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STUDIES OF ION-CONTAINING POLY(ETHERS) AND RELATED POLYMERS

by

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Supervisor: Dr. R.E. Wetton

A doctoral thesis submitted in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy of Loughborough University of Technology.

May 1982

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To my parents for their constant encouragement throughout my studies.
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ORIGINALITY

The work presented in this thesis has been carried out by the author, except where otherwise acknowledged, and has not previously been submitted to this University or any other Institution for a higher degree.
ABSTRACT

The structure and properties of poly(vinyl alcohol), poly(methyl vinyl ether) and poly(ethyl vinyl ether) have been modified by the addition of metal salts to give single phase polymeric compounds. The metals have been selected from the Group I and transition elements of the periodic table.

All the metal salt complexes prepared have been studied using the technique of differential thermal analysis (D.T.A.). The complexes were amorphous and exhibited well defined glass transitions which were elevated or depressed from that of the original polymer depending upon the salt involved.

The complexes have been studied using the technique of dielectric relaxation. The measurements have been carried out at audio frequencies and high dielectric constants and losses have been observed. In certain complexes ionic conduction was observed at temperatures above the glass transition and resistivities comparable with those of semi conductors were measured. The results have been discussed in terms of conventional dielectric theories, however, since many of the conventional methods of representing the data were unsuitable for these systems the results have been discussed in terms of moduli. They are consistent with formation of complexes between the polymer chain and the metal salts.

The systems involving poly(vinyl alcohol) have been investigated using the techniques of mechanical relaxation and small and wide angle X-ray diffraction. Mechanical measurements were carried out under forced vibration and showed enhanced loss with increased salt concentration paralleling the observations from DTA studies. Evidence was obtained which indicated preferential inclusion of small ions into crystalline regions. The use of X-ray diffraction techniques confirmed the presence
of molecularly dispersed salt within the polymers and revealed increased suppression of crystallinity in the polymers.

The experimental data have been interpreted with the aid of two models. It is proposed that for polymers where steric hindrance of the side groups is low and the accepting power of the salt species is high, complexation takes place by chelate ring formation involving two adjacent oxygen atoms pendent to the backbone with the metal salt. For situations in which steric hindrance is greater a cage structure around the cation involving four or more ether oxygens is proposed.

It has been further shown that for complexes formed where steric hindrance effects are high the stability curve will be positioned in the same region as that for $T_g$ elevation effects. Successful interpretation of the observed D.T.A. and dielectric properties has been made by joint application of the concept of complex stability and of the two proposed models.

Complexes of poly(propylene sulphide) and some metal salts have been briefly investigated using D.T.A. techniques and the results interpreted using the aforementioned models.
## CONTENTS

### CHAPTER 1  INTRODUCTION

1.1 The Electrical Properties of Polymers  
1.2 Objectives and Scope of Present Work  
1.3 Modification of Polymers by the Inclusion of Metal Ions  
   1.3.1 Poly(ethers)  
   1.3.2 Poly(amides)  
   1.3.3 Poly(vinyl pyridines)  
   1.3.4 Ionomers  

### CHAPTER 2  THEORY

2.1 The Glass Transition  
   2.1.1 Definition of the Glass Transition  
   2.1.2 Theories of the Glass Transition  
   2.1.3 Factors Influencing the Glass Transition Temperature  
2.2 Dielectric Relaxation  
   2.2.1 Dielectric Dispersion  
   2.2.2 Empirical Distribution Functions  
   2.2.3 Effects of Temperature on the Distribution of Relaxation Times  
   2.2.4 Relationship Between Dielectric Constant and Dipole Moment  
   2.2.5 Dielectric Relaxation Processes  
   2.2.6 Maxwell-Wagner-Sillars Interfacial Polarisation  
   2.2.7 Colloidal Dispersions in Electrolyte Solutions  
   2.2.8 Pohl's Theory of Hyperelectronic Polarisation
2.3 Electrical Conduction in Polymers
   2.3.1 General Features
   2.3.2 Charge Carriers
   2.3.3 Carrier Injection
   2.3.4 The Effect of Structural Features

2.4 Mechanical Properties
   2.4.1 General Features
   2.4.2 Time-Temperature Superposition Principle
   2.4.3 Relationship between Dynamic Mechanical Properties and Structure

2.5 Small Angle X-Ray Scattering
   2.5.1 Introduction
   2.5.2 Scattering Power
   2.5.3 Slit versus Pinhole Collimation
   2.5.4 Porod's Law
   2.5.5 Guinier's Law
   2.5.6 Density Fluctuations within Phases

CHAPTER 3 EXPERIMENTAL

3.1 Purification and Characterisation of Polymers Studied
   3.1.1 Poly(vinyl alcohol)
   3.1.2 Poly(methyl vinyl ether)
   3.1.3 Poly(ethyl vinyl ether)
   3.1.4 Poly(isobutyl vinyl ether)
   3.1.5 Poly(propylene sulphide)
   3.1.6 Molecular Weight Determination

3.2 Preparation of Polymer-Metal Salt Complexes
   3.2.1 Poly(vinyl alcohol)
   3.2.2 Poly(ethyl vinyl ether)
3.3 Differential Thermal Analysis

3.4 Dielectric Measurements

3.5 Wide Angle X-Ray Measurements

3.6 Small Angle X-Ray Measurements

3.7 Mechanical Measurements

3.8 Infra-Red Measurements

CHAPTER 4 RESULTS

4.1 Characterisation of Polymers Studied

4.2 Poly(vinyl alcohol) Containing Metal Salts
   4.2.1 General Properties
   4.2.2 Glass Transition Temperature Data for Poly(vinyl alcohol)-Metal Salt Complexes
   4.2.3 Dielectric Relaxation Studies of Poly(vinyl alcohol)-Metal Salt Complexes
   4.2.4 Effect of Field Strength upon the Dielectric $\alpha'$ Relaxation
   4.2.5 Dynamic Mechanical Relaxation Studies of Poly(vinyl alcohol)-Metal Salt Complexes
   4.2.6 Small Angle X-Ray Scattering Studies of Poly(vinyl alcohol)-Metal Salt Complexes
   4.2.7 Wide Angle X-Ray Scattering Studies of Poly(vinyl alcohol)-Metal Salt Complexes
   4.2.8 Infra-Red Absorption Studies of Poly(vinyl alcohol)-Metal Salt Complexes

4.3 Poly(ethyl vinyl ether) Containing Metal Salts
   4.3.1 General Properties
4.3.2 Glass Transition Temperature Studies of Poly(ethyl vinyl ether)-Metal Salt Complexes 104

4.3.3 Dielectric Relaxation Studies of Poly(ethyl vinyl ether)-Metal Salt Complexes 105

4.4 Poly(methyl vinyl ether) Containing Metal Salts 106
4.4.1 General Properties 106
4.4.2 Glass Transition Temperature Data for Poly(methyl vinyl ether)-Metal Salt Complexes 108
4.4.3 Dielectric Relaxation Studies of Poly(methyl vinyl ether)-Metal Salt Complexes 108

4.5 Poly(propylene sulphide) Containing Metal Salts 110

CHAPTER 5 DISCUSSION OF COMPLEXES OF POLY(VINYL ALCOHOL) AND METAL SALTS 111

5.1 General Properties of Polymer-Metal Salt Compounds Formed 111

5.2 Glass Transition Temperature of Poly(vinyl alcohol)-Metal Salt Complexes 113
5.2.1 Single Phase Model 114
5.2.2 Systems in which T_g was Elevated by Addition of Zinc Chloride 116
5.2.3 Intramolecular versus Intermolecular Coordination 119
5.2.4 Other Transition Metal Chloride Complexes with Poly-(vinyl alcohol) 125
5.2.5 Systems in which T_g was Depressed by the Addition of Salt 133

5.3 X-Ray Scattering Studies 142
5.3.1 Small Angle X-Ray Scattering Studies 142
5.3.2 Wide Angle X-Ray Scattering Studies 143
5.4 Dynamic Mechanical Thermal Analysis 146
5.5 Analysis of Infra-Red Spectra 155
5.6 Dielectric Relaxation Studies of Poly(vinyl alcohol)-Metal Thiocyanate Complexes 157

CHAPTER 6 DISCUSSION OF COMPLEXES OF POLY(ALKYL VINYL ETHERS) AND METAL SALTS

6.1 General Properties of Poly(alkyl vinyl ethers) Containing Metal Salts 164
6.2 Glass Transition Behaviour of Poly(alkyl vinyl ethers) Containing Metal Salts 164
6.2.1 General Comments 164
6.2.2 The Effect of Polymer Side Chain Dimensions 170
6.3 Glass Transition Temperature Studies of Poly(propylene sulphide) Containing Metal Salts 171
6.4 Dielectric Dispersion Studies of Poly(alkyl vinyl ethers) Containing Metal Salts 172
6.5 Dielectric Modulus or Inverse Permittivity Representation of Data 176
6.6 Molecular Interpretation of the Observed Dielectric Permittivity and Glass Transition Data and Calculated Dielectric Modulus Data 178

CHAPTER 7 CONCLUSIONS 185
1.1 The Electrical Properties of Polymers

The electrical conductivity of materials is a property which spans a vast range. Organic compounds have conductivities which are typically eighteenth orders of magnitude smaller than those of metals and many polymers exhibit values which are even lower. Figure 1.1 illustrates typical values for various types of materials.

The inherent insulating properties of most polymers have been exploited for many years to constrain or protect currents flowing in conductors and to sustain high electric fields without breakdown. Early electrical equipment utilised natural polymers such as gutta percha; the advent of synthetic high polymers, however, rapidly increased the range of insulators available and coincided with a concurrently rapidly expanding electronics industry. Typical of the use of high synthetic polymers to electrical applications was the selection of extremely low loss (relative permittivity 2.25, tan $\delta$ less than 0.0003) polyethylene as the insulator for long distance submarine telephone cables across the Atlantic Ocean during the 1960's.

Despite the seeming ideality of polymers for use in situations where highly insulating properties are required the search for plastics having various degrees of conductivity has long been established. Research has primarily centred around the relief of static charge build up on polymer surfaces which at least can be troublesome and at worst, dangerous if they introduce an explosion risk. This problem has frequently been alleviated by the introduction of a heterogeneous conductive filler to the polymer
Figure 1.1

Chart of typical conductivities

$\sigma$ (Ω·m$^{-1}$)

$10^{-18}$  ➞ Polyethylene, dry fused quartz

$10^{-15}$  ➞ Nylon

$10^{-12}$

$10^{-9}$  ➞ Glass, Cotton (50% RH)

$10^{-6}$

$10^{-3}$

$10^{0}$  ➞ Silicon, Germanium (intrinsic)

$10^{3}$

$10^{6}$

$10^{9}$

$10^{12}$

$10^{15}$

$10^{18}$

$10^{21}$ $10^{24}$ $10^{26}$  ➞ Lead at 4K (Superconduction)
matrix or by treatment of the surface by chemical antistatic agents. Carbon black, graphite and powdered metals have been most frequently used as conductive fillers and conductivities of up to $10^{-2} \, (\Omega \, \text{cm})^{-1}$ have been obtained. The heterogeneous nature of such systems means that the conductivity is dependent upon both the shape and size of the conductive filler, and the quality of the interparticle contacts. In addition the mechanical properties are frequently severely impaired and thus the application of the polymers has been limited.

The search for an easily mouldable, flexible conductive polymer for more extensive applications has led to studies of systems in which conduction is inherent. For this situation to exist sufficient overlap of the electron orbitals must exist between neighbouring molecules which themselves have delocalised electronic molecular orbitals. These conditions have been met using various approaches.

a) **Conjugated Chains**

Fully saturated polymer molecules show no significant conductivity, however if the backbone consists of a series of alternating single and double bonds

\[
\begin{array}{c}
\text{\includegraphics[width=0.5\textwidth]{conjugated Chains.png}}
\end{array}
\]

the resulting $\pi$ orbitals can be delocalised over the whole chain length (in a similar manner to that in which the $\pi$ orbitals of benzene are delocalised over the whole ring) to form a so called valence band capable of metallic conduction. The activation energy of conduction for such systems is low (comparable to the thermal energies at room temperature 0.025 eV) and thus high conductivities would be expected.
In reality high conductivities are only observed in relatively few examples of polyacetylenes which have a highly crystalline stereoregular structure. Shirakawa and Ikeda\(^5\) observed values of up to \(10^{-5}\ \Omega\text{cm}^{-1}\) with thin films of trans polyacetylene. Normally, however, values of conductivity are little better than for unconjugated systems. The major reasons for this are two fold. Jahn-Teller stabilisation produces a system of alternating long and short bonds and thus a variation of delocalisation distance and activation energy. Secondly, for conjugation to be fully maintained the molecules must remain planar, rotation about any of the bonds reduces overlap and breaks the conjugation. A typical example of this phenomenon is poly(phenyl acetylene) in which steric hindrance prevents adoption of a planar conformation and the conductivity is less than \(10^{-10}\ \Omega\text{cm}^{-1}\).

The formation of ladder type polymers has overcome the problem of obtaining conjugated chains by locking them into the required configuration. Typical of these are the poly(acene quinone radical) (PAQR) polymers\(^6,7\) which have the general structure

\[
\begin{array}{c}
\text{Conductivities in the range } 10^2 \text{ to } 10^{-5} \ (\Omega\text{cm})^{-1} \text{ have been observed but as with many of the polyacetylenes are generally intractable. The ultimate extension of such systems is represented by the formation of large sheets of fused rings. One such system is produced by the pyrolysis of poly(acrylonitrile) to give conducting filaments known as 'Black Orlon'\(^8\).}
\end{array}
\]
The material has conductivity of \( \approx 10 \ (\mathcal{R} \text{ cm})^{-1} \) but is again intractable. It has the advantage that it can be produced by pyrolysis after fabrication into the desired shape.

b) **Charge Transfer Complexes**

Charge-transfer complexes are formed by partial transfer of an electron from a donor molecule of low ionisation potential to an acceptor molecule of high electron affinity.

\[
D + A \rightarrow D^+ A^- 
\]

The complete transfer of charge would result in the formation of a radical ion (i.e. an ion carrying an odd number of electrons). A good example of the formation of such complexes is given by the reaction between pyrene \((10^{-10} \ (\mathcal{R} \text{ cm})^{-1})\) and iodine \((10^{-5} \ (\mathcal{R} \text{ cm})^{-1})\) to give a complex of conductivity \(10^2 \ (\mathcal{R} \text{ cm})^{-1}\). The complex packs in 'sandwich stacks' and conduction is very directional (being greatest along the direction of the stacks). Polymeric complexes having the donor species attached to the polymer backbone can also be synthesised but show lower conductivity. Examples include poly(phenylene)-iodine\(^9\) \((10^6 \ (\mathcal{R} \text{ cm})^{-1})\) and poly(vinyl-anthracene)-iodine\(^10\) \((10^6 \ (\mathcal{R} \text{ cm})^{-1})\).

The discovery of the compound 7,7,8,8 tetra cyano quinodimethane (TCNQ)\(^11\), a very strong electron acceptor capable of forming first a radical anion and then the dianion has been fundamental to much of the
research towards obtaining a conductive material.

\[ \text{NC} \quad \text{CN} \quad \overset{+e}{\longrightarrow} \quad \overset{-e}{\longrightarrow} \quad \text{NC} \quad \text{CN} \]

TCNQ is capable of forming both charge-transfer complexes and true radical-ion salts. The lithium salt \( \text{Li}^+ \text{TCNQ}^- \) shows conductivity of \( 10^{-1} \) (\( \Omega \text{ cm} \))\(^{-1} \) whilst even higher values have been obtained with some organic cations, e.g.

\[
\begin{array}{c}
\text{N} \\
\text{Me} \\
\text{TCNQ}^-
\end{array}
\]

N-methyl phenazinium TCNQ, conductivity \( \approx 10^6 \) (\( \Omega \text{ cm} \))\(^{-1} \).

Under certain conditions TCNQ may form both simple and complex salts, the latter containing an extra equivalent of neutral TCNQ and showing greater conductivity.

Only limited success has been reported in obtaining polymeric versions of TCNQ complexes. The simplest approach has utilised polymeric cations (ideally with some aromatic nature). Examples\(^{12,13} \) include poly(2-vinyl pyridine), poly(vinyl-methyl imidazole) and poly(1-methyl 2-vinyl pyridine). The increased condition created of obtaining the correct conformation in the solid state to permit the associated TCNQ units to form the necessary face to face stacks for electron transfer has resulted in only limited success. Conductivities of \( 10^2 \) (\( \Omega \text{ cm} \))\(^{-1} \) have, however, been reported\(^4 \).
Examples of radical cation systems also exist, these have been based on a family of heterocyclic compounds known as violenes. An example is tetrathiafulvalene (TTF)

\[
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{S} \\
\text{S}
\end{array}
\]

whose compound with TCNQ shows very high conductivity \((10^7 \text{ S cm}^{-1})\).

c) Organometallic Compounds

The introduction of organometallic groups in polymers have been shown to improve electronic conduction. The metal d orbitals can overlap with the \(\pi\) orbitals of the organic structure, extend the delocalisation and act as bridges to adjacent molecules. Dewar and Talati\(^{14}\) observed conductivities of up to \(1 \text{ S cm}^{-1}\) for the polymeric complex of CuII with 1,5-diformyl-2,6-dihydroxy naphthalene dioxime.

\[
\text{\begin{array}{c}
\text{O} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{O}
\end{array}}
\]

Such complexes are similar to compounds previously described in that they show very poor mechanical stability.

1.2 Objectives and Scope of Present Work

In the previous section the wide range of electrical conductivity in polymeric species was discussed. In particular it was shown that donor-acceptor complexes of organic species though frequently exhibiting high
conductivity showed poor mechanical properties.

The formation of coordination compounds between low molecular weight organic compounds such as the anions of acetyl acetone I and salicylaldehyde II and metal compounds is well established\textsuperscript{15,16} and used frequently in organic synthetic routes\textsuperscript{17}.

\[ \text{acetyl acetone I} \quad \text{salicylaldehyde II} \]

The coordination compounds formed involve donation of electrons from a non-bonding orbital containing electrons on a suitable atom such as oxygen, sulphur or nitrogen to a vacant orbital on the metal atom (normally a hybrid of the available s, p and d orbitals). The bonds thus formed are traditionally represented as being covalent but show some ionic character which is governed by the electronegativity difference between the metal and the ligand atoms. The ability of a ligand to bestow covalent character to a bond which it forms with a metal is frequently termed the donor strength and reflects the ability to increase the electron density on the metal.

Although analogous to their low molecular weight counterparts, relatively few references exist in the literature to complexes in which part of a polymer molecule acts as the donor\textsuperscript{18}.

In addition to the parameters highlighted previously for low molecular weight materials, Davydova\textsuperscript{19} has indicated other factors which will affect complex formation by polymers. The distribution of ligands along, and their position relative to the main chain will affect the efficiency of complex formation. Linked to this will be the requirement of obtaining the correct conformation of the ligand. If the ligand normally exists in a
conformation different to that required by the preferred stereochemistry of
the metal ion, then conformational changes will have to take place before
complexation can take place. In common with their low molecular weight
counterparts chelation will enhance the stability of the metal ion, this
will be especially so if the rings formed by such a process are essentially
unstrained. Suitable donating species are found in several types of
heteroatomic polymers such as poly(ethers), poly(amides), poly(esters),
poly(thio ethers) and poly(vinyl alcohol).

The work presented in this thesis is primarily concerned with the
interaction of metal salts with poly(ethers) in which the ether linkage is
present not as part of the main chain but as a group pendant to the back-
bone. The distance between oxygen atoms was kept constant within the series
such that if complexation occurred involving two oxygen atoms a stable six
member ring could be formed. The polymers differed in the degree of steric
hindrance experienced by the ether linkage, the effect is illustrated by
comparison of poly(vinyl alcohol) \( \left\{ \text{CH}_2-\text{CH} \right\}_n \) \( \text{OH} \)
\( \left\{ \text{CH}_2-\text{CH} \right\}_n \) and poly(ethyl vinyl ether) \( \left\{ \text{CH}_2-\text{CH} \right\}_n \)
\( \text{O-CH}_3 \) poly(ethyl vinyl ether) \( \left\{ \text{CH}_2-\text{CH} \right\}_n \)
\( \text{OCH}_2\text{CH}_3 \) All three poly(ethyl vinyl ether) \( \left\{ \text{CH}_2-\text{CH} \right\}_n \)
polymers were commercially available and dissolved in polar solvents, a
criterion important for the preparation of polymer-metal salt complexes.
In addition to the study of the interaction of metal salts with poly-
(ethers) a brief investigation of sulphur-containing polymers has been
made using poly(propylene sulphide) \( \left\{ \text{CH}_2-\text{CH-S} \right\}_n \).

The selection of the salts to be studied was governed by several
distinct criteria. Of primary importance was the solubility of the salt
in polar organic solvents, a precursor for the preparation of the polymer-
metal salt complexes to be discussed later. Transition metal salts were,
for the most part, ideally suited to the studies, being soluble in solvents
such as alcohols, ethers and ketones and being known to form stable complexes with a wide range of ligands\textsuperscript{15,16}. Other salts were chosen in the light of the ultimate aim of obtaining a conductive polymer system and were selected primarily from Group 1 of the periodic table.

The choice of cation-anion combination was still large despite the above restrictions, however in practice the anion was selected from halides and pseudohalides which were readily available and for which thermochemical data were available.

Care was taken in the choice of metal salt to ensure that it neither degraded the polymer nor was decomposed itself under the experimental conditions used. Where possible and convenient salts were used in the anhydrous state. The hydrated salts being already coordinated to water would require an additional displacement process by the ether oxygens before complexation could take place.

1.3 Modification of Polymers by the Inclusion of Metal Ions

The study of polymers modified by the presence of metal salts has been extensively reviewed\textsuperscript{18,20,21} and will not be considered in depth here. Some studies which are particularly pertinent are, however, given below and are classified by polymer type.

1.3.1 Poly(ethers)

a) Crown Ethers

Crown ethers are macrocyclic compounds with a ring consisting of the repeating unit $\text{\(\text{CH}_2-\text{CH}_2-\text{O}\)}$ and represent an intermediate series of compounds between small organic species and polymers. Crown ethers have been extensively studied by several workers including Pederson\textsuperscript{22,23}, Kopolow\textsuperscript{24,25,26}, Dale\textsuperscript{27} and Alexy\textsuperscript{28}. Their formal names are long, so that trivial names indicating the size of the macrocyclic ring and the number of oxygens
in the ring are frequently used. Thus III is termed 12-crown-4

Crown ethers have the characteristic of being capable of forming stable complexes with a wide range of cations. The complexes have very high stabilities, both in solution and in the solid state in comparison to those formed by other neutral ligands. The complex formed from the potassium cation and 18-crown-6 for example has a stability constant of $10^{6.1}$ in methanol compared with $10^{2.2}$ for the potassium complex of the relatively strong chelating acrylic ligand $\text{Me}(\text{OCH}_2\text{CH}_2)_5\text{OMe}$. Complexes of this type are so strong that they enable inorganic salts such as potassium permanganate and fluoride to dissolve in aromatic solvents when the crown is present, a phenomenon finding great importance in the field of organic chemistry.

In crown ether complexes the ligand oxygens bond solely by electrostatic forces and are located at distinct points on the coordination sphere of the metal. In some complexes such as those formed by IV and potassium thiocyanate the gegen ion remains bonded to the metal, while in others the metal cation is efficiently separated from both the gegen ion and the solvent by the organic framework of the ligand. Under these conditions the basicity and nucleophilicity of the gegen ion are generally enhanced.
The stability of the complexes of crown ethers with alkali metals is highly dependent on the size of the macrocyclic ring and the radius of the cation, and is a maximum when the ring can just accommodate the cation. Thus III will bind with $\text{Li}^+$ but not $\text{K}^+$ \textsuperscript{29}, IV binds with $\text{K}^+$ but not $\text{Li}^+$ or $\text{Na}^+$ \textsuperscript{30}. Similarly V complexes with $\text{Hg}^{2+}$ but not $\text{Cd}^{2+}$ or $\text{Zn}^{2+}$.

b) Poly(ethylene oxide)

The existence of crystalline adducts of mercuryII chloride and poly-(ethylene oxide) have been reported by several workers\textsuperscript{31-34}. The adducts were shown to have two distinct forms which had the empirical formulae $(\text{CH}_2\text{CH}_2\text{O})_4\text{HgCl}_2$ and $(\text{CH}_2\text{CH}_2\text{O})\text{HgCl}_2$ and were designated type I and II respectively. In the former it was found that the normally linear $\text{Cl-Hg-Cl}$ bond had been distorted to $176^\circ$, an occurrence attributed to interaction of salt molecules with the polymer oxygen atoms in which coordination is from one side only. In the second type of complex each oxygen atom of the poly(ethylene oxide) was coordinated to two mercury atoms. Both types of complex are shown in Figure 1.2.

Iwamoto obtained further information about these complexes during studies of ethylene oxide oligomers complexed with mercuryII chloride\textsuperscript{35}. From structural evidence obtained from X-ray diffraction of single crystals Iwamoto was able to suggest that a mercury atom was coordinated to several coplanar oxygen atoms and that the complexes were formed by electrostatic forces acting between the positively charged metal ion and the negatively charged oxygen. A tentative suggestion that structures contained some covalent character in the metal oxygen bonds was also made.

Wright et al.\textsuperscript{36} prepared complexes of poly(ethylene oxide) and various alkali metal salts (in particular halides and thiocyanates) having a molar ratio of salt:polymer repeat unit of 1:4. Complexes of sodium iodide, sodium thiocyanate and potassium thiocyanate were spherulitic and melted at
Figure 1,2
Poly(ethylene oxide)-Mercuric Chloride Complexes

Type 1

Type 2

$T = \text{Trans}, G = \text{Gauche}$
205°, 160° and 100° respectively. Results obtained from X-ray diffraction and infra-red spectroscopy indicated a totally different structure to that of the parent polymer, and that the addition of salt in concentrations in excess of 20 mole percent resulted in recrystallization of the pure salt as displayed by the presence of the characteristic peaks for the salts in the X-ray spectrum of the complex.

In subsequent studies Wright\textsuperscript{37,38} measured the electrical conductivity of these complexes. A transition zone (which for the sodium complexes was situated at approximately 55°C) from a high to a low activation energy of conduction was observed and attributed to the thermal disintegration of the complexes in the amorphous regions. Similarities between the infra-red spectra of these complexes and those of cyclic ethers suggested coordination of the cation to the backbone ether oxygens in a similar manner to that shown in Figure 1.3.

Recent studies\textsuperscript{39,40} have highlighted the potential of such systems as solid electrolytes. Armand\textsuperscript{39} has indicated that the conductivity of the complexes was dependent upon several parameters including cation size, salt concentration and crystallinity. The application of Arrhenius behaviour to the observed experimental results was not successful, and the observed conductivities of better than $10^{-5}$ (S cm)$^{-1}$ at temperatures in the range 40-60°C were explained in terms of a free volume model involving diffusion of the charged species.

It is pertinent at this point to note the studies of Lundberg et al.\textsuperscript{41} also concerning the complexes of alkali metal halides and poly(ethylene oxide). The results obtained indicated depression of melting point and degree of crystallinity of the poly(ethylene oxide) and no formation of any new crystalline complexes of the type described by Wright. The results were again interpreted in terms of ion-dipole interaction. The difference in observed results may be a symptom of the method of preparation.
Figure 1,3
Coordination of poly(ethylene oxide) segments with alkali metal cations

T = Trans
G = Gauche
$\bar{G}$ = Gauche-minus

- Cation
- Carbon
- Oxygen
- Lone pair electrons
Lundberg did not use solution techniques but directly milled the halide into the polymer. Under the latter conditions the mixing would have been less intimate and thus formation of new crystalline phases would not be favoured.

c) Poly(propylene oxide)

The viscoelastic properties of high and low molecular weight poly-(propylene oxide) containing dissolved lithium perchlorate were studied by Moacanin and Cuddihy. For the low molecular weight polymer an elevation of $T_g$ of up to $110^\circ C$ (at 25 wt. % salt loading) above that of the parent polymer was observed. Similar behaviour was observed for the high molecular weight polymer with the exception that at lower salt loadings (< 16 wt. %) two transitions were observed. The first transition occurred at a temperature slightly greater than that of the homopolymer ($-65^\circ C$) whilst the second, at $-10^\circ C$, was interpreted in terms of the transition of polymer helices stabilised by lithium perchlorate present in the helix core. In the low molecular weight polymer the helix core was too small for this to occur and thus the transition was absent. The elevation of $T_g$ was explained in terms of strong interaction forces between the lithium ion and the polyether oxygen atom analogous to those observed in low molecular weight oxygen containing compounds.

In recent studies, James and Wetton have investigated the glass-transition behaviour of poly(propylene oxide) of high and low molecular weight with added zinc chloride. Glass transition temperature elevations of up to $140^\circ C$ above that of the parent polymer were observed. The elevation of $T_g$ was dependent upon the concentration of salt present and followed a sigmoidal curve levelling out at high salt concentrations. The results were interpreted in terms of the formation of a stable five member chelate ring involving the coordination of two adjacent ether oxygen atoms.
in the polymer backbone to the metal salt. The effect is illustrated in Figure 1.4.

Interest in the electrical properties of polyethers in recent years has led to several studies. Delduca et al.\textsuperscript{45} reviewed the formation of complexes between poly(alkyleneoxy) and inorganic salts. The major subjects for their investigations were poly(ethylene glycol) and poly(propylene glycol) in the presence of Group 1 and Group 2 metal tetraphenylborates. It was found from infra-red and NMR spectroscopy that for a given alkylene oxide a cation ratio of 8.5:1 was indicated for complexes of alkali metals and 12:1 for alkaline earth metals. Cheradame\textsuperscript{46} et al. have studied the electrical conductivity of poly(propylene oxide) networks containing sodium tetraphenylborate and have found that in the temperature range 50-150\degreeC conductivity followed an apparent Arrhenius law. In other respects the materials did not follow the typical behaviour of solid electrolytes following the Arrhenius law, an observation interpreted in terms of the fact that the polymers were in the rubbery and not the glassy state.

d) Poly(vinyl alcohol)

The commercial importance of poly(vinyl alcohol) has led to many studies of the effects of the addition of metal salts to the solution properties of the polymer. These have been reviewed by Finch\textsuperscript{47} and Pritchard\textsuperscript{48} in their respective texts and will not be considered in this thesis except to state that in general, addition of metal salt results in an increase in the viscosity of the solution\textsuperscript{49} which may under severe circumstances result in irreversible gel formation\textsuperscript{50}. Both phenomena have been interpreted in terms of coordination of the ions to the polymer molecules.

Hannon and Wissburn\textsuperscript{51} studied the interactions of inorganic nitrates with several polymers including poly(vinyl alcohol). They observed large
Figure 1.4

Coordination of poly(propylene oxide) segments with transition metal halides

$T = \text{Trans}$
$G = \text{Gauche}$

- Metal Halide
- Carbon
- Oxygen
shifts both of the inorganic nitrate and the polymer infra-red absorption frequencies which together with Tg measurements were interpreted in terms of the formation of a complex between the polymer and the salt in the solid state. The solvent was an integral part of the complex. It is pertinent to note that the oxidising nature of the salts used may have led to degradation and hence erroneous results.

Hojo et al.\textsuperscript{52} reported the formation of a complex between poly(vinyl alcohol) and copperII ions from measurements of the absorption spectra in solution. Subsequent studies attempted to quantify the structure of the chelates. Morishima and co-workers\textsuperscript{53} investigated the molecular weight dependence of complex formation. They found that the salt molecules were tetra-coordinated and that a minimum degree of polymerisation of 20 was required to form a complex. They concluded that complexation was a combination of inter- and intra-molecular effects and that some crosslinking may have been present.

Sumita et al.\textsuperscript{54} studied the electron spin resonance (ESR) spectra of poly(vinyl alcohol) and other polymer-CuII complexes. More than five discrete ESR spectra were obtained for the poly(vinyl alcohol)-CuII moiety and were interpreted in terms of various degrees of coordination of the copper ion with the polymer and/or water. The complexes were proposed to take up orthorhombic coordination with the gegen ion taking up the axial positions and the polymer adopting various equatorial positions.

