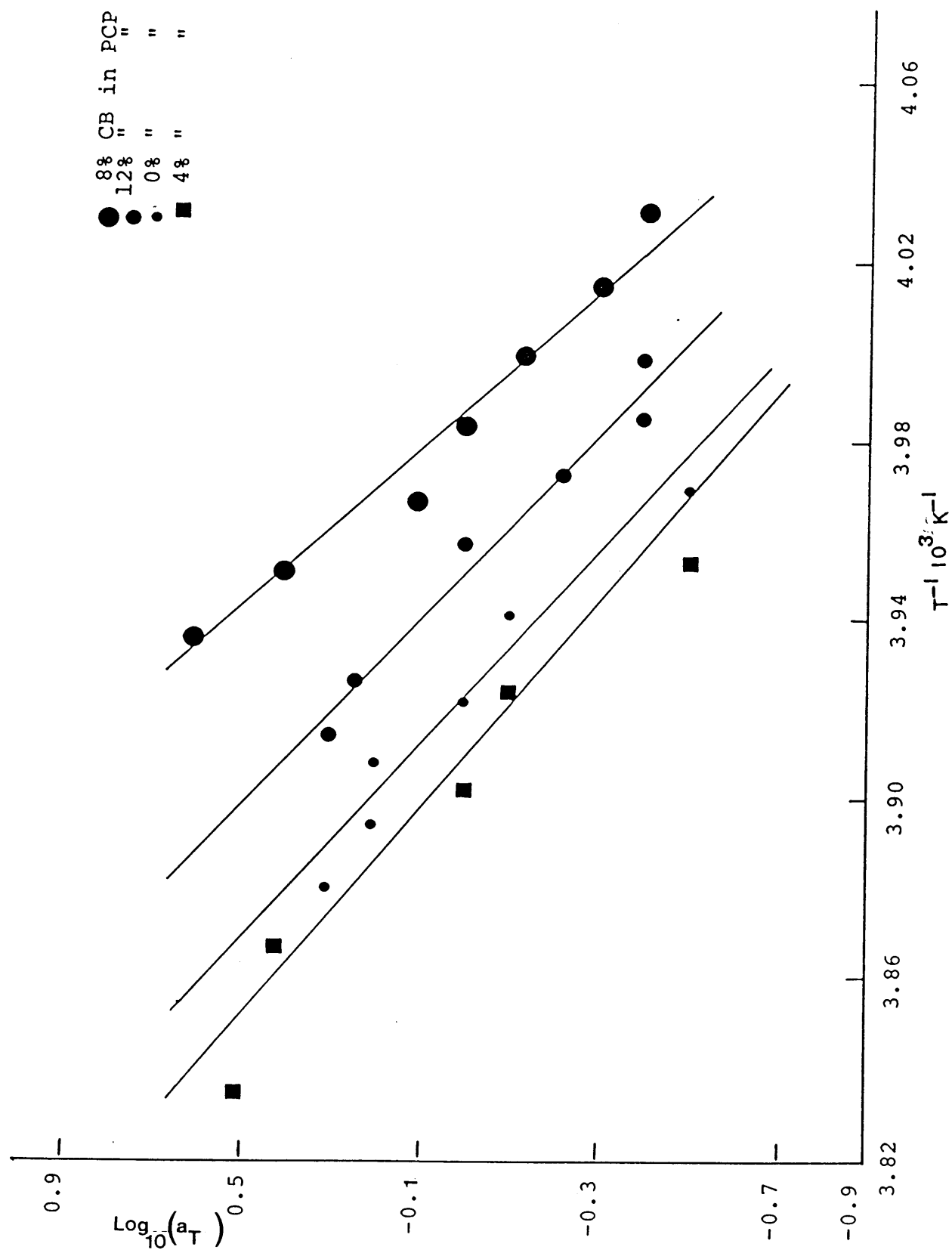


Figure (4.30) Variation of the frequency shift of $f_{\max}$ with reciprocal temperature for carbon black loaded polychloroprene.

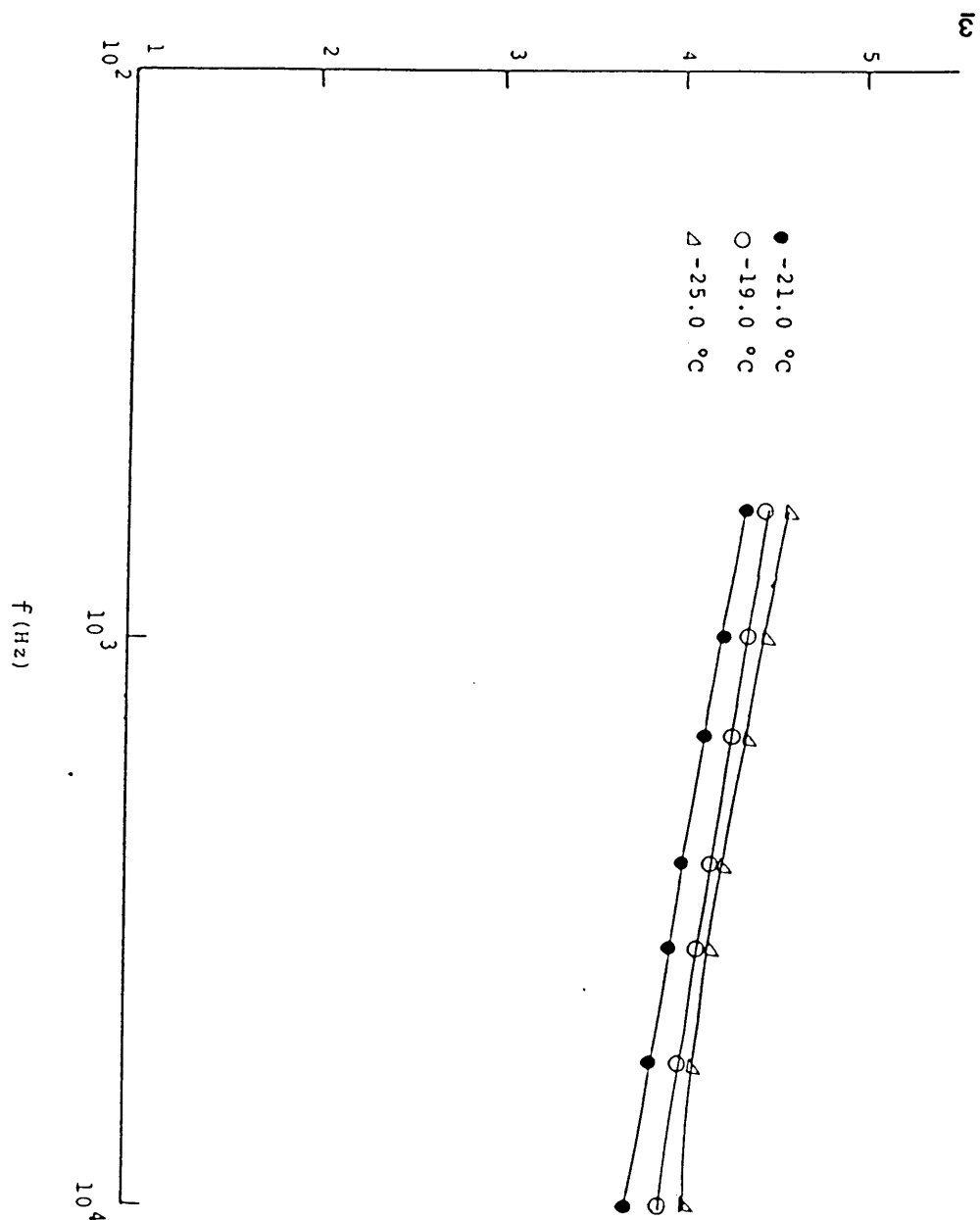


Figure (4.31) The frequency dependence of ϵ'' at various fixed temperature for 8% carbon black in polychloroprene.

part of the complex permittivity ($\bar{\epsilon}$) was found to increase with decreasing frequency as shown in figure 4.32. An analysis was conducted using the Havriliak and Negami circular arc equation (2.54). The results showed that the loss peak was broader than ideal Debye and measured two decades, as shown in figure 4.33. The experimental data on dielectric loss is represented by the normalization plot of $\log_{10} \bar{\epsilon} / \bar{\epsilon}_{\max}$ versus $\log_{10} \omega / \omega_{\max}$ as shown in figure 4.34. The loss peak has a full width at half height of $\lambda = 2.4$ decades. From figure 4.30 the activation energy of relaxation has been found to be 190.4 kJ/mole (1.97 eV). This is significantly higher than for the 0%, 4% and 12% carbon black loading and suggests some polymer carbon black interaction.

C) Characterization of (α) relaxation for 12% carbon black in polychloroprene

In the case of 12% carbon black loaded polychloroprene the whole spectrum of relaxation could be observed. The real part of complex permittivity ($\bar{\epsilon}$) is illustrated in figure 4.35 and was found to increase with temperature and decreasing frequency. The imaginary part of the complex permittivity ($\bar{\epsilon}$), was found to increase with decreasing frequency as shown in figure 4.36. Analysis using the Havriliak and Negami circular arc equation (2.54) produces figure 4.37. The experimental data on dielectric loss is represented by the normalization plot figure 4.38. From figure 4.30 the activation energy of relaxation has been found to be 168 kJ/mole (1.74 eV). Table 4.2 represents the data for the behaviour of dielectric relaxation of the dipole C—Cl bond at high temperatures.

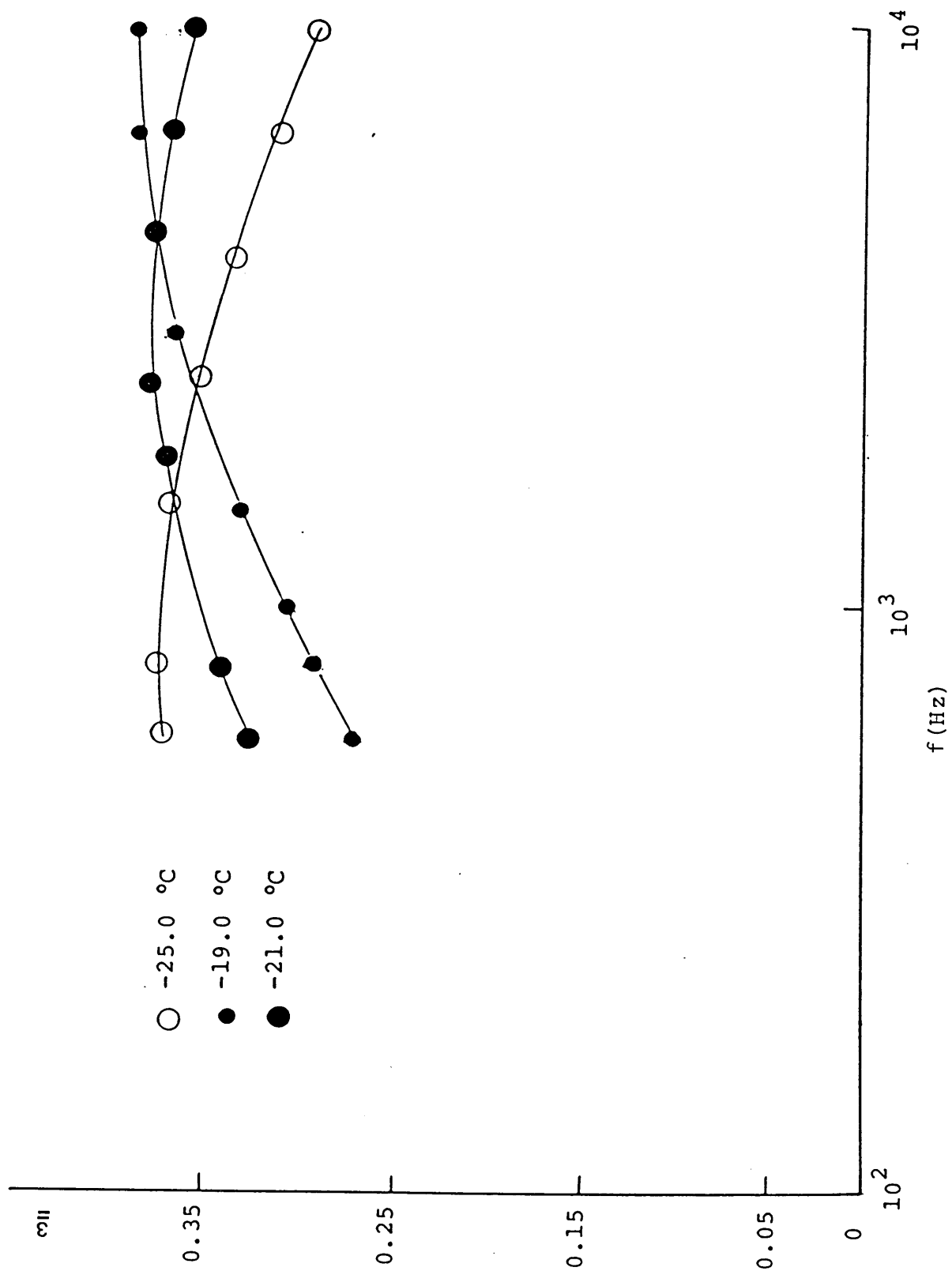


Figure (4.32) The frequency dependence of ϵ'' at various fixed temperature for 8% carbon black in polychloroprene.

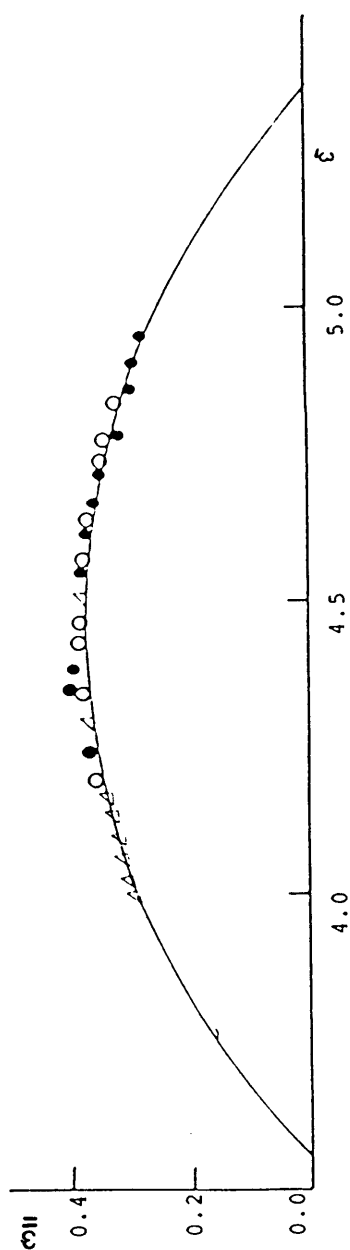


Figure (4.33) Argand diagram of real and imaginary permittivity for 8% carbon black in polychloroprene.

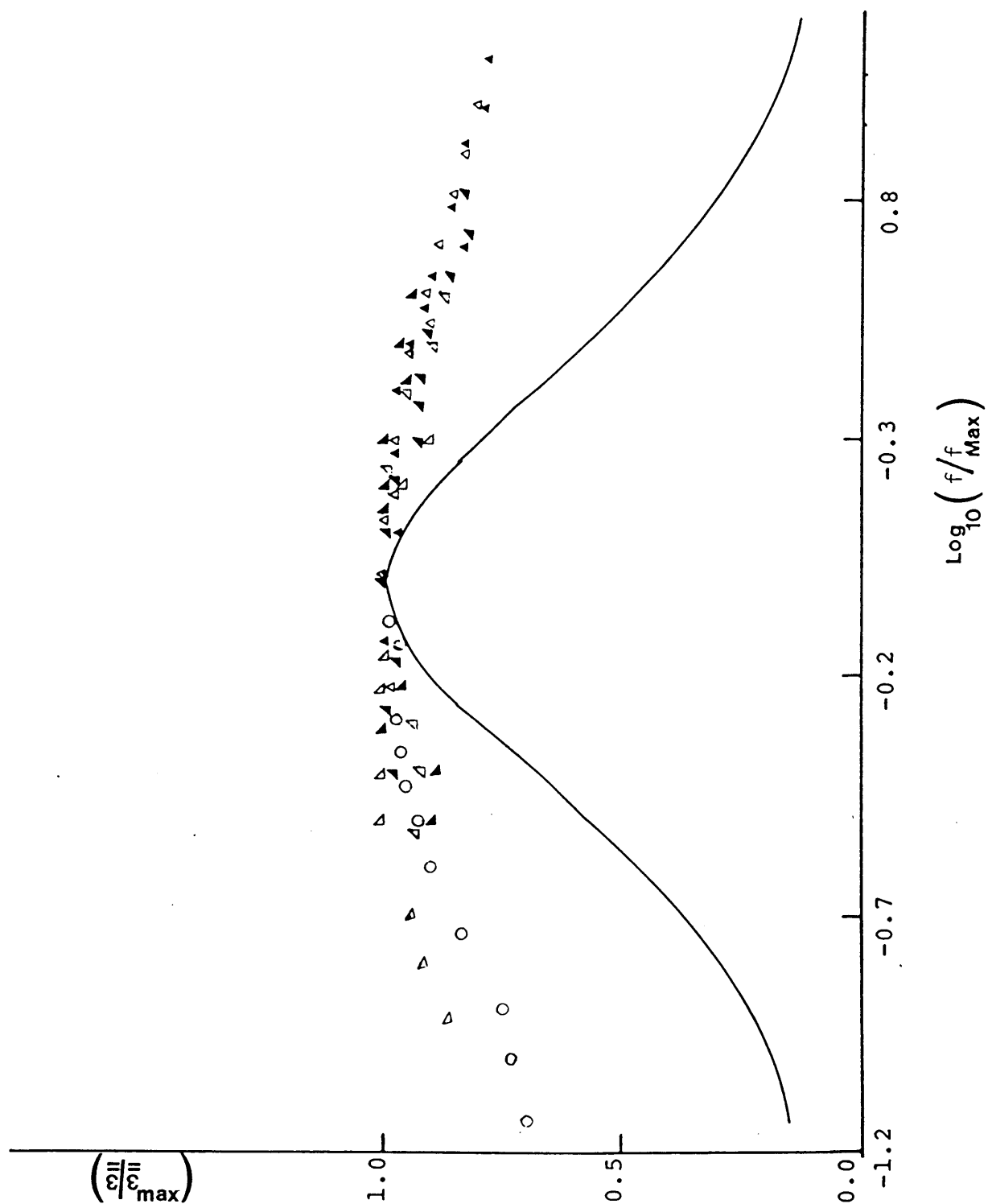
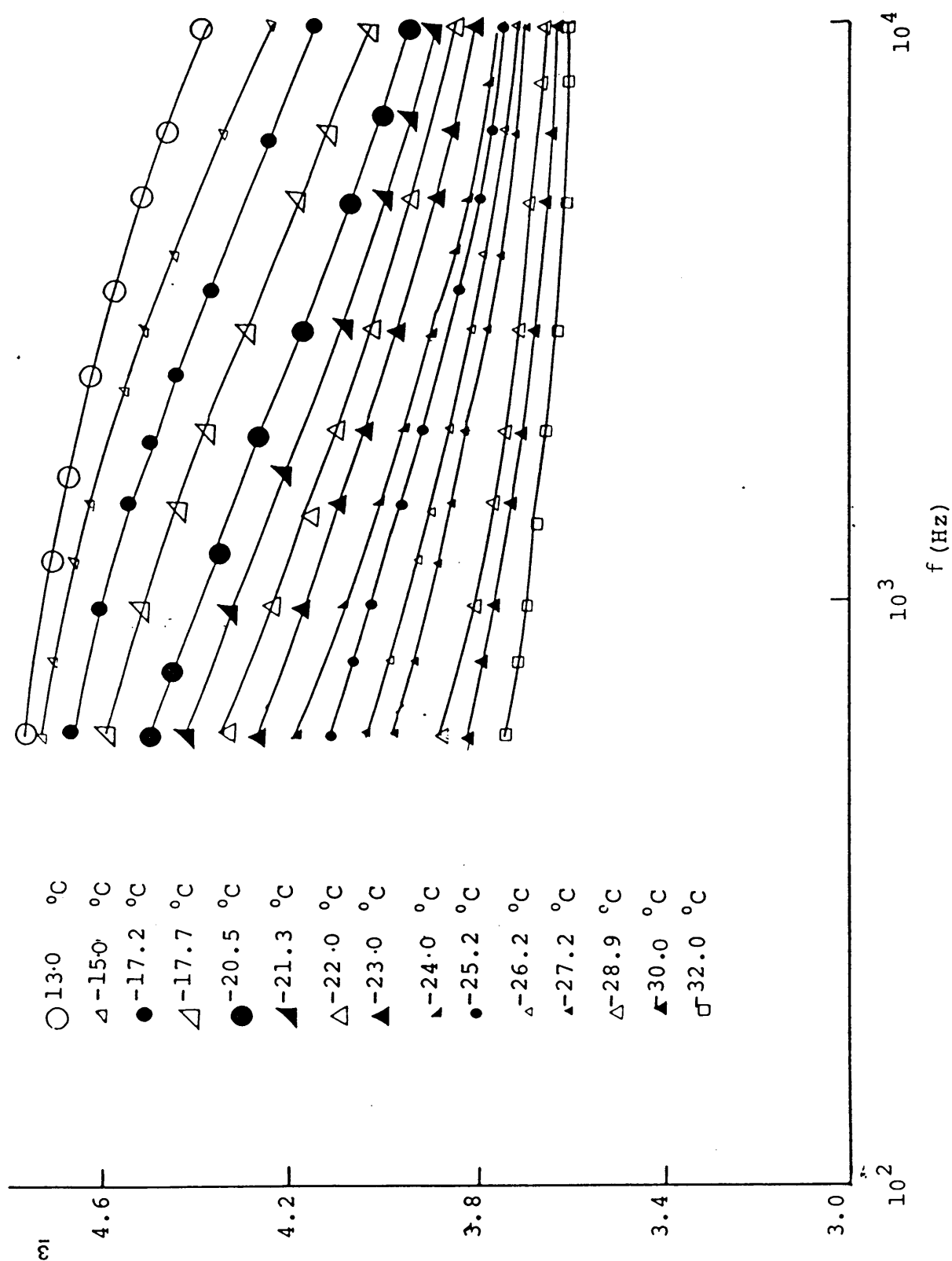


Figure (4.34) Variation of the logarithm of the normalized dielectric loss with normalized frequency for 8% carbon black in polychloroprene.



Figure(4.35) The frequency dependence of ϵ' at various fixed temperature for 12% carbon black in polychloroprene.