Higashi\textsuperscript{55} has reported a new semi-conducting polymer based upon a poly(vinyl alcohol)/copperII salt/iodine chelate. The resistivity was found to vary with the concentration of salt and halogen present. With a salt concentration of 15% and iodine concentration of 4% surface resistivities of $\approx 10^3 \Omega /cm^2$ were reported.
1.3.2 Poly(AMides)

Dunn and Sansom\textsuperscript{56,57} investigated the stress cracking of polyamides (mainly Nylon 6 and Nylon 66) by metal salts in aqueous and non-aqueous solutions. Many halides were found to be active agents, but could be subdivided into types 1 and 2 depending upon the mechanism by which they caused stress cracking. The first involved predominantly transition metals and consisted of a system of coordinated bonds from the metal to the carbonyl groups of the polyamide. The stress cracking in these systems was caused by interference of the polyamide hydrogen bonding.

The second type of complex was observed when compounds of Group 1 and 2 metals were used. In solution these salts formed proton donating solvated species which acted as direct solvents for the polyamide. The two structural forms are shown in Figure 1.5. Similar effects were observed with metal thiocyanates\textsuperscript{58} and nitrates\textsuperscript{59}.

Andrews\textsuperscript{60,61} studied the dynamic mechanical properties of Nylon-6 treated with zinc chloride, cobalt chloride and cobalt thiocyanate. It was found that absorbed salt shifted the tan \(\delta\) peak associated with the \(\alpha\) relaxation to higher temperatures. Accompanying this was a significant increase in the magnitude of the relaxation. Extraction of the zinc chloride or cobalt chloride restored the properties almost to those of the homopolymer (with the exception of the presence of a small residual shift attributed to irreversible morphological changes). Samples treated with cobalt thiocyanate showed permanent changes in structure even after extraction. No molecular interpretations of the observations were proposed.

Ciifferi et al.\textsuperscript{62-64} and Frasci et al.\textsuperscript{65} studied the effects of alkali metal halides, especially lithium chloride and lithium bromide upon Nylon-6. They found that the salts continuously depressed the melting temperature of the polymer with increasing salt content. The addition of salt was also
Figure 1.5

Structure of complexes of Polyamides

(a) with Type 1 metal halides

(b) with Type 2 metal halides
found to reduce the degree of crystallinity and the rate of crystallization of the polymer. The salts could be extracted from the polymer-salt complexes with hot water such that as with the work of Andrews the original characteristics of the polymer were restored. The effects were interpreted in terms of strong interactions between the amide group in the amorphous regions of the polymers and the halides, resulting in the observed reductions of specific volume which were not consistent with a pure addition of polymer and salt. In subsequent work Acierno et al. reported, somewhat surprisingly, in the light of the above observations that the Tg of Nylon-6 was not affected by the type and concentration of the alkali metal salts in the polymer.

In recent studies Kim and Harget and Siegmann and Baraam have reported increases in Tg associated with the incorporation of metal salts in Nyons which was dependent not only on the concentration but the type of salt. Kim and Harget were able to relate the observed increase of Tg with Q/R ratio of the ion, the ratio of oxidation number to ionic radius.

Kakinoki has published results concerning the semi-conducting properties of poly(acrylamide)-copperII chelates with iodine. Treatment of the chelate in a solution of iodine produced films having a surface resistivity of \( \approx 10^3 \Omega/cm^2 \).

Reich and Michaeli polymerised acrylonitrile in the presence of various hydrated metal perchlorates to form solid solutions. They observed a decrease of Tg with increasing salt concentration. The solutions showed high conductivities of \( 10^{-2} (\Omega \text{ cm})^{-1} \). The observations of Tg have been interpreted in terms of plasticisation of the polymer network by the addition of salt. Dewsberry has proposed a conductivity mechanism to account for the observed variation of activation energy with temperature.
1.3.3 Poly(vinyl pyridines)

Interest has been shown since the 1960's concerning the coordination of poly(2-vinyl pyridine)$^{73}$ and poly(4-vinyl pyridine)$^{74-77}$ with the first row transition metal salts. Kopylova$^{78}$ and Agnew$^{79}$ discussed the general features of coordination including the coordination number of the metal ion, the stoichiometry of the complex formed, and the relative merits of the inter- and intra-molecular complexations.

The results published have suggested that complexes were formed through the nitrogen atom of the pyridine ring. Coordination could be either inter- or intra-molecular depending upon the isomer chosen. For 4-(vinyl-pyridine) polymers coordination was predominantly intermolecular such that the metal salt acted as a crosslink between the two polymer chains. In the 2-(vinyl-pyridine) isomer intramolecular coordination was possible since the nitrogen atoms were in favourable positions for such a process. Typical structures are shown in Figure 1.6.

1.3.4 Ionomers

The term ionomer is applied to a material consisting of a polymer of an organic monomer and an ionisable monomer. The number of materials which may be included is enormous, most studies have been conducted upon ethylene containing a small amount of methacrylic acid. The morphology of these compounds is still in dispute but has generated considerable literature which has been reviewed by Otocka$^{80}$ and Eisenberg$^{81,82}$.

At least two structural models have been developed to account for the observed changes in tensile properties, impact resistance and melt viscosity$^{82}$ which occur when some of the acid side groups are neutralised. In the first$^{83}$, a three phase model is envisaged, consisting of a poly-(ethylene) crystal phase, an amorphous hydrocarbon phase and a phase
Figure 1.6

Metal salt complexes of Poly(vinyl pyridines)

(a) Intermolecular Coordination [Poly(4-Vpy)]

(b) Intramolecular Coordination [Poly(2-Vpy)]
Ion cluster model for ionomer systems

Figure 1.7

Hydrocarbon chains

3-13 Å Cluster radius

20-35 Å Short range order distance
consisting of microphase separated clusters of salt groups. The second model postulates a uniform distribution of salt groups throughout the amorphous phase\textsuperscript{84,85,86}. In this latter model the salt groups were assumed to form dimers and not to cluster to any significance.

The first model is supported by evidence obtained from several experimental techniques: X-ray diffraction\textsuperscript{82,87,88}, electron microscopy\textsuperscript{82,89,90}, mechanical and dielectric measurements\textsuperscript{91-94} and thermodynamic parameters\textsuperscript{95}. It is illustrated in Figure 1.7.

Evidence for the second model is less strong, and it has been argued\textsuperscript{18} that much of the experimental data supporting the mechanism can be used equally well to support the Macknight proposal\textsuperscript{83}.

The presence of crystalline regions has complicated the morphology of ethylene-methacrylic acid ionomers and has hindered the interpretation of much of the experimental data. In an effort to overcome this problem Eisenberg and co-workers\textsuperscript{96-98} have studied styrene-methacrylic acid based ionomers. For copolymers containing more than 6 mole \% of ionic comonomer evidence of ion clustering was found from X-ray diffraction. Below this concentration X-ray evidence suggested simple ion multiplet formation.
CHAPTER 2

THEORY

2.1 The Glass Transition

2.1.1 Definition of the Glass Transition

Many substances when sufficiently supercooled below their freezing point exhibit a transition from a viscous liquid to a hard, brittle amorphous solid commonly referred to as a glass. Examples of such substances are numerous and include organic polymers and hydrogen bonded compounds (such as alcohols) in addition to the well known polysilicates.

The glass transition can be defined as the narrow temperature band over which the temperature and pressure derivatives of thermodynamic parameters such as energy $E$, heat content $H$ and volume $V$ suffer a discontinuity, and below which configurational rearrangements of the polymer chain are extremely slow. The effect is that $E$-$T$, $H$-$T$ and $V$-$T$ curves are shallower below the transition temperature than above. Since the change occurs over a relatively narrow temperature band any reasonable measurement which attempts to define the temperature at which the material becomes brittle will be a fair indication of the glass transition temperature $T_g$. The definition of $T_g$ is not however without ambiguity since a $T_g$ thus defined is found to be lower for a slowly cooled material than for a rapidly cooled specimen.

Flory has envisaged an amorphous polymer whether as a glass below $T_g$ or as a rubber above $T_g$ as consisting totally of a random, tangled network. Kargin and Yeh have proposed partially ordered models consisting of bundles of ordered polymer chains in a random matrix. Experimental evidence obtained from Neutron, light, electron and X-ray...
scattering has supported the former assertion and has indicated the adoption of a random configuration in the glassy state which is comparable to those of dilute solutions of polymers in theta solvents.\textsuperscript{101} The glass transition can be explained however, irrespective of the basic element involved in the structure of the amorphous polymer.

2.1.2 Theories of the Glass Transition

There are several theories concerning the glass transition described in the literature. The most widely discussed are the kinetic Free Volume Theory\textsuperscript{105,106} and the more recently proposed statistical mechanical theory of Gibbs and Di Marzio\textsuperscript{107-114} which takes as its premise a thermodynamic viewpoint.

a) Free Volume Theory

The properties of many monomeric and polymeric substances suggest the presence of free volume. In simple terms if the polymer chain is regarded as a solid structure, then the free volume may be regarded as being present as holes of molecular (or monomeric) dimensions due to packing irregularities. Using this concept the thermal expansion coefficient of liquids may be regarded as primarily representing the creation of additional free volume with temperature. The total volume per gram $V$ may be regarded as the sum of $V_f$ the "free volume" and $V_o$ the "occupied volume" (the latter being a composite of the volume of molecules as represented by the Van der Waals radii and the volume associated with vibrational motions). $V_o$ will increase with temperature with expansion coefficient $\alpha_o$. The effect is illustrated in Figure 2.1.

At sufficiently high temperatures to permit motion in the polymeric solid a decrease in temperature is accompanied by a collapse of free volume as molecular adjustments take place within a normal time scale ($T > T_g (\mathcal{C})$). At lower temperatures adjustments are slower and eventually a temperature is
Figure 2.1

Schematic variation total specific volume, occupied volume, and free volume with temperature for a supercooled liquid.
is attained at which collapse cannot occur within experimental times and any residual contraction is due to the solid properties.

Batchinski\textsuperscript{115} applied this concept to the shear viscosity of simple liquids. More recently Doolittle\textsuperscript{116,117} has represented the viscosities of ordinary liquids of low molecular weight in this manner and has derived the equation

\[ \ln \gamma = \ln A + B \left[ V - V_f \right] / V_f \]  
(2.1)

where \( A \) and \( B \) are constants and \( \gamma \) is the viscosity of the system.

Using the concept of fractional free volume \( f \) as given by \( V_f / V \) equation (2.1) can be rearranged in the form

\[ \ln \gamma = \ln A + B \left[ 1/f - 1 \right] \]  
(2.2)

Taking the liquid to be above its glass transition temperature the fractional free volume increases linearly as shown in Figure 2.1. The increase may be represented by the equation

\[ f = f_g + \alpha \left[ T - T_g \right] \]  
(2.3)

where \( f \) is the fractional free volume at temperature \( T \) (\( T > T_g \)) and \( f_g \) is the fractional free volume at temperature \( T_g \). Using the expression for \( f \) derived in equation (2.3) equation (2.2) may be rewritten such that

\[ \ln \gamma \left[ T \right] = \ln A + B \left[ \frac{1}{f_g + \alpha (T - T_g)} \right] - 1 \]  
(2.4)

where \( T > T_g \) and
\[ \ln \frac{\gamma}{\gamma_g} = \ln A + B \left[ \frac{1}{T_g} - 1 \right] \] (2.5)

at the glass transition.

Taking expressions (2.4) and (2.5) subtracting and simplifying Doolittle derived the expression

\[ \log \frac{\gamma}{\gamma_g} = \log \alpha_T = \frac{-B}{2.303 f_g} \left[ \frac{T - T_g}{(f_g(\alpha) + (T - T_g))} \right] \] (2.6)

The above expression has the same form as that of Williams, Landel and Ferry\(^{118}\) for amorphous polymers which, if \( T_g \) is taken as the reference temperature, may be written as

\[ \log \alpha_T = -\frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \] (2.7)

where \( C_1 \) and \( C_2 \) are constants given, from inspection of equations (2.6) and (2.7), by

\[ C_1 = \frac{B}{2.303 f_g} \quad C_2 = f_g / \alpha \] (2.8)

In practice \( B \) has a value approximating to 1 and thus values of \( \alpha \) and \( f_g \) can be determined given knowledge of \( C_1 \) and \( C_2 \).

The values of \( C_1 \) and \( C_2 \) were originally taken as 17.44 and 51.6 respectively for all amorphous polymers, but it has since been shown to be an erroneous deduction since the value of \( C_2 \) is dependent upon \( \alpha \).

b) Statistical Mechanical Theory

The statistical mechanical theory as developed by Gibbs and DiMarzio uses for its premise the assertion that the glass transition observed is an expression of a true equilibrium second order transition. A model was
used in which the polymer chain was fitted into a lattice such that each of the lattice sites were sufficient to accommodate one chain segment each. Vacant sites to permit changes of configuration were also present.

Each molecule is restricted in internal rotation around the chemical bonds of the backbone and thus many conformations may exist under normal conditions. Cooling the molecules reduces the energy available for use in adopting conformations and as a result low energy conformations begin to predominate thus reducing the number of ways in which molecules may pack in the lattice. Lowering the temperature still further eventually results in a state of lowest energy at point $T_2$. This temperature also represents the point at which configurational entropy goes to zero as illustrated in Figure 2.2. There are no further ways in which the lattice may be consistently packed to give lower energy and thus further reduction of temperature and hence available energy does not result in a change in packing arrangement from that adopted at $T_2$. The temperature $T_2$ is referred to as the second order transition temperature.

At temperatures in the region of $T_2$ the free energy barrier which restricts flow of the system from one near ground state to another is very high since the few states which can exist are widely separated within the phase and movement would involve considerable changes in spatial arrangements of molecular entanglements.

The constraints set by such a situation lead to the expectation that at these temperatures the response to externally applied forces would be extremely sluggish. It has been observed that the dielectric and viscoelastic response of polymers show increasingly lengthy relaxation times as $T_2$ is approached from above. The observation confirms the above prediction but shows that the parameter $T_2$ is of little practical use since its existence can only be determined from experiments on an infinitely long time scale. The entity $T_g$ is very similar in character to $T_2$ and many of
Figure 2.2

Variation of configurational entropy with temperature for a glass forming liquid
the predictions which can be made concerning the latter can equally be applied to $T_g$.

The molecular kinetic theory of Gibbs and Adams has extended that of Gibbs and DiMarzio to include non-equilibrium conditions and has yielded a relationship between $T_2$ and $T_g$ which satisfactorily explains the kinetic properties of glass forming liquids within $\pm 100^\circ$ of the glass temperature in terms of the thermodynamic properties of the equilibrium melt.

The theory explained the temperature dependence of the relaxation behaviour in terms of the variation of the size of the cooperatively rearranging body. The size of this region was set by the restraints on configurations which can be adopted in an amorphous packing. A relationship similar to the empirical W.L.F. equation (shown previously in equation (2.7)) was derived from the theory and from comparison of theoretical and experimental values for numerous materials the values of $T_g/T_2$ were determined. The values of the parameter were found to be essentially constant (1.30 ± 8.4%).

2.1.3 Factors Influencing the Glass Transition Temperature

From the preceding section it is evident that any factor which influences the degree of chain stiffness or free volume associated with a polymer will affect the glass transition temperature of the system. In practice the position of the transition is more sensitive to chain stiffness variations than those of intermolecular energy (the latter parameter being related to the number of holes in the lattice and hence free volume). The factors which influence the position of the glass transition and are relevent to the present studies are: chemical structure of the polymer, the degree of crosslinking, the presence of copolymerisation and the addition of fillers.
a) Chemical Structure

The position of the glass transition of a polymer is dependent upon both intra and intermolecular aspects of chemical structure.

The former situation involves purely the structural parameters of the polymer backbone stiffness and is illustrated by comparison of the glass transition of a series of polymers in which the hydrogen of a poly(ethylene) molecule is replaced by various substituents. The replacement of a hydrogen by a methyl group results in a change of $T_g$ of $+100^\circ$ whilst the presence of a benzene ring has an even more dramatic effect elevating $T_g$ by over $200^\circ$C. The statistical mechanical theory explains this observation in terms of the increased flex energy. This is the difference in energy between favoured rotational positions (potential energy minima) of the backbone bonds with respect to their neighbours and is affected by the greater steric hindrance resulting from addition of bulkier side groups.

The creation of symmetrical substitution on a polymer can produce apparently anomalous results as illustrated by the comparison of poly(propylene) ($T_g\ -20^\circ$) and poly(isobutylene) ($T_g\ -70^\circ$). The addition of a second substituent increases the absolute values of the potential energy minima and the barriers; the difference between minima is however reduced.

The nature of the substituents may also affect the glass transition temperature. If we consider a polymer having essentially the same dimensions as that of poly(propylene) but of greater polarity such as polyacrylonitrile then the observed $T_g$ is greatly elevated to $+100^\circ$C as a result of the intermolecular forces. Beuche has interpreted the observation in terms of expansion; a polymer having strong intermolecular forces expanding less readily and requiring a greater temperature before the free volume is of sufficient magnitude for $T_g$ to occur.
b) Crosslinking Effects

Nielson\textsuperscript{119,120} has reviewed the effect of crosslinking upon the $T_g$ of a polymer and has shown that as predicted by both the Free Volume and Gibbs-DiMarzio theories $T_g$ is elevated by such processes. The process of crosslinking a polymer decreases the effective free volume of the system and thus a greater temperature must be attained before the free volume necessary for the glass transition is attained. Statistical mechanics explains the phenomena in terms of decreased configurational entropy in the crosslinked species.

In practice the process of crosslinking produces chemical composition changes in the polymer as more of the crosslinking agent is incorporated. The resulting change in $T_g$ will depend upon two factors; the crosslinking effect which elevates $T_g$ and the copolymerisation effect (as the crosslinking agent may be regarded as a type of comonomer) which may elevate or depress $T_g$ depending upon the nature of the agent.

An empirical relationship has been developed by Nielson\textsuperscript{120} to describe the effect of crosslinking upon $T_g$:

\[
T_g - T_{g_0} = \frac{3.9 \times 10^4}{M_c} = \Delta T_g
\]  

(2.9)

where $\Delta T_g$ is the change of $T_g$ between crosslinked and uncrosslinked polymers and $M_c$ is the molecular weight between crosslinks. The relationship does not, however, account for changes resulting from copolymerisation effects.

A mathematical relationship derived by DiMarzio\textsuperscript{112} relates the shift of $T_g$ with degree of crosslinking in terms of the parameters of the statistical mechanical theory. The equation takes the form
where $T_g$ is the $T_g$ of a polymer of equivalent composition and having no crosslinks, $X_c$ is the mole fraction of monomer units crosslinked and $n_c$ is the average number of atoms in the backbone between crosslinks. $K$ is a function of segmental mobility and the cohesive energy density of crosslinked and uncrosslinked polymer taking a value $\approx 1$. $T_{g_0}$ includes a term accounting for copolymerisation effects and thus equation (2.10) represents only contributions from crosslinking.

c) Copolymerisation

The glass transition behaviour of random amorphous copolymers was first predicted during the 1950's using the principles of additive relationship. Fox\textsuperscript{121} derived the relationship

\[
\frac{1}{T_g} = \frac{W_A}{T_{g_A}} + \frac{W_B}{T_{g_B}} \tag{2.11}
\]

whilst Gordon and Taylor\textsuperscript{122} derived the expression

\[
T_g = \frac{T_{g_A} + k[T_{g_B} - T_{g_A}] W_B}{1 - (1 - k) W_B} \tag{2.12}
\]

where $T_g$ is the glass transition of the copolymer containing weight fraction $W_A$ and $W_B$ of two monomers A and B whose homopolymers have $T_{g_A}$ and $T_{g_B}$ respectively, and $k$ is a constant.

Equation (2.12) has been derived both in terms of free volume\textsuperscript{123} and statistical mechanical\textsuperscript{110} theories. In the former approach the erroneous assumption that the free volume contribution of the monomer unit is constant whether in the homopolymer or a copolymer was made. In reality the free volume is influenced by steric and energetic restraints imposed by adjacent
groups on the polymer backbone. The value of $k$ is lower than the predicted value $A_B/A_A$, where $A_A$ and $A_B$ are the differences between the values of the specific volume-temperature coefficients above and below the glass transitions of homopolymers $A$ and $B$ respectively.

The Gibbs-DiMarzio theory derives an average stiffness energy for the copolymer of the form

$$\varepsilon = \frac{E_A}{B_A} \varepsilon_A + \frac{E_B}{B_B} \varepsilon_B$$

(2.13)

where $\varepsilon_A$ and $\varepsilon_B$ are the stiffness energies of rotatable chemical bonds of homopolymers $A$ and $B$, and $B_A$ and $B_B$ are the fraction of rotatable bonds of type $A$ and $B$ respectively.

An expression in the form of the Gordon Taylor Wood equation (2.12) has been derived using the parameters of equation (2.13) such that

$$W_A \left[ \frac{\alpha_A}{N_A} [T_2 - T_{2A}] \right] + W_B \left[ \frac{\alpha_B}{N_B} [T_2 - T_{2B}] \right] = 0$$

(2.14)

where $W_A$ and $W_B$ are weight fractions of $A$ and $B$ monomer units

$\alpha_A$ and $\alpha_B$ are the number of flexible bonds per monomer

$N_A$ and $N_B$ are the molecular weight of monomers $A$ and $B$

$T_{2A}$ and $T_{2B}$ are the second order transition temperatures for $A$ and $B$ homopolymers respectively

$T_2$ is the second order transition temperature for the copolymer.

It is evident from equation (2.14) that the coefficients $\alpha_A/N_A$ and $\alpha_B/N_B$ replace $k$ of equation (2.12). These parameters can be calculated from the chemical structures of the homopolymers. Equation (2.14) relates the second order transition temperature and not the experimentally derived glass transition temperatures. Application of equation (2.14) to the glass transition can however be made within acceptable limits of error.
The above theory is erroneous in that during copolymerisation of A and B monomer units A-B bonds are formed in addition to A-A and B-B bonds. The stiffness energy of the A-B links will bear no unique relationship to the stiffness energies of the links in the pure homopolymers. Thus, even if $\varepsilon_A$ and $\varepsilon_B$ do not differ greatly, the assumptions made in equation (2.13) may not be valid and thus equation (2.14) would not be expected to give accurate predictions of the $T_g$ of copolymers having a large fraction of A-B links.

Different significance is attached to $k$ in the derivation of the Gordon-Taylor-Wood equation from the free volume and statistical mechanical theories, thus the equation is not universally applicable. Deviations from the equation have been discussed by Illers $^{124}$, Kanig $^{125}$ and Johnson $^{126}$. The latter suggested that deviations from the equation could be explained in terms of the sequence distribution within the polymer. For a copolymer, homopolymer $T_g$ values will hold for A-A and B-B sequences since both will experience essentially the same interactions as in their respective homopolymers. The formation of A-B sequences will result in changes in the contributions of A and B units to the $T_g$ but, having assigned values to such sequences, predictions can be made for the $T_g$ of the whole copolymer.

d) Fillers

The addition of fillers to polymers and their effect upon the glass transition has been reviewed by Manson et al $^{127}$. The addition of inorganic compounds dispersed as a second phase normally produces only weak interactions by polymer adsorption at the filler surface and thus increase $T_g$ slightly. The magnitude of the change of $T_g$ will of course be dependent upon the type, concentration and surface area of the filler and polymer. No generalisations may be applied concerning the absolute magnitude of the $T_g$ elevation. The statement is emphasised by two examples from the literature. Landel $^{128}$ studied poly(isobutylene) filled with glass beads. $T_g$
elevations of up to 7°C at 36.7 vol% loading were observed and were explained in terms of the crosslinking effect from polymer adsorption at the glass surface. Kumins et al.\textsuperscript{129} studied poly(vinyl chloride-vinyl acetate) copolymers filled with TiO\textsubscript{2}. In this system a decrease of T\textsubscript{g} was observed and was explained in terms of adsorption of the acetate groups on the filler surface with resulting disruption of the existing hydrogen bonded network.

2.2 Dielectric Relaxation

2.2.1 Dielectric Dispersion

The static dielectric constant or relative permittivity of a substance is defined as the ratio of \( C_s/C_0 \), where \( C_s \) is the capacitance of a capacitor with a dielectric specimen filling the space between the metallic plates and \( C_0 \) is the capacitance of the equivalent vacuum (or in practice air) space. If a dielectric relaxation process occurs then an energy loss term will also be involved.

The application of an alternating (complex) voltage \( V \) of frequency \( f \) to a capacitor having a dielectric \( \varepsilon \) between the plates results in a complex alternating current \( I^* \) given by

\[
I^* = I + j \omega C V
\]  

The effect can be represented in the form of a diagram as shown in Figure 2.3. The current \( I_C \) (equal to \( \omega C V \)) charges the capacitor to the required instantaneous voltage and leads the voltage by 90° as signified by the presence of the \( j(\equiv \sqrt{-1}) \) term. The component \( I_I \) is in phase with \( V \) and arises if polarisation is unable to keep in phase with the applied voltage. The latter component also contains a term resulting from D.C. conductivity.
Figure 2.3

Vector diagram for a capacitor with dielectric exhibiting relaxation
Equation (2.15) can be expressed in terms of $C_o$, the air capacitance of the system such that

$$\mathbf{I} = j\omega (\epsilon' - j\epsilon'') C_o V \quad (2.16)$$

where the quantity $\epsilon' - j\epsilon''$ represents the complex dielectric constant (complex dielectric permittivity) $\epsilon^*$. The real part $\epsilon'$ is frequently known as the dielectric constant or relative permittivity whilst the imaginary term $\epsilon''$ is commonly referred to as the loss factor.

The complex electric field, $E^*$, and the complex electric displacement, $D^*$, are given respectively by

$$E^* = E_o \exp(j \omega t) \quad (2.17)$$

$$D^* = D_o \exp(j \omega t - \delta) \quad (2.18)$$

where $E_o$ and $D_o$ are the field and displacement amplitudes respectively, $\omega$ is the angular frequency and $t$ is time. $D^*$ and $E^*$ are related by the expression

$$D^* = \epsilon^* E^* = (\epsilon' - j\epsilon'') E^* \quad (2.19)$$

In addition to an expression in terms of complex permittivity the response of a material to a periodic electric field may be expressed in terms of complex polarizability or susceptibility

$$\chi^* = \frac{\mathbf{P}^*}{\mathbf{E}^*} = \chi' - i\chi'' \quad (2.20)$$

The complex permittivity as measured experimentally is a compliance term.
analogous to those encountered when considering the viscoelastic properties of polymers and to be discussed later. The response of the material may be expressed \(^{130,131}\) in terms of a complex electrical modulus \(M^*(\omega)\). This complex modulus is frequently referred to as the complex inverse permittivity and is defined by

\[
M^*(\omega) = M'(\omega) + jM''(\omega) \tag{2.21}
\]

This is related to \(\varepsilon^*(\omega)\) by the expression

\[
\varepsilon^*(\omega) = \frac{1}{M^*(\omega)} \tag{2.22}
\]

thus \(M'(\omega) = \frac{\varepsilon'(\omega)}{[\varepsilon'(\omega)]^2 + [\varepsilon''(\omega)]^2} \tag{2.23}\)

\[
M''(\omega) = \frac{\varepsilon''(\omega)}{[\varepsilon'(\omega)]^2 + [\varepsilon''(\omega)]^2} \tag{2.24}
\]

The loss tangent, \(\tan \delta\), is given by

\[
\tan \delta = \frac{M''(\omega)/M'(\omega)}{\varepsilon''(\omega)/\varepsilon'(\omega)} \tag{2.25}
\]

In physical terms \(\varepsilon'\) and \(\varepsilon''\) are measures of the energy stored and energy lost respectively in a given cycle. In the relaxation region \(\varepsilon'\) decreases with frequency from a value \(\varepsilon_R\) to \(\varepsilon_U\), the relaxed and unrelaxed dielectric constants. The effect is illustrated in Figure 2.4.

The frequency dependence of \(\varepsilon'\) is the result of the time dependence of the polarisation of the dielectric. The total polarization of a dipolar material is the sum of three components. These are the electronic polarization \(P_e\), a term derived from polarization of the bonds \(P_a\) and a third term arising from reorientation of existing dipoles \(P_0\).
Figure 2.4

Plot of $\varepsilon'$, $\varepsilon''$ and $\tan \delta$ versus $\log \omega$ for a single relaxation time model with $\varepsilon_R/\varepsilon_u = 5$
At low frequencies all three components contribute to the polarization. The reorientation of dipoles is however generally a slow process so that as frequency increases the contribution from dipole reorientation decreases. At approximately $10^7$ Hz the dipoles become unable to follow the rapidly alternating field and the polarization becomes the sum of merely $P_A$ and $P_E$. A further increase in frequency decreases the contribution of $P_A$ and at $10^{13}$ Hz only the term from electronic polarization remains. It is pertinent to note that although both $P_A$ and $P_E$ are present and contribute to the dielectric constant at low frequencies they do not result in loss until the infra-red or optical frequency ranges where resonance absorption occurs.

In the frequency region where the dipolar polarization decreases the loss factor passes through a maximum as shown in Figure 2.4. At high frequencies the molecular dipoles have no time to change their orientation in the rapidly alternating field since its period is much less than the retardation time $\tau_R$. At low frequencies the period of the applied field is large compared with the retardation time $\tau_R$ of the molecular dipoles and dipolar polarization is able to build up to its full extent. Since the polarization is able to keep up with the applied field power loss is again low. Between these two regions of constant relative permittivity a step occurs centred about an angular frequency $\omega_m$ (equal to $1/\tau_R$). In this region dipolar polarization cannot keep in phase with the applied field and appreciable power losses occur.

Debye\textsuperscript{133} has shown that for a system having a single retardation time $\tau_R$ the frequency dependence of $\varepsilon'$ and $\varepsilon''$ is given by

\begin{align}
\varepsilon^*(\omega) &= \varepsilon_U + \frac{[\varepsilon_R - \varepsilon_U]}{1 + j\omega\tau_R} \\
\varepsilon'(\omega) &= \varepsilon_U + \frac{[\varepsilon_R - \varepsilon_U]}{1 + \omega^2\tau_R^2} \tag{2.26}
\end{align}
\[ \varepsilon''(\omega) = \frac{\varepsilon_R - \varepsilon_U}{1 + \omega^2 \gamma^2_R} \omega^\gamma \]  

(2.28)

where \(\omega\) is the angular frequency (= 2\(\pi\)f).

From equations (2.25), (2.27) and (2.28) it can be shown that

\[ \tan \delta = \frac{[\varepsilon_R - \varepsilon_U] \omega^\gamma_R}{[\varepsilon_R + \varepsilon_U \omega^2 \gamma^2_R]} \]  

(2.29)

Simplified single retardation time behaviour has been shown to occur in liquids\(^{13}\) but has never been observed in macromolecules. The dipolar orientation of polymer chains is a complex process with a spectrum of retardation times and the observed \(\varepsilon''(\omega) - \omega\) curve is considerably broader and of less magnitude than that for the Debye model. The effect is illustrated in Figure 2.5.

In the preceding text the process of dielectric relaxation has been discussed as a function of frequency at constant temperature. The range of frequencies required for such measurements is not always practically convenient and it is useful to be able to perform measurements at constant frequency at various temperatures.

The single retardation time model can be regarded as having a retardation time approximately equal to the reciprocal of the rate of dipole orientation. Thus over limited temperature ranges at least it is possible to plot the dependence of retardation time using an Arrhenius plot of the form

\[ \gamma_R = \gamma_0 \exp \left[ \frac{\Delta E}{RT} \right] \]  

(2.30)

where \(\Delta E\) is the energy of activation of dipole orientation. It can be seen from equation (2.30) that a distribution of \(\gamma_0\), \(\Delta E\) or both will lead to a distribution of retardation times and the broadened curves shown...
Figure 2.5

Contrasts in dielectric behavior between that of a single relaxation time model and that of a polymer
in Figure 2.5.