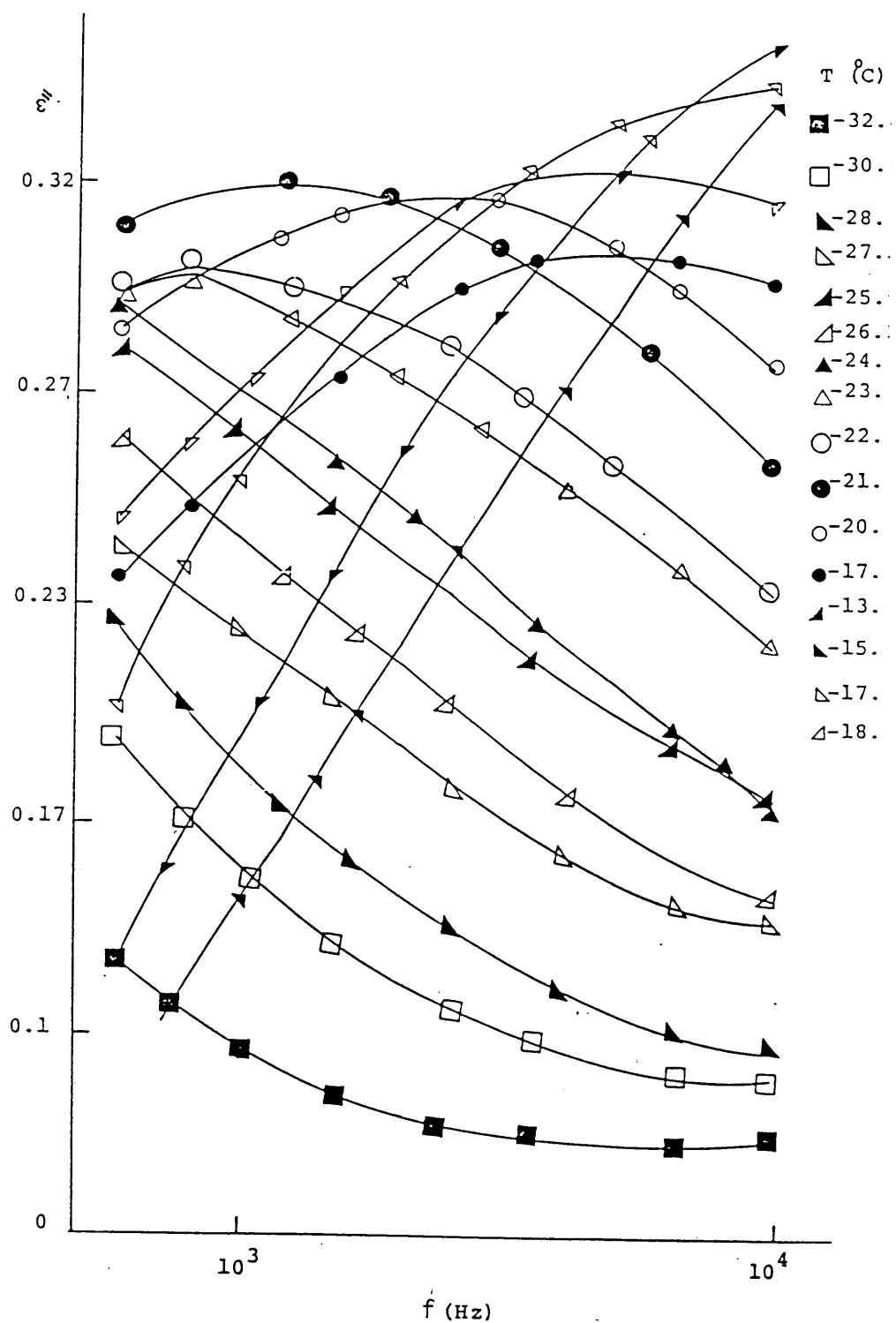


Figure (4.36) The frequency dependence of $\bar{\epsilon}$ at various fixed temperature for 12% carbon black in polychloroprene.

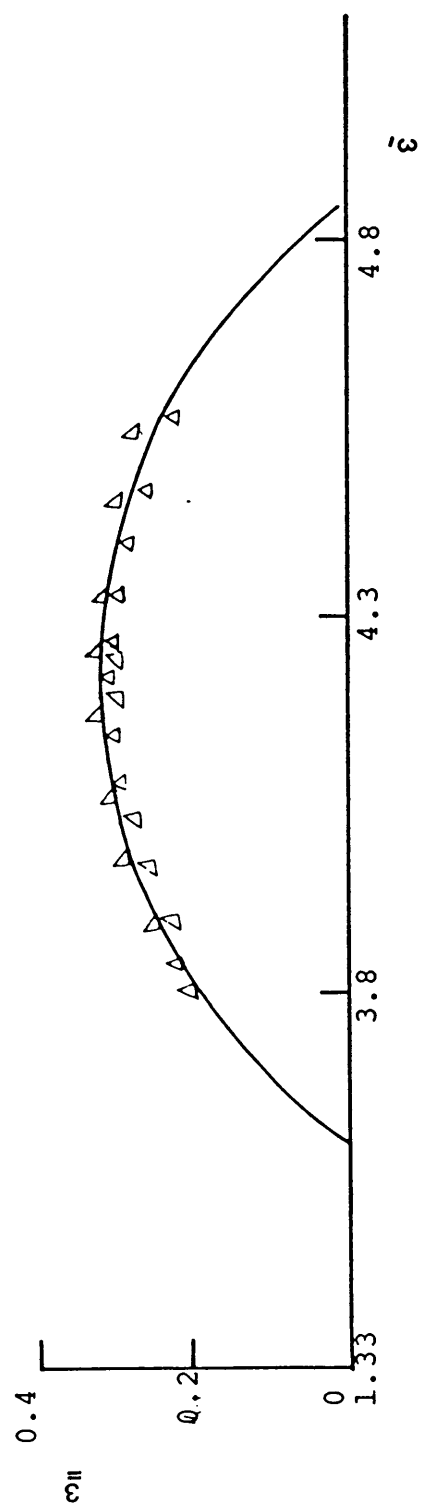
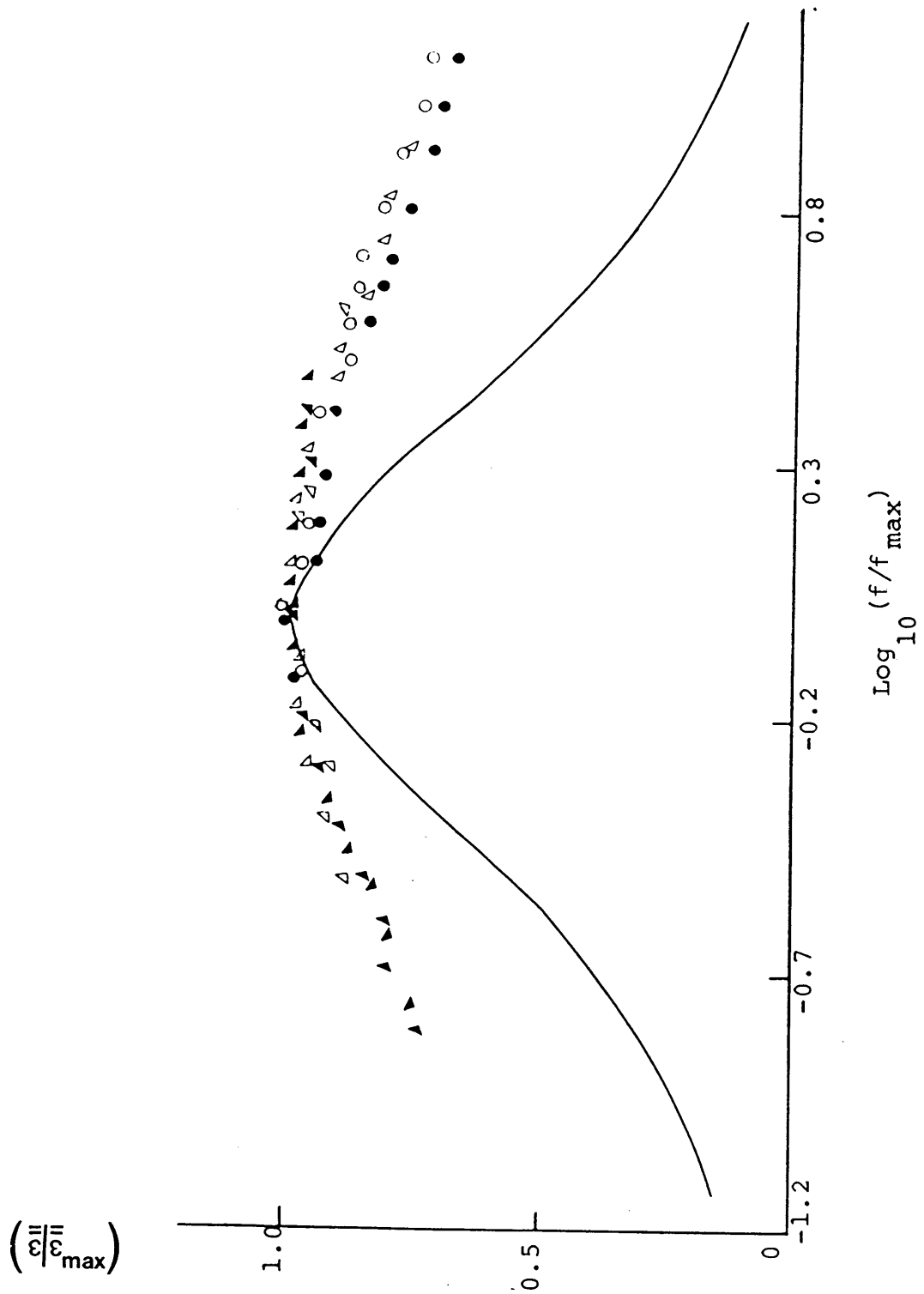


Figure (4.37) Argand diagram of real and imaginary permittivity for 12% carbon black in polychloroprene.



Figure(438) Variation of the logarithm of the normalized dielectric loss with normalized frequency for 12% carbon black in polychloroprene.

Table 4.2. Summary of the Results of α Relaxation at High Temperature for Polychloroprene and Carbon Black Filled Polychloroprene Samples.

Material	Data
0% CB in PCP	$\alpha = 0.5, \quad \beta = 1,$ $\lambda = 2.4 \quad \Delta E_a = 160 \text{ kJ/mole (1.66 eV)}$
4% CB in PCP	$\alpha = 0.5, \quad \beta = 0.85,$ $\lambda = 2.4, \quad \Delta E_a = 156 \text{ kJ/mole (1.52 eV)}$
8% CB in PCP	$\alpha = 0.5, \quad \beta = 0.85,$ $\lambda = 2.4, \quad \Delta E_a = 190.4 \text{ kJ/mole (1.97 eV)}$
12% CB in PCP	$\alpha = 0.5, \quad \beta = 0.85,$ $\lambda = 2.4, \quad \Delta E_a = 168 \text{ kJ/mole (1.74 eV)}$

Two affects appear from these studies:-

- (i) the variation of the activation energy with carbon black content
- and, (ii) the relaxation increment.

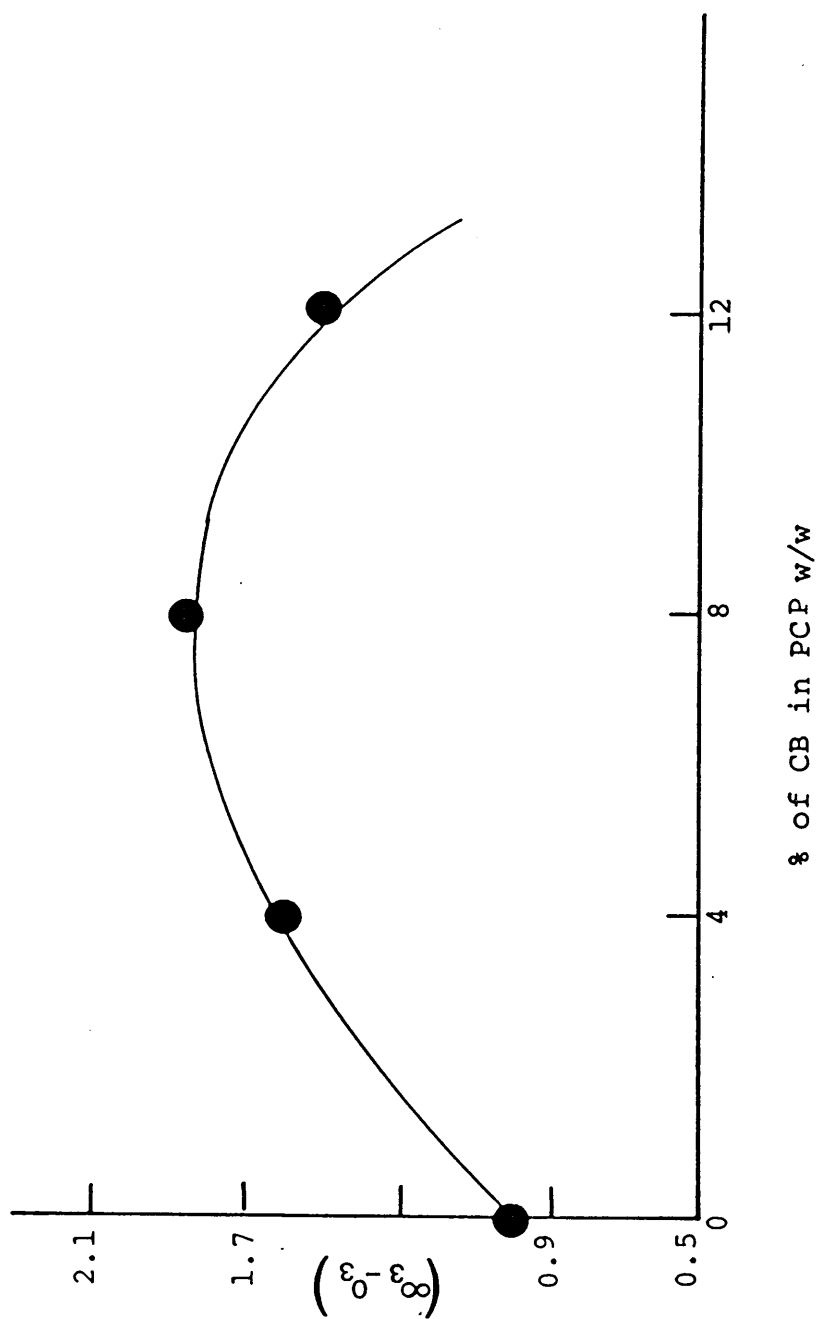
The process being monitored is the reorientation of the C—Cl dipole. An initial decrease in the activation energy may be due to the error in determining the activation or can also be ascribed to the carbon black opening the matrix. But it is clear that this decreasing effect is very small if present at all. Further addition of carbon black leads to an increase in the activation energy consistent with

either removal of free volume or adsorption of chains into the carbon black surface. Still further addition of carbon black leads to a return of the activation energy to a low value but also a reduction in the magnitude of the relaxation increment. This observation is consistent with the idea of a reduction in dipole activity either due to strong adsorption or the dilution effect of the carbon black. It is not possible to differentiate between these two mechanisms. It has been reported previously with the change in carbon black content, there was no effect on the value of (α) and (λ) but there is a slight change in the value of (ΔE_a) and (β) . There is an affect on the magnitude of absorption $(\epsilon_0 - \epsilon_\infty)$, (ϵ_∞) , $(\bar{\epsilon}_{\max})$ and $(\bar{\epsilon}_{\max})$ as the amount of carbon black is increased as shown in figures 4.39, 4.40, 4.41 and 4.42.

This means the addition of carbon black to the polymer can lead to the creation of the filler polymer interaction and these influence the relaxation processes which occur in the composite (19).

4.4. Powles Relation and the Study of Change in the Dielectric Amplitudes of Carbon Black Filled Polychloroprene

Analysis of the shift of the dielectric loss with varying amounts of carbon black, indicates that the addition of the carbon causes a shift initially to low frequency and then a shift to high frequency. The motion of a dipole will depend on the dielectric properties of the environment in which it resides. The effect of introducing a filler of different dielectric properties from that of the matrix might be expected to lead to a change in the effective local permittivity and hence to the motion of the molecular dipole. In this study, Powles relationship (20) has been used in order to examine the effect of change in dielectric permittivity on the relaxation. A variation of



Figure(4.39) Variation of the magnitude of absorption with the concentration of carbon black in polychloroprene .

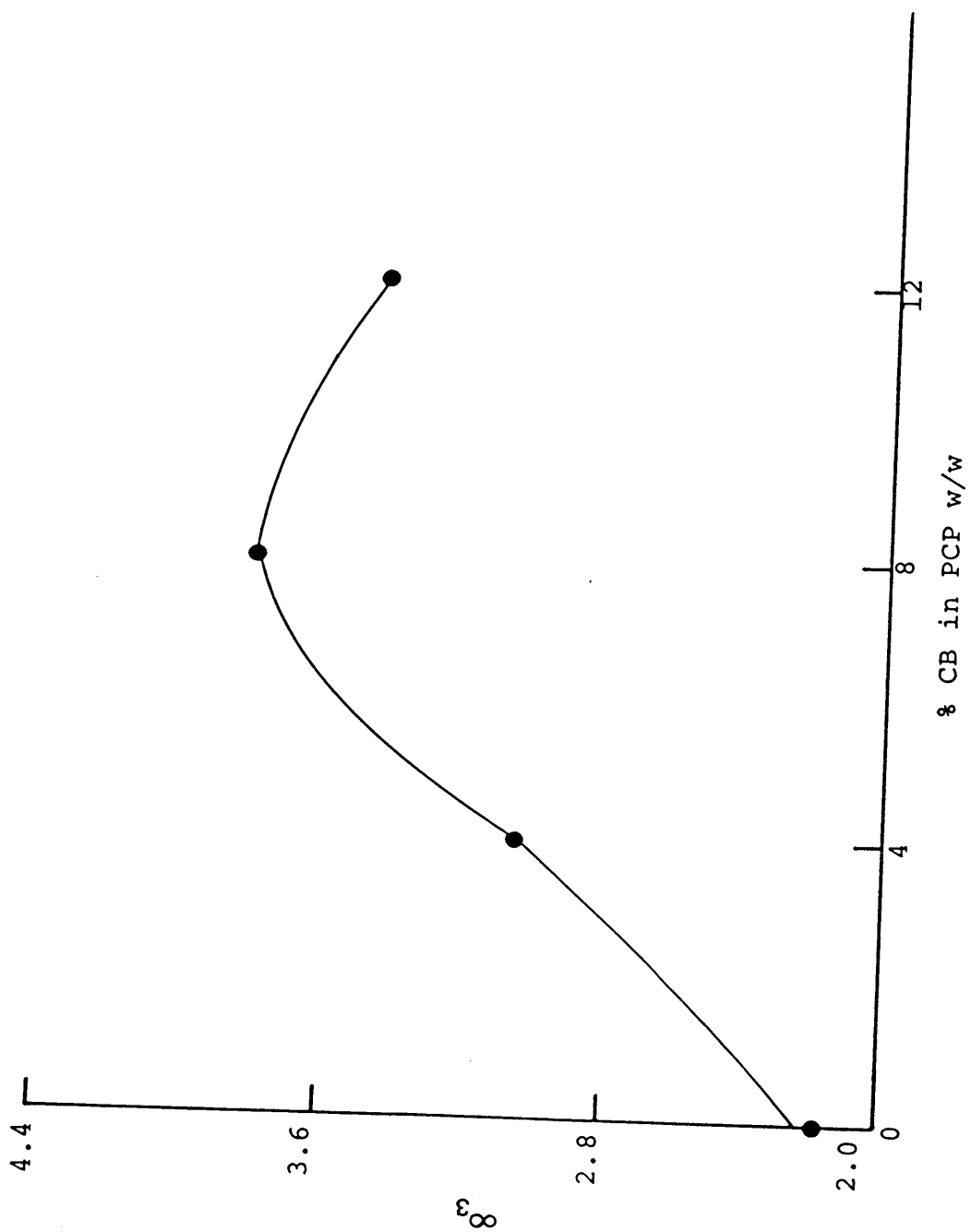


Figure (4.40) Variation of dielectric constant at high frequency with concentration of carbon black in polychloroprene.

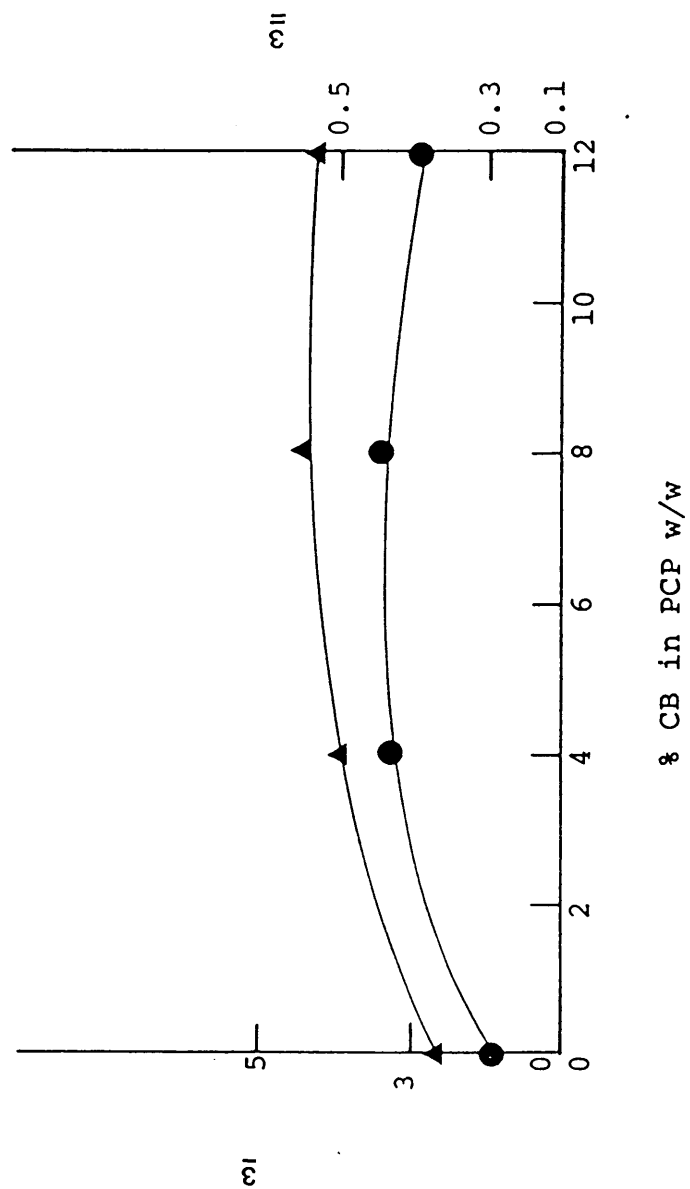


Figure (4.41) Variation of dielectric constant and dielectric loss at the maximum with the concentration of carbon black in polychloroprene.

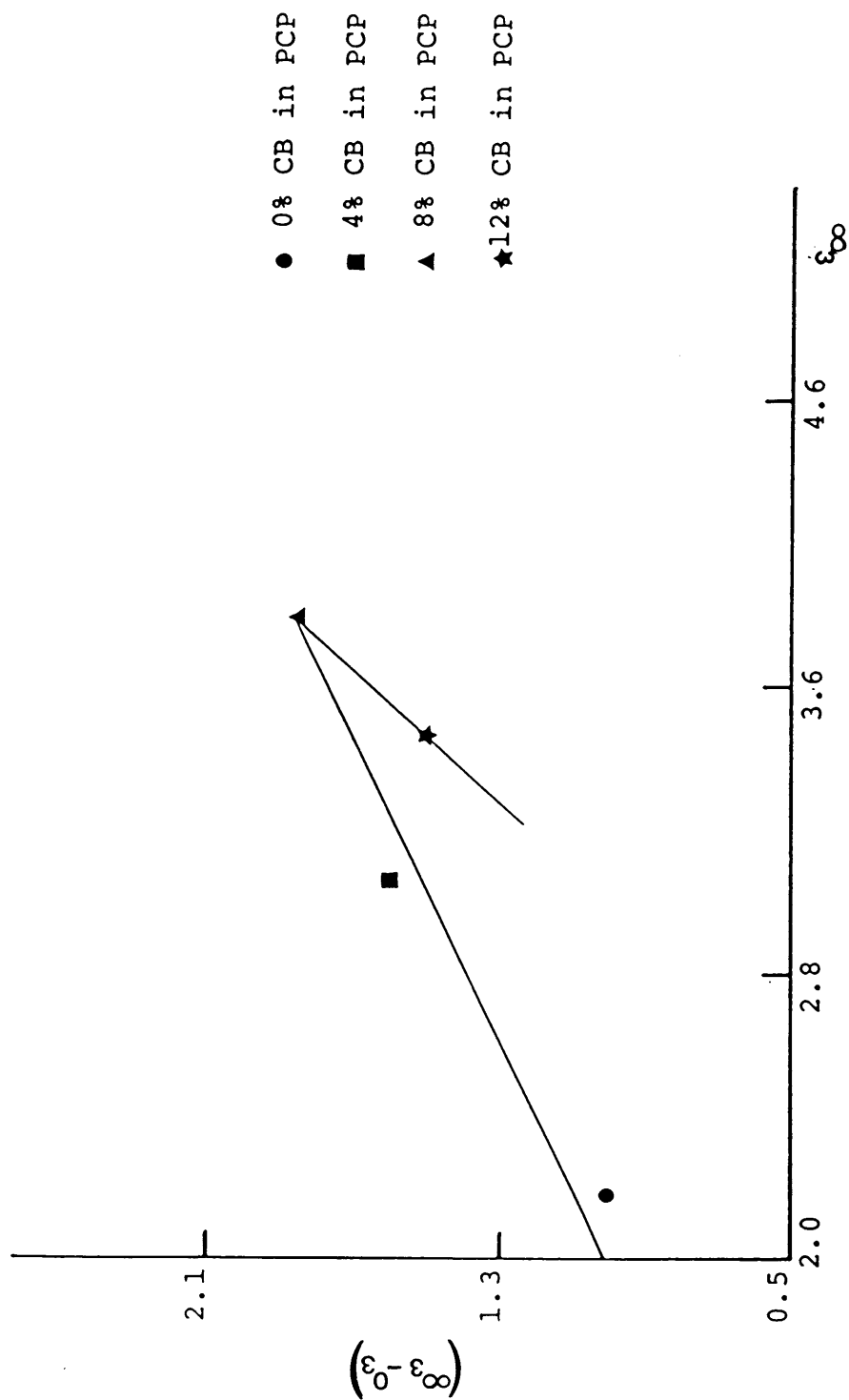


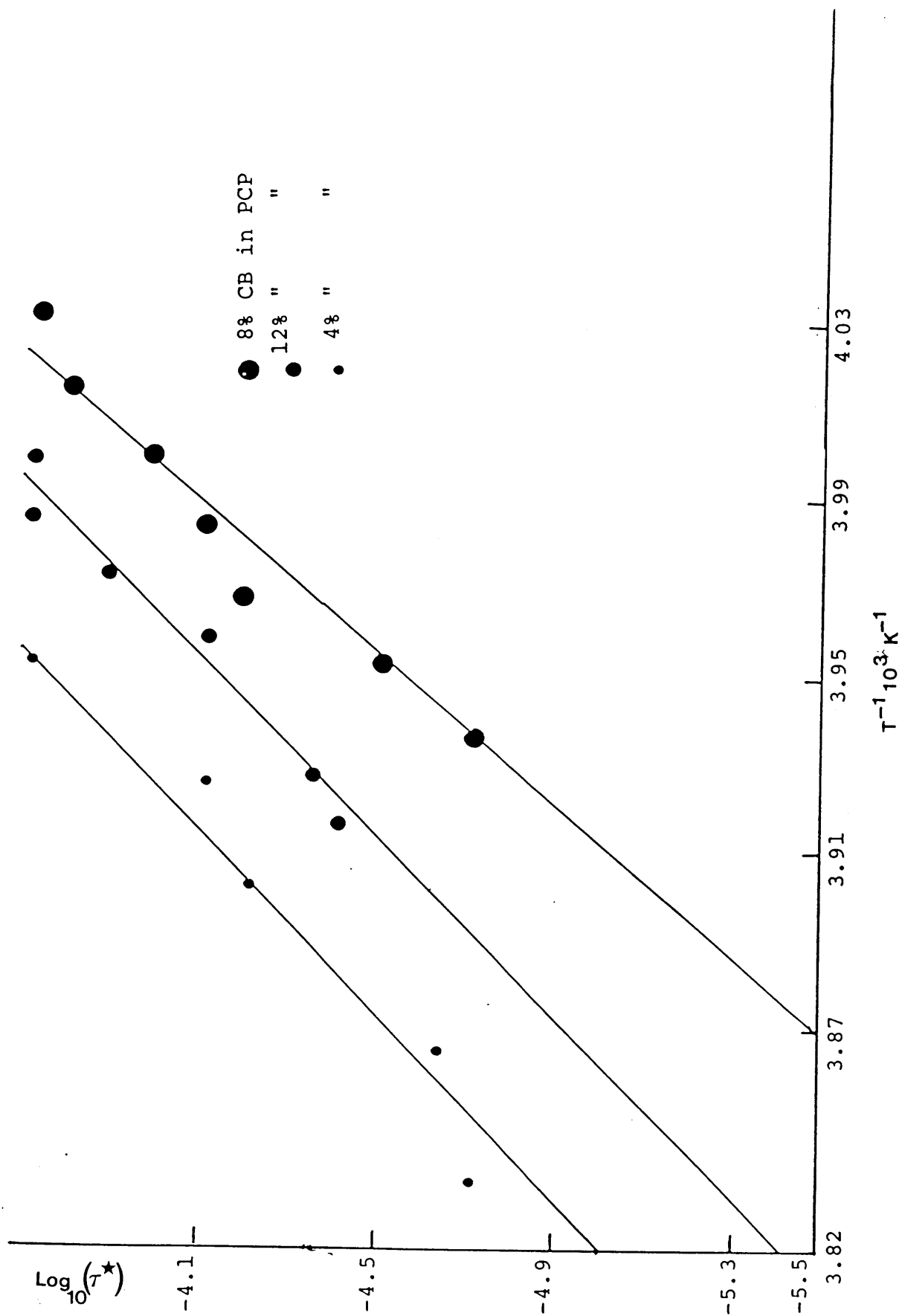
Figure (4.42) Variation of the magnitude of absorption with the dielectric constant at high frequency.

logarithm of (τ) with reciprocal of temperature is shown in fig. 4.43 and table 4.3. Analysis of the data indicates $\frac{\tau^*}{\tau}$ is not unity, this means that the dielectric effect does not explain the observed effects of the shift in the position of the dielectric loss on the temperature axis. It can be seen that shifts are not simply described by the change in the bulk permittivity of the sample and it is probable that these shifts are really the manifestation of real changes in the polymer matrix.

4.5 Discussion

4.5.1 Influence of Carbon Black on the Dielectric Relaxation of Polychloroprene

It is found experimentally that the addition of carbon black to the polymer can lead to the creation of filler-polymer interactions and these may be expected to influence the molecular relaxation processes occurring in the composite. Interaction between polymer chains and the surface of the carbon black can lead to a reduction in the mobility of the dipoles and this will cause a broadening of the relaxation towards the low frequency side of the curve as in the 8 and 12 percentage by weight of carbon black in polychloroprene samples. Alternatively, the filler can open the chain structure creating additional free volume and either lower the (T_g) (glass-transition temperature, i.e. the glass-to rubber transition) or broaden the relaxation towards the high frequency as in the 4 percentage by weight of carbon black in polychloroprene samples. It is assumed in all these cases the changes in dielectric behaviour are associated with motion of dipoles attached to the polymer. It was found in this study that the dielectric effect is not dominant because the ratio $\frac{\tau^*}{\tau}$ depends



Figure(4.43) Variation of the logarithm of time constant for the immediate molecular dipole relaxation with reciprocal temperature for carbon black loaded polychloroprene.

Table 4.3. Variation of the logarithm of time constant for the immediate molecular dipole relaxation with reciprocal of temperature for carbon black loaded polychloroprene.

4% CB in PCP			8% CB in PCP			12% CB in PCP		
$T^{-1} 10^3 \text{ K}^{-1}$	$\log_{10} \tau^*$	τ^*/T	$T^{-1} 10^3 \text{ K}^{-1}$	$\log_{10} \tau^*$	τ^*/T	$T^{-1} 10^3 \text{ K}^{-1}$	$\log_{10} \tau^*$	τ^*/T
3.836	- 4.724	0.95	3.937	- 4.724	0.95	3.917	- 4.419	0.96
3.866	- 4.635	0.95	3.953	- 4.509	0.97	3.928	- 4.363	0.95
3.902	- 4.219	0.95	3.968	- 4.199	0.99	3.959	- 4.119	0.95
3.926	- 4.122	0.95	3.984	- 4.113	0.97	3.973	- 3.898	0.95
3.953	- 3.728	0.94	4.000	- 3.987	0.97	3.986	- 3.722	0.95
			4.016	- 3.811	0.97	4.002	- 3.721	0.96
			4.032	- 3.725	0.95			

upon the system and indicates that other effects in the system are responsible for these changes in the dielectric relaxation.

4.5.2 Influence of Carbon Black on the Conductivity of Polychloroprene and Polystyrene

The dispersion of the carbon black in the matrix has a profound effect on the conductivity as shown in CB/PS and CB/PCP composites. At very low carbon black loading, the conductivity of the composite is low and is close to that characteristic of the polymer matrix. Increasing the concentration of carbon black increases the conductivity of the matrix which is also reflected in relaxation characteristics.

Increasing the concentration of carbon black increases the probability of hopping between the particles. At high concentration a saturation value characteristic of the carbon black itself is obtained. The nature of the dispersion helps to determine the dielectric constant of the matrix which in turn reflects the conductivity of the composite.

There is a connection of $\Delta\bar{\epsilon} = \bar{\epsilon}_{\text{sample}} - \bar{\epsilon}_{\text{unfilled}}$ against dispersion:-

Two situations can be identified, (i) good dispersion of carbon black particles and, (ii) poor dispersion of carbon black particles.

i. Good dispersion of carbon black particles

Let the number of charge carrier be n_i then the increment ($\Delta\bar{\epsilon}$) will be proportional to n_i but in this case the displacement is small and hence the increment is small, which is consistent with a low conductivity.

ii. Poor dispersion of carbon black particles

Touching carbon black particles form the conducting chains: If

the carrier level is the same as above, then the increment ($\Delta \bar{\epsilon}$) is increased by the number of particles forming the chain. Hence the increment is directly proportional to the length of the carbon black chain. The sample at 8% carbon black appears to have a poor dispersion, which is confirmed optically, than the samples of lower carbon black content. Therefore, it has higher conductivity. Further increase in carbon black content beyond 8% increases the conductivity reaching a maximum value at 24% of carbon black content.

It is concluded, therefore, that a correlation exists between the dispersion of carbon black and the conductivity of the polymer composites.

4.5.3 Electronic Conduction Mechanism on the Carbon Black Composites (Carbon Black Filled Polystyrene and Polychloroprene)

The data pertaining to the moderately conducting carbon black composites have been chosen for discussion because of the three points:- (i) frequency dependent conductivity, (ii) frequency independent conductivity and, (iii) because of the conductivity decays with frequency and reaching a limiting value which does not decay further with frequency. This is indicative of the bulk conduction saturation having been achieved as shown in fig. 4.8.

A conductivity which increases with frequency is usually interpreted as evidence for hopping-type conduction rather than unrestricted (not-trapped) band-type conduction.

There are three mechanisms of charge transport observed in this study which can contribute to the a.c. conductivity as follows:-

a) Transport by carriers (electron or holes) excited to the extended

states near E_C or E_V which is indicated by the conductivity independent on the frequency i.e. does not follow $\sigma(\omega) \propto \omega^S$ and have been found for 15% and above CB/PCP and 7% and above CB/PS in the frequency range 600 Hz to 10 kHz.

b) Transport by carriers excited into the localized state at the edges of the valence or conduction band i.e. the conductivity dependence on the frequency, indicates that conductivity follows the typical law $\sigma(\omega) \propto \omega^S$.

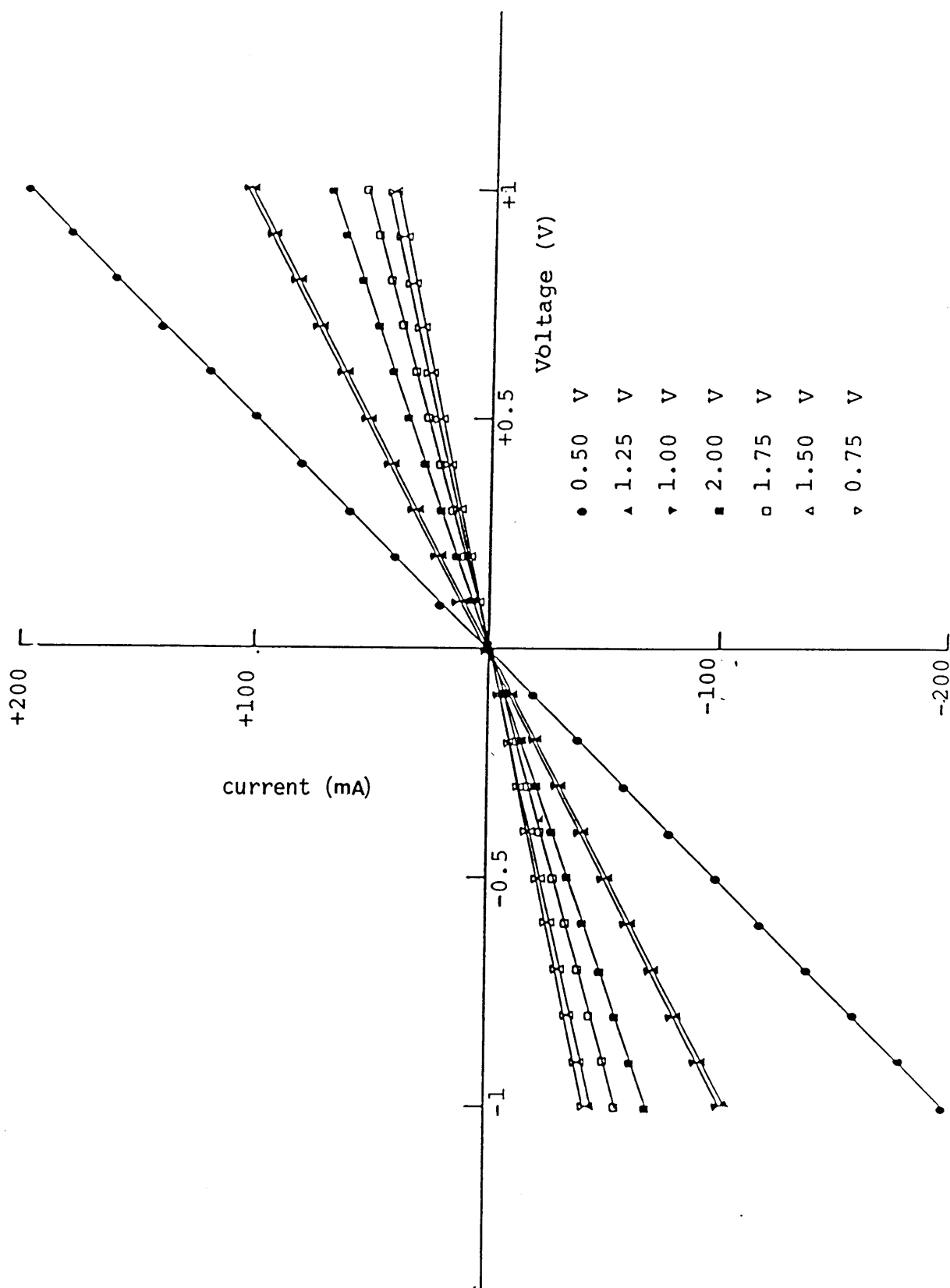
c) Hopping transport of electrons with energies near the Fermi level provided $N(E_F)$ is finite. The frequency dependence predicted by Austin and Mott can be written as $\sigma(\omega) \propto \omega^S$. In the present study, a, b or c mechanisms have been found to be applicable for 1 to 14% CB/PCP and 1 to 6% CB/PS in the frequency range of 600 Hz to 10 kHz. They are represented in figures 4.5 and 4.12 for CB/PS and CB/PCP respectively.

Part II: Electrical Properties of Polypyrrole Para-Toluene Sulfonate

4.6 D.C. Measurement Results

A) Effects of variation of current with the applied voltage (I-V) plots

The current voltage characteristics plotted for PPTS prepared at various voltages in the range 0.5V to 2V are given in figure 4.44. Straight line plots are obtained for voltage versus current measurements as expected if the material exhibits ohmic characteristics. From these graphs it is clear that the (I-V) relationship is ohmic within the measured range of applied voltage. It was also found there was no

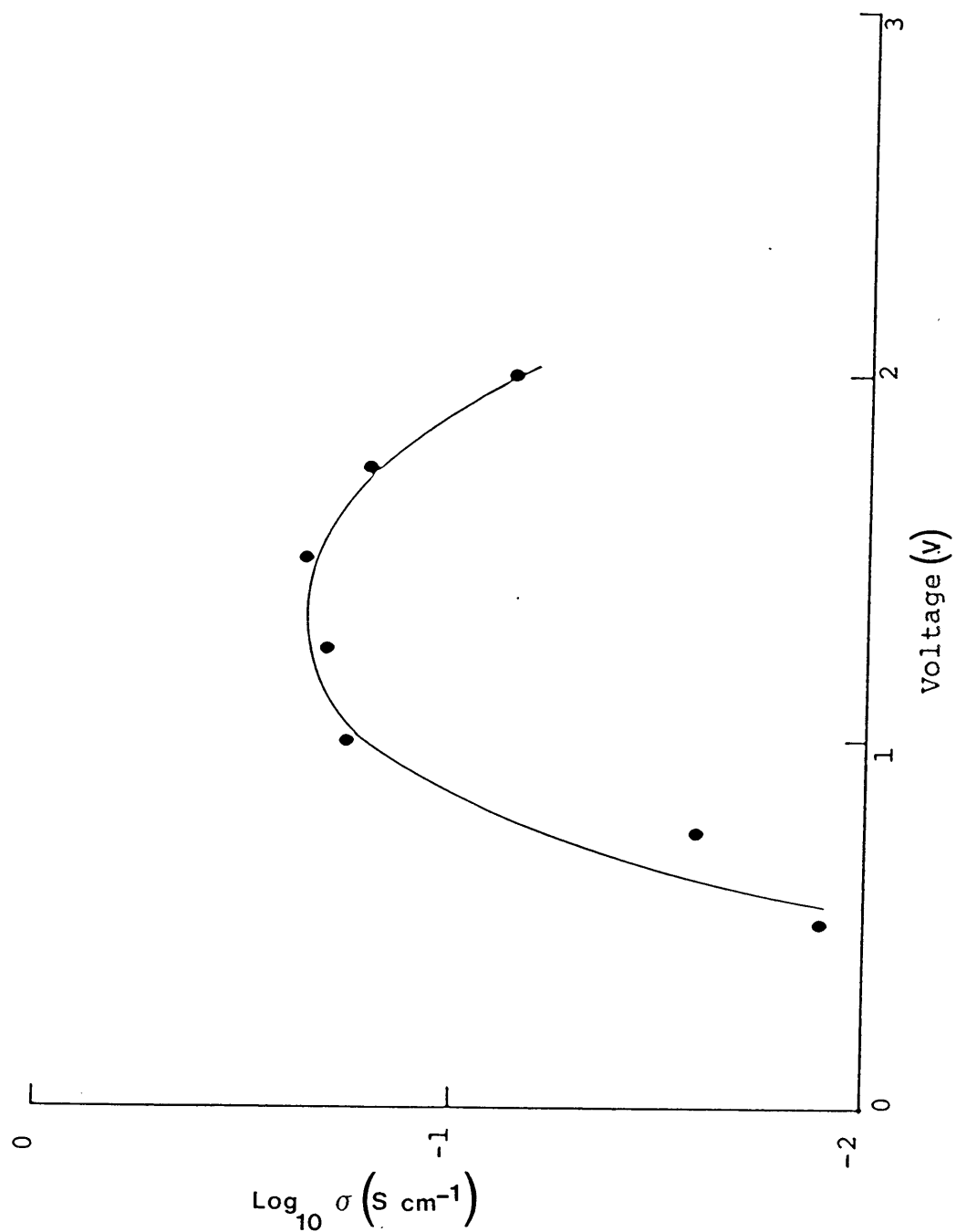


Figure(4.44) Variation of current with voltage of PPTS prepared at various voltages.

effect of the ambient atmosphere on the measurements, data having been obtained under normal atmospheric pressure, vacuum and also under nitrogen and produced the same results. Ohmic conduction is rather surprising as one would expect that during conduction, mass transport of the counter ions might occur and this would lead to internal field gradients which would generate non ohmic conduction. This data clearly indicates that this is not the case, however, it does not indicate the nature of the conduction process occurring in these systems.

B) Effects of variation of voltage on the preparation of polypyrrole para-toluene sulfonate and study of its conductivity

The conductivities of films of polypyrrole synthesized at one salt concentration and a range of potentials 0.50 to 2.00 volts are shown in fig. 4.45. It is found that as the voltage is increased the conductivity increases until a critical voltage is reached (1.50V), a further increase in the voltage leads to a decrease in the conductance. The oxidation reduction potential determined by cyclic voltametry for this film is close to this value. Decrease in the conductivity probably reflects the fact that as the growth rate (see section D) is increased the amount of anion incorporated may be slightly reduced and this variation might be as little as 0.5% and would probably lead to a decrease in the hopping probability, hence, the observed decrease in the conductivity. We shall consider this point later in this chapter. There is some doubt regarding the accuracy of the thickness of these films and hence, of the absolute values of the conductivity, however, the relative trends are significant. The rise in the conductivity does not appear to correlate with any significant variation in the elemental composition. The rise in the conductivity of the polypyrrole films



Figure(4.45)Variation of conductivity with voltage of PPTS used in the preparation of these films.

must clearly be connected with changes in the film structure which are evident in its optical texture. The maximum conductivity coincides with the oxidation reduction voltage and implies that the oxidised state of the film is also of importance. We will discuss these effects later.

C) Effects of variation of conductivity with the temperature

The conductivity and temperature characteristics plots are shown in fig. 4.46. It is found from these graphs that the conductivity increases with temperature for films prepared at voltage above 1V, and decreases for films prepared at voltages below 1V. In general the conductivity slightly increases and decreases with temperature in both the cases as shown in fig. 4.46 i.e. the conductivity is slightly dependent on temperature and such a behaviour suggests a hopping or metallic conduction mechanism (21-31). From fig. 4.46 and table 4.4 the activation energy of PPTS films have been estimated. These values are low which is consistent with the high values of the conductivity of these materials.

Table 4.4. Variation of Activation Energy with the Voltage Applied in the Preparation of PPTS

Voltage V	Activation energy $\times 10^{+3} \text{ eV}^{-1}$
0.5	-7.72
0.75	-7.73
1.00	-3.51×10^{-3}
1.25	+ 1.28
1.50	+ 6.97
1.75	+ 5.02
2.00	+ 3.42

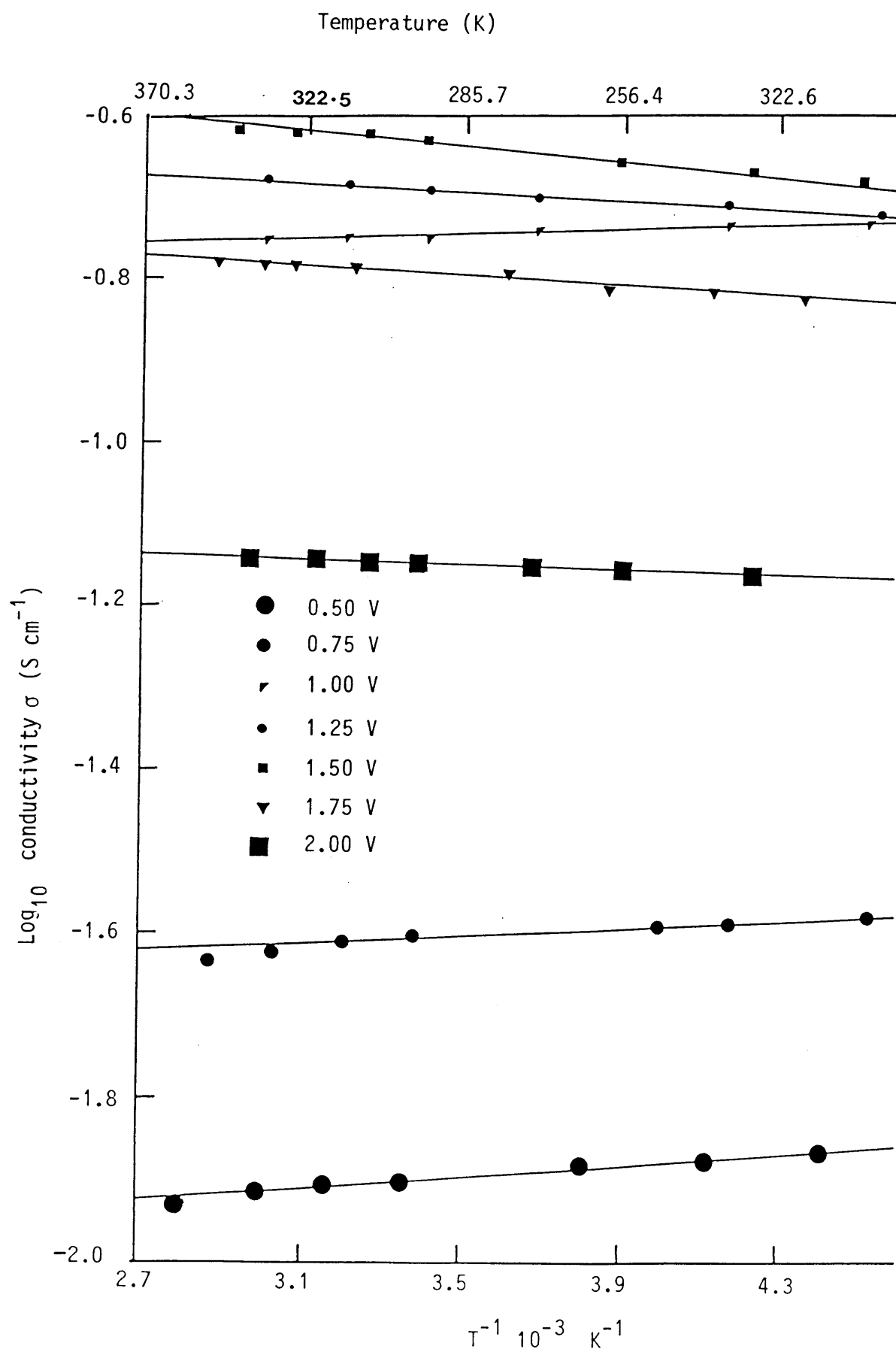


Figure 4.46. Temperature dependence of the conductivity (σ) of PPTS prepared at various voltages.