2.2.2 Empirical Distribution Functions

Dielectric measurements provide data on permittivity and dielectric loss as a function of frequency and temperature which are conveniently displayed graphically as functions of $\log_{10} \omega$ or temperature. The data are however frequently incomplete and as a result several expressions involving empirical parameters have been developed which allow characterisation by means of a small number of parameters.

a) Cole-Cole Distribution

The earliest and perhaps most widely used method of representing data consists of plotting $E"(\omega)$ for a certain frequency against $E'(\omega)$ at the same frequency. This complex locus or Argand diagram was first applied to dielectrics by Cole and Cole (135). The single retardation time expression of equation (2.26) was modified to account for a spectrum of relaxation times by replacing the expression $[1 + j\omega \tau_R]$ by $[1 + j\omega \tau_0]^{1-\alpha}$ where $\alpha$ is a parameter taking value $0 \leq \alpha \leq 1$ and giving a measure of the retardation time distribution, and $\tau_0$ is the most probable retardation time corresponding to frequency $E"(\omega) = E"_{\max}$. Thus

$$E^*(\omega) = E'(\omega) - jE"(\omega) = E_U + \frac{[E_R - E_U]}{1 + [j\omega \tau_0]^{1-\alpha}} \quad (2.31)$$

Equation (2.31) can be written in terms of the real and imaginary components so that

$$E'(\omega) = E_U + \frac{1}{2} \left[ \frac{E_R - E_U}{\sinh \left[ 1-\alpha \right] \chi} \right] [1 - \frac{\sinh \left[ 1-\alpha \right] \chi}{\cosh \left[ 1-\alpha \right] \chi + \cos \frac{1}{2} \alpha \pi}] \quad (2.32)$$

$$E"(\omega) = \frac{\frac{1}{2} \left[ E_R - E_U \right] \cos \frac{1}{2} \alpha \pi}{\cosh \left[ 1-\alpha \right] \chi + \sin \frac{1}{2} \alpha \pi} \quad (2.33)$$
where \( X = \ln \left[ \omega \right] \).

Recombination of equations (2.32) and (2.33) and simplification gives

\[
\left[ \varepsilon''(\omega) - \frac{\varepsilon_R^2 + \varepsilon_U^2}{2} \tan \pi \alpha / 2 \right]^2 + \left[ \varepsilon'(\omega) - \frac{\varepsilon_R^2 - \varepsilon_U^2}{2} \right]^2 = \frac{\varepsilon_R^2 - \varepsilon_U^2}{2} \sec \pi \alpha / 2
\]

Equation (2.34) represents a circle of centre \( \left[ \frac{\varepsilon_R^2 + \varepsilon_U^2}{2} - \frac{\varepsilon_R^2 - \varepsilon_U^2}{2} \tan \pi \alpha / 2 \right] \) and radius \( \frac{\varepsilon_R^2 - \varepsilon_U^2}{2} \sec \pi \alpha / 2 \). The circle bisects the \( \varepsilon'(\omega) \) axis at \( \varepsilon_R \) and \( \varepsilon_U \) when \( \varepsilon''(\omega) = 0 \).

For the condition of \( \alpha = 0 \) equations (2.32) and (2.33) reduce to the Debye expressions (2.27) and (2.28) as expected. When \( \alpha \) takes values greater than zero the dispersion region is broader and the maximum value of \( \varepsilon''(\omega) \) at \( \omega = 1 / \sqrt{\omega} \) is decreased.

A typical Cole-Cole diagram is shown in Figure 2.6. The measurement of the angle of depression \( \pi \alpha / 2 \) enables determination of the distribution of retardation times, whilst the intercepts at the \( \varepsilon'(\omega) \) axis provide a convenient method of assessing \( \varepsilon_R \) and \( \varepsilon_U \) for symmetrical relaxations.

b) Fuoss-Kirkwood

Fuoss and Kirkwood\(^{136}\) rearranged the single retardation time expression for dielectric loss into the form

\[
\varepsilon''(\omega) = \varepsilon''_{\text{max}} \text{sech} \left[ \ln \omega \gamma_R \right]
\]

The inclusion of a parameter \( \beta \) into equation (2.35) extended the scope of the approach to account for a distribution of retardation times, so that

\[
\varepsilon''(\omega) = \varepsilon''_{\text{max}} \text{sech} \left[ \beta \ln \omega \gamma_{AV} \right]
\]
Figure 2.6

A typical Cole-Cole diagram
where $\beta$ is a measure of the breadth of distribution and $\gamma_{AV}$ is the most probable retardation time defined by $1/\omega_{\text{max}}$, where $\omega_{\text{max}}$ is the angular frequency of maximum loss.

The value of $\beta$ can be determined from experimental data using several methods which have been discussed by McCrum et al.\textsuperscript{137} and Wetton and Allen\textsuperscript{138}. Typical amongst these methods are

i) Using the equation

$$\beta = \frac{\epsilon''_{\text{max}}}{\epsilon'_R - \epsilon'_U} \quad (2.37)$$

If the frequency range is sufficient $\beta$ may be determined from the values of $\epsilon'_R$ and $\epsilon'_U$, alternatively $[\epsilon'_R - \epsilon'_U]$ can be determined from the Cole-Cole diagrams.

ii) The equation

$$\cosh^{-1} \left[ \frac{\epsilon''_{\text{max}}}{\epsilon''(\omega)} \right] = \beta \ln \omega \gamma_{AV} \quad (2.38)$$

can be graphically displayed as a plot of $\cosh^{-1} \left[ \frac{\epsilon''_{\text{max}}}{\epsilon''(\omega)} \right]$ vs. log $\omega$ with a sign change at $\epsilon''(\omega) = \epsilon''_{\text{max}}$. The slope of this plot takes a value of $2.303 \beta$.

iii) The equation

$$\cosh^{-1} 2 = \beta / \ln \left[ \frac{\omega_1}{\omega_{\text{max}}} \right] \quad (2.39)$$

where $\omega_1$ is the angular frequency at which $\epsilon''(\omega)$ has dropped to $\frac{1}{4} \epsilon''_{\text{max}}$. can be used in conjunction with measurements of the half-width of the loss peak to obtain $\beta$.

With a knowledge of $\beta$ theoretical $\epsilon''(\omega)$ vs. $\omega$ curves can be
generated and compared to experimental values. Loss curves of similar shape but not identical to those of Cole and Cole may also be generated using equation (2.36).

c) Davidson-Cole Distribution

The Cole-Cole and Fuoss-Kirkwood empirical equations relate only to dispersion and absorption curves which are symmetrical about a point \( \omega \tau = 1 \). Dielectric loss curves frequently have a high frequency broadening such that the Cole-Cole arcs for such systems are said to be 'skewed'. Davidson and Cole\(^{139,140}\) have attempted to fit experimental results to the following function

\[
\frac{\varepsilon^*(\omega) - \varepsilon_U}{[\varepsilon_R - \varepsilon_U]} = \frac{1}{[1 + j\omega \tau_1]^\alpha} \quad 0 < \alpha < 1
\]

(2.40)

where \( \tau_1 \) is a characteristic relaxation time.

Equation (2.40) may be resolved into real and imaginary components having the following form

\[
\frac{\varepsilon'(\omega) - \varepsilon_U}{[\varepsilon_R - \varepsilon_U]} = [\cos \phi]^\alpha \cos \alpha \phi
\]

(2.41)

\[
\frac{\varepsilon''(\omega)}{[\varepsilon_R - \varepsilon_U]} = [\cos \phi]^\alpha \sin \alpha \phi
\]

(2.42)

where \( \tan \phi = \omega \tau_1 \)

(2.43)

At the maximum loss \( \omega \tau_1 \neq 1 \) but is given by

\[
\omega_{\text{max}} \tau_1 = \tan \left[ \frac{1}{(8+1) \cdot \frac{\tau}{2}} \right]
\]

(2.44)

A typical Davidson-Cole plot is shown in Figure 2.7. At low frequencies
Figure 2.7

A typical Davidson-Cole diagram
the curve is circular but at high frequencies the curve approaches the abscissa along a straight line of slope $\theta \pi/2$.

d) Williams-Watts Approach

The use of the 'skewed arc' approach has been extensive in the representation of dielectric experimental data\textsuperscript{141} but was found by Williams and Watts\textsuperscript{142} to be inadequate to explain the observed non-symmetrical behaviour associated with the primary or $\alpha$ relaxation of many polymers.

Taking the complex dielectric permittivity

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \quad (2.45)$$

Williams and Watts expressed it by the superposition principle in the form

$$\frac{\varepsilon^*(\omega) - \varepsilon_U}{\varepsilon_R - \varepsilon_U} = \int_0^\infty \left[ -\frac{d\gamma(t)}{dt} \right] \exp(-j\omega t) dt \quad (2.46)$$

where $\gamma(t)$ is the normalised decay function obtained upon removal of a steady electric field from a sample.

A simple empirical decay function

$$\gamma(t) = \exp\left(-\frac{t}{\tau_0}\right)^\beta \quad 0 < \beta \leq 1 \quad (2.47)$$

where $\tau_0$ is some effective retardation time.

was proposed which when inserted into equation (2.46) gave

$$\frac{\varepsilon^*(\omega) - \varepsilon_U}{\varepsilon_R - \varepsilon_U} = \mathcal{L} \left[ \beta \lambda t^{\beta-1} \exp(-\lambda \tau_0) \right] \quad (2.48)$$

where $\mathcal{L}$ represents the Laplace transform and $\lambda = \frac{\tau_0}{\tau_0} - 1$.

Using this expression Williams and Watts\textsuperscript{143} were able to represent
the \( \alpha \) relaxations of many amorphous polymers by choosing suitable values of the parameter \( \beta \). The Argand diagrams from the Williams-Watts empirical functions showed similar trends to those of Davidson and Cole shown in Figure 2.7, but had marked deviations at higher frequencies.

The Williams-Watts approach has been successfully applied to systems in which conduction processes mask the underlying dielectric relaxation. Using the previously defined dielectric modulus (equation (2.21)) the conduction relaxation of alkali silicate glasses\(^{130}\) and poly(arylene vinylenes)\(^{131}\) have been studied using this method. In both systems the imaginary part of the dielectric modulus \( \varepsilon''(\omega) \) was not only broader than a single relaxation time but was asymmetric and skewed to the high frequency side of the maximum. Application of the distribution function (equation (2.47)) gave good agreement with the observed data.

e) Grant Complex Conductivity

It was shown in equation (2.45) that the observed complex permittivity from experimental measurements can be resolved into real and imaginary components. For materials of low conduction the imaginary component may be resolved into the linear sum of a relaxation and conduction components such that

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - j(\varepsilon''_{\text{relax}} + \sigma_0/\omega \varepsilon_0) \tag{2.49}
\]

where \( \varepsilon_0 \) is the permittivity of free space and \( \sigma_0 \) is the d.c. conductivity.

In materials where conduction is significant analysis of the complex permittivity is not always convenient and an alternative approach must be considered. It has been shown previously that the use of the complex inverse permittivity or dielectric modulus is in many cases convenient. Grant\(^{144}\) has approached the problem in terms of the admittance of a unit
cube of the substance $Y$ as defined by

$$Y = \omega \varepsilon^* = \sigma^*$$  \hspace{1cm} (2.50)

Thus

$$\sigma'(\omega) + i \sigma''(\omega) = i \omega (\varepsilon'(\omega) - i \varepsilon''(\omega))$$  \hspace{1cm} (2.51)

and

$$\sigma' = \omega \varepsilon''$$  \hspace{1cm} (2.52)

$$\sigma'' = \omega \varepsilon'$$  \hspace{1cm} (2.53)

Figure 2.8 shows a comparison of conductivity and permittivity plots for four equivalent circuits. The presence of $\varepsilon_U$ distorts the conductivity plot and may be eliminated by using $\varepsilon'(\omega) - \varepsilon_U$ to formulate $\sigma''(\omega)$.

2.2.3 Effects of Temperature on the Distribution of Relaxation Times

It has been shown previously that empirical distribution functions can be calculated as a function of frequency at constant temperature. Temperature itself is also a powerful variable affecting the distribution of relaxation times. The effect is reflected in the possible temperature variability of the parameters $\alpha$, $\beta$, $\gamma$ as defined previously if $\gamma_0$ and/or $\varepsilon_U$ are temperature dependent.

It was shown that for many transitions Eyring's general theory of rate processes could be applied such that the temperature dependence was characterised by an Arrhenius plot of the form

$$\gamma_R = \gamma_0 \exp \left[ \frac{\Delta \varepsilon}{RT} \right]$$  \hspace{1cm} (2.30)

If the distribution of relaxation times is independent of temperature it is possible to superimpose the normalised experimental $\varepsilon''(\omega)/\varepsilon_{\text{max}}$ vs.
Figure 2.8

Complex conductivity and permittivity plots for some equivalent circuits
\[ \frac{\varepsilon'(\omega)}{\varepsilon_R - \varepsilon_U} \text{ vs. } \omega \text{ curves, obtained at different temperatures to form master curves. The Time-Temperature superimposition is described by the semi-empirical Williams-Landel-Ferry (WLF) equation (2.7) which is derived from the general principle discovered by Leaderman whilst measuring polymer creep-temperature relationships.} \]

In the case of the Arrhenius equation the shift \( \ln \alpha_C \) is

\[ \ln \alpha_C = \frac{\Delta E}{R} \left[ \frac{1}{T} - \frac{1}{T_g} \right] \quad (2.54) \]

The W.L.F. equation is valid at temperatures higher than the glass transition but significant deviations occur at low temperatures. The W.L.F. approach has, however, been applied to temperatures of \( T_g - 100^\circ C \) by introducing an effective temperature to account for the non-equilibrium state of the glass. \(^{148}\)

McCrum and Morris\(^ {149}\) have further modified the W.L.F. equation to account for the effect of temperature upon the relaxed and unrelaxed moduli (permittivities) of polymers.

### 2.2.4 Relationship Between Dielectric Constant and Dipole Moment

It has been stated previously that the application of a static electric field to a system of dipolar molecules in the liquid or gaseous state results in a net orientation of the dipoles such that they align with the field. Debye\(^ {133}\) has calculated the static dielectric constant in terms of the contributions from all the orientation processes and has related it to the dipole moment of the molecule for gaseous systems.

\[ \frac{\varepsilon_R - 1}{\varepsilon_R + 2} = \frac{4}{3} \pi N \left[ \alpha_e + \frac{\mu_0^2}{3kT} \right] \quad (2.55) \]

where \( \varepsilon_R \) is the static dielectric constant, \( \mu_0 \) is the dipole moment of...
the molecule, \( N \) is the number of molecules per unit volume, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature and \( \alpha_e \) is the deformation polarizability due to the displacement of the molecule. This function is given by the Clausius-Hosotti equation

\[
\frac{\varepsilon_U - 1}{\varepsilon_U + 2} = \frac{4}{3} \gamma N \alpha_e
\]  

(2.56)

where \( \varepsilon_U \) is the dielectric constant measured at frequencies such that contributions from dipole orientation are not present.

Equation (2.56) is limited to gases and very dilute solutions of dipolar molecules in non-polar solvents. Onsager\(^{150}\) has expanded the expression to account for polarization of the surrounding medium by dipolar molecules in a condensed phase. The resulting equation

\[
\mu_0^2 = \frac{3kT}{4N} \left[ \frac{2\varepsilon_R + \varepsilon_U}{3\varepsilon_R} \right] \left( \frac{3}{\varepsilon_U + 2} \right) (\varepsilon_R - \varepsilon_U)
\]  

(2.57)

is, however, applicable only for a system with no orientation correlation between dipoles.

Kirkwood\(^{151}\) modified the Onsager equation to account for short range interactions between molecules in the liquid state. The modification omitted to account for the deformation polarizability of the molecules and a term was empirically added to give the final equation:

\[
\frac{\varepsilon_R - 1}{9\varepsilon_R} \frac{2\varepsilon_R + 1}{2\varepsilon_R} = \frac{4}{3} \gamma \varepsilon N \left[ \alpha_e + \frac{\mu^2}{3kT} \right]
\]  

(2.58)

where \( \mu \) is the 'liquid dipole moment' of the molecule (\( \mu_0 \) is the dipole moment for an isolated molecule in vacuo whilst \( \mu \) accounts for the surrounding liquid environment), \( g \) is the Kirkwood Correlation Function and is used to characterise orientational correlations between the
reference dipole and its nearest neighbours. For a molecule surrounded by z equivalent nearest neighbours then

$$g = 1 + z \frac{\cos \varphi}{1}$$  \hspace{1cm} (2.59)$$

where $\cos \varphi$ is the average cosine of the angle made between the reference molecule and one of its nearest neighbours. Thus when $g = 1$ there is no orientational correlation.

Fröhlich\textsuperscript{132} has improved upon the theory of Kirkwood to account for orientation processes in terms of statistical mechanics. He considered small regions surrounding the specimen molecule in an infinite matrix of the dielectric. Using statistical mechanics for the elementary dipoles and regarding the region as a continuum of dielectric constant $\varepsilon_U$ the following relationship was derived

$$\left[ \varepsilon_R - \varepsilon_U \right] = \left[ \frac{3\varepsilon_R}{2\varepsilon_R + \varepsilon_U} \right] \frac{4\pi N}{3kT} \left[ \frac{\varepsilon_U + 2}{3} \right] g \mu^2$$  \hspace{1cm} (2.60)$$

where $g$ is the orientation correlation function given by

$$g = 1 + \sum_{i \neq j} \cos \frac{\varphi_{ij}}{2}$$  \hspace{1cm} (2.61)$$

and $\cos \frac{\varphi_{ij}}{2}$ is the average of the cosine of the angles $\varphi_{ij}$ made between the reference molecule $i$ and a molecule $j$. For no orientation correlation between molecules $g = 1$, and the Fröhlich equation then reduces to the Onsager equation as would be expected.

The theory of Fröhlich can be used to explain systems such as water and alcohols which consist of small molecules possessing intermolecular dipole orientation correlations. Thus with the Onsager equation the dielectric properties of rigid dipolar molecules may be predicted.
The continued Brownian motion of polymer chains results in the dipole moment being a vectorial sum. In addition a strong mechanical correlation in orientations between the components of the chain will exist which have to be considered in any theory. Single polymer chains cannot be taken as the basic dipole unit since a polymeric medium will consist of an intermingled network of molecules and it is only if the basic dipole unit is taken to be the chemical repeat unit that Fröhlich's theory may be applied.

2.2.5 Dielectric Relaxation Processes

In order to compare the location of loss peaks for different polymers the relaxation processes need to be labelled. Two basic systems have been proposed. Boyer\textsuperscript{152} suggested labelling the glass-rubber transition by $T_g$, glass-glass transitions by $T_{gg}^{(1)}, T_{gg}^{(2)}$, ... and liquid transitions by $T_{1l}^{(1)}, T_{1l}^{(2)}$, ... in order of their relative positions to $T_g$. The currently adopted system is based upon the nomenclature first proposed by Deutsch et al.\textsuperscript{153}. In this system peaks were labelled $\alpha, \beta, \gamma$, ... in order of decreasing temperature (for a given frequency) and were subscripted to denote the phase responsible for the transition.

For a solid amorphous polymer the $\alpha_a$ relaxation is associated with the glass transition where large segments of the polymer chains move from one equilibrium conformation to another (micro-Brownian motion). The second or $\beta_a$ transition occurs in the glassy state where motion is limited and is usually attributed to side groups or limited segment motion. The latter may take two forms, crankshaft movement\textsuperscript{154} or local mode mechanisms\textsuperscript{155}. A third relaxation $\gamma_a$ has been observed in certain substituted polymers\textsuperscript{156}. The origin of this relaxation remains obscure, but has been attributed to the independent movement of side groups.

For crystalline polymers a series of transitions designated $\alpha_m, \alpha_c$. 
\( \beta_c, \gamma_c \) associated with crystalline melting and crystal-crystal transitions have been similarly defined \(^{157}\).

In recent studies concerning the addition of metal salts to polar polymers, James, Wetton and Brown \(^{144}\) observed the evolution of two new transitions occurring at higher temperatures than the \( \alpha_a \) relaxation. To avoid renaming the traditional \( \alpha_a \) and \( \beta_a \) relaxations they were designated \( \alpha' \) and \( \beta' \). The magnitude of these relaxations were larger than could be explained using the conventional theories of dielectric relaxation \(^{137}\).

As will be shown later, similar large magnitude relaxations have been observed for some of the systems which have been studied here. Several alternative theories may be applied to explain these results and below three are briefly outlined.

2.2.6 Maxwell-Wagner-Sillars Interfacial Polarization

If an otherwise loss-free dielectric contains a second trapped phase of higher conductivity an effect known as Maxwell-Wagner-Sillars Interfacial Polarization \(^{158-160}\) may result. The effect involves migration of charge from the conducting phase to the interface with the dielectric causing a rise in the apparent dielectric constant. The dielectric loss is also affected at certain frequencies since ohmic conduction takes place as current flow in the conducting phase produces polarization changes at the interphase with the insulator.

The magnitude of this effect and its position in the frequency plane will depend upon the dielectric constants for the two phases, the volume ratio of each, and the size and geometry of the conducting phase.

With a knowledge of these parameters relaxation times may be calculated. In his work, Van Beek \(^{161}\) derived equations for several phase geometries such as spheres, spheroids, rods, cylinders and lamellae. It was found that
application of the equations to dispersions of ellipsoid particles gave very high predicted values of permittivity and loss, especially if the ratio of the major and minor axes \((a/b)\) was large. The Maxwell-Wagner-Sillars relaxation is narrow and only slightly wider than that predicted for single relaxation time models.

2.2.7 Colloidal Dispersions in Electrolyte Solutions

Schwan et al.\(^{164}\) observed high dielectric constants associated with suspensions of non-conductive colloid particles in aqueous electrolytes. Schwarz\(^{165}\) later developed a theory to explain this phenomenon.

The theory predicts that charging of the colloid particles will take place by the ions and that they will then attract a shell of counter ions. The counter ions are strongly bound by attraction and to escape into solution must overcome a large potential barrier. Movement along the surface is less restricted and thus upon application of an external electrical field longitudinal movement occurs. Polarisation of the ion atmosphere results and a dipole is formed. The extent of counter ion polarisation within the double layer will depend upon the mobility and surface concentration of the ions and will be opposed by the tendency of the ion to counter diffuse and destroy the surface concentration gradient.

The polarisation leads to an increase in the dielectric constant of the system which in some circumstances can be greater than that contributed by the bulk phases.

Schwarz showed that the magnitude of the relaxation could be shown thus

\[
E_R - E_U = \frac{2}{4} \frac{p}{(1 + p/2)^2} \frac{e_o^2 R \sigma_o}{\varepsilon_o k T}
\]  

(2.62)

where \(p\) is the volume fraction of dispersed spheres, \(e_o\) is the electrical charge of the counter ion, \(R\) is the sphere radius, \(\sigma_o\) is the counter ion
density in the double layer, \( \varepsilon_0 \) is the permittivity of free space, \( k \) is the Boltzmann Constant, and \( T \) is the absolute temperature. A characteristic frequency of the relaxation was defined by

\[
f = \frac{1}{2\pi C_R} = \frac{u k T}{\pi R^2}
\]

where \( C_R \) is the characteristic retardation time, \( u \) is the counter ion surface mobility. The surface mobility was shown to be governed by an exponential relationship with the free solution mobility \( u_0 \)

\[
u = u_0 \exp \left(-\frac{\alpha}{kT}\right)
\]

From equations (2.62) and (2.63) it can be shown that

\[
C_R = C_0 \exp \left(\frac{\alpha}{kT}\right)
\]

with

\[
C_0 = \frac{R^2}{2u_0 kT}
\]

Thus the theory predicts Debye-type behaviour for a system of equal size spheres; if the spheres are not of uniform dimensions then a relaxation spectrum will exist.

The primary requirements for Schwarz-type dielectric behaviour are:

1) A system of mobile ions electrostatically associated with immobile counter ions existing in the structure.

2) The regions containing the mobile ions must be isolated from other similar regions.

3) The continuous matrix must have a conductivity sufficiently high and/or a dielectric constant sufficiently low to ensure an adequate potential gradient across the ion-containing region to induce ion displacement.
The theory has been successfully applied to several systems having anomalous dielectric behaviour. Examples are dispersions of poly(styrene) spheres in potassium chloride solutions\textsuperscript{164}, and of polysalts (poly(vinyl-benzyl trimethyl ammonium)-poly(styrene sulfonate)) containing water and sodium bromide\textsuperscript{166}.

From inspection of section 2.2.6 it would be expected that since the colloid particles are suspended in a heterogeneous system, Maxwell-Wagner-Sillars-type relaxation might be expected. Calculations for both systems\textsuperscript{164,166} showed that the observed relaxations were of several orders of magnitude greater than those predicted for M.W.S.-type behaviour and took place at far lower frequencies.

2.2.8 Pohl's Theory of Higher Electronic Polarisation

During a study of highly conjugated macromolecules based upon polyacene radical quinones, Pohl\textsuperscript{167,168} found very high dielectric constants (between 50 and 900) which were strongly frequency, field strength and temperature dependent but which varied only slightly with pressure.

The results were accounted for by postulating a new type of electronic polarisation by the applied field of groups of highly mobile charges in very low resistance regions (such as \textepsilon\textital{TT} orbitals). The polarisation effect was termed 'hyper electronic' and calculations predicted the observed frequency, temperature, field strength and pressure dependences.

In contrast to M.W.S. and Schwarz-type relaxations, the Pohl effect shows a dependence of dielectric constant upon field strength and this observed effect can prove a useful tool in the identification of relaxation processes in polymers.
2.3 Electrical Conduction in Polymers

2.3.1 General Features

The low conductivity, low dielectric loss and high breakdown strength of most plastic materials normally leads to their application as insulators. Recent research has, however, led to a range of high molecular weight materials which exhibit conductances high enough to class them as semi-conductors (specific conductance $\sigma = 10^{-12}$ to $10^2 \Omega^{-1} \text{cm}^{-1}$).

It has been shown previously that the complex morphology of polymeric materials precludes the application of the conventional theories of dielectric polarisation developed for low molecular weight inorganic and organic substances to high molecular weight materials without special considerations. A similar situation exists for application of conventional electrical conduction theories to polymeric materials.

The electrical conductivity $\sigma$ of every substance depends upon the direction (e.g. $X$) and absolute temperature, and follows the general relationship

$$\sigma(T,X) = \sum_i |q_i| n_i(T) \mu_i(T,X) \quad (2.67)$$

where $q_i$ is the charge, $\mu_i$ its mobility and $n_i$ the number of carriers of type $i$.

Experimentally it has been found that conductivity frequently varies with temperature (reflecting the presence of two temperature dependent quantities in equation (2.67)) following the relationship

$$\sigma = \sigma_0 \exp \left(-\frac{E_a}{kT}\right) \quad (2.68)$$

where $\sigma_0$ is a constant, $E_a$ is the thermal activation energy, and $k$ is the
Boltzmann constant. Thus plots of \( \log \sigma \) vs. \( 1/T \) may be obtained which are usually linear and from which \( E_a \) may be calculated from the slope.

For some systems the plots consist of a series of intersecting lines of different slopes; these reflect the various activation energies for individual regions (such as below and above the glass transition \( T_g \))\(^{38}\).

Equation (2.68) does not predict the effect of increased temperature upon the number of carriers and a further equation

\[
n(T) = n_o \exp\left(-\frac{E_n}{2kT}\right)
\]

(2.69)

may be proposed in which \( n_o \) is a constant and \( E_n \) is the activation energy of carrier generation.

Conduction processes in polymers take one of two general forms, either that of an electronic nature arising from the formation of electron-hole pairs in an energy band structure or thermally activated hopping of electrons or ions. The primary modes of conduction are summarised in Table 2.1.

Table 2.1 Conduction Modes in Polymers

<table>
<thead>
<tr>
<th>Electronic Processes</th>
<th>Ionic Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Conduction by Electrons</td>
<td>1) Electrolytic (cationic, anionic)</td>
</tr>
<tr>
<td>a) Intrinsic</td>
<td>a) Intrinsic (self dissociating)</td>
</tr>
<tr>
<td>b) Extrinsic (impurities donate electrons)</td>
<td>b) Extrinsic (impurities or dopants)</td>
</tr>
<tr>
<td>2) Conduction by Holes</td>
<td>2) Protonic</td>
</tr>
<tr>
<td>a) Intrinsic</td>
<td></td>
</tr>
<tr>
<td>b) Extrinsic (impurities other than electrons)</td>
<td></td>
</tr>
<tr>
<td>3) Metallic Conduction</td>
<td></td>
</tr>
<tr>
<td>e.g. poly(acetylenes)</td>
<td></td>
</tr>
</tbody>
</table>
2.3.2 Charge Carriers

The formation of electron-hole pairs in an ordered system can result in conduction via an energy band structure. The holes will arise from vacancies in the valence band following the promotion of an electron to a conduction band by thermal energy $169$. The effect is illustrated in Figure 2.9a.

If electronic conduction takes place without the presence of traps then the parameter $E_n$ of equation (2.69) corresponds to the forbidden energy gap of the band theory and the observed activation energy takes a value $E_n/2$. The mobility $\psi(T)$ will be high when the effective mass is small, decreasing with temperature increase owing to scattering. Thus equation (2.68) shows deviations because of the dominance of the exponential term of equation (2.69). In the presence of traps mobility is governed by

$$\psi(T) \propto \exp \left( -E \psi / kT \right)$$

(2.70)

where $E \psi$ is the energy of activation for mobility. The conductivity is now given by

$$\sigma \propto \exp \left( -((E_n/2) + E \psi) / kT \right)$$

(2.71)

and thus by comparison with equation (2.67)

$$E_a = E \psi + E_n/2$$

(2.72)

Similar considerations may be made for electronic hopping processes which give rise to conduction. If conduction is ionic then $E_n$ corresponds to
the work required to create and separate ions. The mobility will be similarly activated and $E\psi$ will take values similar to those for diffusion of ions so that equation (2.72) will still hold.

This simplified theory is difficult to apply to systems where, as in the case of polymers, the bulk mobility is low and the material is not ordered.

For a disordered system a very complex analysis is involved, Hott$^{17}$ has however suggested a number of qualitative generalisations which can be made.

a) The lowest energy states in a band will usually be localised and there will be a critical energy $E_c$ above which states are not localised. An electron in a localised state may be able to move by hopping to another localised state or by thermal excitation to energies above $E_c$.

b) Localised states may exist in the forbidden energy gap.

The features of these systems are illustrated in Figure 2.9b.

Band conduction will not normally occur in bulk materials where intermolecular charge transfer is involved because of discontinuities between molecules. It is however frequently difficult to distinguish between band-type hopping-type conduction in many systems when a constant electric field is being used. It has been shown$^{171}$ that for band-type conductors the conductivity decreases as frequency increases, whereas for hopping-type conduction conductivity increases as frequency increases.

The nature and source of charge carriers in many of the more insulating polymers remains obscure despite the differences of frequency dependence outlined above. Whilst ionic conduction has been reported for numerous polymers$^1$ it has been substantiated in relatively few$^{172,173}$; in many cases the postulated electronic conduction processes are equally supported$^{174}$ so that for polymers such as poly(ethylene terephthalate) (PET) the arguments for both systems are equally strong. Amborski$^{175}$ suggested that the
Figure 2.9

Band formation in ordered and disordered structures

a) Ordered

- Potential wells
- Conduction band
- Valence band

N(E)

Fermi level

Energy E

Eg

b) Disordered

- Potential wells
- Conduction band
- Valence band

N(E)

Fermi level

Energy E

Eg
non-linear relationship between current, field strength and temperature in PET was indicative of ionic conduction; Fowler\textsuperscript{174} proposed electronic conduction processes for the same polymer and was even able to calculate the distribution of traps required to give the observed results. Subsequent studies by Seanor\textsuperscript{172} suggested a process involving both mechanisms but in which the ionic component predominated at higher temperatures.

2.3.3 Carrier Injection

In more highly insulating polymers conduction may result from injection of a charge carrier from the electrodes. If the carriers have to surmount a potential barrier $U$ to enter or leave the polymer then the current is given by

$$i \propto \exp\left[\frac{-U}{kT}\right]$$

(2.73)

A slight variation of the polymer-electrode interface will affect the potential barrier $U$ and will thus have a large effect upon the conductivity. If high electric fields ($E$) are used, the effective potential barrier at the electrode will be reduced (the Schottky effect) and the current will then be given by

$$i \propto \exp\left[\frac{-\left(U - \frac{e \beta E^2}{kT}\right)}{kT}\right]$$

(2.74)

where $\beta = \left(\frac{e}{4\pi \varepsilon' \varepsilon_o}\right)^{\frac{1}{2}}$

$\varepsilon'$ is the relative permittivity of the polymer and $e$ is the electronic charge.

The currents in polymers may be space-charge limited. For a material with a well-defined band system without traps and with electrodes making ohmic contacts, the current density changes from proportionality to applied
voltage $V$ (ohmic) at low voltages (where injection is negligible) to quadratic behaviour at higher voltages, where the space-charge-limited current density $J$ is given by Child's law

$$J = 9 \varepsilon_s \frac{\psi v^2}{8t^3}$$  \hspace{1cm} (2.75)

where $\varepsilon_s$ is the static dielectric constant of the material, $t$ its thickness and $\psi$ its drift mobility. In general the current lies within a 'triangle' as shown in Figure 2.10.

---

**Figure 2.10** Behaviour of Dielectrics with Space Charge Limited Currents

The upper curve represents the restraints set by Child's law (equation (2.75)) for a solid free of traps. The lower curve represents the limits set by Ohm's law for the neutral solid (normal volume conductivity) and the right corresponds to the situation in which all the traps in the solid have been filled before the voltage is applied (the traps filled limit or T.F.L.)
2.3.4 The Effect of Structural Features

a) Molecular Weight

In Chapter 1 some of the parameters required for electronic conduction were briefly reviewed. It was shown that for electronic conduction to take place a series of alternating single and double bonds were required so that delocalisation could provide a path for electrons. Any process which increases the extent of this delocalisation will increase the conductivity, thus higher molecular weight polymers show enhanced electronic conductivity. For ionic conductors the effect of molecular weight is negligible except below 10,000 where plasticisation by the increased number of chain ends (to give a higher free volume and thus ion mobility) can increase conductivity. The contrasts in electrical behaviour are highlighted by studies of poly(ethylene terephthalate). Measurements on the solid polymer at 170°C\textsuperscript{175} of conductivity showed essentially no change upon increasing molecular weight from 13000 to 22000; whilst those on the molten polymer at 283°C\textsuperscript{176} revealed almost an order of magnitude change fall in (ionic) conductivity by increasing the molecular weight from 9000 to 18000.

b) Morphology and Crystallinity

Any process which increases the order of a system such as crystallisation or orientation will decrease the available free volume and thus the mobility of the ions for conduction. The expected reduction in ionic conduction with increasing order (both crystalline and orientational) have been observed in poly(ethylene terephthalate)\textsuperscript{175,176}. Increasing the crystallinity by between 10 and 50\% reduced the conductivity by a factor of between 10 and 1000. The expected increase in activation energy which results from a reduction in ion mobility was also observed.

The effect of morphology changes still remains poorly understood, a situation highlighted by apparent anomalies encountered during studies of
polymer semiconductors. Studies of the effect of increased crystallinity upon the conductivity of polyacetylene\textsuperscript{177} showed an increase of conductivity with increasing crystallinity. The results have been explained in terms of the formation of a longer conjugated system with improved intermolecular transfer of electrons. By contrast poly(vinyl anthracene)-iodine complexes, which also exhibit enhanced electronic conductivity, show little dependence of conductivity upon crystallinity\textsuperscript{10}.

c) Crosslinking

The process of crosslinking results in marked reductions in free volume and thus causes a decrease in the mobility of the ions involved in transport. The predicted decreases in conductivity with the onset of crosslinking have been observed in thermosetting polymers and has been used as a method of determining structural parameters and the glass transition in such systems\textsuperscript{178}.

d) Ionizing Radiation

The exposure of polymers to high energy radiation (\(\alpha\), \(\beta\) or \(\gamma\) electrons) can induce changes which may at first be temporary but after sufficient dosage can become permanent\textsuperscript{179}.

Irradiation of poly(ethylene) with X-rays of dose rate 8 kR/min resulted in a reduction of resistivity of approximately four orders of magnitude at room temperature\textsuperscript{180}. The induced current was found to be proportional to \(I^n\) where \(I\) is the radiation intensity and \(0.5 < n < 1\), and was not instantaneous with irradiation but rose gradually.

These observations were interpreted\textsuperscript{174} in terms of the production of free electrons and holes through the volume of the dielectric and the consequential formation of conduction bands, the energy distribution of which was governed by the parameter \(n\).
e) The Effect of Relative Permittivity

The dielectric constant of a polymer can have an important effect upon the conductivity. The presence of plasticisers, fillers and moisture may also enhance conduction either by self-dissociation or by increasing the relative permittivity of the mass \(^1\). The degree of dissociation of ion-pairs is proportional to \(\exp\left(-\frac{V_o}{\mathcal{E}'kT}\right)\), where \(V_o\) is the energy required to separate the ions, \(T\) is the absolute temperature and \(k\) is the Boltzmann constant. It can be shown that

\[
\log \mathcal{E} = B + \frac{A}{\mathcal{E}'} \quad (2.76)
\]

where \(A\) and \(B\) are constants, and \(\mathcal{E}\) is the volume resistivity.

A linear relationship of negative slope between \(\log \sigma\) and \(1/\mathcal{E}'\) has been similarly derived and verified using cellulose acetate doped with Group 1 metal halides \(^{181}\). In this study it was suggested that moisture was an important source of charge carriers and that the theory of weak electrolytes could be applied to ionic salts in moist solid polymers.

An increase in dielectric constant may also affect the creation of mobile electrons, and the effect of water absorption on charge-carrier generation has been evaluated \(^{182}\) and a general expression derived

\[
\sigma [T, \mathcal{E}'] = \sigma_0 \exp\left[\frac{-E_d}{2kT} \exp\left[\frac{k}{T}\left(\frac{1}{\mathcal{E}'} - \frac{1}{\mathcal{E}_1'}\right)\right]\right]. \quad (2.77)
\]

where \(E_d\) is the work required to separate the electron and hole in the dry material, \(k\) is a constant, \(\mathcal{E}'\) the dielectric constant of the dry material and \(\mathcal{E}_1'\) is that of the moist material. At constant temperature equation (2.77) simplifies to equation (2.76).

Rosenberg \(^ {182}\) has predicted
where \( m \) is the moisture content and \( C \) and \( D \) are constants. Equation (2.78) has been fitted to some experimental data with good agreement.

In addition to other modes of action Eley and Leslie\(^\text{183}\) have shown water to act as an electron donor such that

\[
\log_{10} \sigma = F + \log_{10} (m^4) + km^x
\]  

(2.79)

where \( F \) and \( k \) are constants, \( x \) is another constant dependent upon the distribution of water molecules.

The difficulty in determining conduction processes in polymers was again highlighted by the use of Rosenberg's data\(^\text{182}\) by Eley and Leslie\(^\text{183}\). Equation (2.79) was shown to give almost as good a fit with \( x = 1/3 \) as equation (2.78).

2.4 Mechanical Properties of Polymers

2.4.1 General Features

Polymers show mechanical properties which have the characteristics of both perfect solids (Hookean)\(^\text{184}\) and of perfect liquids (Newtonian)\(^\text{185}\). A perfect solid obeying Hooke's law shows stress which is directly proportional to strain, whilst for a perfectly viscous liquid Newton's law of viscosity is obeyed and stress is directly proportional to the rate of strain. Polymers are classed as viscoelastic bodies and show behaviour intermediate between the two extremes. Constant deformation is not maintained under the application of constant stress (i.e. the material creeps) and under conditions of constant deformation the stress required to maintain it diminishes with time (i.e. the material is subject to stress...
relaxation). If a polymer is subjected to a sinusoidally oscillating stress then the strain will neither be exactly in phase with the stress (as for Hookean behaviour) or 90° out of phase (as for a Newtonian liquid) but will be somewhere in between. For a given cycle some of the energy input will be stored and recovered whilst some will be dissipated as heat. The measurement of the viscoelastic behaviour of a polymer is normally carried out by study of creep, stress relaxation and dynamic mechanical properties.

a) Creep

To measure creep a shear stress $\sigma_{xy}$ is suddenly applied to a specimen at time zero and is held constant during the test. The resulting strain $\varepsilon_{xy}$ is measured as a function to time such that the tensile compliance $D(t)$ is given by

$$D(t) = \frac{\varepsilon_{xy}}{\sigma_{xy}} \quad (2.80)$$

Figure 2.11 illustrates a typical log $D(t)$ vs. time plot and demonstrates the characteristic features of viscoelastic behaviour in polymers.

At short times the material acts as an elastic solid and is termed 'glassy' with $D(t) = J_U$, the unrelaxed or glassy state compliance. As time progresses the material deviates from Hookean behaviour, the creep compliance increases and the material softens showing elastic deformations characteristic of a rubber. The transition from perfect elastic behaviour to finite behaviour occurs over several decades of time and is characterised by a retardation time $\tau_R$. Following the transition a rubbery region is reached in which $D(t) = J_R$, the relaxed compliance, and the behaviour is dependent only upon the chemical structure. $D(t)$ remains constant with further time increase for crosslinked polymers but continues to increase slowly in uncrosslinked specimens which are subject to Newtonian flow.
Figure 2.11

Typical creep compliance curves for polymers
b) **Stress Relaxation**

If a sample of polymer is subjected to an instantaneous strain \( \varepsilon_{xy} \) which is held constant during the test period then the tensile stress to maintain the given strain \( \sigma_{xy} \) can be measured as a function of time such that the tensile stress modulus \( E(t) \) is given by

\[
E(t) = \frac{\sigma_{xy}}{\varepsilon_{xy}}. \tag{2.81}
\]

Figure 2.12 illustrates a typical log \( E(t) \) vs. time plot. At short times the glassy state predominates and the polymer shows an unrelaxed modulus \( E_U \). With increasing time a relaxation region characterised by a relaxation time \( \lambda \) is observed in which the modulus falls. At longer times a relaxed modulus \( E_R \) is attained. For crosslinked systems the value of \( E(t) \) remains constant with further increase in time. For uncrosslinked polymers values of \( E(t) \) continue to decrease with time for the same reasons as the increase in \( D(t) \) previously described.

c) **Dynamic Mechanical Measurements**

Dynamic mechanical measurements of polymers are carried out by subjecting a sample to a sinusoidal stress (strain) and observing the resulting strain (stress) as a function of frequency. The effect is illustrated in Figure 2.13.

If we consider a stress variation \( \sigma_{xy} \) given by

\[
\sigma_{xy} = \overline{\sigma_{xy}} \sin \omega t \tag{2.82}
\]

where \( \overline{\sigma_{xy}} \) is the amplitude of the stress in any cycle and \( \omega \) is the angular frequency, then the observed strain will vary with the same frequency as the stress but will lag behind by an angle \( \phi \) such that
Figure 2.12

Typical stress relaxation behavior for polymers

--- Linear polymers

Crosslinked polymers

$G_U$

$G_R$

Log $G(t)$

Log $t$

Log $\tau$
Figure 2.13

Dynamic mechanical behavior of polymers
\[ E_{xy} = \overline{E_{xy}} \sin [\omega t - \delta] \]  

(2.83)

Equations (2.82) and (2.83) describing dynamic mechanical stress-strain relationships show similarities to those previously derived for electric field (equation (2.17)) and electric displacement (equation (2.18)). It is possible to describe viscoelastic behaviour in terms analogous to the complex dielectric permittivity and complex inverse dielectric permittivity described in section 2.2.1. The corresponding compliance \( J^*(\omega) \) and modulus \( G^*(\omega) \) for mechanical measurements are thus given by

\[ J^*(\omega) = J'(\omega) - j J''(\omega) \]  

(2.84)

\[ G^*(\omega) = G'(\omega) + j G''(\omega) \]  

(2.85)

where \( J'(\omega) \) and \( G'(\omega) \) are the storage compliance and modulus representing energy stored in the sample and \( J''(\omega) \) and \( G''(\omega) \) are the loss compliance and modulus representing input energy lost as heat.

The variation of storage and loss compliance and modulus is shown in Figure 2.14. The behaviour is again analogous to that described in section 2.2.1 for dielectric response. At high frequencies glassy state behaviour predominates with \( J' = J_U \) and \( G' = G_U \). At frequencies near to \( 1/\zeta_R^{-1} \) \( J'(\omega) \) increases rapidly (\( G'(\omega) \) decreases rapidly near to \( 1/\zeta \)) whilst the value of \( J''(\omega) \) (and \( G''(\omega) \)) rise to a maxima at \( \omega = 1/\zeta_R^{-1}(1/\zeta) \) and then falls. Further reduction of frequency results in \( J'(\omega) \) and \( G'(\omega) \) attaining constant values of \( J_R \) and \( G_R \) as the polymer enters the rubbery or relaxed state. As in the case of creep and stress relaxation experiments the onset of flow in linear polymers can result in a second relaxation in both compliance and modulus terms, as frequency is further reduced.

The complex compliance \( J^* \) and modulus \( G^* \) may be represented in the form
Figure 2.14

Variation of storage and loss compliance and modulus with frequency
of Argand diagrams similar to those of Figure 2.3. Thus the loss tangent may be defined as

$$\tan \delta = \frac{J''(\omega)}{J'(\omega)} = \frac{G''(\omega)}{G'(\omega)} \tag{2.86}$$

It can also be shown\textsuperscript{157} that mechanical compliance and modulus are related by the expression

$$J^* = \frac{1}{G^*} \tag{2.87}$$

and hence

$$J' = \frac{G'}{|G^*|^2} \tag{2.88}$$

$$J'' = \frac{G''}{|G^*|^2} \tag{2.89}$$

Debye\textsuperscript{133} has derived expressions for $\varepsilon^*(\omega)$, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ in terms of the relaxed and unrelaxed permittivities and relaxation (retardation) times for a single relaxation time model. Using similar arguments it is possible to derive\textsuperscript{137} similar expressions for viscoelastic response such that:

$$J'(\omega) = J_U + \frac{[J_R - J_U]}{1 + \omega^2 \tau_R^2} \tag{2.90}$$

$$J''(\omega) = \frac{[J_R - J_U] \omega \tau_R}{1 + \omega^2 \tau_R^2} \tag{2.91}$$

$$\tan \delta_m = \frac{[J_R - J_U] \omega \tau_m}{J_R + J_U \omega^2 \tau_m^2} \tag{2.92}$$

and

$$G'(\omega) = G_R + \frac{[G_U - G_R] \omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2} \tag{2.93}$$

$$G''(\omega) = \frac{[G_U - G_R] \omega \tau_R^2}{1 + \omega^2 \tau_R^2} \tag{2.94}$$
\[
\tan \delta_m = \frac{\left[ G_U - G_R \right]}{G_R + G_U \omega^2 \Gamma_m^2}
\]  
(2.95)

where \( \Gamma_m = (\Gamma_R \Gamma_m)^{\frac{1}{2}} \).

If \( G'(\omega) \) and \( J'(\omega) \) are plotted against \( \log \left( \frac{1}{\omega} \right) \) the curves coincide with \( E(t) \) and \( D(t) \) plotted against \( \log t \) on the same scale. Thus the reciprocal relationship between log frequency and temperature characteristic of viscoelastic behaviour is established.

In common with observations of dielectric relaxation processes mechanical relaxation times have a temperature dependence given by an Arrhenius expression of the form of equation (2.30).

\[
\chi = \chi_o \exp \left[ \Delta E/RT \right]
\]  
(2.30)

It may be shown that

\[
\log \omega_{\text{max}} = \log \frac{1}{\chi_0} + \left( \frac{R}{\Delta E} \right) T
\]  
(2.96)

and thus at constant \( \omega \) and variable temperature plots of \( G' \), \( G'' \), \( J' \) and \( J'' \) vs. temperature plots analogous to \( \log \omega \) plots may be obtained.

2.4.2 Time-Temperature Superposition Principle

Viscoelastic relaxation takes place over large time scales which frequently make it inconvenient if not impossible to measure the full spectrum of relaxation at a given temperature. It is therefore convenient to exploit the reciprocal frequency-temperature relationship and employ an extrapolation method to obtain the full spectrum of the relaxation.

A method was first developed by Leadermann who studied the creep response of materials. He observed that the response curves obtained at different temperatures could be superposed by a translation along the
logarithmic time axis. A factor $a_T$ was defined such that data obtained at a temperature $T$ when multiplied by $a_T$ could be superposed upon data at a reference temperature $T_0$. The factor $a_T$ was experimentally determined at each temperature by noting the shift required to make data at $T$ and $T_0$ coincide. Using data superposed from various temperatures, a master curve at the reference temperature could be obtained which covered more decades than experimentally determinable.

Provided the polymer follows linear viscoelastic theory a similar time-frequency variable $(a_T)$ can be applied to stress relaxation-time curves and dynamic modulus-frequency curves.

Williams, Landel and Ferry defined the shift factor $a_T$ by the semi-empirical equation

$$\log a_T = \frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \tag{2.7}$$

which has been modified to account for deviations at temperatures below the glass transition as discussed previously in section 2.1.

2.4.3 Relationship Between Dynamic Mechanical Properties and Structure

a) Molecular Weight and Crosslinking

The molecular weight and weight distribution of rigid polymers have little effect upon their dynamic mechanical behaviour except at very low frequencies. Uncrosslinked polymer melts are, however, strongly sensitive to molecular weight. High molecular weight polymers have more entanglements and thus the plateau region becomes more prominent and covers a larger temperature range as molecular weight increases. The loss peak is similarly shifted to higher temperatures and has greater magnitude.

Crosslinking of rubbers prevents much of the viscous flow from taking
place and thus the second drop of modulus does not occur and in some cases the modulus may actually increase slightly in the rubbery state. It was shown previously that crosslinking elevates $T_g$ and this trend is reflected in the position of the mechanical loss peak associated with the $\alpha$-transition which is shifted to higher temperatures with increasing degree of crosslinking. The peak is also broadened and decreased in magnitude such that at high levels of crosslinking there is no indication of the glass transition.

b) Plasticisers and Copolymerisation

The effect of plasticisers upon the mechanical behaviour of polymers reflects the trends exhibited in thermal studies. In general, addition of plasticiser causes the transition to shift down the temperature axis. Associated with this shift there is a broadening of the loss peak which reflects the nature of the plasticiser and its compatibility with the polymer. If the plasticiser has limited solubility in the polymer or tends to associate in the presence of the polymer then the peak will be broadened. This effect has been illustrated by Nielson et al. who studied poly(vinyl chloride) containing diethyl phthalate (a good solvent for PVC), dibutyl phthalate (a poorer solvent) and dioctyl phthalate (a very poor solvent). The transition region was found to broaden and was accompanied by an associated reduction of the maximum value. The slope of the log modulus vs. temperature curve was also observed to decrease with increasing breadth of transition.

The effect of copolymerisation upon the dynamic mechanical properties of polymers may similarly be predicted from glass transition behaviour. The glass transition of a copolymer is intermediate between that of the respective constituent homopolymers. It may be predicted as previously described by the Fox equation (equation (2.11)) or the Gordon-Taylor-Wood equation (equation (2.12)). Using similar criteria the position of maximum
damping of the mechanical relaxation may be predicted from the composition of the copolymer and the position of the relaxation peaks for the respective homopolymers.

For a homogeneous copolymer all molecules will have the same chemical composition and thus will have a single sharp glass transition relaxation. In reality most copolymers consist of molecules with different chemical compositions (i.e. different sequence distributions) arising from differences in reactivity ratios between the comonomers. Heterogeneity of chemical composition can lead to broadening of the relaxation peaks. Nielsen\textsuperscript{190} has related this observation to the mutual compatibility of the individual homopolymers. If the molecular interactions between individual homopolymer sequences is high then the interchain heterogeneity will be small and the peak will be sharp. If the homopolymers are insoluble in each other then interchain heterogeneity will be high and as a result a broad transition will result.

2.5 \textbf{Small Angle X-Ray Scattering}\textsuperscript{191-193}

2.5.1 \textbf{Introduction}

When X-rays of a given wavelength impinge upon an atom its electrons become secondary emitters of X-rays and the atoms are said to be scattering the incident radiation. The scattering may take two forms, either that of coherent (unmodified) or incoherent (modified). The former represents the major part of the energy of scattering and may be utilised for structural studies as the phase relationship between incident and scattered X-rays is unchanged. Incoherent or Compton scattering contributes to the diffuse background of an X-ray diffraction pattern and is derived from the interaction of X-rays with loosely bound or free electrons and the subsequent longer wavelength emission.
Variations of electron density produce variations in the intensity of the coherent scattering geometry governed by the familiar Bragg equation 194

\[ n\lambda = 2d \sin \Theta \]  

(2.97)

where \( \lambda \) is the wavelength of the x-rays, \( d \) is the interplanar distance, \( n \) is an integer number and \( \Theta \) is half the angle of deviation of diffracted rays from the incident X-rays. The effect is illustrated in Figure 2.15.

If the variations of electron density occur on an atomic level then interference will be observed in the wide angle scatter region (WAXS). The reciprocity between interatomic distance and \( \sin \Theta \) indicated in equation (2.97) leads to scattering and interference effects by inhomogeneities of colloidal dimensions at very small angles (SAXS). For copper k\( \alpha \) radiation of wavelength 1.542 \( \AA \) the angle 2\( \Theta \) is typically less than 3°. The dependence of SAXS intensities only upon large scale inhomogeneities and not those of atomic dimensions results in no scatter at low angles from single crystals and pure or homogeneous substances.

Two types of inhomogeneity are most likely to produce small angle X-ray scattering from solid polymers. The first consists of a network of alternate crystalline and amorphous regions which in general will have different electron densities. The second type arises from the presence of particles or microvoids dispersed in the polymer matrix. A difference of electron density between the particles (or microvoids) and the matrix produces the observed scattering. It is not possible to distinguish between scattering by a system of particles in space and from a complementary system of voids in a matrix because of the Babinet principle of reciprocity. Under normal circumstances independent evidence concerning the nature of the system is available to facilitate the choice between the alternatives.
Figure 2.15

Geometry of Bragg reflection
2.5.2 Scattering Power

The intensity of small angle scattering is proportional to the mean square fluctuation of the electron density between the two or more kinds of regions that produce the heterogeneity \( (\bar{\rho} - \bar{\rho})^2 \) and is termed the 'Scattering Power'. For a two phase system of electron densities \( \rho_1 \) and \( \rho_2 \) for the respective phases and having a sharp boundary between them then

\[
(\bar{\rho} - \bar{\rho})^2 = [\rho_2 - \rho_1]^2 \phi_1 \phi_2 = \Delta \rho^2 \phi_1 \phi_2
\]  

(2.98)

where \( \phi_1 \) and \( \phi_2 \) are the volume fractions of the phases and \( \phi_1 + \phi_2 = 1 \). For scattering to occur an electron density difference must exist between the two phases and will be a maximum when \( \phi_1 = \phi_2 = 0.5 \).

2.5.3 Slit versus Pinhole Collimation

The original theory of small angle scattering was developed for primary beams with a point-like cross-section, a situation which in practice is only realised with pinhole collimation of the radiation. The requirement for higher intensities of radiation has lead to the use of slit collimators with the associated necessity of modifying the mathematical treatment of the data.

There are two methods in which slit-distorted or 'smeared' experimental data may be treated:

1) Derive formulae to correct the scattered intensity for the collimation errors, the corrected data (desmeared) approximating to that obtained from pinhole optics.

2) Derive a new scattering theory to obtain directly from smeared intensity data the parameters previously only found from pinhole collimated data.

Treatment of the results by application of Guinier's law requires desmeared data whilst use of Porod's law can be made using smeared data. Methods of
desmearing small angle X-ray scattering data have been recently reviewed and will not be considered here.

2.5.4 **Porod's Law**

Porod has shown\(^{195}\) that for a two phase system the tail end of the small angle scattering curve should conform to the asymptotic course \(\Theta^{-4}\) for pinhole collimation and \(\Theta^{-3}\) for collimation by infinitely long narrow slits. This is equivalent to saying that for smeared intensity data the product \(\Theta^{-4}I(\Theta)\) or \(\Theta^{-3}I(\Theta)\) should assume a constant value.

Positive deviations from Porod's law can occur due to electron density fluctuations\(^{196,197}\) within phases whilst negative fluctuations may result from diffuse interphase boundaries\(^{198}\). Luzzati et al.\(^{199}\) have shown that electron density fluctuations lead to an additional constant term in the smeared intensity \(I\) scatter curve. Combining this effect with Porod's law gives an overall form for the tail of the scattering intensity curve:

\[
\tilde{I}(\Theta) = k_1 \Theta^{-3} + k_2
\]

or

\[
\tilde{I}(\Theta) \Theta^3 = k_1 + k_2 \Theta^3
\]

(2.99)

(2.100)

Thus from equation (2.100) it can be seen that a plot of \(\Theta^3\tilde{I}(\Theta)\) vs. \(\Theta^3\) should yield a straight line slope \(k_2\) from which the correction factor \(\Theta^3.k_2\) which must be applied to the scattering \(\Theta^3.I(\Theta)\) can be determined.

2.5.5 **Guinier's Law**

For a dilute, monodisperse system in which the particles may assume all orientations with equal probability Guinier\(^{200}\) described the scattering intensity by the function
I(\Theta) = I(0) \exp\left(-\frac{1}{3}\left[\frac{4\pi}{\lambda}\right]^2 R^2\right) \tag{2.101}

where I(\Theta) and I(0) are the desmeared intensities at \Theta and zero angle respectively, \lambda is the wavelength of the radiation and \bar{R} is the electronic radius of gyration.

Guinier's law is commonly expressed in a logarithmic form

$$\log_e I(\Theta) = \log_e I(0) - \frac{1}{3} \left[\frac{4\pi}{\lambda}\right]^2 \Theta^2 \tag{2.102}$$

From equation (2.102) it is evident that a plot of \log_e I(\Theta) versus \Theta^2 will be linear with intercept \log_e I(0) and slope \(-\frac{1}{3} \left[\frac{4\pi}{\lambda}\right]^2\).

Guinier's law is most closely obeyed for monodisperse systems of spherical particles, but even for departures from this behaviour the limiting slope as \Theta approaches zero will still yield the mean radius of gyration.

2.5.6 Density Fluctuations within Phases

It was stated in section 2.5.4 that fluctuations of electron density within phases can give rise to positive deviations from Porod's law for two phase systems such as amorphous polymers. The scattering from amorphous polymers has been interpreted in terms of a 'nodule' structure in which ordered domains exist within a disordered matrix\textsuperscript{201-203}.

Fischer et al.\textsuperscript{196,197} have shown that for some amorphous polymers the diffuse scattering is strongly dependent upon the thermal history of the polymer. Although much of the scattering could be attributed to the presence of foreign particles such as stabilisers and catalyst residues, residual scattering remained after purification. The residual scattering has been interpreted in terms of thermal density fluctuations within an homogeneous phase.
The measurement of SAXS at various temperatures above and below $T_g$ revealed an increase of scatter intensity with temperature both above and below the glass transition but which showed a change of slope at $T_g$. It was shown that for a one component system the fluctuation of particle density was given by

$$\frac{(N - \overline{N})^2}{\overline{N}} = K T \chi d$$

(2.103)

where $N$ is the number of particles in volume $V$, $K$ is the Boltzmann constant, $T$ is the temperature, $\chi$ is the isothermal compressibility and $d$ is the average number density. The theory assumes that many degrees of freedom are present on a local level. From scatter theory it was possible to show that

$$\frac{(N - \overline{N})^2}{\overline{N}} = I(0) / Z^2$$

(2.104)

where $I(0)$ is the extrapolated scatter at zero angle and $Z$ is the number of electrons per particle.

Similar studies have been made by Ruland on semi-crystalline polymers and comparable relationships have been shown to hold.
CHAPTER 3

EXPERIMENTAL

3.1 Purification and Characterisation of Polymers Studied

3.1.1 Poly(vinyl alcohol)

Poly(vinyl alcohol) (B.D.H. Laboratory reagent, degree of hydrolysis 98.5%) was purified to remove residues present from the commercial hydrolysis of poly(vinyl acetate). A clear solution of poly(vinyl alcohol) (5% wt./vol.) in water was precipitated by slow addition, with stirring, to a large volume of acetone. The filtered polymer was then re-dissolved and the process repeated. Following the second precipitation the polymer was filtered and dried under vacuum (< 0.1 mm Hg) at 70°C for two weeks, until constant weight was attained. The polymer was subsequently stored, under vacuum, until required.

3.1.2 Poly(methyl vinyl ether)

Low molecular weight poly(methyl vinyl ether) (supplied by Polysciences Inc.) was received as a highly viscous liquid. The polymer was degassed and dried under vacuum at 50°C and stored until required.

3.1.3 Poly(ethyl vinyl ether)

Poly(ethyl vinyl ether) (Trade name Lutonal A50, supplied by B.A.S.F. Ltd.) was received as a viscous, colourless gel. The polymer was dissolved in dry methanol to give a 5% wt./vol. solution which was then filtered to remove insoluble particles derived from crosslinking processes occurring during the commercial polymerisation. The filtered solution was evaporated and subsequently stored, under vacuum, until required.
3.1.4 Poly(isobutyl vinyl ether)

Poly(isobutyl vinyl ether) (Trade name Lutonal I.C.I.25, supplied by B.A.S.F. Ltd.) was received as granules coated with talc. The polymer was dissolved in methyl ethyl ketone to give a 5% solution which was then centrifuged, at 9000 r.p.m. for 20 minutes, to remove talc particles. The centrifuged solution was evaporated and stored subsequently, under vacuum, until required.

3.1.5 Poly(propylene sulphide)

Poly(propylene sulphide) (obtained from Dunlop Canada Ltd.) was degassed at 50°C under vacuum; no further purification was undertaken prior to use.

3.1.6 Molecular Weight Determination

The nature and compatibility of the polymers used in these studies precluded the use of G.P.C. techniques to obtain the number average and weight average molecular weights.

Dilute solution viscometry to determine the viscosity average molecular weight was carried out using a capillary viscometer of the Ubbelohde type. Measurements were carried out using a constant temperature bath set at 25°C with a solution (3.5 g/100 ml) of the relevant polymer in a suitable solution which was successively diluted. The efflux times were measured until agreement within 0.1 sec was obtained.

The molecular weight of the polymer was determined using the following method: the viscosity data as a function of concentration are extrapolated to infinite dilution by means of the Huggins\(^{206}\) equation.

\[ \eta_sp C = [\eta] + k'[\eta]^2 C \]  \hspace{1cm} (3.1)
where \( \gamma_{sp} \) = specific viscosity = \( \gamma = 1 \)

\( [\gamma] \) is the intrinsic viscosity

\( K' \) is a constant for a series of polymers of different molecular weights in a given solvent

\( C \) is concentration.

The Kraemer\(^{207}\) relationship provides an alternative definition of intrinsic viscosity\( [\gamma] \):

\[
\ln \frac{\gamma}{C} = [\gamma] + K''[\gamma]^2 C
\]

\( (3.2) \)

where \( \gamma \) is the relative viscosity = \( \frac{\text{solution elution time}}{\text{solvent elution time}} \)

\( K'' \) is a constant such that \( K' - K'' = \frac{1}{2} \).

A plot of \( \frac{\gamma_{sp}}{C} \) and \( \frac{\ln \gamma}{C} \) vs. concentration (in g/100 ml solvent) yields a common interception at \( C = 0 \), such that:

\[
[\gamma] = \frac{[\gamma_{sp}]}{C=0} = \frac{[\ln \gamma]}{C=0}
\]

Standing and Mark and Houwink\(^{208}\) have shown that the intrinsic viscosity of a polymer shows proportionally to the molecular weight, such that:

\[
[\gamma] = KM^a
\]

\( (3.3) \)

where \( K \) and \( a \) are constants determined from the double logarithmic plot of intrinsic viscosity and molecular weight (normally determined from a series of polymer fractions). The exponent \( a \) lies between 0.5 (for a \( \Theta \) solvent) and 1; \( K \) typically lies between 0.5 and \( 5 \times 10^{-4} \). Both values depend upon the polymer, solvent and temperature. Values of \( K \) and \( a \) exist in the literature\(^{209}\) for standard conditions and from these the molecular weight of a given polymer may be determined.
3.2 Preparation of Polymer-Metal Salt Complexes

All the complexes were prepared in essentially the same manner. The salt and polymer were dissolved separately in a mutual solvent and the two solutions thoroughly mixed together. The solvent was then removed to leave the complex.

It is evident that the mutual solvent chosen must be a good solvent for the salt and the polymer, and should ideally have a low boiling point to facilitate its removal by evaporation.

A summary of the solvents used is given in Table 3.1.

All metal salts were anhydrous, were stored under vacuum for long periods prior to use and in general required no further treatment before use.

Having discussed the general criteria for the production of polymer samples, the preparation of poly(vinyl alcohol) and poly(ethyl vinyl ether) will now be discussed in more detail. The former polymer required specialised techniques of preparation due to the curious nature of the polymer. The method of preparation for the second polymer is general and may be applied to any of the other systems stated.

3.2.1 Poly(vinyl alcohol)

Purified polymer (3 g) was dissolved in distilled water (60 ml). To achieve dissolution of the polymer it was found to be advantageous to allow the polymer to swell overnight in the solvent, and to subsequently heat the mixture carefully to 60°C to complete the process. A solution of the salt under test with concentration 5% w/v was prepared from the dry salt and distilled water.