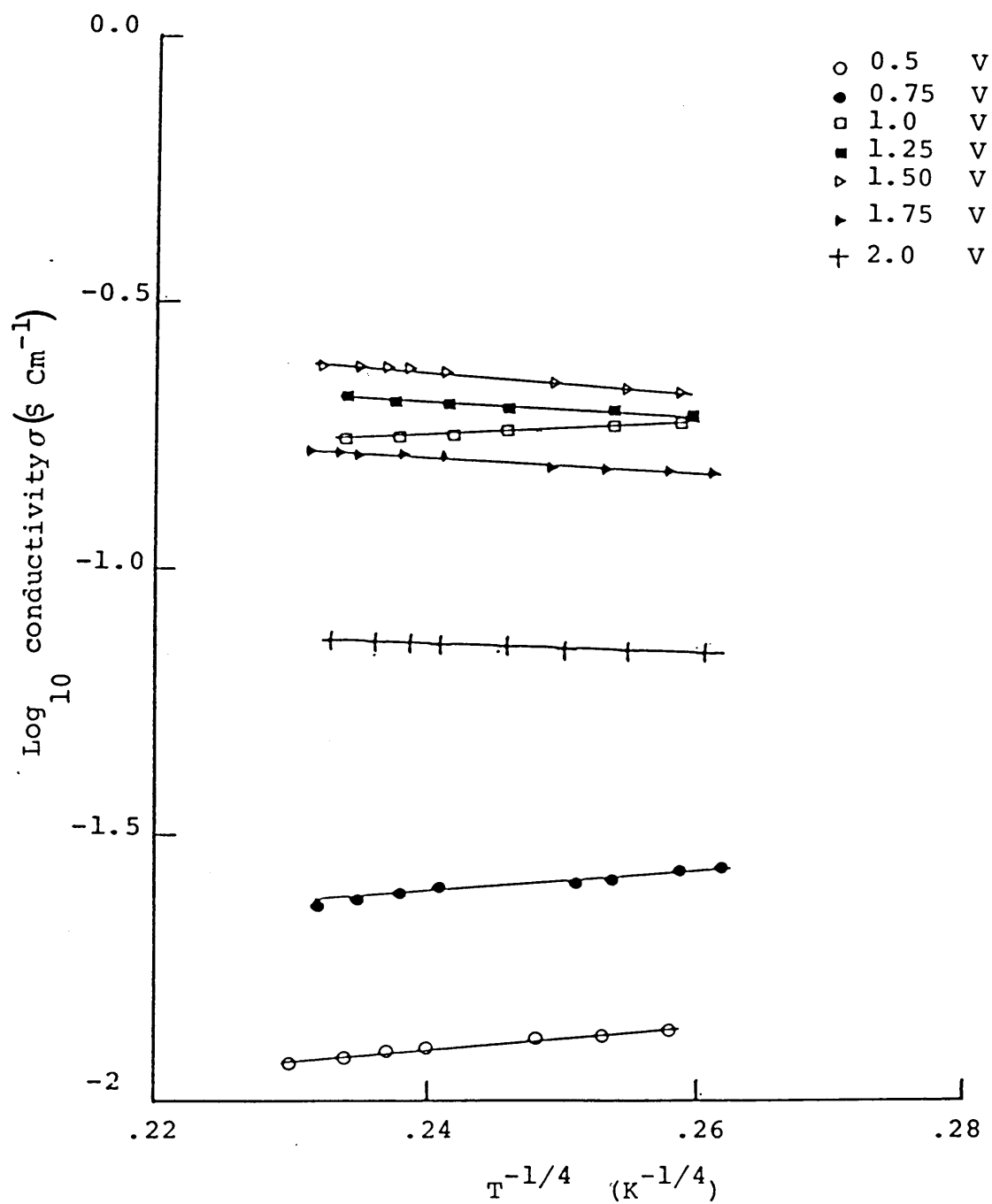
The data, although very restricted in temperature range, shows reasonable linearity when plotted as $\log_{10} \sigma$ versus $T^{-1/4} K^{-1/4}$ as shown in fig. 4.47. This functional form is predicted by model for so-called three dimensional variable range hopping (32-34), which is in agreement with the data of other workers (24,28, 35-43).

D) Effects of variation of salt-electrolyte concentration in the synthesis of films and subsequent effect on the conductivity of films

The effect of variation of the salt-electrolyte concentration is shown in fig. 4.48, the concentration of freshly redistilled pyrrole was held constant at 0.01m and the potential used in the growth of the films was maintained constant at 1.0V. An increase in the salt concentration (silver para-toluene sulfonate) during the preparation from a value of 0.001 to 0.1m has a marked effect on the conductivity of the films produced. The initial increase is very marked, thereafter the rise is slower. Elemental analysis of the films did not indicate any significant variation in the concentration of anion incorporated in the films, however, solvent contamination and other effects limit the precision of these data and do not preclude the possibility of variations of the order of 8% in composition. It was anticipated that the change in the electrolyte concentration might lead to different levels of anion incorporation, and this is consistent with the range of ratios of anion to monomer found in this study and also by Street et al.

4.7 Dielectric Measurement Results

In the case of the most insulating of the PPTS films the behaviour of the dielectric absorption could be observed. The real part and



Figure(4.47)Logarithm of the conductivity σ versus $T^{-1/4}$ for PPTs prepared at various voltages.

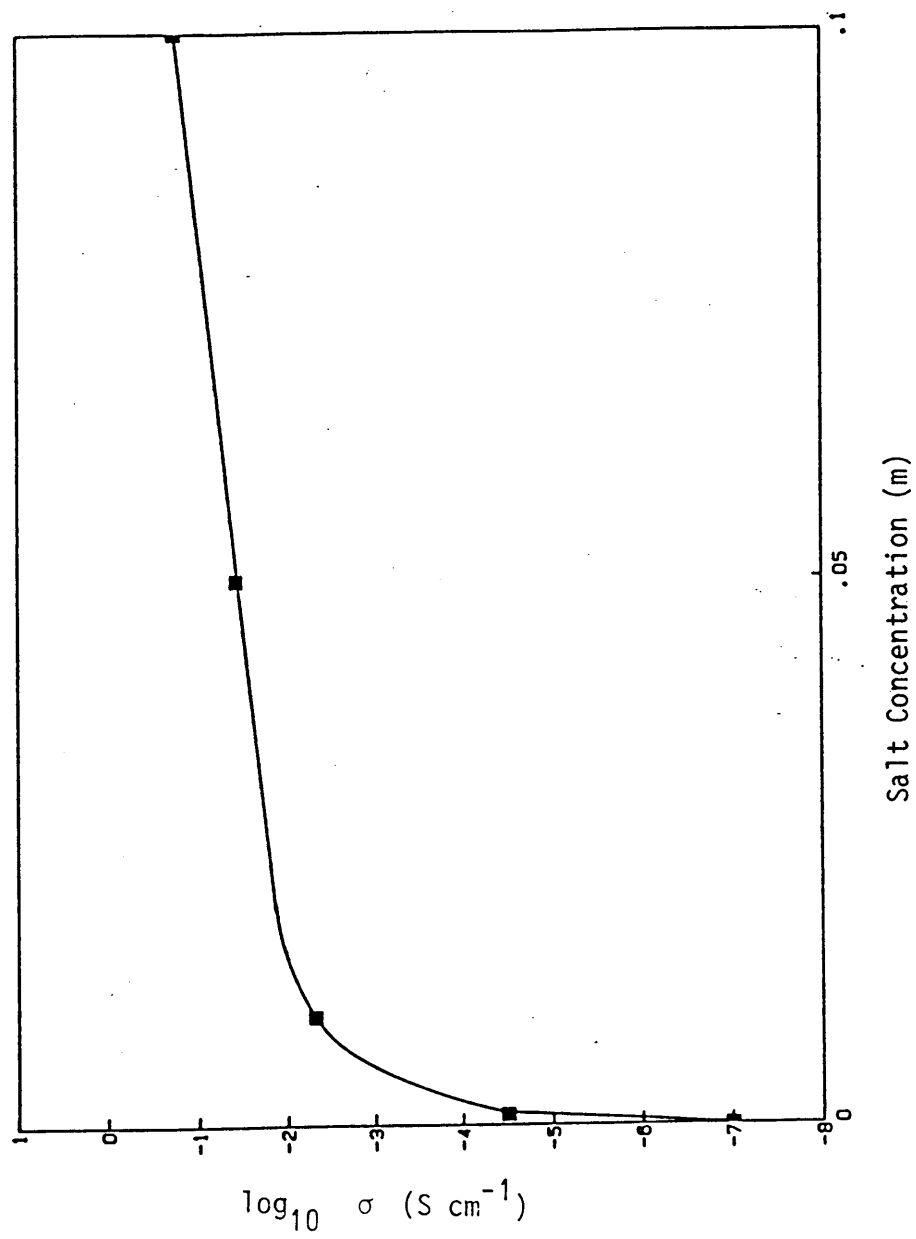


Figure 4.48 Variation of the salt-electrolyte concentration used in preparation of PPTS films with conductivity.

imaginary part of the complex permittivity are illustrated in fig.

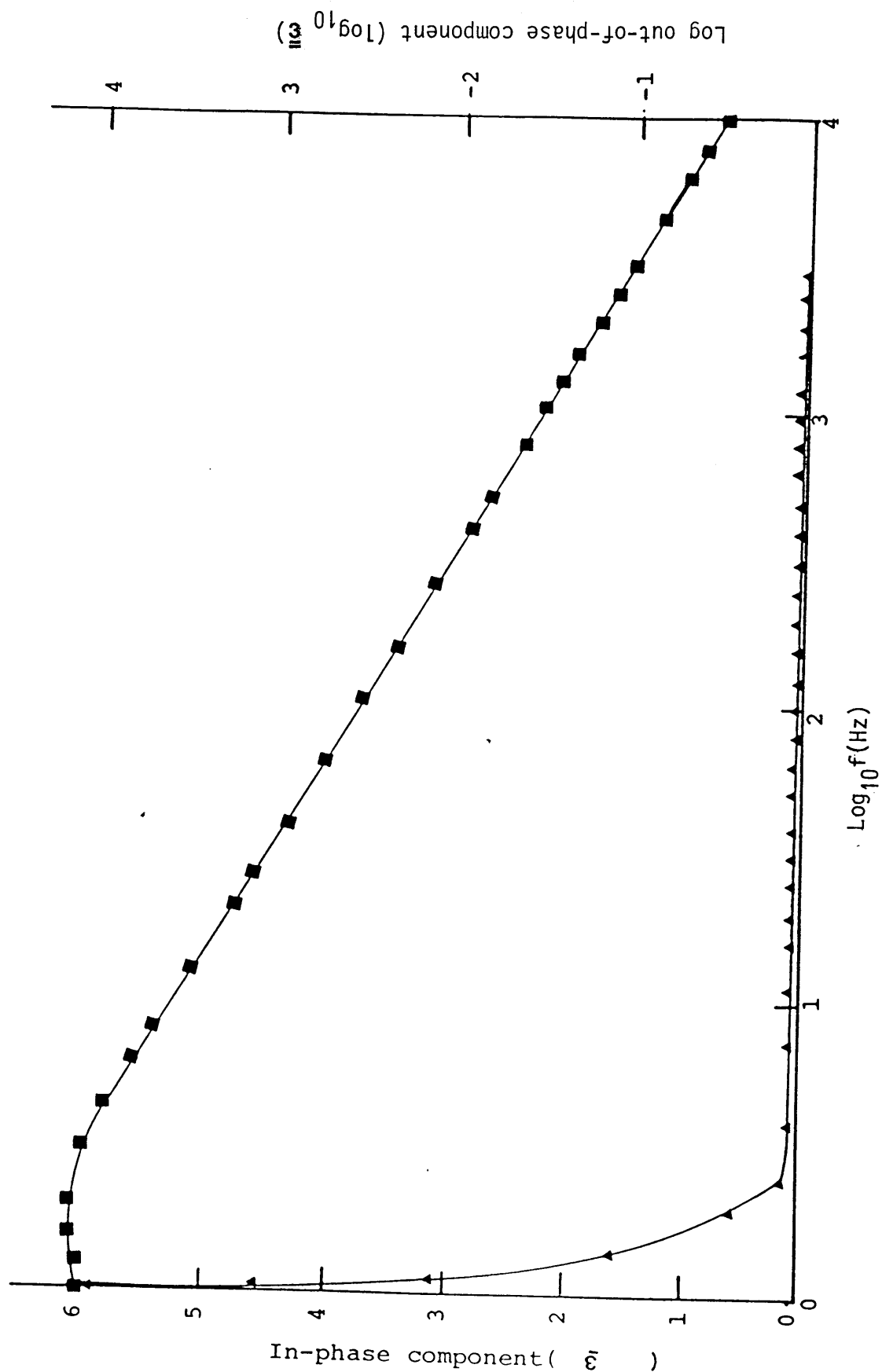
4.49. Dielectric constant ($\bar{\epsilon}$) increases with frequency and the rate of increase of ($\bar{\epsilon}$) with decreasing frequency is slow at high frequencies and increases rapidly at low frequencies. The imaginary part of the complex permittivity ($\bar{\epsilon}''$) is found to increase with decreasing frequency and the rate of increase of ($\bar{\epsilon}''$) with decreasing frequency is small at high frequencies and increases markedly at low frequencies. These results show that no clear relaxation process is observed at room temperature in the frequency range of these measurements and these effects may be associated with the conductance process.

4.8 Results of Variation of Anions and Cations in the Supporting Electrolytes, Electrolytes and Voltage on the Morphology of Doped Polypyrrole

Polypyrrole morphology is dependent on the conditions used in the preparation:-

A) Electrolyte variation

The electrochemical preparation of doped polypyrrole has been described previously, and the morphology dependence on the electrolyte has been recorded. The topology of the growing surface of the film is influenced by the electrolyte (44). The dielectric constant of electrolyte and the rate of growth increases proportionally; because changes in the electrolyte can alter the rate of growth as shown by changing the electrolyte study in the previous experiments. It is found that when the rate of growth increases it produces uniform films, however, at high growth rates the surface covered becomes irregular. This indicates that the rate of growth alters the morphology of the



Figure(4.49) Variation of dielectric constant and dielectric loss as a function of frequency at room temperature for PPTS film.

films. In addition the redox reaction is quite sensitive to the nature of the electrolyte, since it involves movement of the anion. The anion is a counter ion to the incipient cations on the polymer chain and hence can markedly influence the chain packing and also the interchain distances.

B) Cation variation

The action of the cations in the supporting electrolytes produces changes in the morphology of polypyrrole as shown in previous experiments. It is found that polypyrrole tetrafluoroborate has a different surface when prepared by different supporting electrolytes such as silver tetrafluoroborate and tetraethylammonium tetrafluoroborate. The mole ratio of anions has not been determined, but it might be possible that some form of complex bonding between the anions and the polymer is occurring. In the case of the silver salt the electrochemical process is simple, because the tetraethylammonium tetrafluoroborate will undergo a complex series of electrochemical processes, i.e. the counter ion species, however, have been shown to influence the conductivity of polypyrrole films as well as their morphologies (41,43,44). Differences in the morphology of this case must be attributed to the influence of the cation in the chemistry. Although the reactions involving the cation should occur at the other electrode, for electrical neutrality to be achieved it is necessary that the cations should be in the electrical double layer close to the growing polymer and this is probably the way in which they influence the structure of the growing films.

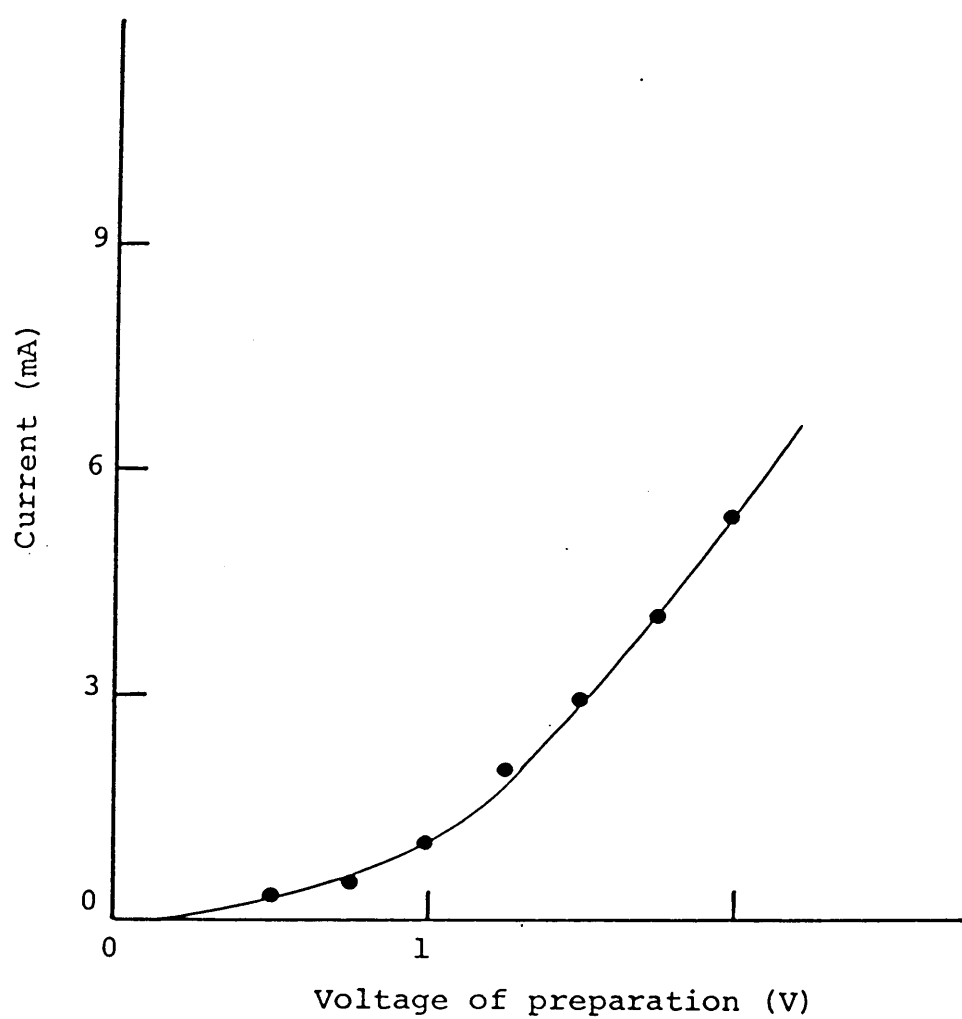
C) Anion variation

Variation of the anions also produces a small change in the flotation density of the films obtained and show very dramatic changes on the topology of growing surface. This variation changes the stability and conductivity of the films upon heating as shown experimently in polypyrrole perchlorate and polypyrrole para-toluene sulfonate. It is likely that these variations result from the chemical nature of the anions and not from the changes in the stoichiometry of the unit in the films which remains in the narrow range of 0.2 to 0.33. It is also possible that the growth rate will influence the micro structure and hence the polymer chain packing. This ratio agrees with the electrochemical results and again suggests that the level of oxidation of the polymer in the film is determined by the chemical nature of the polymer and much less by the nature of the anion. The anion of the electrolyte produced changes, as indicated by cyclic voltamogram for the oxidation reduction potentials of the polymer films. Changes in the size, shape, and charge on the anion can be expected to markedly influence the extent and type of chain packing which occurs and this will be reflected in the gross structure of the films of polypyrrole (44). The anion reacted chemically with the cationic polymer. This variation in the form of the voltamogram with anion was observed and explained in terms of the generation of electrochemically discrete centers in the film (45).

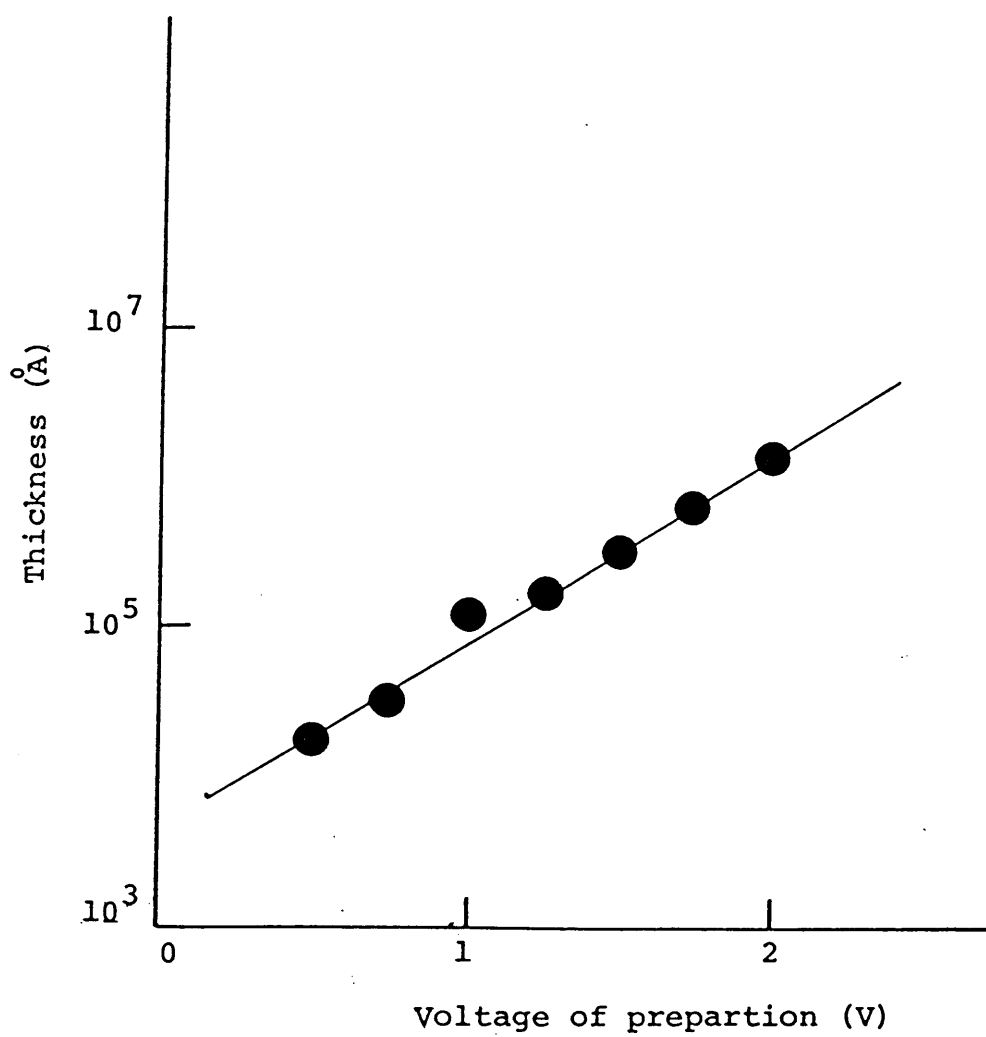
D) Voltage variation

Variations in voltages in the preparation of polypyrrole para-toluene sulfonate by the electrochemical methods played a role in the morphology and conductivity. It is found that as the voltage is

increased, the rate of growth of the films appeared to increase and also the thickness linearly altered as shown in figures 4.50 and 4.51 respectively. The rate of growth is dependent on the voltage at low voltages and is uniform. As shown in previous experiments on polypyrrole tetrafluoroborate and polypyrrole para-toluene sulfonate, different surfaces are obtained when prepared at different voltages. It was found by other workers (21,46,47) that polypyrrole tetrafluoroborate of different thicknesses produced different cyclic voltamogram. The cyclic voltamograms are produced when polypyrrole tetrafluoroborate electrode in pure (blank) electrolyte with a platinum electrode are used. Only a broad background current is observed with the thicker films (0.8-5 μ m) (21,46,47), while thinner film (.1 μ m) give a broad peak near 0.2V (48) due to the oxidation and reduction reactions of the films, fig. 4.52. Films of intermediate thickness (0.5-2 μ m) produce cyclic voltamograms that are consistent with this, fig. 4.52. The electrode reaction yields figure 4.52 which is associated with the extended π -system of the polymer being oxidized and the film switches from neutral to the oxidized state. This involves a π delocalized radical cation structure. This reaction is accompanied by a visible colour change, the neutral film is yellow and the oxidized film is brown/black. Generally speaking as the thickness varies so does the surface structure. The wide variation in the topologies of the surfaces again emphasize the complexity of the electropolymerization process which among other things, produces regions in the films with different growth rates. The differences observed in the surface topologies are not reflected in the packing structure of the bulk material since the flotation densities of the films show little variation (21,46,47).