To the cooled polymer solution an aliquot of salt solution was added such that the desired molar ratio would be obtained in the resulting polymer. The mixture was agitated thoroughly to ensure complete mixing and was poured
Table 3.1. Solvents Used for Polymer-Metal Salt Complex Preparations

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>BP/°C</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>Distilled water</td>
<td>100</td>
<td>Only solvent for poly(vinyl alcohol), required warming to dissolve polymer.</td>
</tr>
<tr>
<td>Poly(methyl vinyl ether)</td>
<td>Ethanol*</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Poly(ethyl vinyl ether)</td>
<td>Methanol**</td>
<td>64.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethanol*</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetone*</td>
<td>66</td>
<td>Not always suitable, high volatility frequently lead to evaporation before kinetics of complex formation possible.</td>
</tr>
<tr>
<td>Poly(isobutyl vinyl ether)</td>
<td>Methyl ethyl ketone*/ isopropyl alcohol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(propylene sulphide)</td>
<td>Tetrahydrofuran+</td>
<td>65</td>
<td>Most polar solvent capable of dissolving polypropylene sulphide.</td>
</tr>
</tbody>
</table>

* AR grade solvents dried over fresh 3 Å molecular sieve.
** Dried by refluxing with magnesium followed by storage over fresh 3 Å molecular sieve.
+ Dried over calcium hydride and freshly distilled prior to use.
into a poly(methyl methacrylate) mould. The solvent was slowly removed by evaporation at room temperature until a solid film was formed. The polymer was then thoroughly dried under vacuum at elevated temperature for several weeks. The resulting complex was stored under vacuum at room temperature until required.

The concentration of the salt in the polymer was calculated with respect to the moles of monomer repeat units in the polymer.

3.2.2 Poly(ethyl vinyl ether)

Poly(ethyl vinyl ether) (2 g) was dissolved in A.R. grade ethanol (20 ml) (dried over 3 Å molecular sieve). A solution of the required anhydrous salt was prepared from the dried chemical in dry ethanol (dried over 3 Å molecular sieve) such that the concentration was approximately 5% w/v. An aliquot of salt solution was added to the polymer solution to give the desired molar ratio of salt to monomer units. Following agitation to ensure thorough mixing, the solution was poured into a circular glass mould with a tin bottom. The majority of the solvent was removed by blowing a stream of dry nitrogen/air over the solution at room temperature for one week. The gas was dried by passage through silica gel columns and concentrated sulphuric acid. Last traces of solvent were removed under vacuum and the sample subsequently stored until required.

The use of a tin foil base in the mould was necessitated by the high tack of the polymer which precluded the preparation method which would normally be applied prior to measurement of the samples to obtain a uniform specimen.
3.3 Differential Thermal Analysis

a) Apparatus

The glass transition temperature \( T_g \) of the polymer-salt complexes was determined using a Du Pont 900 Differential Thermal Analyser equipped with the Differential Scanning Calorimetry Accessory (Catalogue no. 900600). A diagram of the cell is shown in Figure 3.1. A sample pan and a reference pan were positioned on the two raised platforms on the constantan disc as shown. The cell operated at constant heating rate using a single heating block. In the calorimetric mode the temperature difference (\( \Delta T \)) between the sample and the reference junction was plotted against the reference pan temperature. The instrument was calibrated using mercury and benzoic acid which melt at -39°C and 122°C respectively.

Figure 3.2 shows a typical step response thermogram, characteristic of the glass-rubber transition and indicates the parameters used in the measurement of \( T_g \). Several parameters have been applied to define \( T_g \). For this work, however, \( T_g \) has been defined such that:

\[
T_g = \frac{1}{4} (T_H + T_J)
\]

(3.4)

where \( T_J \) and \( T_H \) are as defined by the diagram.

b) Experimental Technique

Samples of the polymer-salt complex (\( \approx 5-10 \) mg) were accurately weighed into aluminium sample pans and sealed to prevent the absorption of water. Samples were weighed so that correlation of the sample weight with the magnitude of the \( T_g \) step as measured by the baseline shift could be made. The sample pan was placed into the cell together with an empty aluminium pan which acted as a reference. The calorimetry cell was cooled to -100°C using
Figure 3.1
Calorimetry Cell
Figure 3.2

An Idealized Glass Transition

\[ T_g = 0.5 \left( T_J + T_H \right) \]
liquid nitrogen, care being taken to prevent ice formation during the process. Samples of the polymer-metal salt complex were scanned at a heating rate of 15°C/min up to a temperature of 150°C.

3.4 Dielectric Measurements

a) Apparatus

The values of tan δ (the loss tangent) measured were normally reasonably large, thus it was possible to carry out all measurements of dielectric behaviour of the polymer-metal salt complexes using a Wayne Kerr B221 Universal Bridge, a Wayne Kerr A321 waveform analyser and an Advance Instruments low frequency oscillator. Each piece of equipment was operated as described in their respective instruction manuals.

The Wayne Kerr Bridge is designed for measurement of high loss systems and is of the transformer ratio arm type. The bridge treats the sample as equivalent to a capacitance $C$ in parallel with a resistance $R$. For such a system it can be shown\textsuperscript{137} that:

\[ \varepsilon' = \frac{C}{C_0} \]  
\[ \varepsilon'' = \frac{1}{R \omega C_0} \]  
\[ \tan \delta = \frac{1}{RC \omega} \]

where $C_0$, $\varepsilon'$, $\varepsilon''$, tan $\delta$ and $\omega$ are as previously defined. The bridge gives a direct reading of capacitance $C$ and of the conductance $G$ where $G = 1/R$.

The value of $\varepsilon'$ could be found directly from equation (3.5) and $\varepsilon''$ could be calculated from:
\[ E'' = \frac{10^6 G}{2\pi f C_0} \] (3.8)

with \( G \) in \( \mu \)Mho, \( C_0 \) in \( \text{pf} \) and \( f \) is in Hz. From values of \( E' \) and \( E'' \) the loss tangent could be calculated from:

\[ \tan \delta = \frac{E''}{E'} \] (3.9)

The capacitance measurements could be made to within \( \pm 0.1\% \) and conductance measurements to within \( \pm 1\% \).

Measurements were made in the frequency range \( 5 \times 10^2 \) to \( 2 \times 10^4 \) Hz and in the temperature range \(-60^\circ \text{C} \) to \(+100^\circ \text{C} \). The sample in the form of a flat disc was positioned in a three terminal cell which was essentially a modified Wayne Kerr Solid Dielectric Permittivity Jig (Model DJ21) as described previously by Fielding-Russell\textsuperscript{210}. The cell is shown in Figure 3.3. The three terminal cell eliminated fringing fields and surface conduction across the ends of the sample. The electrode \( E \) was shielded by a guard ring \( G \) separated from it by a 0.23 mm wall of epoxy resin. Thus the effective area of the sample exposed to the field was given by:

\[ A = \pi (r + \delta r/2)^2 \] (3.10)

where \( r \) is the radius of the electrode \( E \), and \( \delta \) is the thickness of the epoxy resin wall. The electrode \( E_2 \) could be moved up or down using micrometer screw \( M \). The temperature of the cell was monitored using a copper/constantan thermocouple adjacent to the sample and the whole assembly fitted into a vacuum tight brass container.

The capacitance of the dielectric cell with space between the electrodes evacuated was given by;
Figure 3.3

A Three-terminal Dielectric Cell
\[ C_0 = \frac{A}{3.6\pi d} \text{ pf} \]  

(3.11)

where \( A \) is the effective area as previously defined and \( d \) is the thickness of the sample.

b) Experimental Technique

The preparation of samples for dielectric measurements followed two courses dependent upon the nature of the polymer to be investigated. Samples of poly(vinyl alcohol) containing metal salts were compression moulded into circular discs measuring about 4 cm in diameter and up to 2 mm thick. The temperature of the mould was dependent upon the glass transition temperature, \( T_g \), of the sample, but the temperature was usually about 50°C above \( T_g \). To ensure good contact between the sample surfaces and the electrodes, tin foil was pressed into the specimen faces and a thin film of silicone grease was used to prevent air gaps. Samples of poly(vinyl ethers) containing metal salts were cast directly onto tin foil as previously stated and thus it was unnecessary to modify the samples further prior to carrying out dielectric measurements.

The cell was securely located inside the brass container which was evacuated to prevent water absorption. The container was immersed in methanol placed in a well insulated Dewar vessel. The cell was cooled from room temperature to \(-50^\circ\text{C}\) by addition of solid carbon dioxide to the methanol. Using this method the temperature could be controlled to within \( \pm 0.5^\circ\text{C}\). Temperatures above ambient were achieved by immersing the cell in an oil bath thermostated to \( \pm 0.1^\circ\text{C}\). Readings were taken at approximately 5°C intervals over the entire temperature range studied and from the data obtained values of \( \varepsilon' \), \( \varepsilon'' \) and \( \tan \delta \) for each temperature and frequency were calculated.
3.5 **Wide Angle X-Ray Scattering**

a) **Apparatus**

Wide angle X-ray data were obtained for a series of poly(vinyl alcohol)-metal salt complexes using a Phillips PW 1050/25 Goniometer with symmetrical reflection geometry. The goniometer is illustrated in Figure 3.4 and a block diagram of the ancillary equipment is shown in Figure 3.5.

The X-rays were of nickel filtered CuKα radiation generated at a tube voltage of 40 KV and a current of 20 mA. They were detected by a xenon-filled proportional counter (Phillips PW 1965/10) operating at 1650 V in conjunction with a pulse height analyser (Phillips PW 4082). The equipment was operated as directed in the manufacturer's instruction manuals.

b) **Experimental Technique**

Sections of polymer-salt complex were cut from the previously cast films such that they fitted a 2 cm x 1 cm recess in an aluminium sample holder. A sample thickness of 2 mm was sufficient to ensure that it was effectively infinitely thick with respect to the X-ray beam.

Each complex was scanned in the angular range \(2\Theta = 4^\circ\) to \(50^\circ\) automatically over a scan period of 20 minutes.

3.6 **Small Angle X-Ray Scattering**

a) **Apparatus**

Small angle X-ray scattering data were obtained for various poly(vinyl alcohol)-metal salt complexes using slit collimated, nickel filtered CuKα radiation in a Rigaku-Denki goniometer (Model 2202). The optics of the Rigaku-Denki system are shown in Figure 3.6, whilst the associated electronics are shown in block diagram form in Figure 3.7.
Figure 3.4

Geometry of Symmetrical Reflection Diffractometer
Figure 3.5

Block Diagram of Diffractometer Electronics

E.H.T GENERATOR
(Philips PW 1010 / 25)

Cu Kα X-Ray Tube

DIFFRACTOMETER
(Philips PW 1050 / 25)

PROPORTIONAL COUNTER
(Philips PW 1965 / 10)

LINEAR AMPLIFIER
(Philips PW 4072/01)

PULSE HEIGHT ANALYSER
(Philips PW 4082)

COUNTER
(Philips PW 1051)

POWER SUPPLY
(Philips PW 4029/01)
The Rigaku Denki Small Angle Goniometer
Figure 3.7

Block Diagram of SAXS Electronics
The scattering X-rays were detected by means of a sodium iodide scintillation counter in conjunction with a pulse height analyser. The data thus received were stored in a 100-channel multichannel analyser (Laben Spectroscope Model 100) operating in multiscalar mode and being controlled by a step scanner. The step scanner advanced the goniometer through the required angular increment (normally 0.01° at angles below 1° and 0.03° at angles between 1° and 4°) at the conclusion of the desired count period for each channel. Following the completion of the automatic measurement in each of the 100 channels the data could be accessed via a teleprinter output.

b) Experimental Technique

The goniometer was aligned prior to each experiment by adjusting the second and third slits according to the manufacturer's instruction manual. Samples of the polymer-salt complexes were cut from the previously cast sheets such that they were sufficiently large to fit in a sample holder of dimensions 2.5 cm x 0.5 cm. Where possible the thickness of the sample was chosen such that absorption effects were minimised. For such a condition to be attained the thickness is given by

\[ t_m = \frac{1}{\mu} \]  

(3.12)

where \( \mu \) is the linear absorption coefficient of the specimen.

The samples were scanned in the angular range \( 2\Theta = 0.055° \) to \( 3.025° \), using a count time of 100 seconds per increment. The background intensity was determined by placing the sample in an absorbing position just in front of the detector and rescanning over the same angular range. The data were smoothed manually to remove statistical counting fluctuations. All measurements were carried out at 19°C.
3.7 Mechanical Measurements

a) Apparatus

Mechanical measurements were carried out using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (P.L.-D.M.T.A.), operated as described in the instruction manual.

The P.L.-D.M.T.A. uses a rectangular sample of polymer which is clamped firmly at both ends. A third clamp mounted at the centre of the specimen is linked to a mechanical oscillator. The resistance to the applied deformation, as measured by the magnitude and phase of the displacement of the sample, is automatically converted to Young's Modulus data by the associated electronic equipment. Figure 3.8 shows the head of a mechanical analyser and the associated electronics are shown in the form of a block diagram in Figure 3.9.

For such a sample geometry and deformation it may be shown that:

\[ M \ddot{x} + kE^* + A_x = F_p \exp(i\omega t) \]  

where \( M \) is the mass of the vibrating system
\( x \) is the linear displacement of the drive clamp
\( E^* \) is the complex Young's modulus of the specimen
\( F_p \) is the maximum driving force
\( \omega \) is the angular frequency of the driving current
\( t \) is time

\( A \) is the restoring force per unit displacement of the suspension system
\( k \) is a geometric factor \( = \frac{2bh^3}{t^3} \)

where \( b \) is the sample width
\( h \) is the sample thickness
\( t \) is the distance between each rigid sample clamp and the central oscillating clamp.
Figure 3.8

DMTA Cell Assembly
Figure 3.9

Block diagram of DMTA electronics

- VIBRATOR
- VIBRATOR DRIVER
- DIGITAL SINE WAVE GENERATOR
- FREQUENCY SELECT
  - manual
- DISPLACEMENT SELECT
  - manual
- CONTROL PROCESSOR
- A/D CONVERTER
- DISPLACEMENT TRANSDUCER AND LINEARIZER
- AMPLIFIER SYSTEM
- V/I CONVERTER AND COUNTERS
- COMPUTATION PROCESSOR
- D/A CONVERTER
- DISPLAYS
- THUMBWHEEL REGISTERS

- Gain control
- Offset control
- Calibration data
- Sample data
It has been shown\textsuperscript{211} that from equation (3.13) the complex Young's modulus may be resolved into its measurable real and imaginary parts such that

\[
E' = C \left[ \frac{V_i}{V_o} \cos \beta \right] + \frac{M}{k} [\omega^2 - \omega_R^2] \tag{3.14}
\]

\[
E'' = C \left[ \frac{V_i}{V_o} \sin \beta \right] \tag{3.15}
\]

and

\[
\tan \delta = \frac{E''}{E'} \tag{3.16}
\]

where \( \omega_R \) is the free resonant frequency of the system

\( C \) is a constant

\[
\beta = \tan^{-1} \left( \frac{kE''}{kE' + A - M\omega^2} \right) = \text{phase angle}
\]

\( V_i \) is the input voltage

\( V_o \) is the output voltage.

b) Experimental Technique

Samples of poly(vinyl alcohol)-metal salt complexes for dynamic mechanical measurements were prepared by cutting rectangular shaped specimens from previously cast sheets of polymer. The dimensions were accurately measured using a micrometer and vernier calipers and the relevant parameters programmed into the analyser. Samples having dimensions 5 cm x 1 cm x 0.2 cm proved to give the most consistent results without the onset of shear in the specimens.

The sample was securely clamped into the measuring head which was in turn surrounded by a stainless steel outer cover assembly. The cell could be cooled by the passage of liquid nitrogen through internally mounted cooling coils. The temperature of the cell was both monitored and controlled by a platinum resistance probe mounted adjacent to the specimen and con-
nected to the temperature programming unit. A heating rate of 5°C/min together with a frequency of 1 Hz was chosen for most measurements.

3.8 Infra-Red Measurements

Infra-red spectra of some of the poly(vinyl alcohol)-metal salt complexes were obtained using a Perkin-Elmer Grating Spectrometer (Model 457) calibrated using a polystyrene film. The samples to be measured were dissolved in water and thin films cast onto poly(methyl methacrylate) sheet. The films were removed and thoroughly dried at elevated temperature under vacuum. The specimens were subsequently cooled to room temperature and mounted on film sample holders. No special precautions were taken to eliminate water during measurements. The samples were, however, allowed to stand in the beam for five minutes prior to measurement to permit water absorbed during the transfer process to be removed.
CHAPTER 4

RESULTS

4.1 Characterization of Polymers Studied

The molecular weights, glass transition temperatures, trade names and suppliers of the polymers studied in this thesis are given in Table 4.1. The relatively low molecular weight and high polarity of the polymers used precluded the use of techniques other than viscometry to determine the molecular weight.

4.2 Poly(vinyl alcohol) Containing Metal Salts

4.2.1 General Properties

The general properties of poly(vinyl alcohol) containing metal salts which are discussed in this thesis and prepared as described in Section 3.2 are given in Table 4.2. It can be seen from this table that three types of compounds were observed.

Compounds of the first type were prepared when salts of transition metals were introduced into poly(vinyl alcohol). The compounds were optically transparent (though frequently deeply coloured by the metal ion) and their glass transition temperatures were higher than the glass transition temperature of the parent polymer. At room temperature all the compounds were below their glass transition temperature and were thus brittle; they were, however, thermoplastic and could be readily moulded above their $T_g$ using conventional techniques. The compounds were water sensitive and absorption of water lead to plasticisation and an associated reduction of $T_g$; they were, however, considerably less deliquescent than the parent chemicals. During
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>$T_g$ (°C)</th>
<th>$\bar{M}_v$</th>
<th>Comments</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>-</td>
<td>BDH Chemicals Ltd.</td>
<td>75</td>
<td>20,900</td>
<td>Viscometry carried out in distilled water, using $k$ and $\alpha$ values from Brandrup et al. $^{209}$ Literature $T_g$ 75°C $^{205}$</td>
<td></td>
</tr>
<tr>
<td>Poly(ethyl vinyl ether)</td>
<td>Lutonal A50</td>
<td>BASF (U.K.) Ltd.</td>
<td>-27.5</td>
<td>37,200</td>
<td>Viscometry carried out in ethyl methyl ketone using $k$ and $\alpha$ values from Hanson et al. $^{212}$ Literature $T_g$ -19°C $^{209}$</td>
<td></td>
</tr>
<tr>
<td>Poly(methyl vinyl ether)</td>
<td>-</td>
<td>Polysciences Inc.</td>
<td>-24.5</td>
<td>4,800</td>
<td>Viscometry carried out in ethyl methyl ketone using $k$ and $\alpha$ values from Brandrup et al. $^{209}$ Literature $T_g$ -13°C $^{209}$</td>
<td></td>
</tr>
<tr>
<td>Poly(propylene sulphide)</td>
<td>-</td>
<td>Dunlop (Canada) Ltd.</td>
<td>-37.5</td>
<td>-</td>
<td>No viscometry undertaken, quoted $[\gamma]$ 0.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 Characterisation of the Polymers Studied
<table>
<thead>
<tr>
<th>Metal Salt</th>
<th>Colour of Complex</th>
<th>Optical Clarity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc chloride</td>
<td>Colourless</td>
<td>Transparent</td>
<td>Single phase, glassy solids becoming more brittle as salt concentration increased. Less water sensitive than the constituent chemicals.</td>
</tr>
<tr>
<td>Cobalt chloride</td>
<td>Dark Blue</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>Leaf Green</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>Copper chloride</td>
<td>Deep Green</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>IronIII chloride</td>
<td>Red/Brown</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>CobaltII thiocyanate</td>
<td>Dark Blue</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>Lithium thiocyanate</td>
<td>Colourless</td>
<td>Transparent</td>
<td>Type II Complexes</td>
</tr>
<tr>
<td>Sodium thiocyanate</td>
<td>Colourless</td>
<td>Transparent</td>
<td>Single phase, glassy solids becoming less brittle with increasing salt concentration. At high salt loadings blooming of salt and formation of two phase systems observed. Less water sensitive than the constituent chemicals.</td>
</tr>
<tr>
<td>Potassium thiocyanate</td>
<td>Colourless</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>Ammonium thiocyanate</td>
<td>Colourless</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>Colourless</td>
<td>Opaque</td>
<td>Type III Complexes</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>Colourless</td>
<td>Opaque</td>
<td>Two phase, glassy solids, blooming of salt at low salt concentrations. Very water sensitive.</td>
</tr>
</tbody>
</table>
the periods of storage and measurement care was taken to maintain anhydrous conditions and prevent water uptake to ensure that consistent conditions prevailed.

The addition of thiocyanates of monovalent metals to poly(vinyl alcohol) resulted in the formation of a second type of compound which, in common with the first type of complex, were optically transparent. The glass transition temperatures of the second type of compound were lower than that of the parent polymer but were below their $T_g$ at room temperature. In common with the first type of compound, polymers in this group could be moulded at temperatures above their glass transition by conventional techniques and were similarly water sensitive. The deliquescent nature of the compounds increased with salt concentration reflecting the glass transition behaviour and thus great care was taken to achieve and maintain anhydrous conditions throughout measurement and storage periods.

A third type of compound formed by the addition of halides of monovalent metals were opaque and two phase. A depression of $T_g$ was observed but on a lesser scale to that encountered with type II compounds, furthermore the compounds were very water sensitive and blooming of the salt was frequently observed even at low salt loadings.

Subsequent work in this thesis will demonstrate that whilst the first two types of compound were true, single phase complexes, in the third type of compound, the metal salts acted merely as second phase fillers and no chemical interaction between the polymer chains and the salt took place.

4.2.2 Glass Transition Data for Poly(vinyl alcohol)-Metal Salt Complexes

It has been stated previously that the complexes of poly(vinyl alcohol) with metal salts exhibited two distinct patterns of glass transition behaviour which were dependent upon the nature of the salt used.
Figure 4.1 illustrates the glass transition behaviour for complexes formed between poly(vinyl alcohol) and various transition metal compounds. The complexes exhibited single glass transitions which were well-defined although some broadening of the transition did occur at high salt loadings. Complexes of poly(vinyl alcohol) and monovalent thiocyanates also exhibited well-defined single glass transitions and typical examples of these are illustrated in Figure 4.2. It is evident from Figure 4.2 that in common with complexes of the first type the glass transitions of these compounds were broader than those of the parent polymer.

Figure 4.3 illustrates the $T_g$ data for several poly(vinyl alcohol)-metal salt complexes as a function of the mole percent metal salt present in the complex. It can be seen that addition of transition metal chlorides results in an elevation of $T_g$ which follows a non-linear relationship with salt concentration. No limiting value of $T_g$ was observed over the relatively low range of salt concentrations studied. In contrast addition of metal thiocyanates resulted in a depression of $T_g$ having a linear relationship over the range of concentrations studied. It is clear from both sets of results that the cation plays an important part in determining the shape and position of the $T_g$ vs. composition curve.

An estimate of the magnitude of the glass transition was obtained by measuring the shift in the base line which occurred on passing through the glass transition. The criteria taken for such measurements are illustrated in the following diagram.
Figure 4.1

Typical Glass Transitions of Poly(vinyl alcohol)

Metal Chloride Complexes

Concentration of salt in mole percent

Temperature (°C)

50 60 70 80 90 100 110 120 130

Exo

Endo

ΔT
Figure 4.2

Typical Glass Transitions of Poly(vinyl alcohol) Metal Thiocyanate Complexes

Concentration of salt in mole percent
Figure 4.3

Glass Transition Temperatures of Poly(vinyl alcohol)-Metal Salt Complexes
Using the above method the magnitude of the glass transition was determined for poly(vinyl alcohol) containing zinc chloride and ammonium thiocyanate; examples which highlight the different behaviour exhibited by the two types of compound.

The results obtained for these two salts are shown in Figure 4.4. Both salts show an increase in the magnitude of the glass transition per unit weight of sample with increasing salt content over the range of concentrations studied. Included in Figure 4.4 are plots of the same data reduced to account for only the polymer present in the sample. If the parent polymer alone were responsible for the observed glass transition then the latter plots would be expected to reduce to a line of zero slope. Though the samples differ in the exact form of the reduced curve it is clear that neither takes the above form and thus it is possible to state that the salt was not present merely as a second phase filler. This statement exemplifies the observation made previously in Section 4.2.1 by visual examination that the salts were molecularly dispersed within the polymers.
Figure 4.4

The Magnitude of the Glass Transition of Poly(vinyl alcohol)-Metal Salt Complexes

![Graph showing the magnitude of the glass transition as a function of mole% metal salt. The graph includes data for NH₄CNS and ZnCl₂. The magnitude is plotted on the y-axis (arbitrary units) and the mole% metal salt on the x-axis. The data points are marked with circles and dots, indicating different units of measurement for the sample and polymer.]
The data presented in Figure 4.4 uses for its premise the assumption that the heat capacity difference between the glassy and rubbery states as estimated by the step height is independent of the salt present in the polymer. If this were true then the plot of magnitude of relaxation (w.r.t. unit weight of sample present) vs. mole % salt present would be expected to take a slope of zero. This is clearly not the case and thus the transition process taking place must involve further energy terms associated with the addition of the salt.

4.2.3 Dielectric Relaxation Studies of Poly(vinyl alcohol)-Metal Salt Complexes

The inherent crystallinity present in poly(vinyl alcohol) caused by a strongly hydrogen bonded network results in a complex series of dielectric relaxation processes. Poly(vinyl alcohol) exhibits a single relaxation process in the temperature and frequency range studied, which can be attributed to the \( \alpha_a \) relaxation process associated with the glass to rubber transition. The addition of metal salts to the polymer produced more complex relaxation behaviour.

Figures 4.5 and 4.6 summarise the temperature plane dielectric relaxation data of poly(vinyl alcohol)-metal thiocyanate complexes measured at 1.5 kHz in the temperature range +20--+130°C.

It can be seen from both figures that the \( \alpha_a' \) relaxation attributable to the relaxation of segments of polymer associated with metal salt groups is not clearly visible in the storage component data. The relaxation processes are distorted to two factors. Firstly, the crystallinity inherently present and its associated relaxation processes are superimposed upon those attributable to the amorphous phase. In addition at higher temperatures and low frequencies further distortion occurs as a result of conductivity effects. It was shown previously in Section 2.2.2 that the onset of conduction can
Figure 4.5

Temperature dependence of $\log\varepsilon'$ and $\tan\delta$ for Poly(vinyl alcohol)-Lithium Thiocyanate solid solutions at 1.5 kHz.
Figure 4.6

Temperature dependence of Log\(\varepsilon\) and Tan \(\delta\) for Poly(vinyl alcohol)-Metal Thiocyanate solid solutions at 1.5 kHz

![Graph showing the temperature dependence of Log\(\varepsilon\) and Tan \(\delta\) for Poly(vinyl alcohol)-Metal Thiocyanate solid solutions at 1.5 kHz. The graph includes data points for 10% Na SCN and 15% NH\(_2\)SCN, showing the concentration of salt in mole percent and the loss tangent as a function of temperature.]
seriously affect the form of the $\varepsilon'$ and $\varepsilon''$ vs. temperature curves. Typically the result is a steady, almost linear, increase of $\varepsilon'$ and $\varepsilon''$ with temperature.

The data when represented in the form of loss tangent ($\tan \delta$) vs. temperature curves shows better resolution of the relaxation processes. From the family of curves resulting from measurements at various frequencies it is possible to plot the frequency-temperature location of the loss tangent maxima for the $\alpha_a$ relaxation. This is shown in Figure 4.7 and it can be seen that whilst the log $f$ vs. $1/T$ plots are essentially linear there is no simple relationship between the location of plot and the mole percent salt present in the complex.

The frequency dependencies of $\varepsilon'$, $\varepsilon''$ and $\tan \delta$ for the $\alpha_a$ relaxation of poly(vinyl alcohol) containing 8.8 mole % LiCNS at various temperatures are shown in Figures 4.8, 4.9 and 4.10. It can be seen that although the range of measurement was limited the data formed a well-defined family of curves and that high values of $\varepsilon'$ and $\varepsilon''$ were observed. From the position of the maxima of the $\tan \delta$ peaks it was possible to construct a temperature-frequency location plot similar to that of Figure 4.7. This plot is shown in Figure 4.11. The peaks in $\tan \delta$ were again used in preference to the peaks in $\varepsilon''$ because, in general, they were less affected by conductivity effects and were again better defined than the corresponding $\varepsilon''$ peaks.

4.2.4 Effect of Field Strength on the Dielectric $\alpha_a$ Relaxation

It has been stated previously $^{167,168}$ that for certain polymeric systems field strength has an important effect upon the magnitude of the dielectric relaxation. The effect of field strength was studied for the system of poly(vinyl alcohol) containing 15.8 mole % NH$_4$CNS, and the results are summarised in Table 4.3. From this summary it is clear that field strength has little effect upon the magnitude of the relaxation process.
Figure 4.7

Frequency-Temperature Plane Location (based on tan θ data) for Poly(vinyl alcohol) Metal Salt Solid Solutions

- 5.3% Li CNS
- 8.8% Li CNS
- 15.3% Li CNS
- 5.1% KCNS
- 5.3% NaCNS
- 10.3% NaCNS

Log$_{10} \varepsilon$

$\frac{1}{T_{\text{MAX}}} \times 10^3$

2.7 2.8 2.9 3.0 3.1 3.2
Figure 4.8

Frequency dependence of $\varepsilon$ at various temperatures for Poly(vinyl alcohol) + 8.8 mole % LiCNS
Figure 4.9

Frequency dependence of $\varepsilon''$ at various temperatures for Poly(vinyl alcohol) + 8.8 mole % LiCNS
Figure 4.10

Frequency dependence of \( \tan \delta \) at various temperature for Poly(vinyl alcohol) + 8.8 mole % LiCNS
Figure 4.11

Frequency-Temperature Plane Location (based on \(\tan \delta\) data) for Poly(vinyl alcohol) Metal Salt Solid Solutions
Table 4.3. Variation of Dielectric Parameters with Field Strength for Poly(vinyl alcohol) containing 15.8 mole % NH₄CNS

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Field</th>
<th>Log $\varepsilon'$</th>
<th>Log $\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500 Hz</td>
<td>332 v/cm</td>
<td>3.902</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>301 v/cm</td>
<td>3.895</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>211 v/cm</td>
<td>3.896</td>
<td>3.802</td>
</tr>
<tr>
<td></td>
<td>151 v/cm</td>
<td>3.903</td>
<td>3.789</td>
</tr>
<tr>
<td></td>
<td>90 v/cm</td>
<td>3.900</td>
<td>3.786</td>
</tr>
<tr>
<td></td>
<td>30 v/cm</td>
<td>3.904</td>
<td>3.784</td>
</tr>
<tr>
<td>5000 Hz</td>
<td>332 v/cm</td>
<td>3.656</td>
<td>3.584</td>
</tr>
<tr>
<td></td>
<td>301 v/cm</td>
<td>3.675</td>
<td>3.601</td>
</tr>
<tr>
<td></td>
<td>211 v/cm</td>
<td>3.666</td>
<td>3.579</td>
</tr>
<tr>
<td></td>
<td>151 v/cm</td>
<td>3.675</td>
<td>3.578</td>
</tr>
<tr>
<td></td>
<td>90 v/cm</td>
<td>3.683</td>
<td>3.578</td>
</tr>
<tr>
<td></td>
<td>30 v/cm</td>
<td>3.689</td>
<td>3.579</td>
</tr>
<tr>
<td>15000 Hz</td>
<td>301 v/cm</td>
<td>3.417</td>
<td>3.343</td>
</tr>
<tr>
<td></td>
<td>211 v/cm</td>
<td>3.418</td>
<td>3.376</td>
</tr>
<tr>
<td></td>
<td>151 v/cm</td>
<td>3.438</td>
<td>3.388</td>
</tr>
<tr>
<td></td>
<td>90 v/cm</td>
<td>3.448</td>
<td>3.392</td>
</tr>
<tr>
<td></td>
<td>30 v/cm</td>
<td>3.458</td>
<td>3.399</td>
</tr>
</tbody>
</table>
4.2.5 Dynamic Mechanical Relaxation Studies of Poly(vinyl alcohol)-Metal Salt Complexes

Poly(vinyl alcohol) exhibited a single mechanical relaxation in the temperature and frequency range studied. This process could be attributed to the $\alpha_a$ relaxation associated with the glass to rubber transition. The addition of metal salts to the polymer produced parallel relaxation processes associated with the glass to rubber transition of the polymer-metal salt complex. The strength of the relaxation process in the homopolymer as measured by the magnitude of the drop in log $E'$ and of the peak in $\tan \delta$ was lower than that normally associated with amorphous polymers. The presence of crystallinity reduces the volume fraction of amorphous phase and diminishes the relaxations which can take place at $T_g$. Residual relaxation to attain a true rubbery state modulus takes place at the crystalline melting point.

a) Poly(vinyl alcohol)-Zinc Chloride Complexes

Figure 4.12 summarises the mechanical relaxation behaviour of poly (vinyl alcohol)-zinc chloride complexes measured at 1 Hz in the temperature range 40 to 180°C. It can be seen from Figure 4.12 that the $\alpha_a$ relaxation occurred at high temperatures above the glass transition temperature of the pure polymer. Further, it can be seen that the magnitude of the $\alpha_a$ relaxation was considerably greater than that of the homopolymer and was dependent upon the concentration of salt present. Addition of relatively small amounts of salt resulted in a dramatic increase in the difference between the glassy state and rubbery state moduli though the associated $\tan \delta$ values did not increase by proportionally as much. Addition of larger quantities of zinc chloride to the polymer had less effect upon the modulus change between the glassy and rubbery state but produced larger changes proportionally in the size of the $\tan \delta$ peak. The $\tan \delta$ peak remained asymmetric, larger values of $\tan \delta$ being adopted on the high temperature side of the transition. This
Figure 4.12

D.M.T.A data for various Poly(vinyl alcohol)-Zinc Chloride complexes

Concentration of salt in mole percent

Temperature (°C)
observation reflects the relaxation of crystalline segments of the polymer systems which begin to take place above the glass transition of the system.

b) Poly(vinyl alcohol)-Ammonium Thiocyanate Complexes

Figures 4.13 illustrate the mechanical relaxation behaviour of poly(vinyl alcohol)-ammonium thiocyanate complexes measured at 1 Hz and in the temperature range -40º to 160ºC. It can be seen in Figure 4.13 that the α-relaxation of this system occurred at temperatures below that of the homo-polymer, the position of mechanical relaxation process reflecting that previously observed by thermal measurements. The magnitude of the relaxation as measured by the difference between the relaxed and unrelaxed moduli increased rapidly with salt addition up to 10 mole %. A relatively small further increase in magnitude was observed with further addition of salt up to 15 mole percent. The observation supports the proposal that crystallinity inherently present in the polymer is rapidly destroyed by the addition of only small amounts of salt. It can also be seen in Figure 4.13 that the values of tan δ_max increase as the amount of salt present in the complex is increased. The magnitude of the relaxation as reflected by values of the maxima remains small with a value of only 0.4 being observed for the system containing 15 mole percent salt. In common with poly(vinyl alcohol) containing zinc chloride the peaks remained asymmetric with a high temperature (rubbery state) tail.

c) Poly(vinyl alcohol)-Metal Thiocyanate Complexes

Figures 4.14, 4.15 and 4.16 summarise the mechanical relaxation behaviour of poly(vinyl alcohol)-potassium thiocyanate, sodium thiocyanate and lithium thiocyanate complexes measured under similar conditions to those used for the poly(vinyl alcohol)-ammonium thiocyanate system. The data presented in these figures follow similar trends to those observed for the ammonium thiocyanate-poly(vinyl alcohol) system. The magnitude of the relaxation as reflected by
Figure 4.13

D.M.T.A. data for various Poly(vinyl alcohol) Ammonium Thiocyanate complexes

Temperature (°C)

Concentration of salt in mole percent

Log $E'$ (Nm$^2$)

Tan $\delta$
Figure 4.14

D.M.T.A. data for various Poly(vinyl alcohol)-Potassium Thiocyanate complexes

![Graph showing D.M.T.A. data for various Poly(vinyl alcohol)-Potassium Thiocyanate complexes.](image-url)
Figure 4.15

D.M.T.A data for various Poly(vinyl alcohol) - Sodium Thiocyanate complexes

Concentration of salt in mole percent

Loss Tangent

Temperature (°C)
Figure 4.16

D.M.T.A. data for various Poly(vinyl alcohol)-Lithium Thiocyanate complexes

Concentration of salt in mole percent

Loss Tangent

Temperature (°C)
the modulus change between glassy and rubbery states again increased rapidly with small salt addition, but at concentrations of salt greater than 10 mole percent the incremental increase in modulus difference with increased salt content became less marked.

The position of the loss tangent (\(\tan \delta\)) peak maxima reflected the trends previously observed from thermal data showing a gradual shift to lower temperatures with increased salt content. The value of \(\tan \delta_{\text{max}}\) became larger as the amount of salt present increased, an effect reflecting the increased importance of the \(\alpha_a\) relaxation in the polymer system as crystallinity was disrupted and complex formation took place.

Comparison of Figures 4.14, 4.15 and 4.16 indicates a variation of relaxation strength (reflected by the strength of \(\tan \delta_{\text{max}}\)) such that \(K^+ > Na^+ > Li^+\). This trend does not parallel the reduction of cationic radius across the series as expected and is thought to reflect inclusion of small ions into crystalline segments. The topic will be discussed in Chapter 5.

4.2.6 Small Angle X-Ray Scattering of Poly(vinyl alcohol)-Metal Salt Complexes

Small angle X-ray scattering data were obtained for a series of poly(vinyl alcohol)-metal salt complexes containing different concentrations of metal salt. The data were smoothed manually to remove statistical counting fluctuations and were corrected such that each sample had the same effective thickness and absorption coefficient as the poly(vinyl alcohol) parent polymer. This permitted absolute comparison to be made of the scattering curves from different samples. The correction was executed using equation (3.12) as previously described. The linear absorption coefficient used for the absorption correction was derived from mass absorption coefficients calculated as described in Appendix A.
Corrected scattering data for poly(vinyl alcohol) containing zinc chloride, ammonium thiocyanate and lithium thiocyanate are given in Figures 4.17, 4.18 and 4.19 respectively. It is evident that as the concentration of salt in the complex increased the scattering in the tail of the small angle curve also increased. No peaks were observed in any of the scattering curves and the scattering intensity from the original polymer was very low.

Figures 4.20-4.22 and 4.23-4.25 show the Porod Law plot and deviation from Porod Law plot respectively for each of the above systems.

4.2.7 Wide Angle X-Ray Scattering of Poly(vinyl alcohol)-Metal Salt Complexes

Wide angle X-ray scattering data were obtained for a series of poly(vinyl alcohol)-metal salt complexes containing different amounts of salt. The data was smoothed manually to remove statistical variations but was not treated further. Data obtained in this way is shown in Figures 4.26 and 4.27 as a function of scattering angle. It can be seen that in the angular region under observation there was a monotonous reduction of crystalline scattering with addition of salt to the system. Initial addition of salt up to 5 mole percent had a large effect upon the crystallinity of the polymer, but subsequent addition had a diminished effect. At 15 mole percent salt content there was no evidence of scattering from the polymer with the exception of the broad band scattering normally associated with amorphous polymers. Some evidence of a small increase of scattering in the region $2\theta=5-10^\circ$ was observed for samples containing lithium thiocyanate. It is thought that this observation reflects inclusion of salt into crystalline segments and will be discussed in Chapter 5.

No evidence of the incidence of scattering from pure crystalline areas of metal salt within the polymer was obtained for the salt concentrations investigated. The observation is exemplified in Figure 4.26 by the superposition of the major crystalline salt scattering peaks. 213
S.A.X.S. data for various Poly(vinyl alcohol)-
Zinc Chloride complexes

Figure 4.17
SAXS Data for various Poly(vinyl alcohol) Ammonium Thiocyanate complexes
Figure 4,19

S.A.X.S data for various Poly(vinyl alcohol) Lithium Thiocyanate complexes

[Graph showing relative intensity vs. scattering angle with concentration of salt in mole percent]
Figure 4.20

Porod's Law Plot for Poly(vinyl alcohol) - Zinc Chloride Complexes

![Graph showing Porod's Law Plot for Poly(vinyl alcohol) - Zinc Chloride Complexes.](image)

- **Mole % ZnCl₂**
  - 0
  - 5
  - 10
  - 15

- **I(2θ)** (arbitrary units)

- **Scattering angle 2θ (deg)**
Porod's Law Plot for Poly(vinyl alcohol)-Ammonium Thiocyanate Complexes

Figure 4.21
Figure 4.22

Porod's Law Plot for Poly(vinyl alcohol) - Lithium Thiocyanate Complexes

Mole % LiCNS
- 0
- 5
- 10
- 15

$I(2\theta)^3$ (arbitrary units)

Scattering angle, $2\theta$ (deg)
Figure 4.23

Deviations from Porod's Law of Poly(vinyl alcohol) Zinc Chloride Complexes

Mole % ZnCl₂
- ○ 0
- ● 5
- □ 10
- ■ 15

\(\tilde{I}(2\theta)^3\) (arbitrary units)

(Scattering angle, 2\(\theta\))^3 (deg)^3
Figure 4.24

Deviations from Porod's Law of Poly(vinyl alcohol) Ammonium Thiocyanate Complexes
Figure 4.25

Deviations from Porod's Law for Poly(vinyl alcohol) Lithium Thiocyanate Complexes

Mole % LiCNS
- 0
- 5
- 10
- 15

\( \bar{I} (2\Theta)^3 \) (arbitrary units)

(Scattering angle, 2\( \Theta \))^3 (deg)^3
Figure 4.26

W.A.X.S Data for Various Poly(vinyl alcohol) Zinc Chloride Complexes
Figure 4.27
W.A.X.S. Data for Various Poly(vinyl alcohol) Lithium Thiocyanate Complexes

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Graphical Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Solid line</td>
</tr>
<tr>
<td>5</td>
<td>Dashed line</td>
</tr>
<tr>
<td>10</td>
<td>Dotted line</td>
</tr>
<tr>
<td>15</td>
<td>Dash-dotted line</td>
</tr>
<tr>
<td>20</td>
<td>Dashed-dotted line</td>
</tr>
</tbody>
</table>

Scatter Angle 2θ (deg)
4.2.8 Infra-red Data for Poly(vinyl alcohol)-Metal Salt Complexes

Infra-red absorption data obtained for two series of poly(vinyl alcohol)-metal thiocyanate complexes are shown in Figures 4.28 and 4.29. It can be seen from these figures that the infra-red spectrum of the homopolymer contains few well-defined peaks over the range investigated. The presence of crystallinity and hydrogen bonding further broadens the spectrum and in addition creates a peak at \( \approx 2100 \text{ cm}^{-1} \). The spectrum obtained for the homopolymer is however in agreement with that from literature and similar designations may thus be made.

Inspection of the infra-red spectra of the complexed systems shows few distinctive changes in the spectrum from that of the homopolymer either by the appearance of new bands or shifts in existing bands. One notable change was, however, present, a new band at 2050 cm\(^{-1}\) grew in magnitude with increased mole percent salt present. An infra-red spectrum of the pure salts confirmed that its presence was due to the thiocyanate group and was attributable to C=N or C=S stretch as indicated by literature.

4.3 Poly(ethyl vinyl ether) Containing Metal Salts

4.3.1 General Properties

The general properties of poly(ethyl vinyl ether) containing metal salts to be discussed in this thesis and prepared as previously described are given in Table 4.5. It can be seen that two types of compound were formed.

Compounds of the first type prepared from zinc chloride and certain thiocyanates were optically transparent (though deep amber in colour) and showed curious glass transition behaviour. The glass transition temperature of the complex was higher than that for the parent polymer but it was found that a peak transition temperature existed beyond which further addition of salt produced self plasticisation in the samples. At room temperature the
Infra-red spectra of various Poly(vinyl alcohol) Ammonium Thiocyanate complexes
Figure 4.29

Infra-red spectra of various Poly(vinyl alcohol) Potassium Thiocyanate complexes
<table>
<thead>
<tr>
<th>Metal Salt</th>
<th>Colour of Complex</th>
<th>Optical Clarity</th>
<th>General Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc chloride</td>
<td>Amber</td>
<td>Clear</td>
<td>Type I Complexes</td>
</tr>
<tr>
<td>Calcium thiocyanate</td>
<td>Amber</td>
<td>Clear</td>
<td>Single phase, viscous liquids at low salt loadings.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>The viscosity increases with salt concentration to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a given loading but then decreasing again. Less</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>water sensitive than the constituent chemicals.</td>
</tr>
<tr>
<td>Lithium thiocyanate</td>
<td>Amber</td>
<td>Clear</td>
<td></td>
</tr>
<tr>
<td>Sodium thiocyanate</td>
<td>Amber</td>
<td>Clear</td>
<td>Type II complexes</td>
</tr>
<tr>
<td>Ammonium thiocyanate</td>
<td>Amber</td>
<td>Clear</td>
<td>Single phase, viscous liquids at salt loadings up to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 mole percent. Viscosity apparently independent of</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>salt loadings. Less water sensitive than the constituent</td>
</tr>
<tr>
<td>Potassium thiocyanate</td>
<td>White</td>
<td>Two phase</td>
<td>Two phase, very water sensitive.</td>
</tr>
</tbody>
</table>
compounds were above their glass transition temperatures and with the exception of specimens with near optimum salt loading were viscous, tacky liquids. The latter property precluded the use of conventional techniques for moulding samples. All compounds were water sensitive and thus great care was exercised to maintain dry conditions both during periods of measurement and storage to ensure consistent conditions prevailed.

The addition of thiocyanates of metals with a large cationic radius resulted in the formation of compounds of a second type which were also optically transparent though frequently deeply coloured. Compounds of this second type were tacky, viscous liquids at salt loadings of up to 20 mole percent with the glass transition temperature apparently independent of the salt concentration, being equivalent to that of the homopolymer. In common with complexes of the first type these compounds were water sensitive and thus similar precautions had to be taken to maintain dry conditions.

4.3.2 Glass Transition Data for Poly(ethyl vinyl ether) Containing Metal Salts

It has been previously stated that complexes of poly(ethyl vinyl ether) with metal salts exhibited two distinct patterns of glass transition behaviour dependent upon the nature of the salt used. Figure 4.30 illustrates the glass transition behaviour of both types of complex formed by PEVE and various metal salts. It can be seen that the complexes exhibited single, well-defined glass transitions though some broadening at higher salt loadings was noticeable.

Figure 4.31 illustrates the $T_g$ data of various poly(ethyl vinyl ether)-metal salt complexes as a function of mole percent salt present. It can be seen that for compounds of the first type $T_g$ was elevated following a non-linear relationship with salt concentration. Whilst initial addition of salt increased $T_g$ rapidly there was a maximum elevation after which further addition caused a reduction towards the original values. The position of the
Figure 4.30
Glass Transition Data For Various Poly(ethyl vinyl ether) Zinc Chloride Blends
Figure 4.31

Glass Transition Temperatures of Poly(ethyl vinyl ether)-Metal Salt Complexes

Graph showing the relationship between mole % metal salt (w.r.t. moles monomer) and glass transition temperature ($T_g$) for different metal salts:
- $\text{ZnCl}_2$
- $\text{Ca SCN}_2$
- $\text{NH}_4 \text{SCN}$

The graph indicates that $T_g$ increases with increasing mole % of metal salt for each of the complexes, reaching a peak before decreasing.
maximum was not consistent and it is evident that the nature of the cation played an important part in determining its position.

Figure 4.31 exemplifies the observation that compounds of the second type contained molecularly dispersed salt (as indicated by their optical transparency) without any effect upon the glass transition temperature.

4.3.3 Dielectric Relaxation Studies of Poly(ethyl vinyl ether)-Metal Salt Complexes

Poly(ethyl vinyl ether) exhibits a single relaxation process in the temperature and frequency range studied, which can be attributed to the \( \alpha_a \) relaxation process associated with the glass to rubber transition. The addition of metal salts to the polymer resulted in more complex relaxation behaviour. Figures 4.32 and 4.33 summarise the temperature plane data for two poly(ethyl vinyl ether)-metal salt complexes measured at 1.5 kHz in the temperature range -60 to +100°C.

From inspection of the above figures it is clear that the \( \alpha_a \) relaxation of the homopolymer is replaced by a second \( \alpha'_a \) relaxation upon the addition of even small quantities of metal salt. The observed \( \alpha'_a \) relaxation attributable to the glass to rubber transition of associated polymer and metal salt groups is shifted to higher temperatures with addition of salt but is soon masked by a continuum resulting from conduction effects. At high salt loadings the effect is such that the familiar step response in the storage component and peak in the loss term are extinguished.

Comparison of Figures 4.32 and 4.33 suggest that although similar behaviour is exhibited by both halide and thiocyanate systems, the magnitudes of the parameters adopted by the latter are lower.

From the preceding figures it is clear that conventional methods of representing dielectric data are not suitable for systems such as these in which electrical conduction is taking place. To express the data in a clearer
Figure 4.32

Temperature dependence of Log $\varepsilon'$ and Log $\varepsilon''$ for various Poly(ethyl vinyl ether) Zinc Chloride complexes at 1.5 kHz
Figure 4.33

Temperature dependence of Log $\varepsilon'$ and Log $\varepsilon''$ for various Poly(ethyl vinyl ether)-LiCNS complexes at 1.5 kHz
form the concept of dielectric modulus or inverse permittivity has been employed as previously described in Section 2.2.2.

Figures 4.34 and 4.35 illustrate the previously presented PEVE-ZnCl₂ and PEVE-LiCNS dielectric data as real and imaginary parts of dielectric modulus in the temperature plane. It is clear that the data presented in this manner considerably simplifies the observed relaxation phenomena. The real part of modulus takes the form of a step response from an unrelaxed value of log $M'$ -0.5 to a relaxed value of $\epsilon_r$ -6 for zinc chloride systems and -3 for lithium thiocyanate systems. The unreal part of modulus is subjected to a double relaxation process. The lower of these two processes loses strength with increasing salt content whilst the second becomes more dominant and shifts to lower temperatures as the concentration of salt increases. The origin of these relaxation processes will be discussed in Chapter 6.

4.4 Poly(methyl vinyl ether) Containing Metal Salts

4.4.1 General Properties

The general properties of poly(methyl vinyl ether) containing metal salts to be discussed in this thesis and prepared as previously described are given in Table 4.6.

The properties of the complexes prepared were broadly similar to those prepared from poly(ethyl vinyl ether). The compounds were optically transparent, pale amber viscous liquids above their glass transition temperature at room temperature. In common with type I complexes formed by poly(ethyl vinyl ether) the glass transition temperatures of PMVE-metal salt complexes were elevated above those of the pure polymer. The elevation of the glass transition temperature proceeded until an optimum concentration was attained. Beyond this point further addition of salt resulted in internal plasticisation and a reduction of $T_g$. 
Temperature dependence of Log $M'$ and Log $M''$ for various Poly(ethyl vinyl ether) Zinc Chloride complexes at 1.5 kHz.
Figure 4.35

Temperature dependence of Log M' and Log M'' for various Poly(ethyl vinyl ether) Li CNS complexes at 1.5 kHz

![Graph showing temperature dependence of Log M' and Log M'']
Table 4.6  Some Properties of Poly(methyl vinyl ether) Containing Metal Salts

<table>
<thead>
<tr>
<th>Metal Salt</th>
<th>Colour of Complex</th>
<th>Optical Clarity</th>
<th>General Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc chloride</td>
<td>Pale amber</td>
<td>Clear</td>
<td>Single phase, viscous liquids at low salt loadings.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Viscosity increasing to a maximum with salt concen-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tration. Less water sensitive than the component</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>chemicals.</td>
</tr>
<tr>
<td>Lithium thiocyanate</td>
<td>Pale amber</td>
<td>Clear</td>
<td></td>
</tr>
</tbody>
</table>
In common with PEVE-metal salt compounds, samples prepared from poly(methyl vinyl ether) were in general tacky in composition, thus conventional techniques of moulding could not be employed. The compounds were water sensitive and thus in common with samples prepared from other polymers great care was taken to ensure that anhydrous conditions prevailed both during experimental measurements and periods of storage.

4.4.2 Glass Transition Data for Poly(methyl vinyl ether) Containing Metal Salts

It was previously stated that inclusion of metal salts to poly(methyl vinyl ether) resulted in an elevation of the glass transition temperature. Figure 4.36 illustrates the glass transition behaviour of the complexes formed. It can be seen that the complexes exhibited single, well-defined glass transitions, with some broadening at higher salt loadings observable.

Figure 4.37 illustrates the glass transition data for various PEVE-metal salt complexes as a function of mole percent salt present. It can be seen that for both compounds, $T_g$ was initially elevated by the addition of metal salt. A maximum value of $T_g$ was attained beyond which further addition of metal salt resulted in plasticisation and an associated reduction of $T_g$. The position of the maximum was not uniform and it is evident that the nature of the cation is an important factor in determining the position.

4.4.3 Dielectric Relaxation Studies of Poly(methyl vinyl ether)-Metal Salt Complexes

Poly(methyl vinyl ether) exhibits a single relaxation process in the temperature and frequency range studied. The observed relaxation can be attributed to the $\alpha_a$ process associated with the glass to rubber transition. In common with samples prepared from poly(ethyl vinyl ether) the addition of metal salt to poly(methyl vinyl ether) resulted in more complex relaxation
Figure 4.36

Typical Glass Transitions of Poly(methyl vinyl ether) Metal Salt Complexes
Glass Transition Temperatures of Poly(methyl vinyl ether) - Metal Salt Complexes

Figure 4.37
processes. In Figures 4.38 and 4.39 the temperature plane data for two PMVE-metal salt complexes measured at 1.5 kHz in the temperature range -60 to +100°C are illustrated.

Inspection of the above figures indicates that the $\alpha_a$ relaxation of the parent polymer is replaced by a second $\alpha_i'$ process shifted to higher temperatures and showing greater magnitude in both the real and imaginary terms. At higher salt loadings the $\alpha_i'$ process becomes superimposed upon an increasing continuum as a result of conduction effects. Both monovalent thiocyanates and divalent halide systems show this behaviour though the magnitude of the process is clearly dependent upon the nature of the salt.

It is evident from Figures 4.38 and 4.39 that after a relatively small salt addition conventional methods of representing dielectric relaxation data become unsuitable for these systems and thus it is necessary again to consider the data in terms of a real and imaginary part of a complex dielectric modulus.

Figures 4.40 and 4.41 illustrate the same data as that previously shown but in terms of the components of dielectric modulus. In both figures the real terms are reduced to a step response from an unrelaxed value of $\log M' = -0.5$ to a relaxed value of $\omega \rightarrow -6$. For the lithium thiocyanate system the relaxation takes the form of a single process. The system containing zinc chloride however shows a relaxation process which is divided into two distinct mechanisms; a low temperature process of low strength followed by a larger strength relaxation at higher temperatures. The phenomenon is further exemplified by the trends in the unreal terms. The unreal part of the complex modulus passes through a single maximum for systems containing lithium thiocyanate. The positions of the maxima are above that of the homopolymer for all concentrations of salt but is elevated the most for the system containing 5 mole percent salt. The further addition of salt above this concentration results in a shift to lower temperatures. For the system containing zinc
Temperature dependence of $\log \varepsilon'_\infty$ and $\log \varepsilon''$ for various Poly(methyl vinyl ether) Zinc Chloride complexes at 1,5 kHz.
Figure 4.39
Temperature dependence of Log\(\varepsilon'\) and Log\(\varepsilon''\) for various Poly(methyl vinyl ether) Lithium Thiocyanate complexes at 1,5 kHz
Temperature dependence of Log M' and Log M'' for various Poly(methyl vinyl ether) Zinc Chloride complexes at 1.5 kHz.
Figure 4.41
Temperature dependence of Log $M'$ and Log $M''$ for various Poly(methyl vinyl ether) Lithium Thiocyanate Complexes at 1.5 kHz

Concentration of salt in mole percent

- $0$
- $5$
- $10$
- $15$
- $20$
chloride the unreal term passes through a double maxima reflecting the two relaxation processes which take place. The first process occurring at low temperatures (but above the glass to rubber transition of the homopolymer) is at its greatest for 5 mole percent salt content and gradually shifts to lower values as salt concentration is increased. A second process occurring at higher temperatures shows a distinct maxima at the lowest concentration of salt measured and is subsequently shifted to lower temperatures and magnitude with further increase of salt concentration. At high salt loadings the second process takes the form of an inflection on the side of the first relaxation peak.

4.5 Poly(propylene sulphide) Containing Metal Salts

Figure 4.42 illustrates the effect upon $T_g$ of the addition of zinc chloride to poly(propylene sulphide). It is pertinent to note that although the compounds formed by these systems were colourless and optically transparent no elevation of the glass transition temperature was observed over the salt concentration range investigated. This effect contrasts strongly with the observed effects in poly(propylene oxide) systems containing zinc chloride.
Figure 4.42

Typical Glass Transitions of Poly(propylene sulphone) Metal Salt Complexes

![Graph showing the glass transitions of poly(propylene sulphone) metal salt complexes. The graphs display the temperature on the y-axis and the concentration of salt on the x-axis for different metal salts. The graph shows the exothermic and endothermic transitions at various concentrations of salt.](image-url)
Figure 4.43

Glass Transition Temperatures of Poly(propylene sulphide)-Metal Salt Complexes
5.1 General Properties of Polymer-Metal Salt Compounds Formed

In Chapter 4 it was shown that three types of compounds were formed by the addition of metal salts to poly(vinyl alcohol). The properties of these compounds have been discussed previously in section 4.2 but for completeness will be briefly considered again here. Compounds of type I and II were both optically transparent whilst those of the type III system were opaque. These observations could not be taken as evidence of the single phase nature of the first two compounds but was certainly indicative that any heterogeneities present were smaller than 2000 Å in size. The opacity of type III systems was a clear indication of the presence of a two phase system and that the distribution of the salt through the polymer was different from that observed in the first types of compounds.

The glass transition behaviour further exemplifies the differences between the three types of compounds. Compounds of type I and II were characterised by the dramatic change brought about in $T_g$ by a relatively small variation of salt concentration. The former markedly elevated the glass transition over that of the homopolymer whilst for compounds of the second type a depression of $T_g$ was observed. Type III systems also showed a depression of $T_g$ but this was of considerably less strength than that of the former complexes.

The sensitivity of the compounds to water also highlights the differences in salt distribution between type I and II compounds and the type III species. All the salts used were highly deliquescent, salts such as lithium thiocyanate and zinc chloride dissolved rapidly in their own water of crystallisation within minutes if left exposed to the atmosphere.
Samples of poly(vinyl alcohol) containing these salts showed only slight water absorption becoming plasticised after prolonged exposure to a humid atmosphere. Type III systems rapidly bloomed salt to the surface upon storage which could be rapidly dissolved in normal atmospheric moisture.

It is clear therefore from simple observations of the physical appearance and water sensitivity of the polymer specimens that type I and II polymer systems contained metal salt which was finely dispersed throughout the polymer and was retained by some strong physical interaction between the polymer and salt. In compounds of the third type no chemical interaction to form a complex was present and thus the salt acted merely as a filler for the system.

5.2 Glass Transition Temperature of Poly(Vinyl Alcohol)-Metal Salt Complexes

In recent reviews Eisenberg\textsuperscript{18,21} has outlined three major ways in which the glass transition temperature of polymers may be elevated by the addition of ions to the system. The three models were based upon the effects of crosslinking, copolymerisation and ion clustering with particular emphasis on ionomeric systems and can all satisfactorily explain the observed elevations of $T_g$.

Otocka and Eirich\textsuperscript{216} studied copolymers of butadiene with ionic monomers. They found a linear increase of $T_g$ with the increase of ionic groups and a dependence of magnitude of $T_g$ upon the character of the ionic monomer. Studies of the viscoelastic properties of these systems revealed that the observed $T_g$ was not the result of the onset of mobility of the ionic groups but could be attributed to other segments, the ionic groups acted as crosslinks and thus increased $T_g$ through this mechanism.

The second theory of Otocka and Kwei\textsuperscript{85} was based upon studies of
ethylene-metal methacrylate copolymers. Dynamic mechanical measurements revealed a shift of the glass transition to higher temperatures with increasing salt content which followed the familiar copolymer equation (5.1)

$$T_g = n_1 T_{g1} + n_2 T_{g2}$$ (5.1)

Matsuura and Eisenberg have investigated the glass transition behaviour of ethyl acrylate ionomers having different ions present at varying concentrations. The results obtained indicated that for every ion incorporated a plot of $T_g$ vs. ion concentration showed sigmoidal behaviour with the steepest point of the curve corresponding to the failure of time-temperature superposition in viscoelastic properties. The curves could be further superimposed when the $q/a$ or charge to ion separation ratio was accounted for. The observation was interpreted as reflecting ion clustering in which segmental motion would be decreased sufficiently to affect $T_g$.

Tsutsui and Tanaka have proposed that the introduction of ionic structural units in polymers such as ionomers increases intermolecular forces such that they predominate over the other factors which normally influence $T_g$. Thus at relatively high ion content the interactions could be considered as exclusively attributable to electrostatic influences and thus expressable in terms of the cohesive energy density of the polymer calculated from electrostatic theory. A successful correlation between calculated and observed glass transition temperatures was made by Tanaka for several ionic polymers including polyphosphates and ionenes.

It is pertinent at this point to note that the previously described theories have been applied exclusively to systems in which ionisable structural units have been included into the polymer backbone in some manner. The observed phenomena are not, however, restricted solely to these classic types of ionic polymers and it is pertinent to reiterate the previously described studies of Wetton and James on poly(propylene oxide)
containing zinc chloride and those of Hannon and Wissburn\textsuperscript{219} on phenoxy-
calcium thiocyanate mixtures. In both studies $T_g$ was elevated by the
addition of salt. In the former the increase in $T_g$ was ascribed essentially
to electrostatic forces between the zinc atom and the polarizable ether
oxygen with resultant formation of chelate rings. In the latter study the
elevation of $T_g$ was explained in simpler terms as the result of decreased
free volume in the system.

Any of the preceding mechanisms may be used to explain the observed
increases of $T_g$ resulting from the addition of ionic units to polymer
systems. For a given polymer, however, the elevation of $T_g$ may be the com-
bination of any of these mechanisms and supporting evidence from several
sources would be required before an assertion could be made.

In the following sections the observed glass transition behaviour will
be interpreted in terms of these theories and further evidence presented to
support the assertions.

5.2.1 Single Phase Model

It has been stated previously in this Chapter that whilst samples of
poly(vinyl alcohol) containing zinc chloride or various metal thiocyanates
were optically clear and thus did not contain heterogeneities of dimensions
greater than 2000 Å this in itself could not be taken as clear evidence of
single phase character. Evidence obtained from glass transition temperature
data can however provide valuable arguments towards confirming this.

Studies of block and graft copolymers\textsuperscript{220} and blends\textsuperscript{126,127} have shown
that microphase separation of the two polymer domains can result in the
appearance of two distinct $T_g$ processes attributable to each of the respec-
tive homopolymers. The observation of a single glass transition process in
the salt containing poly(vinyl alcohol) as illustrated in section 4.2.2
suggests the presence of a single polymeric phase.
The molecular compatibility of the components of block and graft copolymers and blends can be estimated by the breadth of the transition. Work by Macknight et al.\textsuperscript{221} with poly(phenylene oxide)/polystyrene blends revealed single glass transition temperatures which were broader than those of the two constituent polymers. Had complete homogeneity existed then blending the two polymers would have resulted in a composite having the same breadth of glass transition as that of the constituent polymers.

The glass transition data of poly(vinyl alcohol)-metal salt complexes shown in figure 4.1 indicates the molecular compatibility of the components at lower salt loadings. The broadening of the transitions observed at higher salt loadings was indicative of the onset of homogeneity.

The observed glass transition profiles were broader than those reported by Wetton et al.\textsuperscript{44} for poly(propylene oxide). It is likely that the high crystallinity within the parent polymer resulting from strong hydrogen bonding between hydroxyl groups serves to reduce the magnitude and increase the breadth of the transition relative to comparable polymers. Thus even before the addition of metal salts the observed transitions are relatively broad. The data presented does, however, suggest that dispersion of metal salt on a molecular or near molecular scale would be a prerequisite for the observed large $T_g$ changes to occur.

The existence of a single polymeric phase does not exclude the possibility that the salt is acting only as a conventional filler. It has been well documented\textsuperscript{220} that filled polymer systems can still exhibit single glass transitions although, as detailed in section 2.1.3, the effect upon the position of the glass transition would be minimal.

Further evidence for the presence of a single phase system comes from comparison of samples of type I and II compounds with type III species. In the latter system visual examination of the samples clearly indicated two phase character as revealed by their optical opacity; in an addition there
was no appreciable variation of the glass transition. Type I and II complexes showed marked contrasts to this behaviour as previously described in section 4.2.2 and suggests that only type III compounds existed as simple filled systems.