Figure(4.50)Variation of voltage with current used
in the preparation of PPTS film.



Figure(4.51) Variation of voltage with thickness used in the preparation of PPTS films.

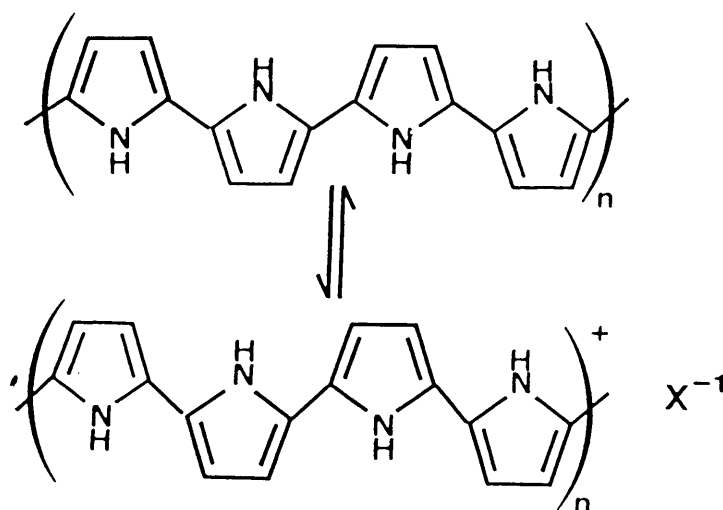


Figure 4.52.

4.9 Elemental Analysis Results

The elemental analysis of polypyrrole sulfate gives a small variation in results for the total carbon, hydrogen, nitrogen and sulphate contents. Two formulae are obtained; $(C_{3.9} H_{3.1} N_1 (SO_4)_{3.5})$ and $(C_4 H_{3.4} N_1 (SO_4)_{4.9})$. The elemental analysis indicates that there is 65% by weight of polymer, 35% anion and 58% polymer, 42% anion respectively. The elemental analysis for polypyrrole perchlorate gives a small variation in results for the total carbon, hydrogen, nitrogen and chlorate content; three formulae are $(C_{3.9} H_{2.9} N_1 (ClO_4)_{0.4})$, $(C_{4.3} H_3 N_1 (ClO_4)_{1.6})$ and $(C_{4.1} H_{3.9} N_1 (ClO_4)_{0.9})$. The ratio of polymer to the anion by weight are respectively (62% : 38%), (69% : 31%) and (56% : 44%). The variation of the elements in the polypyrrole is dependent on the conditions used in the synthesis. The ratio of hydrogen to nitrogen 3:1 and carbon to nitrogen 4:1 indicates that the polymer rings remain intact, hence a

long chain structure is obtained. The chemical analysis of polypyrrole in general appears to indicate the incorporation of the anion is at the 1-4 ratio indicating that every fourth pyrrole ring probably contains an extra proton and this helps to explain the fact that the analysis reveals a higher than expected hydrogen content and this is in agreement with the observation of other workers (49). The conducting polymer is, therefore, more correctly written as shown in fig. 4.53.

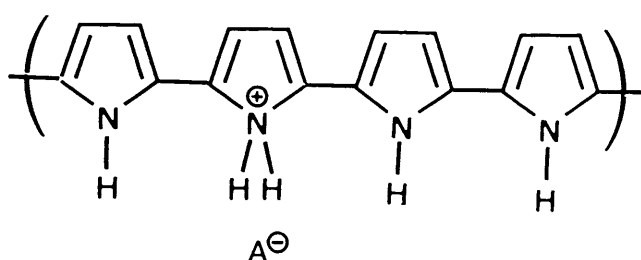


Figure 4.53

The excess hydrogen observed will infact be present in the system protonated ring structures. The extent of protonation will depend on the voltage used in the synthesis and this is in turn reflected in the changes in conductivity.

4.10 Cyclic Voltametry

An example of the type of cyclic voltamogram for this system is shown in fig. 4.54. The number of electrons transferred in the electrode reaction, (n), for a reversible couple can be determined from the separation of the peak potentials (50). This produces a value of (n) equal to 2.23 from this trace. The determination of the peak potentials is subject to quite a large error as a result of the breadth

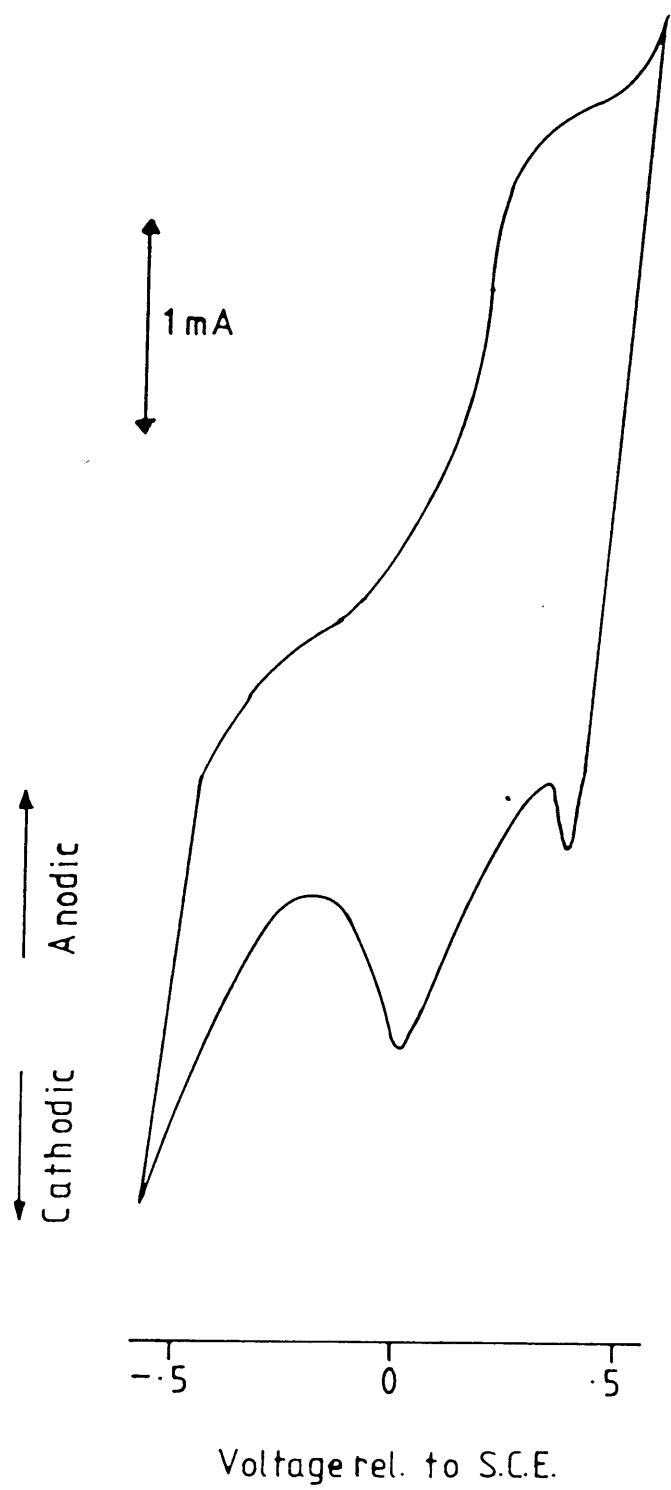


Figure 4.54. Cyclic voltammetry of PPTS using 0.1m silver para-toluene sulfonate in acetonitrile.

of the peaks. The value of 2.23 is reasonably close to a value of 2.25 suggested by Street (51,52). The cyclic voltamogram shows further peaks at -0.34 and +0.37 volts relative to the SCE (standard calomel electrode). These peaks have been ascribed to the effect of the background processes associated with the gold electrode. The polymerization reaction involves two electrons per monomer unit and elemental analysis and the above observations indicate that 0.25 electrons per molecule are used in the partial oxidation of the film (48). This is consistent with the final structure having one anion per four pyrrole units. It is observed from the cyclic voltamogram that whilst the process occurring is not completely electrochemically reversible, repeated scanning can be performed without significant change in shape which is indicative of a certain degree of chemical reversibility in the system.

4.11 Thickness Determination and Structural Properties

The thickness of polypyrrole para-toluene sulfonate PPTS films were determined by using a Dektak II surface profile analyser. Estimation of the thickness of polypyrrole films at the various voltages are shown in figures (4.55, 4.56, 4.57, 4.58, 4.59, 4.60 and 4.61) and table 4.5.

Figure 4.51 illustrates the effects of variation of voltage used in the preparation on the thickness of the film. It is also found that the lowest voltage, close to the limiting voltage for the electrochemical reaction where the oxidation-reduction potential of the growth of the polypyrrole is approximately 1.2V relative to calomel electrode, the growth is very slow. However, under these very poor growth conditions, it is found that the anion incorporated is fairly high. At low voltages the growth is uniform. Once the critical voltage of 1.2V

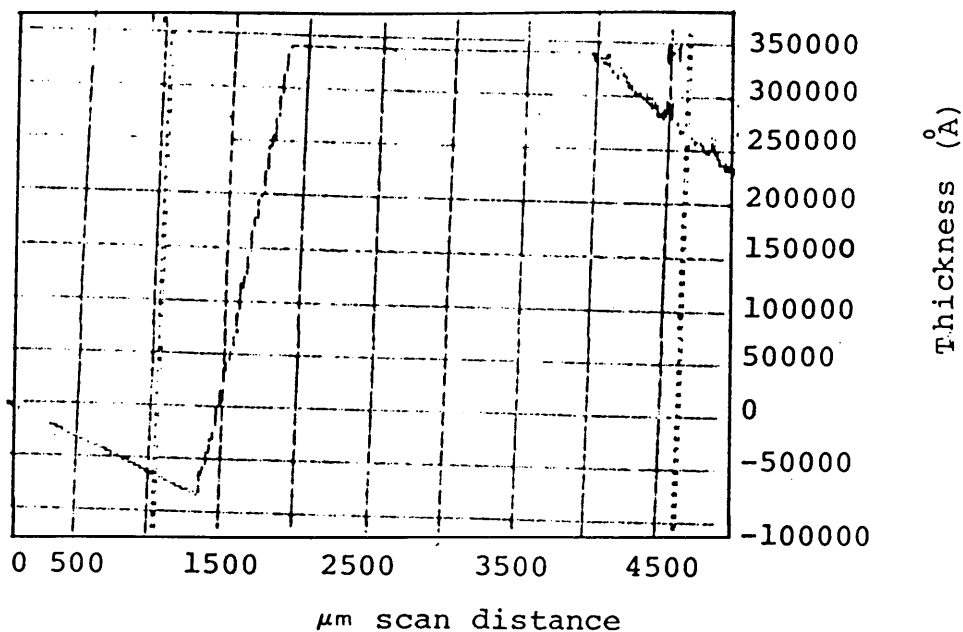


Figure (4.55) Determination of the thickness of PPTS prepared at 2 V and room temperature.

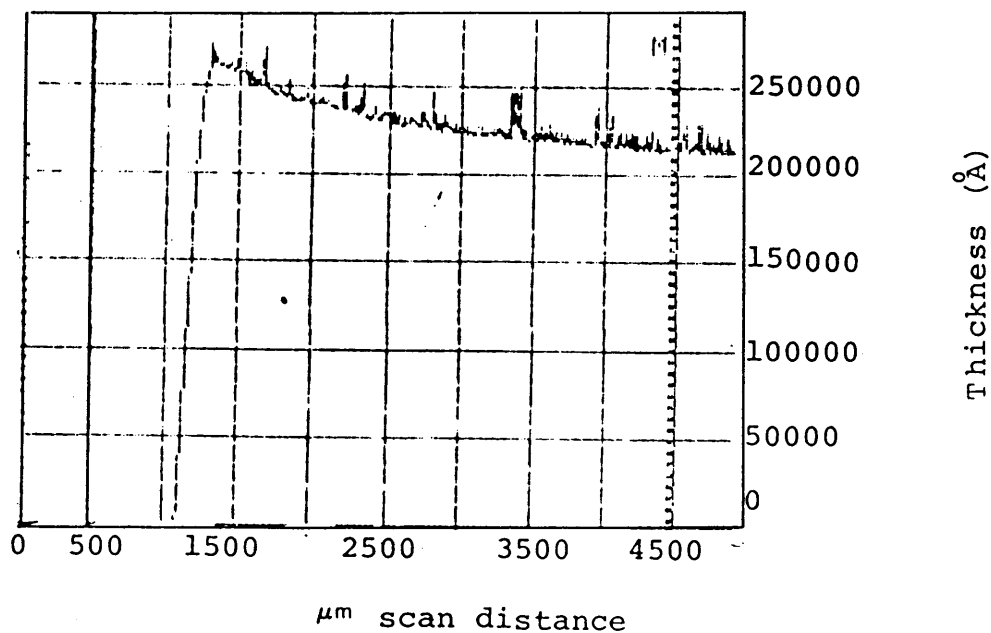


Figure (4.56) Determination of the thickness of PPTS prepared at 0.75 V and room temperature.

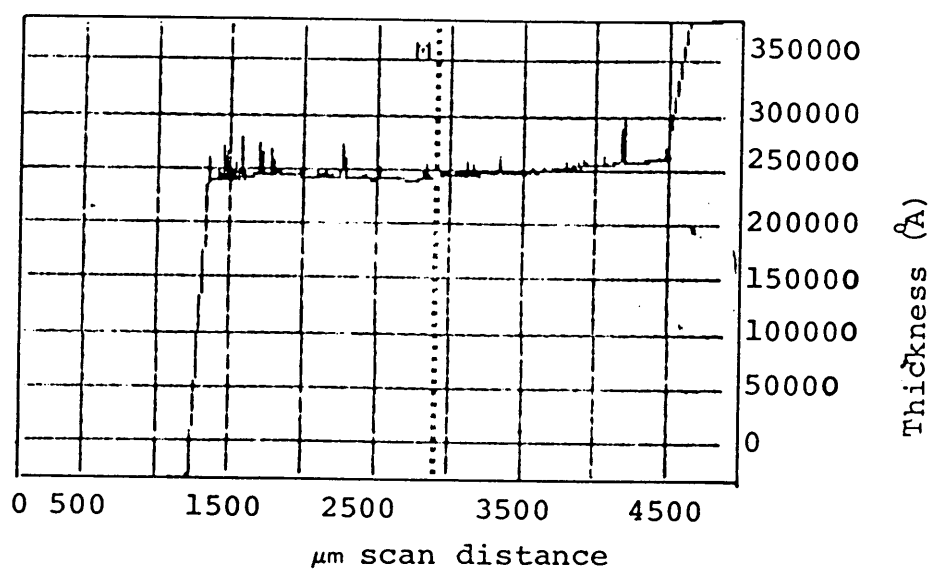


Figure (4.57) Determination of the thickness of PPTS prepared at 0.5 V and room temperature.

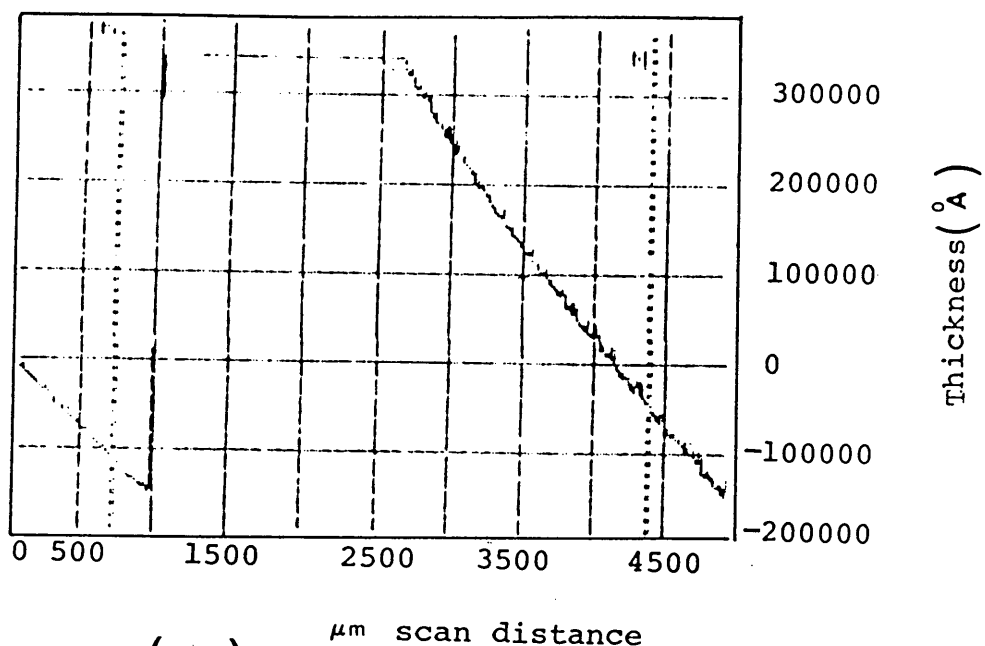


Figure (458) μm scan distance
Determination of the thickness of PPTs prepared at 1.75 V and room temperature.

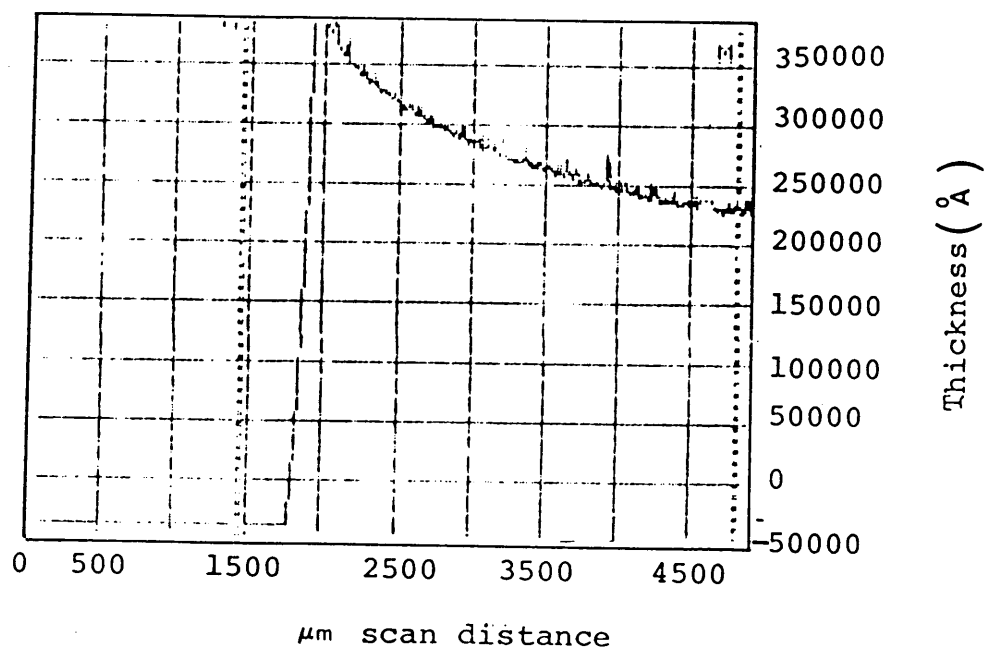


Figure (459) μm scan distance
Determination of the thickness of PPTs prepared at 1.25 V and room temperature.

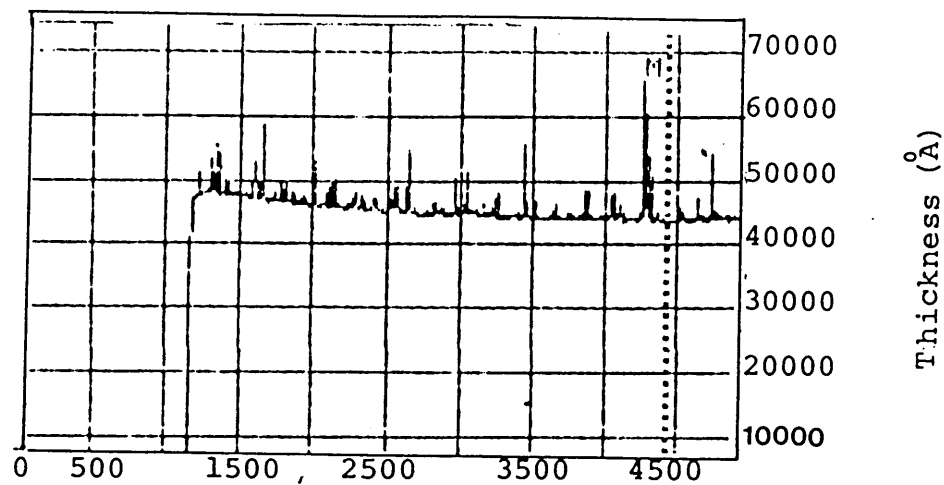


Figure (4.60) μm Determination of the thickness of the PPTS prepared at 0.75 V and room temperature.

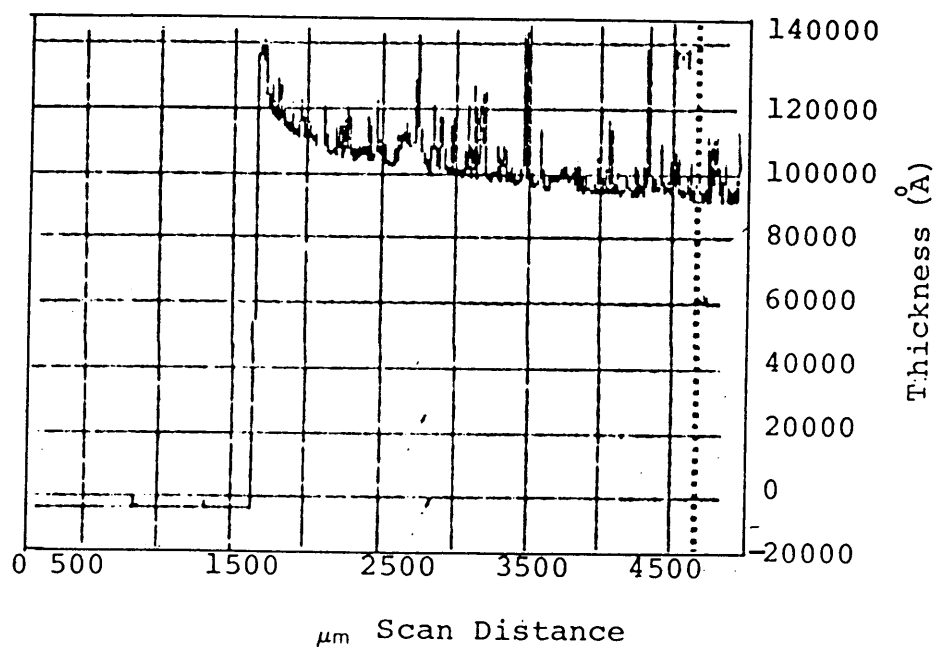


Figure (4.61) μm Scan Distance Determination of the thickness of PPTS film prepared at 1.00 V and room temperature.

has been exceeded there is a very interesting change in the growth pattern. It is found that a lip appears at the point where the gold electrode meets the glass. This lip is small for the lower voltages but rapidly increases and becomes very large for the larger voltages. The size of the lip reflects the enhanced rate of growth of the polypyrrole in the region of the electrode. The reasons for the enhanced growth are as follows:-

i. The edge of the electrode will have associated with it a field gradient. The films formed at the higher growth rates tend to be less conductive than those at the lower voltages, hence, it is found that there is the possibility of a local filled inhomogeneity at the edge of the electrode. This will increase the potential, hence, a corresponding increase in the growth rate.

ii. The larger growth rate will also lead to a reduction in the concentration of the polypyrrole in the region close to the electrode edge and this in turn will create an over potential which will influence the potential difference applied to the system. The results of the two effects is to generate this marked lip at the edge of the films and also to produce a very considerable difference in the thickness of the film in this region compared with the bulk of the polypyrrole film. The abnormal lip is less conductive than the bulk because it has been generated in a region of high overvoltage.