Examination of data illustrating the magnitude of the $T_g$ process for zinc chloride and ammonium thiocyanate containing systems which was presented in Figure 4.4 reveals that the whole sample and not merely the poly(vinyl alcohol) underwent a transition from a glass to a rubber. The relationship is not however as clearly defined as that previously discussed for similar systems. If the transition were due solely to the polymer complex then only a small dependence of the magnitude of relaxation upon the salt content would be expected. This is clearly not the case for either sample although it is evident that it is not merely the polymer which is involved in the transition.

5.2.2 Systems in which $T_g$ was Elevated by Addition of Zinc Chloride

The addition of metal salts to poly(vinyl alcohol) on a molecularly dispersed scale has been shown previously to result in two $T_g$ processes depending upon the nature and quantity of salt added. Many factors may influence the position of $T_g$; it is, however, clear from the observed results that in both systems chemical interactions rather than weaker physical effects must take place to produce the observed $T_g$ variations. The nature of these chemical effects must, however, differ greatly between the two systems.

The most probably chemical interactions occurring in both types of metal-salt complex systems are those between the lone electron pair of the hydroxyl group and the metal cation of the salt. Such interactions would lead to the formation of a coordinate bond between the polymer chain and the metal. The cation may accept more than one lone pair of electrons and thus the involvement of more than one ether linkage is possible. Though
both types of complex will involve such electron transfer processes the extent of donation will clearly be different in each case and will thus lead to differing effects upon the glass transition.

It has been shown previously that salts forming type I complexes were taken from transition metal compounds. Many of the classic criteria applied to coordination chemistry can thus be similarly used with these systems and the polymer regarded merely as an extended ligand.

Commercial poly(vinyl alcohol) contains less than 2% head to head linkages, thus the polymer used may be regarded as having the structure

\[
\left[ \begin{array}{c}
\text{CH}_2 - \text{CH} \\
\text{O} \\
\text{H}
\end{array} \right]_n
\]

For such a molecule the close proximity of oxygen atoms capable of donating results in a strong possibility of involvement of more than one hydroxyl group with any given cationic species. If adjacent hydroxyl groups on the same polymer chain were involved with the same cation then formation of a chelate ring could take place. Involvement of oxygen atoms on neighbouring chains would result in the formation of a crosslink. The nature of the final coordinating system will be a function both of the polymer and the metal salt and a situation in which simultaneous inter- and intra-molecular coordination takes place cannot be discounted for some metals.

The filled d shell of the zinc atom results in no ligand field stabilisation for complexes containing the ion, thus the stereochemistry of the complexes is determined solely by the ionic size and electrostatic forces. A coordination number of 4 and tetrahedral geometry is normally favoured by zinc. Figure 5.1 illustrates some of the possible interactions of zinc chloride with poly(vinyl alcohol). The simplest coordination shown involves
Figure 5.1
Coordination models for Poly(vinyl alcohol) Zinc Chloride complexes

I Single oxygen coordination

II Double oxygen coordination

III Triple oxygen coordination

IV Quadruple oxygen coordination
only a single hydroxyl oxygen and thus does not fulfill the coordination requirements of the zinc atom unless partial ionisation of one of the Zn-Cl bonds takes place.

The coordination of two hydroxyl oxygen atoms results in two possible forms for the complex. The first, an intermolecular process produces a crosslink whilst the second involves intramolecular interactions coordinates hydroxyl groups on adjacent monomer units. The complex thus produced takes the form of a six membered chelate ring containing 3 carbon, 2 oxygen and a single metal atom. The formation of a six member ring is particularly larly significant since it is well documented that ring systems containing 5 or 6 members show the least strain and thus the highest stability.

In developing the models for involvement of a single and pair of hydroxyl groups it has been assumed that the zinc chloride remains entirely covalent. Calculations of electronegativity differences have shown the Zn-Cl bond to contain 39% ionic character. If either or both of the zinc-chloride bonds were ionised then further structures involving coordination of 3 and 4 oxygen atoms could be visualised in which the coordination number of 4 were retained. These models are shown in scheme III and IV of Figure 5.1.

The limit of solubility of the salt in the polymer will be attained when all the available oxygen atoms are fully coordinated to the metal salt. The maximum concentration of salt for each of the four schemes shown in Figure 5.1 will be different and will reflect the number of participating oxygen atoms. Values for the maximum mole fraction of salt in the polyether for each of the systems are given in Table 5.1.

For a system involving two oxygen atoms a value of approximately 33% would be expected. The calculation to determine the relationship assumes that the number of coordinating oxygen atoms is independent of salt concentration in the polymer. This may be an erroneous assumption since at low
concentrations of salt a high level of oxygen atoms may lead to a series of preferred higher coordination states.

A further assumption for such a model is that all oxygen atoms present are capable of coordinating and that steric or conformational restraints are negligible. Even in amorphous polymers this will clearly not be the case since short term order will always be present.

The strong hydrogen bonding present in polymers such as poly(vinyl alcohol) leads to additional problems, although of relatively low strength (5-10 kJ mol\(^{-1}\)) the resulting strong intramolecular bonding leads to the presence of a high degree of crystallinity even in the atactic polymer. The effect of the increased conformational restraints created by such processes are difficult to estimate, they will however be discussed later in this Chapter.

It can therefore be seen that values of the degree of compatibility of the metal for different extents of coordination as calculated for Table 5.1 will be an over-estimate from the experimentally derived values. The observed salting-out phenomena at higher halide concentrations together with the observations of other workers which were reviewed in Chapter 1 suggest that scheme II is probably the major contributor for transition metal-halide poly(vinyl alcohol) complexes.

5.2.3 Intramolecular vs. Intermolecular Coordination

It has been shown previously that on the strength of steric considerations only, interaction between zinc chloride and poly(vinyl alcohol) will probably involve two hydroxyl groups with each salt molecule. For such a process it is clear that coordination can take place either on an intramolecular or an intermolecular basis. Both cases would result in an elevation of \(T_g\), in the former as a result of reduced chain flexibility by formation of cyclic structures and in the latter by formation of crosslinks. The occurrence of chelate complexes of zinc compounds with low molecular
Table 5.1 Theoretical Relationship between Coordination Model and Metal Salt Solubility for Poly(vinyl alcohol)-Metal Salt Complexes

<table>
<thead>
<tr>
<th>Number of Coordinating Oxygen Atoms</th>
<th>Maximum Mole Fraction of Metal Salt Soluble in Polyether</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
</tr>
<tr>
<td>6</td>
<td>0.14</td>
</tr>
<tr>
<td>7</td>
<td>0.12</td>
</tr>
</tbody>
</table>
weight oxygen containing compounds is well documented\textsuperscript{15} and thus it would be logical to suggest that similar compounds would be formed by higher molecular weight systems.

The formation of chelate rings randomly placed along the polymer backbone would result in chain stiffening and hence an elevation of $T_g$. The resulting system could be regarded as a random copolymer formed from coordinated and uncoordinated monomer units.

If the glass transition data is expressed in terms of the weight fraction of salt incorporated then it should be possible to predict the $T_g$ of the random copolymer by application of the Gordon-Taylor-Wood equation (2.12)

$$
T_g = \frac{T_{g_A} + [KT_{g_B} - T_{g_A}] W_B}{1 - (1 - K) W_B}
$$

James\textsuperscript{20} has successfully applied this approach to prove that the coordination of zinc chloride with poly(propylene oxide) is essentially an intramolecular process with deviations only at high levels of salt loading ($\approx 70$ wt. \%) where incomplete complexation was occurring.

The application of the Gordon-Taylor-Wood equation to poly(vinyl alcohol)-metal salt systems is fraught with problems. The value of $K$ must be defined in addition to the weight fractions of monomer present. It was shown in Chapter 2 that $K$ may be difficult to estimate and can require mathematical manipulation to fit the observed copolymer $T_g$ data. In addition to defining $T_{g_B}$ the glass transition temperature of the fully
coordinated monomer unit it is necessary also to calculate $T_g^A$, the glass transition of the uncoordinated unit, when applying the G.T.W. equation to poly(vinyl alcohol) systems.

The glass transition temperature of poly(vinyl alcohol) is artificially high as a result of the strong hydrogen bonding and reduced free volume of the polymer. Addition of any compatible component to the polymer disrupts the hydrogen bonding and plasticises the main chain backbone. Any additional restraints upon the backbone movement caused by chelation processes will therefore be superimposed upon the glass transition temperature of the non-hydrogen bonded polymer and not the polymer in the normal state. The copolymer formed by any complexation process will consist of coordinated monomer sequences, non-coordinated non-hydrogen bonded sequences and non-coordinated hydrogen bonded sequences. Evaluation of the relevant constants and application of the G.T.W. equation to such a system is not easily possible.

The glass transition temperature for totally non-hydrogen bonded poly(vinyl alcohol) cannot be directly measured and thus the use of analogies must be made. Using thermochemical data presented in Appendix B it can be seen that dimensionally the hydroxyl group is similar to a methyl group and thus a $T_g$ similar to that of poly(propylene) (-20°C) could be envisaged. The increased polarity of the hydroxyl group over that of the methyl group could lead to a change in the $T_g$ as outlined in section 2.1.3 such that it would be closer to that of poly(vinyl chloride) (87°C). For the purposes of these calculations an intermediate value of 20°C was chosen. Figure 5.2 shows the predicted $T_g$ vs. wt. % composition of hydrogen bonding curve as determined by the simple Fox relationship (2.11)

$$\frac{1}{T_g} = \frac{W_A}{T_g^A} + \frac{W_B}{T_g^B}$$

(2.11)

and assuming that all hydrogen bonding is intramolecular.
Plot of Tg vs Wt percent hydrogen bonding for Poly (vinyl alcohol) Zinc Chloride complexes assuming a simple hydrogen bonded non-hydrogen bonded parent copolymer.
Figure 5.2 also shows some of the DTA data for poly(vinyl alcohol)-zinc chloride complexes plotted on comparable axes and with the assumption that the inclusion of a single salt molecule results in the disruption of only the minimum number of hydrogen bonds as illustrated below. This is, however, clearly an idealised state.

Numerous assumptions have been made in deriving the preceding argument, however despite these several trends emerge from the modified data. It is evident that the metal salt is not acting merely as a plasticiser or filler by simply disrupting hydrogen bonding. Despite the fact that crystallinity is disrupted there is an overall increase in flex energy for the system which results in an increase in the glass transition.

Taking as a premise that residual uncomplexed hydroxyl groups remain totally intramolecularly hydrogen bonded, it is possible to apply the Fox copolymer equation (2.11). Good agreement for the observed data has been found if a value of 348 K is taken for the glass transition temperature of the homopolymer segments and a value of 400 K taken for the fully complexed
segments. At salt concentrations of greater than 15 mole % salt deviations from the predicted behaviour occurred due to the onset of contributions from intermolecularly complexed species.

If intermolecular coordination occurs then the resulting crosslinks will again result in an elevation of the glass transition temperature. In section 2.1.3 it was shown that the elevation of $T_g$, resulting from crosslinking could be expressed by the empirical relationship

$$
\Delta T_g = \frac{3.9 \times 10^4}{\frac{1}{\bar{M}_c}}
$$

Figure 5.3 compares experimentally obtained DTA data with that calculated using equation (2.9) assuming that all the salt molecules act as conventional crosslinks. Initial inspection of Figure 5.3 reveals considerable discrepancies between the theoretically derived and experimentally determined values. This suggests that either the crosslinks formed are very weak or that they are not formed in any appreciable amount. The presentation of the data is, however, erroneous since the effect of hydrogen bond disruption has not been accounted for. Even if the salt molecule does not interact with the polymer but is incorporated only as a filler disruption of the hydrogen bonded network can occur with a resulting depression of $T_g$. In Figure 5.2 data calculated previously for a crosslinked system was plotted to account for the initial presence of a hydrogen bonded-non hydrogen bonded copolymer. A rapid increase in $T_g$ with a relatively small addition of salt is noticeable and indicates that even if allowances for copolymerisation effects are made the contributions from intermolecularly coordinated species are negligible.

Earlier in this Chapter it was shown that for a coordinating system involving two adjacent hydroxyl oxygens a maximum of 33 mole % salt could theoretically be incorporated. Experimentally, salting-out phenomena are observed at concentrations of 25 mole % or greater, suggesting that
Figure 5.3

Theoretical elevation of $T_g$ by crosslinking for Poly(vinyl alcohol) Zinc Chloride complexes

![Graph showing theoretical and observed $T_g$ data](image-url)
complete chain chelation did not take place. It is reasonable to suggest that unchelated oxygen atoms may arise either because of the random nature of the chelation process or because their conformations are unsuitable for complexation.

An estimate of the effect of isolated hydroxyl groups can be made from the studies of Flory concerning the intramolecular reactions between neighbouring groups on vinyl polymers. Statistics were used to analyse the condensation of consecutive substituents X, in a polymer of structure \( -\text{CH}_2\text{CHX} - \). For a system having a regular head to tail linkage he found that 13.5% of the active groups were prevented from reacting as a result of isolation effects. This argument if applied to chelates would imply that only 86.5% of the available oxygen atoms would chelate, a value corresponding to a salt concentration of 28.5 mole % (55 wt. % \( \text{ZnCl}_2 \)).

The observation of gelation at concentrations of salt below this suggest that crosslinking is taking place. It is probable that oxygen atoms in conformations unfavourable for intramolecular chelation coordinate at higher salt concentrations by an intermolecular process.

5.2.4 Other Transition Metal Chloride Complexes with Poly(vinyl alcohol)

In the preceding section it was demonstrated that the complex between poly(vinyl alcohol) and zinc chloride consisted primarily of six member chelate rings at lower salt concentrations with contributions from single coordination species and intermolecular moieties occurring where all the conformationally suitable groups have been chelated. Figures 4.1 and 4.3 show the dependence of the elevation of \( T_g \) upon the nature of the complexing salt. To interpret this data it is necessary to consider various thermochemical parameters associated with the compounds.

It has been shown that the nature of the anion plays an important part upon elevation and limiting value of \( T_g \) of complexes of poly(propylene oxide)
with zinc halides. A reduction of the effect of addition of salt with increasing size of anion was attributed to electronegativity differences between the halide ion and the cation. Electronegativity can be calculated using the relationship:

\[
\% \text{ ionic character} = 100 \left(1 - \exp \left(-\frac{1}{4} (\chi_A - \chi_B)^2\right) \right)
\]

(5.1)

where \(\chi_A - \chi_B\) is the Pauling electronegativity difference for the A-B bond.

Table 5.2 illustrates typical values for transition metal-halide bonds calculated in this manner using data from Appendix B.

Figure 5.4 illustrates glass transition data expressed as a function of ionic radius. It can be seen that the glass transition behaviour of poly(vinyl alcohol) containing transition metal compounds is not governed by any simple relationship to the aforementioned parameters. If cationic radius were the only determining factor for \(T_g\) elevation then a maximum value would have been expected for \(\text{Cu}^{2+}\) the largest ion studied which would have given the maximum perturbation of the polymer and thus the largest increase in flex energy. Conversely, if polarity as reflected by ionic character of the bonds were the controlling factor, then \(\text{Zn}^{2+}\) would have been expected to have had the greatest effect.

In practice neither factor was dominant and it seems likely that the elevation of \(T_g\) was a balance of both these effects. The ionic radius may be particularly important since it will in itself produce a composite effect being the balance of two opposing factors. An increase in ion dimensions will produce greater perturbation and thus increase \(T_g\). The effect will be opposed by increased steric hindrance influences which will reduce the ability of any ion to coordinate fully to the chain.

The trends described previously are perhaps misleading and to explain
Figure 5.4

Variation of ΔTg with cationic radius for various Poly(vinyl alcohol)-Transition metal chloride complexes.
Table 5.2 Some Parameters for Transition Metal Chloride Bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (covalent)</th>
<th>Bond length (ionic)</th>
<th>$\chi_A - \chi_B$</th>
<th>% ionic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-Cl (II)</td>
<td>2.30</td>
<td>2.55</td>
<td>1.4</td>
<td>38.7</td>
</tr>
<tr>
<td>Cu-Cl (II)</td>
<td>2.34</td>
<td>2.50</td>
<td>1.1</td>
<td>26.1</td>
</tr>
<tr>
<td>Ni-Cl (II)</td>
<td>2.14</td>
<td>2.53</td>
<td>1.2</td>
<td>30.2</td>
</tr>
<tr>
<td>Co-Cl (II)</td>
<td>2.15</td>
<td>2.55</td>
<td>1.2</td>
<td>30.2</td>
</tr>
<tr>
<td>Fe-Cl (II)</td>
<td>2.15</td>
<td>2.45</td>
<td>1.2</td>
<td>30.2</td>
</tr>
</tbody>
</table>
the nature of the complexes formed it is perhaps more relevant to consider
the electronic structure on the cation and in particular the number and
spatial arrangement of ligands around a complexed ion.

It can be shown from Ligand Field Theory\textsuperscript{16} that given suitable con-
ditions the five degenerate d orbitals present on transition metals will
hybridise and split under the influence of octahedral and tetrahedral fields
to give the following splitting.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{splitting_diagram.png}
\caption{Splitting of d orbitals under octahedral and tetrahedral fields.}
\end{figure}

Octahedral field
Tetrahedral field
Electrons fed into these orbitals will normally obey Hund's law of
maximum multiplicity, retaining the same spin and remaining unpaired. Two
electrons placed in the same orbital will undergo electrostatic repulsion
resulting in an unfavourable energy contribution seriously affecting the
stability of the orbital. The magnitude of the effect will depend upon
the relative strength of the pairing energy and the energy difference
between successive orbitals.

Under the influence of an octahedral field a system containing 1,2,
3,8,9,10 electrons will adopt only one configuration whilst those contain-
ing 4,5,6,7 electrons will have the possibility of a high spin (unpaired)
and a low spin (paired) form. Which of the latter states will predominate
will depend upon the balance of the splitting energy $\Delta_0$ and the pairing
energy $P$. Calculations for a tetrahedral field indicate a similar pattern
of behaviour with high and low spin states possible for 3,4,5,6 electron
systems although values of $\Delta_t$ are always lower than those for octahedral
fields. Ligand Field Stabilisation Energies for the two environments are
summarised in Table 5.3 from which it can be seen that stabilisation reaches a maximum for octahedral fields at Ni$^{2+}$ (d8) whilst for tetrahedral fields the maximum occurs for Co$^{2+}$ (d7).

Using the preceding information together with known coordination numbers$^{15}$ and geometry$^{19}$ structures for transition metal-poly(vinyl alcohol) complexes may be proposed. The zinc ion (d10) shows no stabilisation effect and has a preferred coordination number of 4. The chelate ring model proposed earlier in this Chapter satisfies these requirements and can be completed with the minimum of bond distortion to give a tetrahedral structure.

The complexes of cobalt$^{2+}$ may adopt either 6-fold (octahedral) or 4-fold (tetrahedral). To assign a structure to the complex of poly(vinyl alcohol) to cobaltII chloride it is useful to use the addition information gained from the absorption spectra of transition metal complexes.

Figure 5.5 shows the energy level split diagram for the electron orbitals of cobalt$^{2+}$ under the influence of tetrahedral and octahedral fields.

![Energy level diagram for Cobalt$^{2+}$ (d7).](image)

The absorption spectrum results in transitions from similar states, in the influence of an octahedral field the transitions are weak, occur in the blue end of the spectrum and result in the compound having a pale red colour.
Table 5.3  Ligand Field Stabilisation Energies in Octahedral and Tetrahedral Environments

<table>
<thead>
<tr>
<th>No. of Electrons</th>
<th>Octahedral Field</th>
<th>Tetrahedral Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,6</td>
<td>(-2/5 \Delta_o)</td>
<td>(-3/5 \Delta_t)</td>
</tr>
<tr>
<td>2,7</td>
<td>(-4/5 \Delta_o)</td>
<td>(-6/5 \Delta_t)</td>
</tr>
<tr>
<td>3,8</td>
<td>(-6/5 \Delta_o)</td>
<td>(-4/5 \Delta_t)</td>
</tr>
<tr>
<td>4,9</td>
<td>(-3/5 \Delta_o)</td>
<td>(-2/5 \Delta_t)</td>
</tr>
<tr>
<td>0,5,10</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 5.6

Some octahedral coordination models for Poly(vinyl alcohol) transition metal complexes

I

Single chain
Single coordination

II

Single chain
Double coordination

III

Double chain
Three fold coordination

IV

Double chain
Four fold coordination
By contrast under the influence of a tetrahedral field the absorption is strong and occurs at the red end of the spectrum giving the compounds an intense blue colour. The observation of deep blue colouration for complexes of poly(vinyl alcohol) with cobalt chloride is indicative of a tetrahedrally coordinated system and thus a series of structures similar in nature to those proposed for zinc chloride-poly(vinyl alcohol) complexes may be postulated.

The thermoplastic nature of the complexes of cobalt chloride suggests that, in keeping with previous assertions, intermolecular contributions are negligible. The larger increases in the glass transition temperature observed for these compounds may be attributed to the additional stabilisation afforded to the complex by ligand field effects.

The remaining transition metal cations investigated prefer to adopt 6-fold (octahedral) coordination and thus a more intricate series of interactions would be expected between CuII, FeIII, NiII and poly(vinyl alcohol). Under such conditions contributions from intermolecular coordinated species would be expected to be significant although evidence from the glass transition temperature data and the processability of the samples is not consistent with this assertion.

For systems in which 6-fold coordination takes place both geometric and optical isomerisation may be present. The non-equivalence of the two polar positions can lead to geometric isomerisation in which the trans form predominates.
The use of polydentate ligands such as poly(vinyl alcohol) can also result in optical isomerisation in the cis geometric isomer with resulting formation of several enantiomers.

The previously outlined non-equivalence of the polar positions suggests that the associated chlorine atoms will adopt these and that the non-optically active trans form will predominate. Figure 5.6 illustrates a series of compounds formed from such interactions and having various degrees of participation from the polymer chains.

With the exception of scheme IV all models have incorporated in them at least one water molecule. Water has been shown\textsuperscript{15} to have approximately the same d orbital splitting power as the hydroxyl group and in fact any other ligand complexing through the oxygen atom. Thus for schemes I to III competition will always exist between water molecules of the solute and the hydroxyl groups of the polymer backbone to coordinate to the available sites.

All the complexes shown in Figure 5.6 will result in an increase in flex energy and will thus have an elevated glass transition temperature. The relatively low elevations of T_g experimentally observed suggest that contributions from the fully complexed species IV (which effectively creates
a crosslink were negligible.

Hojo et al.\textsuperscript{52} and Sumita and co-workers\textsuperscript{54} have studied the formation of complexes between poly(vinyl alcohol) and copper salts by absorption spectroscopy and electron spin resonance. The E.S.R. studies suggested octahedral coordination with various degrees of involvement by water molecules, whilst those of Hojo on the absorption spectra were indicative of tetra coordination. The copper\textsuperscript{2+} (d9) represents a special case however, in which Jahn-Teller distortion is particularly strong. The effects are so great that repulsion of the two equivalent axial orbitals takes place (with an associated attraction of the remaining isomorphic equatorial orbitals) which in an extreme case can lead to the adoption of planar geometry as by copper\textsuperscript{2+}.

5.2.5 Systems in which \( T_g \) was depressed by the addition of salt

Addition of alkali metal thiocyanates to poly(vinyl alcohol) was shown in Chapter 4 to produce type II complexes in which \( T_g \) was successively depressed with increasing salt concentration. Visual examination of the samples suggested interaction between the polymer and the incorporated metal salt, glass transition temperature data however suggested that this system was not equivalent to those discussed previously and that the polymer chain could not be simply regarded as an extended polydentate ligand.

The existence of systems in which the glass transition temperature is depressed by the addition of salt are well documented and for the most part concern plasticisation effects resulting from the presence of compatible low molecular weight compounds. Reich and Michaeli in their study of poly(acrylonitrile) containing hydrated metal perchlorates\textsuperscript{70,71} observed a decrease in \( T_g \) with increasing salt content. The effect was interpreted in terms of solubilisation of the salt species (of which the anion was very large) without strong interaction and a resulting decrease in polymer mobility. In contrast, Wissburn and Hannon\textsuperscript{51} interpreted decreases in \( T_g \)
observed in samples of polar polymers containing inorganic nitrates (particularly poly(methyl methacrylate) containing zinc nitrate) in terms of conventional chelate ring formation. They argued that water would be an integral part of all complexes formed and that its presence would result in plasticisation effects.

The linear depression of $T_g$ illustrated in Figure 4.3 is consistent with disruption of hydrogen bonds and an associated plasticisation effect resulting from the addition of metal salt. If the observed data were merely the result of plasticisation then the effect of ion type would not have been so marked and a pattern of results consistent with the copolymer relationship of Figure 5.3 would have been expected.

It is clear that neither conventional chelate theory nor plasticisation theory may be applied successfully to type II poly(vinyl alcohol) complexes and thus it is perhaps relevant to consider the unique character of the strongly hydrogen bonded poly(vinyl alcohol) chain and to draw analogies to other metal complexed systems in an attempt to determine structures for the complexes.

Bunn examined poly(vinyl alcohol) by X-ray crystallography and showed that the molecule normally adopted a zig-zag conformation with a two monomer, monoclinic repeat unit. Unlike other crystalline polymers, the pendant hydroxyl groups could lie either side of the plane for crystallinity to be retained. The presence of crystallinity could not therefore necessarily be taken as evidence of stereo regularity.

The disruption of the relatively weak hydrogen bonds (5-10 kJ mol$^{-1}$) by dissolution leaves lone pairs of electrons on the oxygen atoms which are free to associate with suitable species. In section 5.2.3 it was shown that for metals having suitable vacant orbitals conventional coordination could occur with formation of six member chelate rings. In the presence of ions without suitable orbitals to form chelates the interaction takes the
form of an ion-dipole effect between the hydroxyl group and one of the ionic species. In its simplest form this interaction could result in the formation of a poly electrolyte.

![Ions and Hydroxyl Groups Interaction](image)

The nature of the associating species in these structures has been a matter of conjecture for many years. Smith et al.\textsuperscript{224} and Bailey and co-workers\textsuperscript{225} attributed the interaction between poly(ethylene oxide) and poly(acrylic acid) and poly(sodium acrylate) to give crosslinked products to the association of a polymeric anion. Bailey and Callard\textsuperscript{226} have also shown the anion to have a more pronounced effect than the cation upon the salting out phenomena observed in aqueous solutions of poly(ethylene oxide). Evidence for the absence of cationic binding has also been obtained from studies of the interactions of poly(vinyl pyrrolidone)\textsuperscript{227} with salts of organic acids and the triiodide ion.

In contrast to the preceding studies were those of Wright and co-workers\textsuperscript{36-38} studying the interaction of poly(ethylene oxide) with alkali metal halides. In common with Lundberg's earlier studies\textsuperscript{41} a system of ion-dipole interactions were postulated. The deductions contrasted with those Lundberg and supported the arguments of Iwamoto\textsuperscript{33-35} and Blumberg\textsuperscript{31-32} that coordination was between the ethereal oxygen and the cationic species. The assertion was supported by evidence obtained from infrared and X-ray spectroscopy.
The ion-dipole interactions shown previously in schemes I and II will result in the initial disruption of two hydrogen bonds for every associated cation (anion) and will lead to a dramatic increase in chain flexibility which will be reflected as a depression of $T_g$. The reduction of $T_g$ through hydrogen bond disruption will be counteracted by an increase in $T_g$ resulting from the formation of new species by association of ions with the backbone and the accompanying decrease in chain flexibility.

Figure 5.7 illustrates glass transition data taken from section 4.2.1 and plotted as a function of the degree of hydrogen bonding assuming that a simple copolymer equation describes the relationship between hydrogen bonded and non-hydrogen bonded moieties and that two hydrogen bonds are destroyed for each incorporated ion. It is evident that the observed glass transition temperatures are not directly attributable to a simple associative process as shown in schemes I and II. The data obtained indicates that the coordination process is the result of a cooperative effect involving more than one hydroxyl group.

The formation of adducts by cooperative involvement of several hydroxyl groups invites comparison with the complex formation of crown ethers. Macrocyclic or crown ethers are compounds having the repeat unit $-\text{CH}_2-\text{CH}_2-\text{O}-$ and have been extensively studied for their ability to complex to certain metals so strongly that in extreme cases they can provide a method of solubilising the metal in organic media$^{22-30}$. The affinity of crown ether compounds for metals is quite specific and depends upon the dimensions of the cation in relation to those of the cavity in the ring.

In his studies of the thiocyanate complexes of poly(ethylene oxide) Wright$^{36-38,228}$ drew analogies between these compounds and their counterparts formed by crown ethers and argued that complexation occurred through similar interactions with formation of structures similar to those shown in Figure 1.3. He argued that in common with crown ethers the number of
Glass transition data for various Poly(vinyl alcohol) metal thiocyanate complexes replotted to account for simple disruption of hydrogen bonding prior to complexing.
monomer units required to complex a metal would depend largely upon the
size of the cation and the constraints set by the degree of contortion of
the chains demanded to achieve the required conformation. The effect of
the latter parameter would be greater for smaller ions and thus it was
predicted that complexes formed from larger cations such as $K^+$ or $NH_4^+$ would
show greater stability. The involvement of neighbouring chains with result-
ing crosslink formation was considered and analogies were drawn with the
macrobicyclic amine (cryptate) ligand $N(CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2)_3N$ in
which the cation is totally enclosed.

The non-hydrogen bonded poly(vinyl alcohol) chain is in many respects
similar to the poly(ethylene oxide) molecule and it is possible that
similar conformations could be adopted such that a cationic species is
shrouded by a polymeric sheath. In common with the other compounds the
number of monomer units involved in each complex will vary and will depend
upon the size of the cation.

It is relevant to refer to the studies of Pederson$^{22,23}$ on crown ethers
in which estimates of 'hole' dimensions were made and which have been
summarised in Table 5.3. Table 5.3 also illustrates the ionic diameters of
various cations taken from thermochemical data presented in Appendix B
It is clear from this data that the convenient dimensions of the holes in
each of the crown compounds could lead to preferential complexation of
specific cations.

Consideration of each cation in turn shows that a cooperative process
between different numbers of monomer units will be involved. The similar
dimensions of the lithium ion to those of 12-crown-4 suggests a cooperative
process involving four monomer units for an analogous poly(vinyl alcohol)
complex. Anet and co-workers$^{29}$ carried out conformational studies of
12-crown-4 and showed it to adopt a square shape with the oxygen atoms
positioned along the sides structure.
Table 5.3 Diameters of Holes for Various Crown Ethers

<table>
<thead>
<tr>
<th>Polyether</th>
<th>Original Estimate (1)</th>
<th>Estimate (2)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-crown-4</td>
<td>1.8 Å</td>
<td>1.2-1.5 Å</td>
</tr>
<tr>
<td>15-crown-5</td>
<td>2.7 Å</td>
<td>1.7-2.2 Å</td>
</tr>
<tr>
<td>18-crown-6</td>
<td>4.0 Å</td>
<td>2.6-3.2 Å</td>
</tr>
<tr>
<td>21-crown-7</td>
<td>74.0 Å</td>
<td>3.4-4.3 Å</td>
</tr>
</tbody>
</table>

* Data from Pedersen, J.A.C.S. 89 7017 (1967).
** Data from Pedersen, J.A.C.S. 92 386 (1970).

Ionic diameters of cations used are:

<table>
<thead>
<tr>
<th>Cation</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>1.30 Å</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.90 Å</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.66 Å</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>2.84 Å</td>
</tr>
</tbody>
</table>
Using scaled molecular models it has been a relatively simple task to compare the structure of 12-crown-4 with that of poly(vinyl alcohol) and to demonstrate that the conformational changes required of the latter molecule to adopt the same spatial arrangement of oxygen atoms are minor. Figure 5.8 illustrates the equivalent structures and demonstrates that the involvement of a single polymer chain would not result in excessive bond strain.

Similar arguments may be applied to other cations and it can be shown that complexation of sodium ions will require five monomer units whilst that of potassium and ammonium will involve six units. The involvement of more oxygen atoms (and hence more monomer units) results in less rigorous conformational restraints upon each monomer unit and hence a greater overall stability. The increase in stability is, however, accompanied by a decrease in the solubility of the metal in the polymer as progressively more hydroxyl groups are involved.