Examination of the edge profile of the films grown at various voltages indicates that both concentration and voltage used in the synthesis of the film have a significant effect on the product. It can be seen from figures 4.57 and 4.56 that at 0.5V and 0.75V there is a sharp edge to the film conforming to the edge of the gold electrode. As the voltage is raised above 1.0V the edge becomes a pronounced lip.

The lip at 1.25V is now a sharp point and its magnitude increases with increased voltage. The observation of this lip can be attributed to a combination of two effects. The edge will have associated with it a high field gradient and hence the effective potential in this region may be higher than over the main part of the electrode. As shown in the previous figure, the rate of growth depends on the applied voltage and hence the observation of point associated with this high field is consistent with the previous observation. The high growth rate can lead to a depletion of the electrolyte in the region close to the electrode and hence generate an over-voltage which itself will enhance the growth rate. It should be noted that since the higher the voltage the lower the conductivity, then this region will have a larger resistance, hence, generating an even higher over-potential.

Finally it should be noted that the surface roughness of the polypyrrole films as determined by the Dektak do not appear to be dependent on potential used for growth or the electrolyte concentration but are simply a function of the absolute thickness of the films formed. The thin films 17,000 to 32,000 Å grown at potential of 1.0V and 1.5V are very smooth, figure 4.61, whereas films grown under similar conditions and allowed to become 100,000 to 200,000 Å thick are rough. It is possible that the local internal inhomogenities in the films are now leading to differential growth rates and hence microscopic peak formation. This observation is, therefore, consistent with the effects of edges in producing peaks described above. The thick films lose their glossy appearance and become matt. A similar observation has been reported by Tourillon and Garnier (53) in a study of the morphology of polythiophene. These authors however, make no comment on the possible origin of these effects.

Table. 4.5. Variation of the Thickness of the Films with Changing Voltage used in the Preparation of the Film.

Voltage V	Thickness $\times 10^{-4} \text{ A}^0$
0.50	2.7
0.75	4.7
1.00	12
1.25	26
1.50	55
1.75	80
2.00	140

$$\text{Area of the film} = 1.54 \times 10^{+16} (\text{A}^0)^2$$

4.12 Discussion

4.12.1 Electrochemical Polymerization of Pyrrole

The oxidative electrochemical polymerization of pyrrole produces conducting black flexible films (35,50) of polypyrrole doped with various anions. The first step in the electrochemical polymerization of pyrrole is the generation of the radical cation at the anode as shown in figure 4.62. The mechanism involves oxidation and dimerization of pyrrole followed by aromatization and oxidation of the dimer. The last step is included because the aromatic dimer ($E_{PA} = .06\text{V VS SSCE}$) and the higher molecular weight oligomers are known to oxidize more easily than the monomer (54) by extension of these reactions.

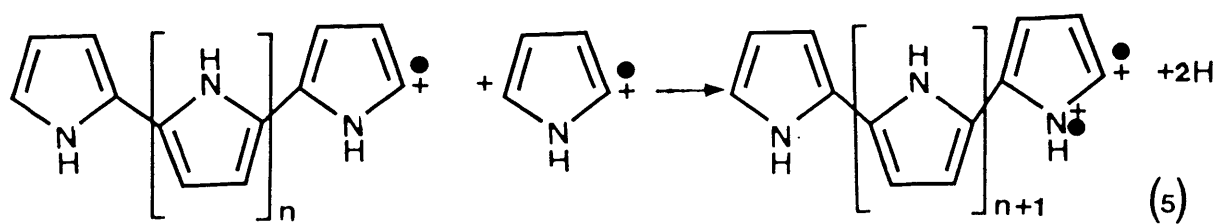
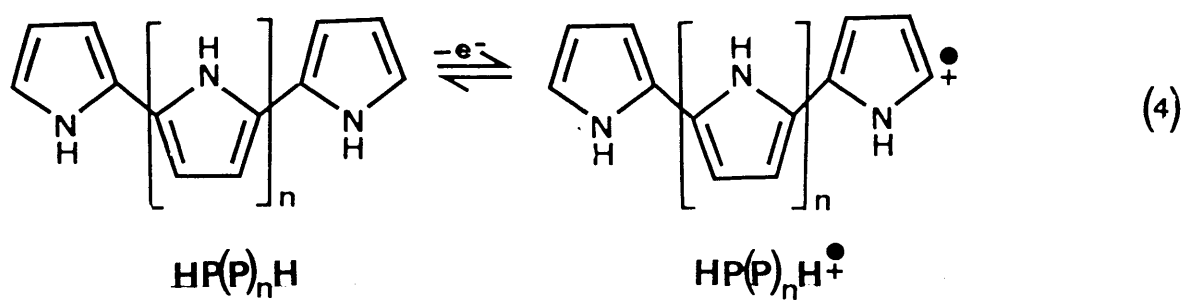
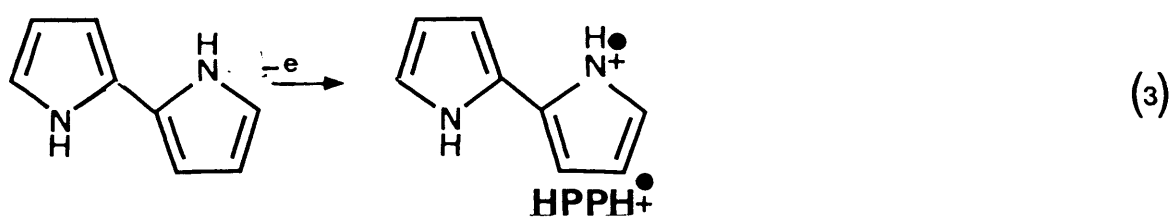
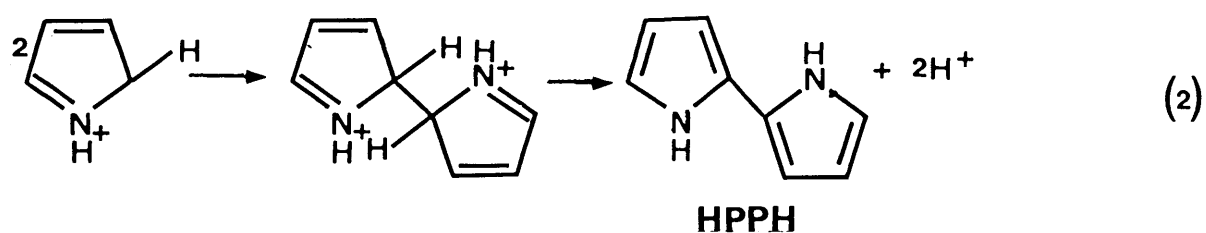
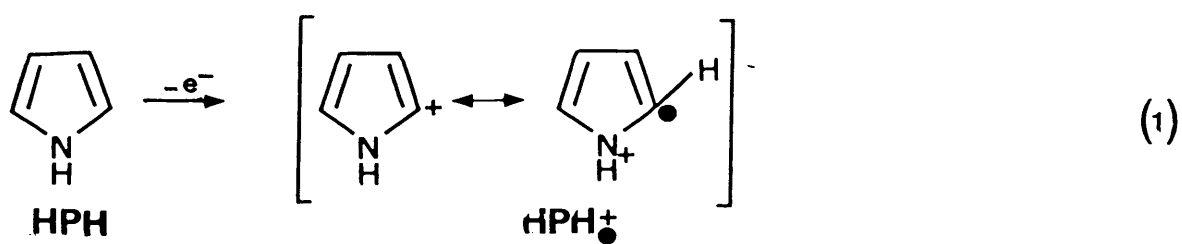


Figure 4.62

The steps for the polymerisation process can be described as in equations 4 and 5 figure 4.62.

The polymerization reaction has been shown to involve 2 electrons/molecule of pyrrole and the resulting polymer is produced in the oxidized state with 0.25 to 0.33 cation centers per pyrrole unit depending on the electrolyte anion used (23,55). This is confirmed by the data presented in this thesis.

This mechanism is also consistent with the number of electrons consumed in the reaction which has been found to be between 2.33 and 2.25 per pyrrole (56). These numbers also agree with the number of anions found in the film. Chain propagation may then proceed by reaction of two radical cations, pairing the spins and eliminating two protons to produce the neutral dimer. The elimination of the protons is confirmed by the slow rise in the pH of the electrolyte solution during the film growth (57, 58). The polymer is not exclusively α , $\bar{\alpha}$ -bonded so to some extent elimination of β -hydrogen can also take place. We believe that the radical cation of the monomer plays a key role in the synthesis of the chains because of its high reactivity and concentration in the region of the anode.

At the potential necessary to oxidize the monomer presumably the dimer and higher oligomers are also oxidized to the corresponding radical cations allowing chain propagation to continue. Reaction of the oligomer radical cations occurs primarily with the radical cations of the monomer, which are present in high concentration in the region of the anode but can also react with other oligomeric species. As the chain grows the pyrrole oligomer becomes insoluble and eventually precipitates out on the electrode, where the chain can continue to grow until the oligomer radical cation becomes too unreactive or until it

becomes prevented from reacting for steric reasons. If polypyrrole is generated in a neutral form it will stop conduction and polymerization will cease.

Elemental analysis reveals that the situation is more complex than this simple mechanism would indicate. Additional oxidation of polypyrrole chain leads to the formation of cationic sites with incorporation of the electrolyte anion to maintain charge neutrality. As regards the electroactive properties of the film, the film can be reversibly switched between the oxidized and neutral forms. The cyclic voltamogram for this reaction shows that it is very sensitive to the nature of the anion in the electrolyte solution. In fact, the switching speeds depend on the mobility of the anions in and out of the film. Results on both polypyrrole and poly (β , $\bar{\beta}$ -dimethylpyrrole (P $\beta\bar{\beta}$ DMP) perchlorate indicated the presence of one perchlorate for every three rings in the polymer chain. However, analysis also indicates the presence of one perchlorate anion for every three pyrrole rings and there is also one more hydrogen than that corresponding to the idealized neutral structure that this would indicate. Although the amounts of hydrogen and perchlorate are almost identical, spectroscopic data would indicate that these species are not present in the form of perchloric acid. Indeed, infrared (57) and ^{13}C NMR studies (59) indicate the presence of $\text{sp}^3\text{C-H}$ moieties in polypyrrole, perhaps arising from the addition of hydrogen to the pyrrole ring under the acidic conditions of the electrochemical polymerization (60). The quaternized pyrrole entity will influence the electro-delocalization on the conjugated backbone as well as giving sites on such which the anion can localize. In addition chain ends would contribute to the excess hydrogen observed in the elemental analysis as would the presence of

the oxidized form.

Because the excess hydrogen may be distributed among several different types of sites the elemental analysis data can not be used to derive either chain length or conjugation length. Thus, if all of the excess hydrogen were present at chain ends the data would indicate a chain length of 7 to 8 pyrrole rings, the presence of hydrogen at internal chain sites makes this a lower limit on the chain length. The effects of the sp^3 hydrogen depends on their currently unknown distribution between α and β -sites. Hydrogen at an α -pyrrole carbon definitely intercepts the π -conjugation along the polymer backbone, whereas substitution at a β -carbon may not, if the excess hydrogen were all at α -sites the average conjugation length would be of the order of three pyrrole rings. In fact, the presence of hydrogen at other positions makes this a lower limit on the conjugation length.

The possibility of a very short conjugation length in polypyrrole is difficult to reconcile with the observation of a single oxidation peak in cyclic voltametry unless a single conjugation length dominates the distribution, also, extrapolations of electrochemical properties and optical data for short chain pyrrole oligomers suggest a conjugation length of the order of six or more pyrrole rings (61). Moreover, EPR results indicate only a spin for every 50 pyrrole rings (62). Single oxidation of a given conjugation segment would result in a polaron state (a radical cation with an unpaired spin) thus, the conjugation length must be long enough to support a doubly oxidized state (bipolarons) which do not have unpaired spins as shown in figure 4.63, (35,38,52,57,63-66) which represents valance band of (a) polaron and (b) a bipolaron on a polypyrrole, more accurately, the charge and spin are delocalized over the whole defect. In conjunction with the

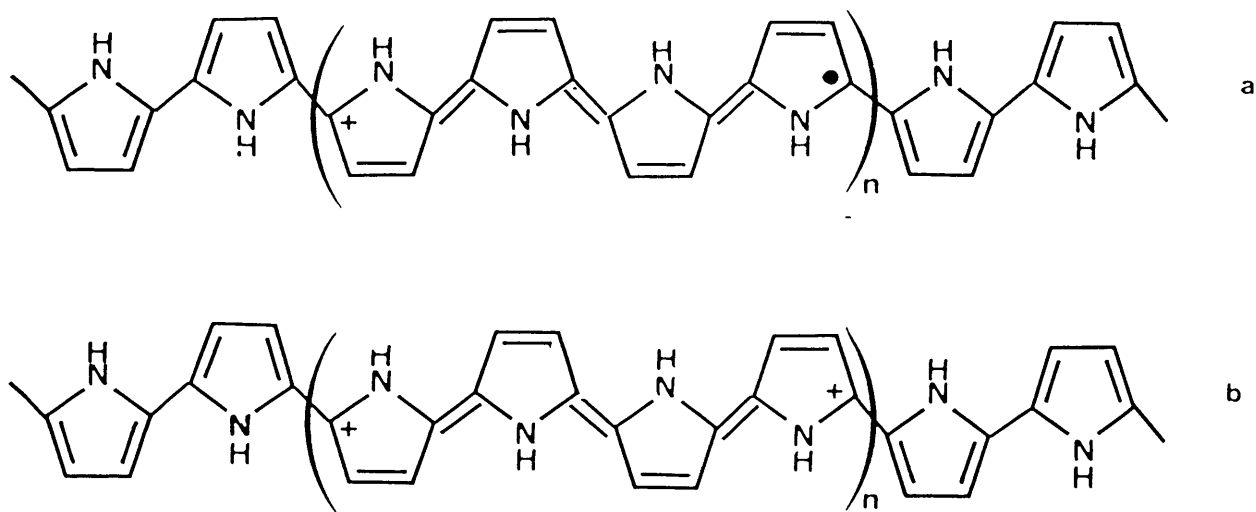


Figure 4.63.

elemental analysis data indicating one perchlorate and thus one charge per three pyrrole rings, a lower limit on the conjugation length of six rings would be indicated. To be consistent with the cyclic voltametry however, this model required that the first and second oxidation potentials for a conjugated segment fall within the same envelope.

4.12.2 Conductivity and Electronic Conduction of PPTS

The conductivity of polypyrrole para-toluene sulfonate film may be related to the morphology, i.e. related to conditions under which PPTS is prepared. It has been reported by various researchers for doped polypyrrole (49,67) values of the electrical conductivity as high as 200 and as low as 0.001 S cm^{-1} . In the present work the conductivity of PPTS varies between 1.27×10^{-2} to $22.65 \times 10^{-2} \text{ S cm}^{-1}$. Therefore, the variation in the conductivity is quite reasonable. In the case of polypyrrole, Street (51) has indicated that defects in the structure of the conjugated system associated with the formation of alpha-beta

rather than alpha-alpha linkages, oxidation during the polymerization process as well as variation in the dopant level all contribute to the observed variations in the electrical conductivity of polypyrrole. It is also important to note that the oxidation reduction potential for the polypyrrole system is 1.2V and it appears that at this point maximum conductivity is achieved. At lower voltage the two electron reduction will occur but the product will be neutral. Above 1.0V there will be a pyrrole ring in four oxidized state, therefore, the growth becomes very rapid and whilst oxidation can occur, the incorporation of the anion will be less effective, this will decrease the probability of inter chain hopping and hence the conductivity of the films. In figure 4.47; the conductivity (σ) of the PPTS films is plotted versus $T^{-1/4}$ where (T) is the temperature. All the data fits rather well with straight lines in this type of plot, which indicates that (σ) follows the typical law $\sigma(T) \propto \exp(-T^{-1/4})$ i.e. Mott's model, a conventional model of variable range hopping process, gives the right qualitative behaviour of the conductivity. Scott et al (38), Bredas et al (66) and Kaufman (65) presented evidence that the species responsible for the conductivity are either polaron or bipolaron. Although qualitatively good, this model does not provide a satisfactory quantitative description of the transport properties in polypyrrole partly because the nature of the conduction mechanism in this polymer has proved extremely difficult to determine because of the high degree of disorder (68) inherently produced by the electrochemical polymerization process, and partly because the transport properties themselves defy description in terms of any conventional model (53, 57).

4.12.3 Conclusions

I. Behaviour of Polypyrrole

This study indicates that very large, yet consistent changes in the electrical conductivity of polypyrrole films can be obtained by the variation in the voltage and concentration of electrolyte used in the synthesis of films. There is also a close correlation between the conductivity, rate of growth and the voltage used in the preparation of the films. If we correlate all the above observations, a possible origin of the phenomena of synthesis of the films may emerge. Although the elemental analysis of the films indicates an anion incorporation of 1:4, it is possible that changes in the effective level of incorporated anion at the 2-5% level could have a significant effect on the conductivity. If we assume that inter-chain charge transfer must involve the anions, then the concentration near ends or at points of close contact can have a dominant effect on the probability of charge transfer. If this is accepted then it is easy to see for a high molecular weight conjugated system that only small changes can have a profound effect on the electrical conductivity. It is also apparent that shorter chains suitably complexed could lead to high levels of conductivity and these in turn will be soluble. From the data presented here it is only possible to conjecture at the origins of the effects and more detailed studies are necessary to establish the validity or otherwise of this hypothesis.

II. Comparison between the behaviour of PPTS and carbon black composites ((CB/PS) and (CB/PCP))

Clearly the two parts of the thesis connect by being concerned

with electronic conductivity. However, the factors influencing these observations are very different and reflect the way in which various parameters influence the observed electronic mobility. In the case of PPTS, the d.c. conductivity is slightly dependent on temperature and seems to fit the possibility of the three dimensional variable range hopping conduction. The charge carrier is either polaron or bipolaron. In the case of carbon black composites (CB/PS) and (CB/PCP), the a.c. conductivity is dependent on temperature and seems to fit the possibility of hopping conduction and the charge carrier is an electron or hole. The type of conduction depends on the activity of the supporting matrix. Both polypyrrole and the carbon black are intrinsic electron conductors ; polypyrrole can be protonated and when highly anion doped leads to highly conducting systems. The conductivity in the case of the carbon black system is controlled more by particle-particle contact than by any active effects of the supporting matrix.

APPENDICES

APPENDICES

Appendix A

Spectroscopic Measurements

Examination of the purity of pyrrole before and after purification by proton magnetic resonance ^1H -NMR and ^{13}C -NMR.

Proton magnetic resonance ^1H -NMR and ^{13}C -NMR were obtained on a Perkin - Elmer R-32 instrument (90 MHz) using deuterium chemical shifts. The measurements were expressed in parts per million (ppm) with respect to tetramethyl silane (TMS) as an internal standard.

It was found that the spectra of ^{13}C -NMR before and after purification of pyrrole were identical as shown in figures (a), (b), (c) and (d). Figures (a) and (b) were proton noise decoupled spectra (fully decoupled with all carbon atoms as singlets). The study of the spectra revealed identical peaks in the regions of 108 and 118 ppm. These were due to the β and α -carbon atoms respectively. Moreover, figures (c) and (d), which were off-resonance decoupled technique (i.e. shows coupling to directly bound protons), show identical peaks in the regions of 106, 110, 118 and 120 ppm which were due to the α and β - carbon coupling to the directly bound protons. The ^1H -NMR spectra before and after purification of pyrrole were also identical as shown in figures (e) and (f). The spectrum of the purified pyrrole indicated a reduction in the impurities, which might be due to the formation of the oligomers. The study of the spectra revealed identical peaks in the regions of 6.2 and 6.5 ppm which were due to the β and α C-H groups respectively.

Appendix B

The data illustrates the range of values obtainable with several types of carbon black (13) (chapter 4) loaded polychloroprene (Neoprene).

Type of Black	A.C. Resistivity, ohm cm	
	50 parts	100 parts
acetylene	2.7×10^2	1.2×10^2
soft black	1.6×10^8	2.0×10^7
reinforcing	1.0×10^8	6.7×10^4
channel	8.5×10^7	1.7×10^6

Appendix C

Normalised plots of $\log_{10} \bar{\epsilon} / \bar{\epsilon}_{\max}$ vs. $\log_{10} f / f_{\max}$

Defining the normalised loss $\bar{\epsilon} / \bar{\epsilon}_{\max} = y$ and the normalised frequency $f / f_{\max} = x$ where $\bar{\epsilon}_{\max}$ and $f_{\max}$ represent the values at the loss peak, the normalised curve may be represented as the result of the reciprocal addition of two power law contributions

$$\frac{1}{y} = ax^{-m} + bx^{1-n}$$

where (a) and (b) are constants and in the present instance (m) = 0.5 and (n) = 0.77.

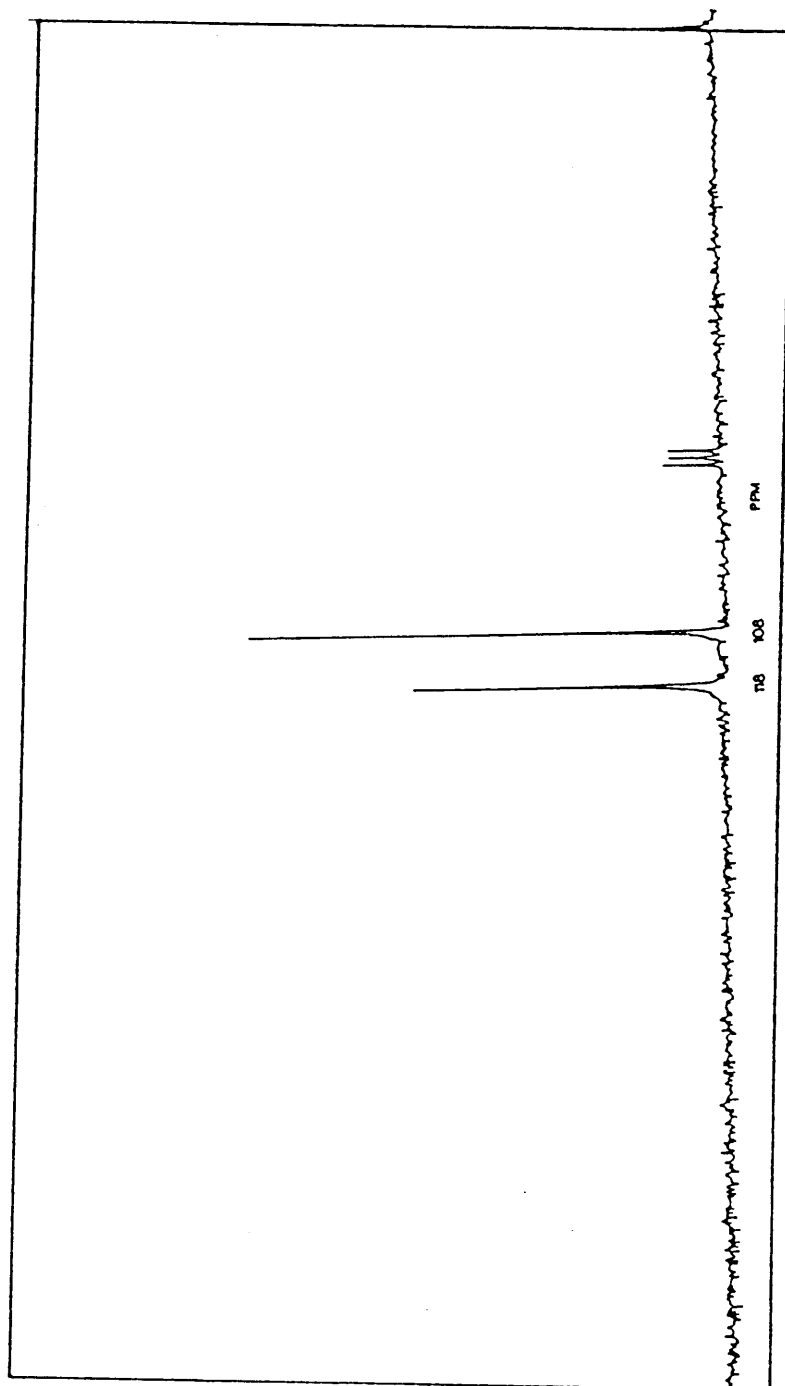


Fig (a) ^{13}C - NMR spectrum of unpurified Pyrrole using proton noise decoupling.

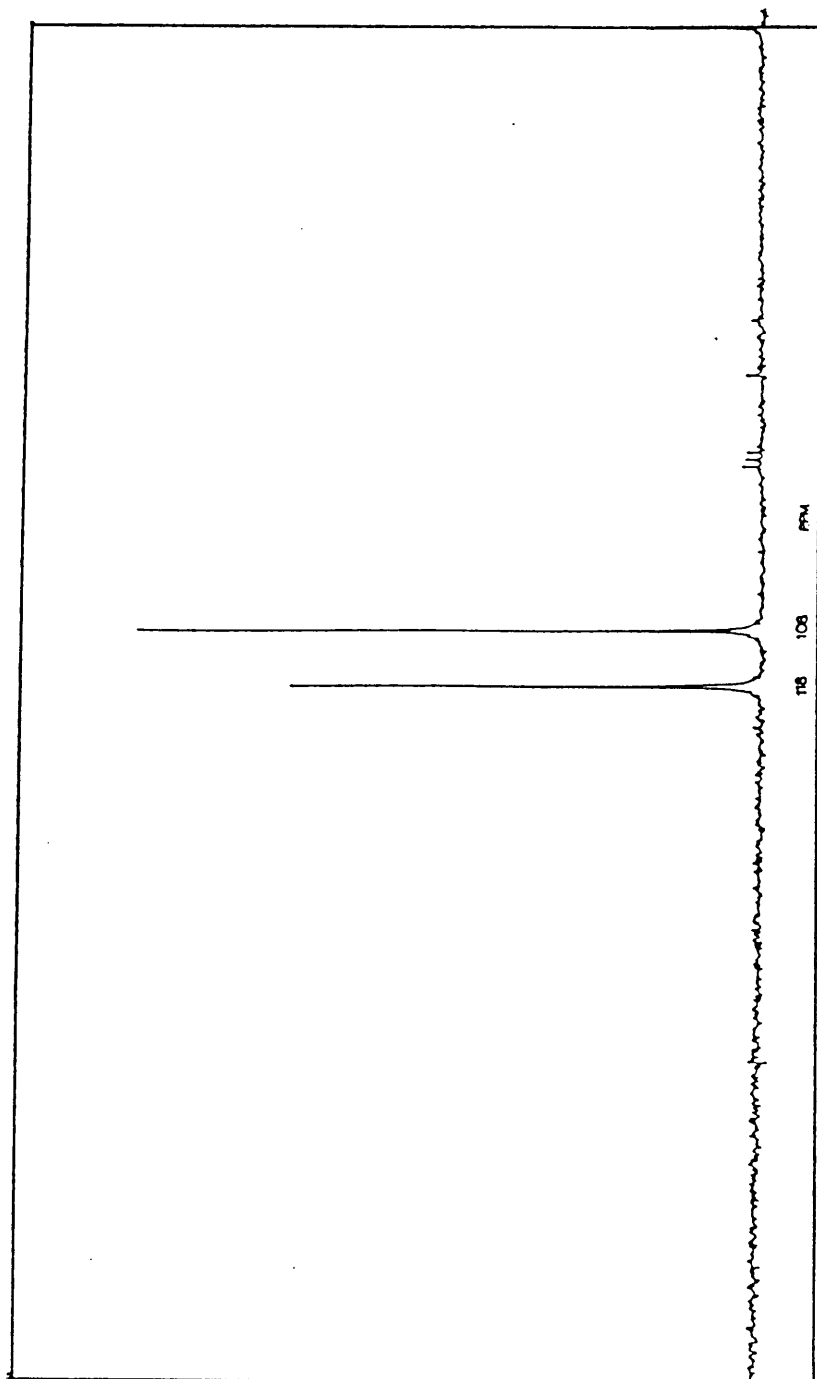


Fig (b) ^{13}C -NMR spectrum of purified Pyrrole using proton noise decoupling.

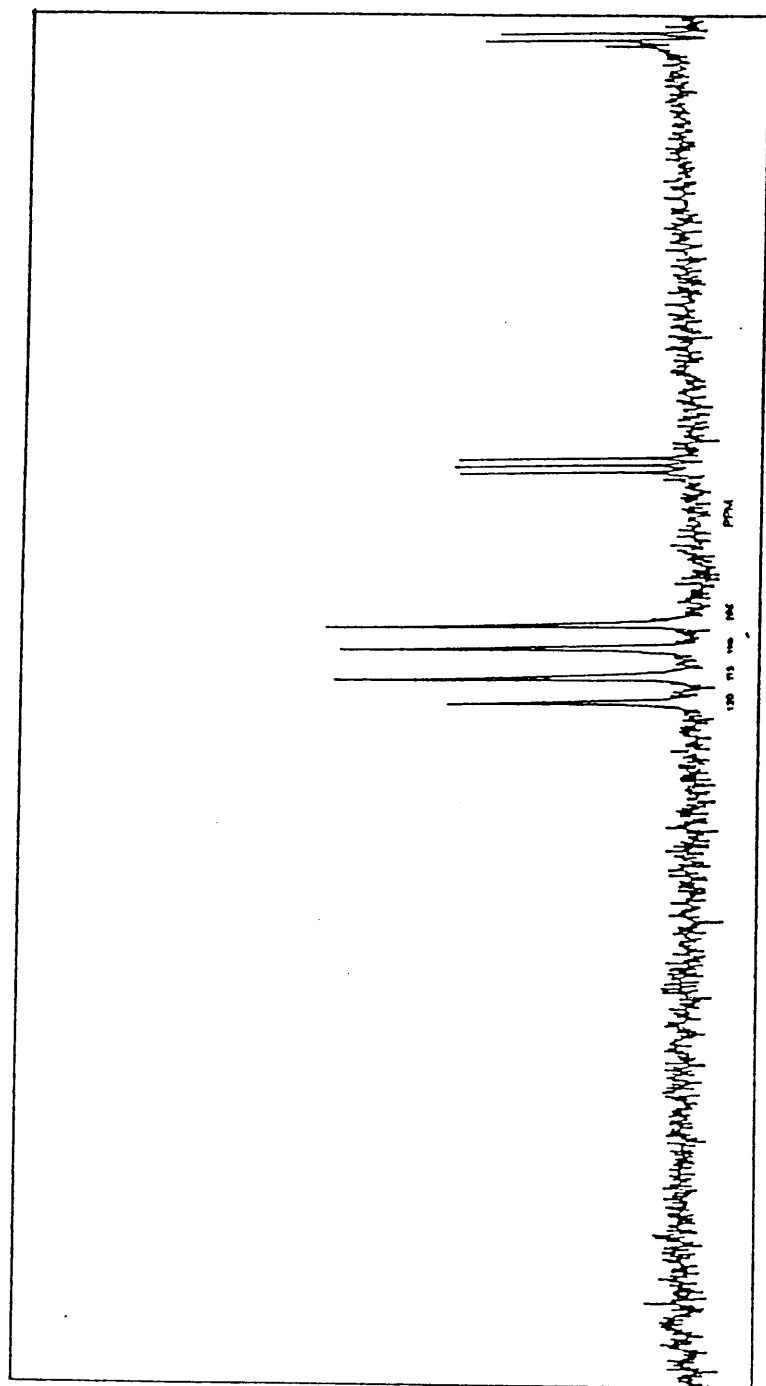


Fig (c) ^{13}C -NMR spectrum of purified Pyrrole using off-resonance decoupling.

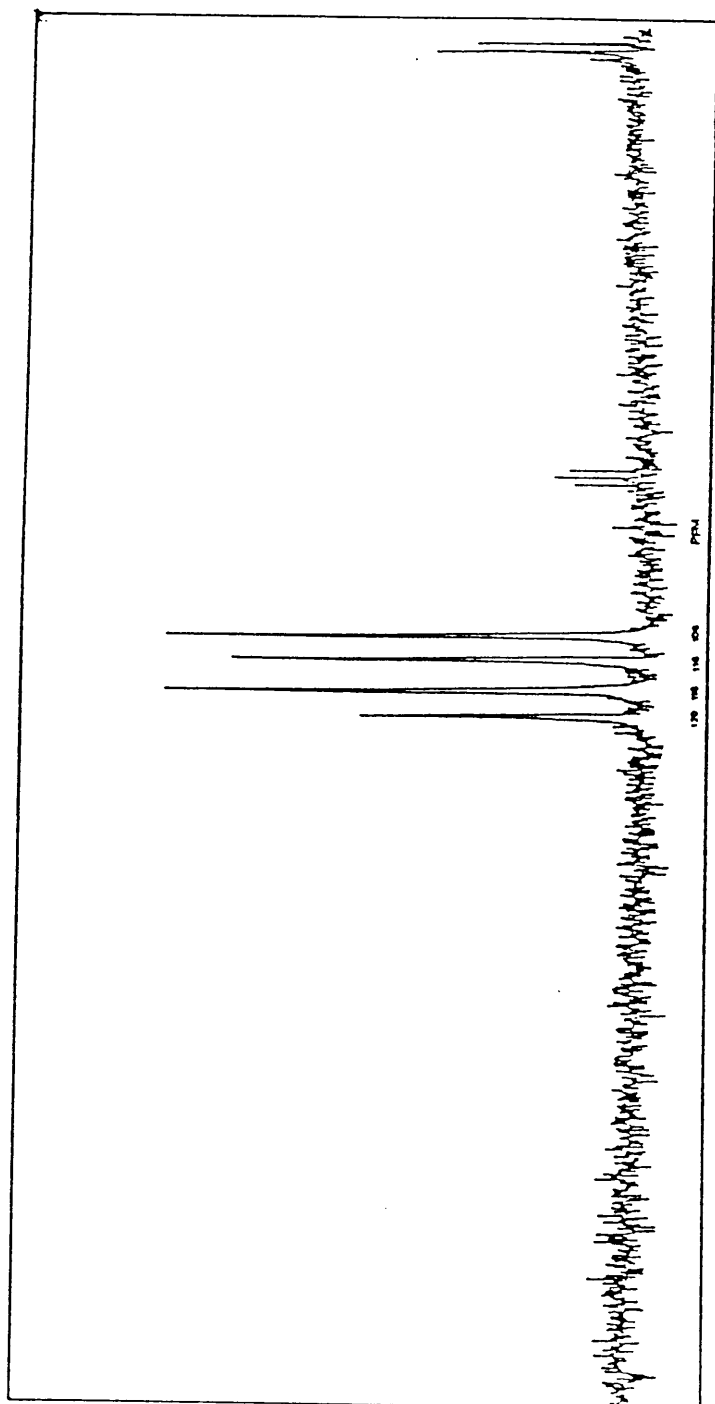


Fig (d) ^{13}C - NMR spectrum of unpurified Pyrrole using off-resonance decoupling.

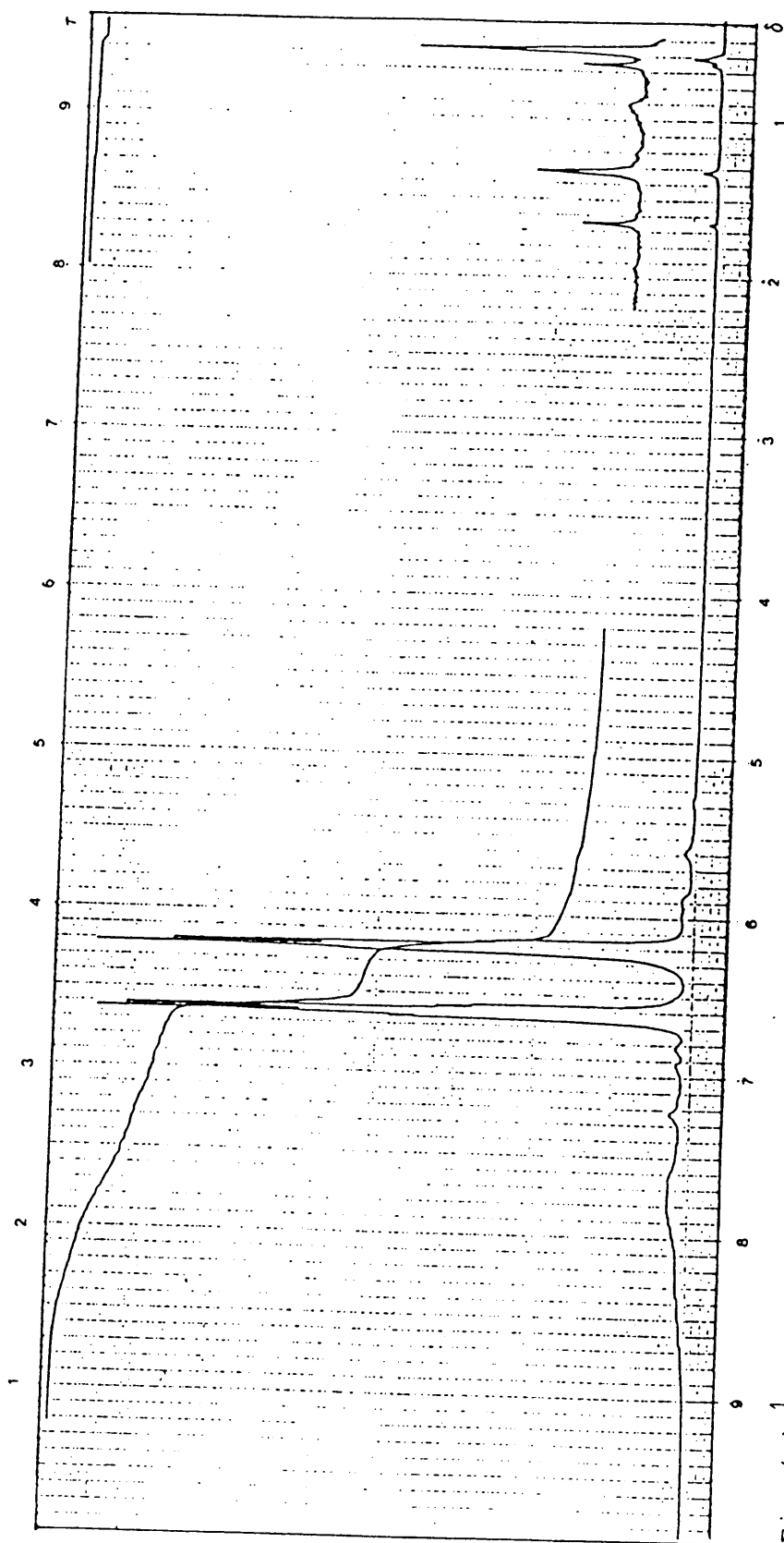


Fig (e) ^1H -NMR spectrum of purified Pyrrole.

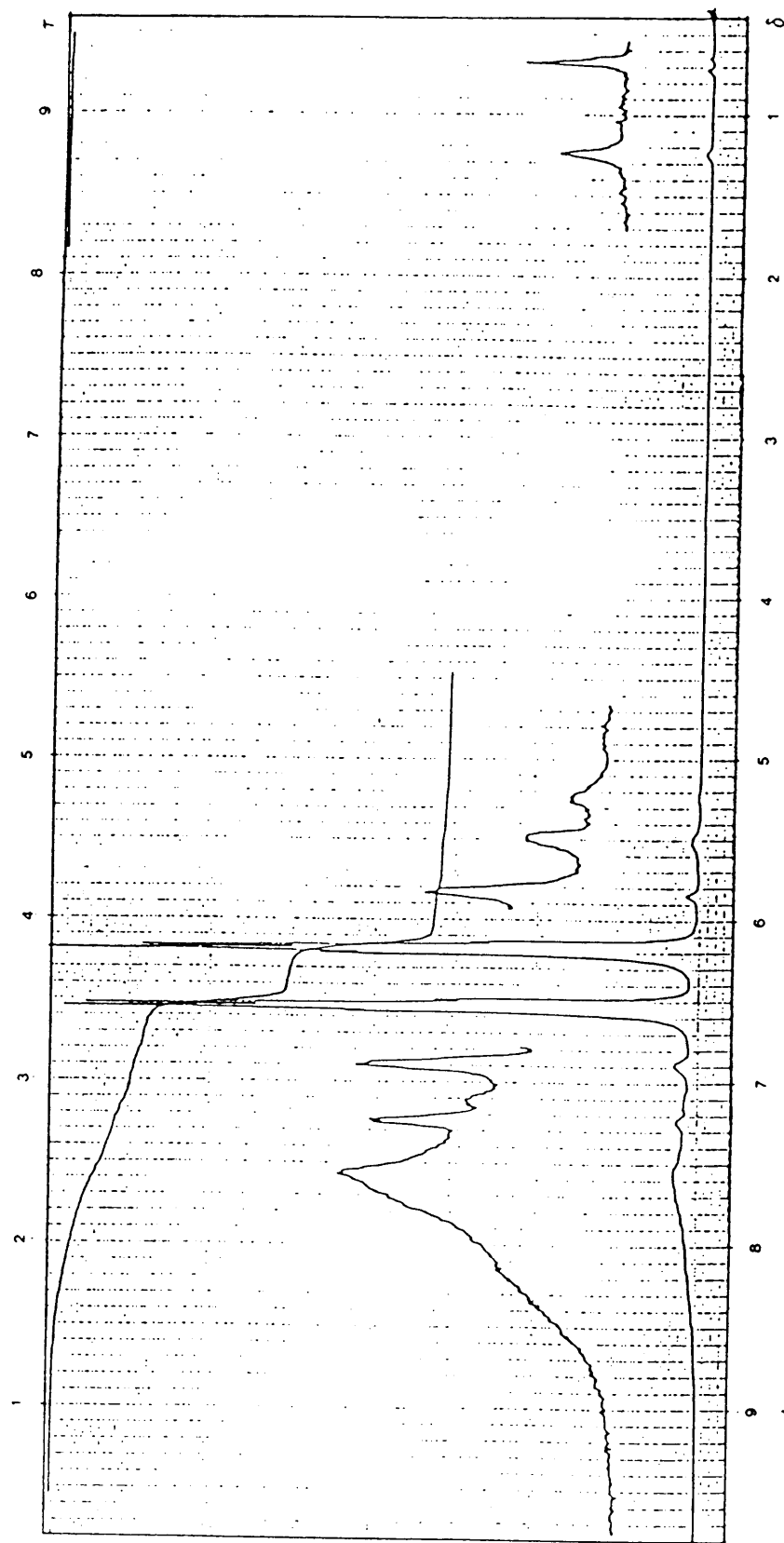


Fig (f) ^1H -NMR spectrum of purified Pyrrole.

REFERENCES

REFERENCES

Chapter One

1. J. Ferrans et al, J.Am. Chem. Soc., 95, 948, (1973)., L.B. Coleman et al, Solid State Commun., 12, 1125, (1973).
2. Szent Györgyi, Nature, 148, 157, (1941).
3. D.D. Eley, Nature, 162, 819, (1948).
4. Kenneth D. Wynne and G. Bryan Street, Ind. Eng. Chem. Prod. Res. Dev., 21(1), 23, (1982).
5. V.V. Walatka et al, Phys. Rev. Lett., 31, 1139, (1973).
6. G.B. Street et al, J. Chem. Soc. Chem. Commun., 464, (1977).
7. M. Akhtar et al, Inorg. Chem., 17, 1539, (1978).
8. W.D. Gill et al, Phys. Rev. Lett., 38, 1305, (1977).
9. C.K. Chiang et al, J. Solid State Commun., 23, 607, (1977).
10. G.B. Street and R.L. Greene, IBM J. Res. Dev., 99, 21, (1977).
11. A.G. MacDiarmid and A. Heeger, J. Synth. Met., 1, 101, (1980).
12. C.K. Chiang et al, Ber. Bunsenger. Phys. Chem., 83, 407, (1979).
13. G.B. Street and T.C. Clarke, IBM J. Res. Dev., 25, 51 (1981).
14. G.E. Wnek et al, Am. Chem. Soc., Div. Org. Coat. Plast. Chem. Pap. 43, 882, (1980).
15. D.M. Ivory et al, J. Chem phys., 71, 1506, (1979).
16. L.W. Shacklette et al, J. Chem. Phys., 73, 4098, (1980).
17. J.F. Rabolt et al, J. Chem. Soc. Chem. Commun., 347, (1980).
18. R.R.Chance et al, J. Chem. Soc. Chem. Commun., 348, (1980).
19. P.J. Nigrey et al, J. Chem. Soc. Chem. Commun., 594, (1979).
20. A.F. Diaz and T.J. Clarke, J. Electroanal. Chem., 111, 115, (1980).
21. K.K. Kanazawa et al, J. Chem. Soc. Chem. Commun., 854, (1979).
22. K.K. Kanazawa et al, synth. Met., 1, 329, (1980).
23. K.F. Schoch et al, J. Am. Chem. Soc., 101, 7071, (1979).

24. P.M. Kuznesof et al, J. Chem. Soc. Chem. Commun., 121, (1980).
25. R.S. Nohr et al, Abstr. Inorg. 161, Am. Chem. Soc., Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug, (1980).
26. R.S. Nohr et al, J. Am. Chem. Soc., 103, 4371, (1981).
27. J. Bacon and R.N. Adams, J. Am. Chem. Soc., 96, 6596, (1968).
28. G.P. Gardini, "Advances in Heterocyclic Chemistry" A.R. Katritzky and A.J. Boulton (Eds.), Vol 15, (1973).
29. A. Dall'Olio et al, C.R. Acad. Sci. Ser., C267, 433, (1968).
30. A.F. Diaz et al, J. Electrochem. Soc. 133, 237, (1981).
31. K.K. Kanazawa et al, synth. Met., 4, 119, (1981).
32. H. Shirakawa et al, J. Chem. Soc. Chem. Commun., 578, (1977).
33. A.F. Diaz, Chem. Scr., 17, 145, (1981).
34. G. Tourillon and F. Garnier, J. Electroanal. Chem., 135, 173, (1982).
35. J. Bargon et al, IBM J. Res. Dev., 27, 330, (1983).
36. C.K. Chiang, Rev. Lett., 39, 1098, (1977).
37. A.F. Diaz et al, J. Chem. Soc. Chem. Commun., 635, (1979).
38. W. Deits et al, Synth. Met., 4, 189, (1982).
39. A.F. Diaz et al, IBM J. Res. Dev., 27, 342 (1983).
40. G.B. Street et al, Mol. Cryst. Liq. Cryst., 83, 253, (1982).
41. M. Salmon et al, J. Polym. Sci. Polym. Lett. Edn., 20, 187, (1982).
42. W.D. Gill et al, Appl. Phys. Commun., 2, 211, (1982).
43. G.B. Street et al, Proceedings of Conference on Electronic Excitation and Interaction Processes in Organic Molecular Aggregates, P. Reineker et al (eds.), Springer Series in Solid State Sciences, 49, 242, (1983).
44. A.F. Diaz et al, J. Electroanal., 108, 377, (1980).
45. Randy A. Bull. et al, J. Electrochem. Soc. Electrochemical Science and Technology, 129No5, 1009, (1982).
46. R. Naufi et al, J. Am. Chem. Soc., 103, 1849, (1981)., R. Naufi et al, J. Electrochem. Soc. Electrochemical Science and

- Technology, 127, 2310, (1980)., T. Skotheim et al, J. Electrochem. Soc Electrochemical Science and Technology, 128, 1625, (1981).
47. F-R. F. Fan et al, Ibid, 128, 2042, (1981).
 48. T.A. Skotheim et al, J. De. Physique Colloque C3, supplement au N°6 Tome 44, 615, (1983).
 49. A.F. Diaz and K.K. Kanazawa, "Extend Linear Chain Compound", J.S. Miller (ed.), Plenum Publishing, New York, 3, 417, (1983).
 50. A.F. Diaz et al, "Conductive Polymer Science Technology", R.B. Seymour (Ed.), Plenum Press, 15, 179, (1981).
 51. A.F. Diaz et al, J. Electroanal. Chem., 129, 115, (1981).
 52. A.F. Diaz et al, J. Electroanal. Chem., 133, 233, (1982).
 53. A.F. Diaz et al, IBM J. Res, Dev., 25(1), 42, (1981).
 54. A.F. Diaz et al, J. Chem. Soc. Chem. Commun., 397, (1980).
 55. Tooru Inoue and Toshihiyo Yamase, Bull. Chem. Soc. Jpn., 56, 985, (1983).
 56. M. Salmon et al, "Acs Symposium Services", J.S. Miller (ed.), American Chemical Society, Washington, 65, (1982).
 57. E.M. Genies and G. Bidan, J. Electroanal. Chem. 149, 101, (1983).
 58. A.F. Diaz et al, J. Electroanal. Chem., 130, 181, (1981).
 59. Proceedings of the International Conference on the Physics and Chemistry of Low Dimentional Synthetic Metals (ISCM 84), Mol. Cryst. Liq. Cryst., 118(1-4), 50, (1985).
 60. M.G.B. Mahabun-Jones and R.A. Pethrick, Polymer Yearbook, II, Gordon and Breech, London and New York, (1985).
 61. G.B. Street et al, Mol. Cryst. Liq. Cryst., 118, 137, (1985).
 62. R.J. Waltman et al, Tetrahedron, 40(20), 3963, (1984).
 63. Yoshino Katsumi et al, Jpn. J. Appl. Phys., 23(12), 899, (1984).
 64. Sizuo Tokito et al, Chem. Lett., 531, (1985).
 65. J.P. Travers et al, Mol. Cryst. Liq. Cryst., 118(1-4), 149, (1985).
 66. J.H. Kaufman et al, Mol. Cryst. Liq. Cryst., 118(1-4), 171, (1985).

67. Pierre Audebert et al, Mol. Cryst. Liq. Cryst., 118(1-4), 187, (1985).
68. M. Ogasawara et al, Mol. Cryst. Liq. Cryst., 118(1-4), 159, (1985).
69. J.C. Scott et al, Mol. Cryst. Liq. Cryst., 118(1-4), 163, (1985).
70. Nigel Bates et al, J. Chem. Soc. Chem. Commun., 871, (1985).
71. S.B. Mainthia et al, J. Chem. Phys., 37, 2509, (1962).
72. Wolfgang Wernet et al, Makromol. Chem. Rapid. Commun., 5, 157, (1984).
73. Keiichi Kaneta et al, Jpn. J. Appl. Phys., 21(9), L567, (1982).
74. Atsuchi Watamabe et al, Bull. Chem. Soc. Jpn., 54, 2278, (1981).
75. Keiichi Kaneto, Tech. Reports. Osaka University, 33(1693), 75, (1983).
76. M. Tanaka et al, Mol. Cryst. Liq. Cryst., 83, 277, (1982).
77. G. Tourillon et al, J. Phys. Chem., 87, 2289, (1983).
78. K. Kaneto et al, Solid State. Commun., 46(5), 389, (1983).
79. G.B. Street et al, Mol. Cryst. Liq. Cryst., 118, 137, (1985).
80. W. Wernet et al, Mol. Cryst. Liq. Cryst., 118, 193, (1985).
81. G.B. Street, "Handbook of Conducting Polymers", T. Skotheim (ed.), Marcel Dekker, New York. (1984).
82. J.C. Scott et al, Synth. Mets., 9, 165, (1984).
83. A.R. Blythe, "Electrical Properties of Polymers", Cambridge University Press, (1979).
84. E. M. Cashell et al, J. Appl. Phys., 52, 1542, (1981).
85. J. Mort and G. Pfister, "Electronic Properties of Polymer", 267, (1982).
86. Norman, "Conductive Rubbers and Plastics", Elsevier Publishing Co. Ltd., New York, Chapter 3, (1970).
87. M.H. Polley et al, Chem. Tech., 30, 170, (1957).
88. A. Veot et al, Rubber World, 176, 77, (1962).
89. V.P. Petrosyon, IZV. Akad. Naur. Arm. SSR. SKM. Nauki., 19(2), 122, (1964).

90. B. Pouaert et al, Polymer, 24, 841, (1983).
91. W.C. Schneider et al, J. Amer. Chem. Soc., 67, 959, (1945).
92. M.R. Fuoss, J. Amer. Chem. Soc., 63, 369, (1941).
93. W. Reddish, Trans. Faraday Soc., 46, 459, (1950).
94. E.K. Deutsch et al, J. Polym. Sci., 13, 565, (1954).
95. H. Thum and F. Wurstlin, Kolloid. Z.U.Z. Polym., 145, 134, (1956).
96. T. Nakajime and S. Satio, J. Polym. Sci., 31, 423, (1958).
97. P.G. Mikhilou, J. Polym. Sci., 30, 605, (1958).
98. L. Brouckere and G. Offergeld, J. Polym. Sci., 30, 105, (1958).
99. H.F. Müller and K. Huff, Kolloid. Z.U.Z. Polym., 164, 34, (1959).
100. S.K. Cole and R.H. Cole, J. Chem. Phys., 91, 341, (1941).
101. A.K. Jonscher, Colloid and Polymer Sci., 253, 231, (1975).
102. G.T. Powles, J. Chem. Phys., 21, 633, (1953).
103. M. Narkis et al, J. Appl. Sci., 22, 1163, (1978).
104. I. Nass, "Encyclopedia of PVC", Marcel Dekker (Ed.), New York, 2, (1977).
105. A. Veot, J. Phys. Chem., 61, 301, (1957).
106. H.M. Polley and B.B.S.T. Boonstra, Rubber Chem. Tech., 30, 170, (1957).
107. S. Chandrasekhar, Rev. Mod. Phys., 15, 86, (1943).
108. B. Abeles et al, Adv. Phys. 24, 407, (1975).
109. P. Sheng et al, Phys. Rev. Lett., 31, 44, (1973).
110. W.F. Werhelst et al, Rubber. Chem. Tech., 50, 735, (1977).
111. Y. Okamoto and Walter Brenner, "Organic Semiconductors", Reinhold Publishing Corporation, London, 82, (1964).
112. O. Niwa and T. Tamamura, J. Chem. Soc. Chem. Commun., 817, (1984).
113. K.E. Sichel et al, Phys. Rev., B18, 5713, (1978).

Chapter Two

1. R.W. Christy, J. Appl. Phys., 31 1680, (1960).
2. R.W. Christy, J. Appl. Phys., 35 2179, (1964).
3. J.R. Hanscomb and Y. Kaabwa, J. Phys. D., 12, 579, (1979).
4. C.A. Hogarth and M. Zor, Thin Solid films, 27, L5, (1975).
5. C.A. Hogarth and T. Iqbal, Thin Solid Films, 51, L45, (1978).
6. A.M. Mearns, Thin Solid Films, 3, 201, (1969).
7. M. White, Thin Solid Films, 18, 157, (1973).
8. A.C. Rastogi and K. L. Chopra, Thin Solid Films, 18, 187, (1973).
9. A.K. Jonscher, International Meeting Electrostatic Charging, Frankfurt (1972), Verlag Chemie, (1974).
10. N.F. Mott, Advances Phys., 16, 49, (1967).
11. A.K. Jonscher, Thin Solid Films, 1, 213, (1967).
12. N.F. Mott and W.D. Twose, Advances in Physics, 10, 107, (1961).
13. A. Miller and E. Abrahams, Phys. Rev., 120, 745, (1960).
14. M. Pollak and T.H. Geballe, Phys. Rev., 122, 1742, (1960).
15. K.L. Chopra, "Thin Film Phenomena", McGraw - Hill, London. (1969).
16. J. Dresner and F.V. Shallcross, J. Appl. Phys., 34, 2390, (1963).
17. J.G. Simmons, J. Phys. D. Appl. Phys., 4, 613, (1971).
18. J.G. Simmons, Physical Review, 155, 3, 15 March (1967), 657, (1967).
19. C.A. Mead, Phys. Rev., 128, 2088, (1962).
20. H. Hirose and Yasaku Wada, Japanese J. Appl. Phys., 3, 4, April (1964), 179, (1964).
21. J. Frenkel, Tech. Phys. USSR, 5, 685, (1938); Phys. Rev., 54, 647, (1938).
22. J.J. O'Dayer, J. Appl. Phys., 37, 2, February 1966, 599, (1966).
23. Junkichi Nakai and T.M. Tazaki, Japanese J. Appl. Phys., 3, 11, 677, (1964).

24. M. Stuart, Phys. Stat. Sol., 23, 595, (1967).
25. S.R. Pollack, J. Appl. Phys., 34, 4, (Part I), 877, (1963).
26. A. Rembaum, T. Meaconin and J.A. Pohl, Progr. Dielect., 6, 41, (1965).
27. A. Rembaum and A.F. Landel, J. Polm. Sci., C17 Polym. Symp., (1967).
28. D.R. Lamb, "Electrical Conduction Mechanism in These Insulating Films", Methuen and Co Ltd., London. (1967).
29. C. Kittle, "Elementary Solid State Physics", John Wiley and Sons, New York, (1962).
30. N.F. Mott and E.A. Davis, "Electronic Processes in Non-Crystalline Materials", Clarendon Press, Oxford. (1979).
31. E.A. Davis, "Amorphous Semiconductors" In Topics in Applied Physics, M.M. Brodsky (ed.) Vol 36, (1980).
32. L.W. Barr and A.B. Lidiard, "In Physical Chemistry An Advanced Treatise", H. Eyring et al, (eds.) Academic Press, New York, Vol 10, (1970).
33. P.W.M. Jacobs and P. Pantelis, Phy. Rev(B), 4, 3757, (1971).
34. T.J. Lewis and A.J. Wright, J. Phys. D3, 1329, (1970).
35. A.B. Lidiard, "In Handbuch der Physik, S. Flugg (ed.) Springer Verlag, Berlin, (1957).
36. N.F. Mott and W.R. Gurney, "Electronic Processes in Ionic Crystals", Clarendon Press, Oxford, (1948).
37. N.F. Mott, Philos, Mag., 19, 835, 1969.
38. J. Stuke and G. Weiser, Phys. Status Solidi, 17, 343, (1966).
39. M.H. Cohen, H. Fritzsche and S.R. Ovshinsky, Phys. Rev. Lett., 22, 1065, (1969).
40. C.G. Kuper and G.D. Whitfield, "Polaron and Excitations", Plenum Press, New York, (1963).
41. S.A. Brazovskii and N.N. Kirova, Jetp. Lett., 33, 4, (1981).
42. K. Fesser et al, Phys. Rev., B27, 4804, (1983).
43. J.L. Bredas et al, Phys. Rev., B26, 5843, (1982), J. Chem. Phys., 78, 6137, (1983)., Bredas., J. Phys. (Paris) Colloq, 44 C3-373, (1983).
44. G.B. Street, "Handbook of Conducting Polymers", T. Skotheim (ed.) Marcel Dekker, New York, (1984).

45. J.L. Bredas et al, Phys. Rev., B30, (1984).
46. J.C. Scott et al., Mol. Cryst. Liq. Cryst., 118(1-4), 163, (1985).
47. P.W. Anderson, Phys. Rev., 109(5), 1492, (1958).
48. K. Hulls, "Electrical and Optical Properties of Chalcogenide Glasses", Ph.D. Thesis, University of Warwick, (1970).
49. A. Miller and E. Abrahams, Phys. Rev., 120(3), 745, (1960).
50. J.C. Slater, "Quantum Theory of Molecules and Solids", McGraw-Hill, New York, Vol.1., (1963).
51. A.I. Gubanov, "Quantum Electron Theory of Amorphous Conductors", 10-12, (1965).
52. a). W. Siebrand, J. Chem. Phys., 40, 2223, (1964).
b). W. Siebrand, J. Chem. Phys., 41, 3574, (1964).
53. T. Holstein, Ann. Phys., 8, 343, (1959).
54. M. Pollak and T.H. Geballe, Phys. Rev., 122, 1742, (1961).
55. J.R. Wyhop and H.A. Pohl, J. Polym. Sci., A28, 1741, (1970).
56. A.K. Jonscher, J. Non-Cryst. Solids, 8-10, 293, (1972).
57. G. Williams and D.C. Watts, Trans. Far. Soc., 66, 80, (1970).
58. T.J. Lewis, Nauk. Inst. Org. Phys., Wroclow, 7, 146, (1974).
59. J.P. Travers et al, Mol. Cryst. Liq. Cryst., 118(1-4), 149, (1985).
60. A.F. Diaz, Chem. Scr., 17, 145, (1981).
61. A.F. Diaz et al, J. Chem. Soc. Chem. Commun., 635, (1979).
62. A.F. Diaz et al., IBM J. Res. Dev., 27, 342, (1983).
63. K.K. Kanazawa et al, Synth. Met., 1, 329, (1980).
64. K.K. Kanazawa et al, Synth. Met., 4, 119, (1981).
65. Wolfgang Wernet et al, Makromol. Chem. Rapid. Commun., 5, 157, (1984).
66. Keiichi Kaneta et al, Jpn. J. Appl. Phys., 21(9), L567, (1982).
67. Atsuchi Watamabe et al, Bull. Chem. Soc. Jpn., 54, 2278, (1981).
68. Keiichi Kaneto, Tech. Reports. Osaka University, 33(1693), 75, (1983).

69. M. Tanaka et al, Mol. Cryst. Liq. Cryst., 83, 277, (1982).
70. G. Tourillon et al, J. Phys. Chem., 87, 2289, (1983).
71. K. Kaneto et al, Solid State Commun., 46(5), 389, (1983).
72. G.B. Street et al, Mol. Cryst. Liq Cryst., 118, 137, (1985).
73. W. Wernet et al, Mol. Cryst Liq. Cryst., 118, 193, (1985).
74. J.C. Scott et al, Synth. Met., 9, 165, (1984).
75. I.G. Austin and N.F. Mott. Adv. Phys., 18, 41, (1969).
76. P.G. Le-Comber et al, J. Non-cryst Solids, 11, 219, (1972).
77. C.H. Seager et al, Phys. Rev., 138, 4746, (1973).
78. H. Scher and E.W. Montrall, Phys. Rev., B12, 2455, (1975).
79. N.F. Mott, "Electrons in Non-crystalline Materials", In Electronic and Structural Properties of Amorphous Semiconductors", P.G. Le-Comber and J. Mort (Eds.), Academic Press, London, New York, 1, (1973).
80. M.H. Cohen, J. Non-cryst. Solids, 4, 391, (1970).
81. N.F. Mott. Philos. Mag., 22, 7, (1970).
82. M. Cutler and N.F. Mott, Phys. Rev., 181, 1336, (1969).
83. A.R. Blythe, "Electrical Properties of Polymers", Cambridge University Press, (1979).
84. Vera. V. Daniel, Dielectric Relaxation, Academic Press, London and New York, (1967).
85. M. Davies, Quart. Rev., 8, 250, (1954).
86. M. Davies, "Some Electrical and Optical Aspects of Molecular Behaviour", Pergamon, Oxford and London, (1965).
87. C.P. Smyth, Ann. Rev. Phys. Chem., 17, 433, (1966).
88. P. Debye, "Polar Molecules". Chemical Catalog Co., New York, Chapter 7, (1939).
89. H. Frochlich, "Theory of Dielectrics, Oxford University Press, Oxford, 36, (1949).
90. C.P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York, (1955).
91. N. Hill et al, Dielectric Properties and Molecular Behaviour, Van Nostrand-Reinhold, London, (1969).
92. S.K. Cole and H.R. Cole, J. Chem. Phys., 9, 341, (1941).

93. W.D. Davidson and H.K. Cole, J. Chem. Phys, 19, 1484, (1951).
94. S.Havriliak and S. Negami, Polymer, 8, 161, (1967).
95. G. Williams and C.D. Watts, Trans. Faraday. Soc., 66, 80, (1970).
96. R.T. Bailey, A.M. North and R.A. Pethrick, "Molecular Motion in High Polymers", Clarendon Press, Oxford, (1981).
97. G.N. McCrum et al, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, (1967).
98. M.G. Bartener and V.Yu. Zelenev, "Relaxation Phenomena in Polymers", Wiley, New York, (1974).
99. L.K.H. Van. Beek, Progr. Dielectrics, 7, 69, (1967).
100. J.C. Maxwell, "Electricity and Magnetism", 1, Claredon Press, Oxford, 452, (1982).
101. K.W. Wagner, Arch. Electrotech, 2, 378, (1914).
102. R.W. Sillers, J. Inst. Electr. Eng., 80, 378, (1937).

Chapter Three

1. A.R. Blythe, "Electrical Properties of Polymers", Cambridge University Press, (1979).
2. W. Crawford Dunlap and Jr., "Conductivity Measurements on Solids", Chapter 7.2, Vol. 6, 13, Academic Press, New York, (1959).
3. Felix Gutmann and Lawrence E. Lyons, "Organic Semiconductors", John Wiley & Sons, Inc, New York, London, Sydney, 44, (1967).
4. L.B. Valdes, Proc. I.R.E., 42, 420, (1954).
5. A. Uhlir and Jr., BSTJ, 34, 105, (1955).
6. L.J. Swartzendruher, Solid State Electronics, 7, 413, (1964).
7. Helmut F. Wolf, "Semiconductors", Wiley-Interscience, a division of John Wiley & Sons, Inc. 503, (1971).
8. C.M. Huggins and A.H. Sharbaugh, J. Chem. Phys., 38, 393, (1963).
9. P.L. Kronick and M.M. Labes, "Organic Semiconductors", J. Chem. Phys., 35, 2016, (1961).
10. A.N. Gerritsen, "Hundbuck der Physik (Encyclopedia of Physics), S. Flugge (ed.), Springer, Berlin, Val 19, 137, (1956).

11. B. Hague, "Alternating Current Bridge Methods", Pitman, London, (1946).
12. A. Dall'Olio et al, C.R. Acad. Sci., C267, 433, (1968).
13. A.F. Diaz et al, J. Chem. Soc. Chem. Commun., 635, (1979).
14. G.B. Street et al, Mol. Cryst. Liq. Cryst., 83, 253, (1982).

Chapter Four

1. E.M. Cashell et al, J. Appl. Phys., 52(3), 1542, (1981).
2. W.F. Verhelst et al, Rubber. Chem and Tech., 50, 735, (1977).
3. Y. Okamoto and Walter, "Organic Semiconductors", Reinhold Publishing Corporation, 82, (1964).
4. E.K. Sichel and J.I. Gittleman, J. Electric Materials, 11(4), 699, (1982)
5. N.F. Mott and E.A. Davis, "Electronic Processes in Non-crystalline Materials", Oxford, London (1979).
6. Abdul Abu Baker and A.M. North, Eur. Polym. J., 13, 799, (1977).
7. J.T. Lewis, Specialist Periodical Reports, Dielectric and Related Molecular Processes, Chem. Soc., (London), M. Davies (ed.), 13, 186, (1977).
8. M.F. Mott, Adv. Phys., 18, 41, (1969).
9. E.G. Pike, Phys. Revs., B6, 1572, (1972).
10. J.T. Lewis and R. Pethig, "Excited States of Biological Molecules", J.B. Birks (ed.), Wiley, London, 342, (1976).
11. Derek J. Crofton and Richard A. Pethrick, Polymer, 22, 1048, (1981).
12. Derek J. Crofton and Richard A. Pethrick, Polymer, 23, 1615, (1982).
13. Masato Matsuo et al, Kolloid. Z.U.Z.F. Polymer, 201, 7, (1965).
14. W.C. Schneider et al, J. Amer. Chem. Soc., 67, 959, (1945).
15. A.K. Jonscher, Colloid and Polymer Sci., 253, 231, (1975).
16. Y.M. Matsuo et al, Kolloid. Z.U.Z.F. Polymer, 201, 89, (1965).
17. S. Havriliak and S. Negami, Polymer, 8, 161, (1967).

18. G. William and P.J. Hains, Faraday Symposia Chem. Soc., 6, 12, (1972).
19. John H. Daly and Richard A. Pethrick, Polymer, 23, 1619, (1982).
20. G.T. Powles, J. Chem. Phys., 21, 633, (1953).
21. A.F. Diaz et al, J. Chem. Soc. Chem. Commun., 635, (1979).
22. A.F. Diaz and B. Hall, IBM J. Res. Develop., 27(4), 342, (1983).
23. A. Diaz, Chemica Scripta, 17, 145, (1981).
24. Wolfgang Wernet et al, Makromol. Chem. Rapid. Commun., 5, 157, (1984).
25. K.K. Kanazawa et al, Synth. Met., 4, 119, (1981).
26. Keiichi Kaneto et al, Jpn. J. Appl. Phys., 21(9), L567, (1982).
27. Atsushi Watamabe et al. Bull. Chem. Soc. Jpn., 54, 2278, (1981).
28. Keiichi Kaneto et al, Tech. Reports. Osaka University, 33(1693), 75, (1983).
29. M. Tanaka et al, Mol. Cryst. Liq. Cryst., 83, 277, (1982).
30. G. Tourillon et al, J. Phys. Chem., 87, 2289, (1983).
31. K. Kaneto et al, Solid State Commun., 46(5), 389, (1983).
32. N.F. Mott, Philos. Mag., 19, 835, (1969).
33. N.F. Mott and E.A. Davies, "Electronic Processes in Non-crystalline Materials", Clarendon Press, Oxford, (1979).
34. E.A. Davies, "Amorphous Semiconductors", In Topics in Applied Physics, M.H. Brodsky (ed.), 36, (1980).
35. K.K. Kanazawa et al, Synth. Met., 1, 329, (1980).
36. W. Wernet et al, Mol. Cryst. Liq. Cryst., 118, 193, (1985).
37. J.P. Travers et al, Mol. Cryst. Liq., 118, 149, (1985).
38. J.C. Scott et al, Mol. Cryst. Liq., 118, 163, (1985).
39. J.C. Scott et al, Synth. Met, 9, 165, (1984).
40. A. Watanabe et al, Bull. Chem. Soc. Jap., 54, 2278, (1981).
41. A.F. Diaz and K.K. Kanazawa, "Extended Linear Chain Compounds", J.S. Miller (ed.), Plenum Press, New York. 3, 417, (1982).
42. M. Tanaka et al, Mol. Cryst. Liq. Cryst., 83, 277, (1982).

43. Sizuo Tokito et al, Chemistry Letters, 531, (1985).
44. M. Salmon et al, Mol. Cryst. Liq. Cryst., 83, 265, (1982).
45. A.F. Diaz et al, J. Electroanal. Chem. 1, (1981).
46. K.K. Kanazawa et al, J. Chem. Soc. Chem., 834, (1979).
47. A.F. Diaz et al, J. Electroanal. Chem., 108, 377, (1980).
48. A.F. Diaz et al, J. Chem. Soc. Chem. Commun., 397, (1980).
49. M.G.B. Mahoubin-Jones and R.A. Pethrick, Polymer Yearbook, II Gordon and Breech, London and New York, (1985).
50. P.T. Kissinger and W.R. Heineman, J. Chem. Education, 60, 702, (1983).
51. C.B. Street et al, Mol. Cryst. Liq. Cryst., 118, 137, (1985).
52. G.B. Street, "In Handbook of Conducting Polymers", T. Skotheim (ed.) Marcel Dekker, New York (1984).
53. G. Tourillon and F. Garnier, J. Poly. Sci. Poly. Phys. Ed., 22, 33, (1984).
54. A. Diaz et al, J. Electroanal. Chem., 121, 355, (1981).
55. A. Diaz et al, Mol. Cryst. Liq. Cryst. 83, 1297, (1982).
56. A.F. Diaz et al, J. Electroanal. Chem., 129, 115, (1981).
57. G.S. Street et al, Mol. Cryst. Liq. Cryst., 83, 253, (1982).
58. G.B. Street et al, "Proceedings of Conference on Electronic Excitation and Interaction Processes in Organic Molecular Aggregates", P. Reineker et al, (eds.) Springer Series in Solid State Sciences, 49, 242, (1983).
59. T.C. Clarke et al, IBM J.Res. Dev., 27(4), 313, (1983).
60. R.A. Jones and G.P. Bean, "The Chemistry of Pyrrole", Academic Press, London, 117, (1977).
61. A.F. Diaz et al, J. Electroanal. Chem., 121, 265, (1982).
62. J.C. Scott et al, Mol. Cryst. Liq. Cryst., 23, 119, (1982).
63. J.C. Bredas et al, J. Phys., 44, C3-373, (1983).
64. J.C. Bredas et al, Phys. Rev., B27, 7827, (1983).
65. J.H. Kaufman et al, Mol. Cryst. Liq. Cryst., 118, 171, (1985).
66. J.L. Bredas et al, Phys. Rev., 1330, (1984).

67. Proceedings of the International Conference on the Physics and Chemistry of Low Dimensional Synthetic Metals (ISCM 84). Mol. Cryst. Liq. Cryst., 118, 1-450, (1985).
68. R.H. Geiss et al, IBM J. Res. Dev., 27, 321, (1983).