Earlier in this Chapter it was shown that an estimate of the glass transition temperature of the partially disrupted hydrogen bonded chain could be made by application of the copolymer equation to sequences of hydrogen bonded and non-hydrogen bonded polymer. A cooperative interaction involving $n$ hydroxyl groups will result in the effective disruption of $n+1$ hydrogen bonds present on the polymer backbone. Thus for a polymer containing 10 mole % salt a salt to monomer unit ratio of 1:9 will exist and in that given sequence $9 - (n+1)$ hydrogen bonds will exist. Assuming the polymer to be fully hydrogen bonded where possible, an estimate of the % hydrogen bonded character can be made and the $T_g$ of the base polymer estimated. Figure 5.9 illustrates the glass transition temperature data in terms of these parameters for sodium and potassium ions. Even with the inherent weaknesses present due to over-simplified model chosen it is clear that the observed data fits well to a single normalised curve. Data for the ammonium ion is, however, not totally consistent with that obtained
Figure 5.8

Comparison of proposed structure of Poly(vinyl alcohol) metal thiocyanate complexes with the conformation of Crown ethers\textsuperscript{29}

\begin{equation}
12\text{-}\text{Crown}\text{-}4
\end{equation}

\begin{equation}
\text{Poly(vinyl alcohol)}
\end{equation}

Hydrogen atoms omitted for clarity
Figure 5.9

Glass transition data for various Poly(vinyl alcohol) metal thiocyanate complexes plotted to account for different degrees of hydrogen bond disruption by cations upon interaction.
that obtained for other ions; the observation is simply explained in terms of ionic dimensions. An interaction involving six hydroxyl groups is proposed for both potassium and ammonium ions although the latter shows a considerably larger ionic radius. This effect will result in greater disruption of the polymer matrix and hence the free volume of the system. The larger increases in free volume experienced by the ammonium-containing systems leads to a more marked depression of $T_g$.

The maximum theoretical concentration of salt in the polymer will occur when all the available hydroxyl groups in the polymer are involved with cationic binding and have been shown previously in Table 5.1. These figures represent the upper limits and for reasons similar to those proposed for the chelated complexes approximately 20% of available hydroxyl groups will not be conformationally suitable. Experimental observations indicated that the practical upper salt concentrations were close to those theoretically predicted. It is probable that at salt concentrations near those of the theoretical maximum the formation of less well defined species takes place in which less than the ideal number of hydroxyl groups are involved. The restraints set even by these systems soon become apparent and incompatibility becomes apparent with the formation of a two phase system.

It is clear both from Figure 4.3 and Figure 5.9 that the process of complexation leads unusually to a net reduction of $T_g$ which is indicative of an overall increase in free volume or reduction of chain stiffness. In view of the proposed structures these results appear initially surprising, as an interaction process must have greater strength than the original hydrogen bonded system for complexation to occur. It must, however, be remembered that any complexation process involving $n$ hydroxyl groups will disrupt $n+1$ hydrogen bonds. Thus the increased chain stiffness resulting from the complexation process does not match the decrease in stiffness produced by hydrogen bond disruption.
Figure 5.10

Schematic representation of the equilibrium present in the metal salt complexes of Poly(vinyl alcohol)
The conformational restraints and apparent anomalous $T_g$ behaviour lead to the postulation that the structure is not static but even in the glassy state consists of a dynamic system. Figure 5.10 illustrates such a model for a four coordinate system. The contributions from each of the four hydroxyl groups can vary and thus an equilibrium state exists. Given extreme conditions, involvement by one of the peripheral oxygen atoms could cease with the inclusion of a new ligand from a different part of the chain. Such a process would lead to a slow diffusion of the ion through the polymer matrix.

It is not unreasonable to expect that if the conformational restraints set by complexation are great, then involvement of more than one chain could be possible as simply shown below in Figure 5.11 for the lithium species.

Figure 5.11
Possible Intermolecular Interaction of Lithium ions with Poly(vinyl alcohol)
If the bonds formed between the hydroxyl group and the lithium metal were of normal character then a structure of the type shown in Figure 5.11 would constitute a crosslink and marked increases in $T_g$ would be expected. The weakness of the overall interaction in these systems may however have led to a less dramatic effect upon the glass transition temperature.

The conformational stress created in the polymer backbone may also be relieved if water acts as one or more of the participating species. Estimates of the effect of such a process are difficult to make, however, experimental evidence suggests that this process is unlikely. If water did participate then the maximum compatible salt concentrations would have been higher than the values observed; in addition the thorough drying process and reproducibility of the experimentally determined parameters following thermal cycling suggests that water was not an active species.

5.3 X-Ray Scattering Studies

5.3.1 Small Angle X-Ray Scattering Studies

The intensity of scattered X-rays is generally lower for amorphous species than those containing crystalline entities\(^{197}\). Several theories have been proposed to explain the scattering from amorphous polymers and it was shown in section 2.5.6 that these may involve 'nodule' structures in a disordered matrix\(^{201-203}\), heterogeneities\(^{201-203}\) such as microvoids or foreign particles, or thermal density fluctuations\(^{196-197}\).

The observed scattering from uncomplexed poly(vinyl alcohol) was weak as was shown in Figure 4.17. The purification process adopted to remove traces of catalyst residues described in Chapter 3 is believed to have been efficient and it is unlikely that the observed scattering was the result of the presence of included heterogeneities from this source. Preliminary investigations have indicated the presence of thermal density fluctuations within the polymer species and it is likely that the residual scattering is attributable to this source.
The small angle scattering data illustrated in Figures 4.17 to 4.19 show no peaks although there was a general trend towards an increased level of scattering with increased salt concentration especially for complexes containing zinc chloride. The absence of a peak in the small angle region supports the assertion that the polymer complexes are homogeneous whilst the increased level of scattering with salt concentration is believed to be attributable to increased density fluctuations within the system.

It is useful to compare the small angle X-ray scattering data for poly(vinyl alcohol)-metal salt complexes with that from ionomeric systems. In recent reviews Eisenberg\textsuperscript{18,21} has discussed scattering data from several types of ionomers. The frequent presence of peaks in the small angle region was indicative of ion clustering although the assignment of the spacing associated with the peaks has been a matter of dispute. Three models have been proposed. The first\textsuperscript{98} suggests that the peak is associated with the spacing between scattering centres, whilst the second\textsuperscript{82,87} relates it to the internal structure of the scattering centres and the third\textsuperscript{83} to short range order of ionic groups around ionic clusters.

The absence of a peak in the small angle scattering of poly(vinyl alcohol)-metal salt complexes suggests that no ion clustering was present, however, the dimensions of the clusters may have been inappropriate to scatter in the small angle region. The latter assertion is unlikely and in general the experimental data suggests a uniform distribution of salt through the polymer either as single molecules or as multiplets similar to those proposed by Otoka and Kwei\textsuperscript{84-86} for ionomeric systems.

5.3.2 Wide Angle X-Ray Studies of Poly(vinyl alcohol)-Metal Salt Complexes

Several methods have been employed to study the crystalline structure of atactic poly(vinyl alcohol)\textsuperscript{47}. All are in agreement with the X-ray diffraction data of Bunn\textsuperscript{214} who proposed a structure involving two monomer groups.
per unit cell and shown in Figure 5.12. The monoclinic unit cell had dimensions \( a = 7.81 \, \text{Å}, \quad b = 2.52 \, \text{Å}, \quad \text{and} \quad c = 5.51 \, \text{Å} \) with \( \beta = 91^\circ 42' \). By applying equation (5.2) outlined by Alexander\cite{191} probable 2\( \Theta \) values calculated for given Miller indices

\[
\left( \frac{1}{d_{HK\ell}} \right)^2 = \left( \frac{h}{d_{100}} \right)^2 + \left( \frac{k}{d_{010}} \right)^2 + \left( \frac{l}{d_{001}} \right)^2 - 2\left( \frac{h}{d_{100}} \right)\left( \frac{l}{d_{001}} \right) \cos \beta \quad (5.2)
\]

where \( d_{100} = a \sin \beta \)
\( d_{010} = b \)
\( d_{001} = c \sin \beta \)

Table 5.4 compares experimentally derived X-ray scatter peaks with the corresponding Miller indices as derived from equation (5.2) allowing for the presence of any systematic absences. The observed crystalline peaks shown in Figure 4.26 are superimposed a broader band of scattering associated with limited order present in the amorphous polymer.

<table>
<thead>
<tr>
<th>Obs. 2( \Theta )</th>
<th>Miller Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.25(^\circ)</td>
<td>100</td>
</tr>
<tr>
<td>19.5(^\circ)</td>
<td>101</td>
</tr>
<tr>
<td>22.9(^\circ)</td>
<td>200</td>
</tr>
<tr>
<td>40.7(^\circ)</td>
<td>011</td>
</tr>
</tbody>
</table>

The wide angle X-ray scattering data for poly(vinyl alcohol)-metal salt complexes showed major changes over that of the parent polymer. The addition of salt resulted in a monotonic depression of the magnitude of the crystalline scattering until at concentrations of \( \approx 15 \) mole \% there was
Figure 5.12

Crystal structure of atactic Poly(vinyl alcohol)\textsuperscript{214}
merely broad scattering from amorphous areas. The observation supports the assertion that hydrogen bonding (and crystallinity) is disrupted by the process of complexation. It is important to note that the observed trends were not indicative of simple inclusion of the metal salt as a second phase filler in which case evidence of the wide angle crystalline peaks for the metal salt superimposed upon those of the polymer would have been expected.

There is little evidence from WAXS data for the evolution of new scattering peaks associated with the formation of the polymer-metal salt complexes except in the system of poly(vinyl alcohol)-lithium thiocyanate which showed the development of a broad peak for $2\Theta = 9.5^\circ$ and associated with a spacing of 9.3 Angstrom.

The origin of this peak remains obscure and several interpretations of its origin may be made. Macknight et al. observed comparable peaks during studies of the caesium salts of ethylene-methacrylic acid copolymer and attributed them to the interchain spacing. James in studies of poly(propylene oxide)-zinc chloride thelates asserted that the presence of peaks of similar spacings were the manifestation of the interchain distance between successive zinc atoms along the backbone. Thus the observed peaks in the poly(vinyl alcohol)-metal salt WAXS spectra may represent the interatomic distance between successive associated cations on the polymer backbone. It is pertinent to note that no corresponding peaks were observed in the WAXS spectrum of poly(vinyl alcohol) containing zinc chloride and thus it is unlikely that the observed spacings were attributable to this phenomenon. A third possibility for the origin of the peak at 9.3 Angstrom is that it represents the inclusion of metal ions within the crystalline phase of the polymer creating a system with unit cell dimensions different from those of the parent polymer. This assertion is supported by the observation that the peak shows little dependence upon the concentration of the metal salt.
This suggests that initial inclusion of salt takes place in crystalline areas in which the lattice structure is maintained, subsequent addition takes place in the remaining matrix and destroys the residual crystallinity still present in the polymer.

The X-ray scattering data obtained from poly(vinyl alcohol)-metal salt complexes indicated single phase character with a molecular dispersion of salt throughout the polymer matrix. The absence of data of sufficient accuracy to perform radical distribution function analysis has, however, precluded the making of further assertions concerning the nature of the polymer systems.

5.4 Dynamic Mechanical Thermal Analysis

The mechanical properties of poly(vinyl alcohol) have been studied by several workers and in particular Takayanagi. Several relaxation processes have been identified which have been assigned to transitions within the crystalline and amorphous phases. Two transitions, designated \( \alpha \) and \( \beta \) occurring at 180°C and 135°C respectively, were assigned to translational motion along and twisting vibration about the chain axis in the crystalline phase. A sharp tan peak, designated \( \delta \), was observed at 80°C which increased in magnitude with decreasing crystallinity and was accompanied by a sharp fall in modulus with increasing temperature. The proximity of the T relaxation for poly(vinyl alcohol) to this temperature led to the assignment of the relaxation process to micro-brownian motions of long chain segments in the amorphous regions of the polymer. Broad peak at lower temperatures were assigned to local mode relaxations similar in nature to those described in section 2.2.5.

The dynamic mechanical results for poly(vinyl alcohol) described in section 4.2.4 show the presence of only one broad transition centred about 80°C in agreement with the observations of Takayanagi. The modulus change
through the relaxation was small (≈ 2 decades) and is indicative that a complete relaxation process had not taken place. There was no evidence for a relaxation process taking place at 135°C although it is clear that had temperatures of 150°C been exceeded a further modulus change to a value of log E' ≈ 7 attributable to the previously described crystalline transitions would have been observed.

The magnitude of the loss (tan δ) peak for the 80°C relaxation process was in general agreement with that of Takayanagi although there was no evidence of the transition due to local mode relaxations in the region of 35°C nor or the broad absorption in the region -60°C as observed by the latter worker. The absorption observed at -60°C has been shown to be a result of the presence of traces of water in essentially dry samples. Systematic addition of water to poly(vinyl alcohol) shifted the primary amorphous absorption peak to lower temperatures with subsequent loss of the secondary peak by submergence beneath the primary peak. The tertiary peak was increased in magnitude and shifted to temperatures as low as -90°C. The absence of the two lower peaks at -60°C and 35°C suggests that water may have been present in the samples. The absence also of transitions below -60°C and the position of the primary amorphous relaxation indicate that this was erroneous and that it is likely that the absence of peaks was merely a function of the method in which the mechanical behaviour was investigated.

The thermo-mechanical behaviour of the complexes of poly(vinyl alcohol) with metal salts show trends which are in agreement with the observed differential thermal analysis results. Figure 4.12 illustrates the data obtained from a type I complex between zinc chloride and poly(vinyl alcohol). The position of the 80°C relaxation peak in the homopolymer was shifted to higher temperatures with increased salt content and was accompanied by simultaneous increase in the magnitude of the relaxation. For a zinc
chloride concentration of ~20 mole % the relaxation strength was comparable with those expected for a totally amorphous polymer. In a similar manner the mechanical behaviour for type II complexes is shown in Figures 4.13 to 4.16 and again follow the trends of depressed \( T_g \) with increasing salt content as previously disclosed in thermochemical data.

Figure 5.13 illustrates the thermomechanical data for various poly(vinyl alcohol)-metal salt complexes in terms of a \( \tan \delta \) vs. mole % salt plot. Comparison of this figure with the thermochemical data previously obtained and shown in Figure 4.3 reveals similar trends and indicates that both techniques are merely reflecting different manifestations of the same glass to rubber transition.

It would be interesting to compare the magnitude of the relaxations as measured by the loss peak areas. Read and Williams have proposed a relationship between the area of the loss curve and the activation energy of the relaxation process of the form

\[
\left\langle \frac{1}{\Delta H} \right\rangle_{AV}^{-1} = (G_U - G_R) \frac{R}{2} \int_{0}^{\infty} \frac{1}{G''(1/T)} d(1/T)
\]

where \( \Delta H \) is the activation energy and other terms are as previously defined in Chapter 2. Thus measurement of the area of \( G'' \) vs. \( 1/T \) plots can lead to an estimate of the activation energy of the observed relaxation process. From such an equation it would be expected that \( \tan \delta \) (and \( E'' \)) would be influenced by the nature of the bound cation and the mode of complexation employed. If the structures proposed in section 5.2.5 are correct for type II complexes then the greater perturbation of the polymer chain resulting from the addition of successively larger cations would be postulated to lead to an increase in the magnitude of the relaxation and a subsequent reduction of the activation energy.

The area of the mechanical loss peak in the temperature plane is
Figure 5.13

Position of the mechanical tan $\delta_{\text{max}}$ for $\alpha'$ relaxation of Poly(vinyl alcohol) metal salt complexes
governed primarily by the normalised strength of the transition S

\[ S = \frac{(C_U - C_R)}{(C_U - C_R)^2} \]  

(5.4)

thus equation (5.3) may be redefined such that

\[ \int_{0}^{\infty} \tan \delta \, d(1/T) = \frac{1}{4} S \pi R / \Delta H^*_a \]  

(5.5)

where \( \Delta H^*_a \) is the average activation energy.

Provided the loss peaks are narrow (< 100°C) then

\[ \frac{1}{T_{\text{max}}} \int_{T_{\text{U}}}^{T_R} \tan \delta \, dT = \frac{1}{4} S \pi R / \Delta H^*_a \]  

(5.6)

The left hand side of equation (5.6) is the area of the \( \tan \delta \) loss peak in the temperature plane over a limited temperature interval, divided by the peak temperature squared. The averaging process is such that

\[ \Delta H^*_a = \langle \frac{1}{H} \rangle_{\text{AV}}^{-1} \]  

(5.7)

Despite the assymetry of the relaxation peaks of poly(vinyl alcohol) and poly(vinyl alcohol)-metal salt complexes application of equation (5.7) can be made. Results obtained from such calculations are shown in Table 5.5.

Inspection of Table 5.5 and of Figures 4.12 to 4.16 suggests that no simple relationship exists between either the type or quantity of salt added and its effect upon the activation energy of the glass transition process observed by mechanical measurements.

The addition of monovalent thiocyanates, salts which form type II complexes, results in a steady linear reduction of the temperature at which
Table 5.5 Calculated Activation Energies for Various Poly(vinyl alcohol)-Metal Salt Complexes from the Area of DMTA Loss Tangent Curves

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration</th>
<th>$T_{\text{max}}/^{\circ}\text{C}$</th>
<th>$\Delta H_a^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mole %</td>
<td></td>
<td>kJ/mol$^{-1}$</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>5</td>
<td>96.5</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>105</td>
<td>33.1</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>117</td>
<td>27.7</td>
</tr>
<tr>
<td>LiCNS</td>
<td>5</td>
<td>81</td>
<td>30.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>74</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>55</td>
<td>19.1</td>
</tr>
<tr>
<td>NaCNS</td>
<td>5</td>
<td>76.5</td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>66</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>60</td>
<td>17.9</td>
</tr>
<tr>
<td>NH$_4$CNS</td>
<td>5</td>
<td>70</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>54</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>40</td>
<td>21.3</td>
</tr>
<tr>
<td>PVA Homopolymer</td>
<td>-</td>
<td>86</td>
<td>37.9</td>
</tr>
</tbody>
</table>
the mechanical glass transition occurs. This effect reflects the observations made from differential scanning calorimetry and discussed in section 5.2. The depression of the mechanical glass transition is accompanied as expected by a steady reduction of the activation energy for the process. The magnitude of this reduction is, however, very dependent upon the nature of the salt and is worthy of further discussion.

In section 5.3.2 it was shown that inclusion of lithium thiocyanate into poly(vinyl alcohol) resulted in the evolution of a new scattering peak in the wide angle X-ray scattering spectrum. The small lithium cation could be included into the crystalline segments of the polymer without major disruption of the crystal lattice but with formation of a new unit cell. Only initial inclusion of salt takes place in this mode and subsequent addition takes place in the remaining matrix, destroying residual hydrogen bonding.

The observations made from WAXS measurements are borne out in the DMTA data. Figure 4.16 showed the DMTA data for various poly(vinyl alcohol)-lithium thiocyanate blends. It is clear that whilst inclusion of the salt increases the magnitude of the glass transition relaxation, the breadth of the relaxation remains wide for all concentrations. The data support the assertion that at least some salt is included into crystalline segments. The increase in magnitude of the loss peak (tan δ peak) reflects the disruption of hydrogen bonded networks and the formation of well defined complexed segments. If inclusion of salt took place in all regions of the polymer with subsequent destruction of networks then a gradual sharpening of the loss peak would be expected with increasing salt concentration. This is not observed and the continued presence of broad peaks even at high salt concentration reflects inclusion of small amounts of salt into crystalline segments.

The dimensions of the sodium cation are sufficiently greater than those
of lithium. Inclusion of the former ion into the crystalline matrix cannot take place without disruption of the lattice structure. As a result there is no new peak evolved in the WAXS spectrum and the effect upon the dynamic behaviour is more dramatic. Addition of sodium ions to poly(vinyl alcohol) destroyed crystallinity and hydrogen bonded networks present in the polymer. The result was a significant increase in the magnitude of the relaxation accompanied by a reduction in the breadth of the process.

The complexation of sodium involves a larger number of monomer sequences, and thus for any given concentration there is greater depression of T_g than for the lithium-containing species.

The addition of ammonium thiocyanate resulted in broad relaxation peaks which were, in some cases, ill defined. The reduction of T_g followed the pattern adopted from DSC data although there was little sharpening of the transition or reduction of its breadth.

The interaction of six or more monomer sequences resulted in only minor involvement of each unit. It is possible that the involvement of several sequences from different parts of the same chain or even other chains may have taken place. In such a situation the steric contortion required by each chain would be minimal. For such a model despite the fact that hydrogen bonding was disrupted and complexation occurred there would be little overall effect upon the conformations adopted by the chains and thus little so called ordering of the amorphous regions. This proposal is supported by the absence of a marked effect upon the characteristics of the transition.

The calculated activation energies shown in Table 5.5 support the assertions made for the mechanical behaviour of type II compounds. For all salts there is a marked reduction of activation energy over that of the homopolymer with the addition of salt, an observation which reflects the destruction of crystallinity and hydrogen bonded networks taking place.
The effect is more marked as cation dimensions increase. The observation reflects the involvement of more monomer sequences (and hence destruction of more hydrogen bonded sequences) with larger ions.

The activation energy data obtained from samples containing ammonium thiocyanate is subject to greater errors because the peaks were in some cases ill-defined. Several additional comments can however be made. Initial addition of salt results in a reduction of activation energy as predicted from the behaviour of the two smaller ions investigated. Data obtained from samples containing higher contributions of salt do not, however, follow the expected trends. Ammonium thiocyanate had a low solubility in poly(vinyl alcohol) (≈16 mole %) and its interaction with the polymer involved the cooperative involvement of at least six monomer sequences. It has been stated previously that to obtain such a complex several isolated sequences from one or more chains could be involved. Despite the low steric contortion required by each monomer unit it is likely that necessary sequences may not exist in the polymer. Thus even at low concentrations of ammonium thiocyanate in poly(vinyl alcohol) incomplete complexation can occur in which fewer than the required six hydroxyl groups are involved. This is reflected by the higher than expected values of activation energy observed.

Figure 4.12 and Table 5.5 also highlight the contrasts in behaviour between type I and II complexes. The addition of zinc chloride to poly-(vinyl alcohol) results in the formation of a typical type I complex with associated elevation of the glass transition temperature. The pattern of behaviour is reflected in the dynamic mechanical data in which there is observed a shift to higher temperatures of the $T_g$ loss peak and a sharpening of the relaxation. The process reflects a net decrease in chain mobility. The data obtained from activation energy calculations further exemplifies the above observations. As with type II complexes there is initially a reduction of activation energy with addition of salt. This
reflects the disruption of the crystalline sequences caused by the addition of salt. Contrary to that expected, $T_g$ is elevated due to decreased flexibility of the now more abundant, amorphous sequences which have been chelated. Further addition of salt takes place in the amorphous phase and as a result there is an increase in activation energy and $T_g$. At higher salt concentrations non-stoichiometry of complexation can occur as hydroxyl groups previously in conformations not suitable for chelation become associated. This effect is reflected as a downturn in activation energy.

The absence of simple plasticisation behaviour with addition of salts further confirms the single phase nature of the systems. Comparison of the results with those obtained by Nielson\textsuperscript{189,190} from studies of poly(vinyl chloride) containing phthalate plasticisers illustrates this point. In the latter studies introduction of plasticiser produced not only the expected shift in the position of the loss peak but also a broadening and a reduction of the maxima, the magnitude of which was dependent upon the plasticiser-polymer compatibility. A decrease in the slope of the modulus vs. temperature curve accompanied the increase in the breadth of the transition. The dynamic mechanical data obtained for poly(vinyl alcohol)-metal salt complexes was in complete contrast to these observations and support the assertion that incorporation of the salt is not as a second phase but as an integral part of the polymer backbone.

In section 5.2.3 it was shown that formation of any complex between poly(vinyl alcohol) and a metal salt could be either intramolecular, with resulting formation of a copolymer containing complexed and uncomplexed sequences, or intermolecular, with the formation of a crosslinked network.

Application of conventional copolymerisation theory may be made to thermochemical data. Thus for the former model of the complex a mechanical tan $\delta$ loss peak intermediate between those of the respective parent polymers (the homopolymer and the fully complexed chain) and slightly sharpened
would be predicted. In reality the presence of heterogeneities between monomer sequences would lead to peak broadening. Similarly, regarding the polymer complex as a crosslinked network results in a mechanical loss peak shifted to higher temperatures with decreased magnitude and broadened.

The results obtained from dynamic mechanical analysis support the assertion made previously that complexation is an essentially intramolecular process and that contributions from intermolecular processes are negligible.

5.5 Analysis of Infra-Red Spectra

The infra-red absorption spectra of poly(vinyl alcohol) of different stereoregularities have been studied by several workers\(^4,47,48\) and the bands shown to be broad and severely overlapped especially in the region 600 to 1500 cm\(^{-1}\). The effects are caused by several factors. The polymer bulk consists of crystallites embedded in an amorphous matrix of glassy material and symmetry differences between the two regions can lead to two sets of frequencies. In addition there are also regions of intermediate crystallinity and the crystalline regions themselves will also have mixed symmetry due to the predominately atactic placement hydroxyl groups along the polymer chain. The presence of individual isotactic and syndiotactic sequences introduces additional problems. Typical infra-red spectra for the two stereoregular forms of poly(vinyl alcohol) are shown in Figure 5.14, their main characteristics have been summarised in Appendix C.

The band at 1141 cm\(^{-1}\) has been shown to be strongly dependent upon crystallinity and a relationship between intensity and film thickness has been established.\(^2,32\) A further relationship between the band intensities \(I\) has also been reported which has provided a useful, though \(\alpha\) semiquantitative method of estimating stereoregularity using the following equations.
Syndio = $60 \left( \frac{D_{916}}{D_{849}} \right) + 7$ per cent \hspace{1cm} (5.8)

Iso = $-78 \left( \frac{D_{916}}{D_{849}} \right) + 59$ per cent \hspace{1cm} (5.9)

Atactic = $18.7 \left( \frac{D_{916}}{D_{849}} \right) + 34$ per cent \hspace{1cm} (5.10)

Using equations (5.8), (5.9) and (5.10) it can be shown that the poly(vinyl alcohol) used for these studies had a composition of 28.4% isotactic, 30.4% syndiotactic and 41.2% atactic.

The broad nature of the infra-red spectra as indicated previously precluded the adequate use of measurements of band shifts which could be associated with any complexation taking place. Of primary interest were the bands occurring at 3340, 1446, 1326, 1144, 1096 and 640 cm\(^{-1}\) associated with the C-O-H linkage which should have shown differences if complexation occurred. Tadokoro\textsuperscript{232} has observed the formation of additional bands in
the spectrum of PVAIc-0D which were attributable to intensity increases and isotopic shifts. The reduction of mobility of the -OH groups in any complexed system can be likened to that caused by the presence of a heavy isotope and similarly a new set of bands could be predicted. James in studies of poly(propylene oxide)-zinc chloride complexes observed shifts in the existing C-O frequencies of the homopolymer to higher energies as complexation took place. By similarity it is possible to envisage similar mechanisms in complexes of poly(vinyl alcohol) and metal salts. The absence of infra-red absorption shifts does not preclude the possibility that complexation has taken place but merely indicates the inadequacies of the method adopted for measurement.

The appearance of a new band at 2050 cm\(^{-1}\) in the infra-red spectrum of type II compounds indicates the presence of the thiocyanate group only and is not the manifestation of a new frequency associated with any complex formed. The observed absorbance is in agreement with that measured for the salt alone as a nujol mull and with that reported by Nakamoto in which assignments were made to the stretching of various isomers.

5.6 Dielectric Relaxation Studies of Poly(vinyl alcohol)-Metal Thiocyanate Complexes

The dielectric properties of poly(vinyl alcohol) have been studied by numerous workers. Ishida and coworkers found that in the range -30\(^\circ\) to +30\(^\circ\) poly(vinyl alcohol) exhibited a single broad relaxation process dependent upon the degree of crystallinity present. The activation energy of the process was found to remain essentially unaffected by crystallinity although for a given temperature the frequency of maximum loss increased with crystallinity. The observation was surprising since motions within disordered segments are frequently more restricted by an increase in crystallinity (i.e. \(f_{\text{max}}\) decreases). Ishida interpreted the results not in
in terms of the primary amorphous transition but to a secondary mode mechanism as previously discussed.

Kurosaki and Furamaya observed similar results to those of Ishida but noted that the activation energy was small despite the long relaxation times and that values of $\varepsilon'$ and $\varepsilon''$ were higher than expected. The results were interpreted in terms not of the concept of simultaneous hindered rotation of individual dipoles but in terms of the proposal of Slack that there were successive dipole rotations within linear hydrogen bonded chains. For the hydrogen bonded poly(vinyl alcohol) there may exist a series of 'fault' sites such as two protons intervening between two oxygen atoms

\[
\begin{align*}
\cdots \mathrm{O} - \mathrm{H} \cdots \cdots \cdots \mathrm{O} - \mathrm{H} & \quad \mathrm{H} - \mathrm{O} \cdots \cdots \cdots \mathrm{H} - \mathrm{O} \\
\begin{array}{c}
\mathrm{CH}_2
\
\mathrm{CH}_2
\
\vdots
\end{array}
& \begin{array}{c}
\mathrm{CH}_2
\
\mathrm{CH}_2
\
\vdots
\end{array}
\end{align*}
\]

I

or no proton between two oxygen atoms

\[
\begin{align*}
\begin{array}{c}
\mathrm{H} - \mathrm{O} \cdots \cdots \cdots \mathrm{H} - \mathrm{O}
\
\mathrm{CH}_2
\
\mathrm{CH}_2
\
\vdots
\end{array}
& \begin{array}{c}
\mathrm{O} - \mathrm{H} \cdots \cdots \cdots \mathrm{O} - \mathrm{H}
\
\mathrm{CH}_2
\
\mathrm{CH}_2
\
\vdots
\end{array}
\end{align*}
\]

II

Application of constant field along the chain causes the dipole at the fault site to turn resulting in transfer of the fault to an adjacent site. The broad shape of the dispersions was attributed to the wide range of hydrogen bonded sequence lengths present.

The dielectric response from samples of poly(vinyl alcohol) containing various metal salts is illustrated in Figures 4.5 and 4.6 from which it is evident that as proposed by Ishida no clear relaxation phenomena take place in the temperature range investigated. At low concentrations of salt a
relaxation process is present as a peak centred at $\approx 110^\circ$. Allowing for differences between DSC and dielectric measurements it is likely that this process is associated with the glass to rubber transition of homopolymer sequences. A new relaxation process designated $\alpha'$ and located around $60^\circ$C appears at higher concentrations of salt and in enhanced by the addition of further salt.

Figures 4.7 and 4.8 illustrated the data in the form of $\log f_{\text{max}}$ vs. $1/T$ plots which showed linear character which was essentially independent of salt concentration. For a conventionally bonded complex an addition of salt would be expected to reduce mobility and increase the activation energy of the system, a feature observable as a change in slope of the $\log f_{\text{max}}$ vs. $1/T$ plots. In studies of the chelated system between poly(propylene oxide) and zinc chloride James observed such changes which were interpreted in the conventional manner. The absence of this effect in complexes of poly(vinyl alcohol) and metal thiocyanates suggests that complexation occurs through dipole shielding effects. To interpret the observed results it is perhaps relevant to consider again the problems associated with complexation of the polymer.

Initial addition of salt to the polymer results in partial disruption of the hydrogen bonding present and hence in some cases crystallinity. For small ions such as lithium it has been previously demonstrated from dynamic mechanical and X-ray data that initial incorporation may not be restricted to amorphous regions but that some penetration of the crystalline lattice may occur. The dielectric loss tangent data reveals the evolution of a new relaxation region designated $\alpha'$ and associated with the relaxation of complexed sequences of monomer units. Addition of successively larger quantities of salt enhances the contribution from this species and reduces the effect from uncomplexed sequences until at concentrations near to the maximum solubility only the former relaxation process is present.
It is interesting to note the marked contrasts in behaviour recorded by the frequently synonymous techniques of dielectric and mechanical spectroscopy. These reflect the different processes monitored by each technique. Mechanical measurements reflect local scale movement of the backbone, whilst those derived from dielectric techniques give an indication of the corresponding electrical perturbations.

Figure 5.15 compares temperature plane data from both techniques and highlights the differences in behaviour for samples containing lithium thiocyanate. The mechanical loss tangent returns essentially to zero at either side of the glass transition relaxation region. In contrast the electrical loss tangent falls only slightly with increasing temperature and then gains magnitude rapidly. The rapid take-off of $\tan \delta_{\text{DIEL}}$ represents the onset of conduction effects and reflects the acquisition of sufficient thermal energy in the system to supply the necessary free volume required for transport of ions through the polymer matrix.

The onset of conduction is dependent only upon the activation energy of the carrier species, thus as the concentration of salt increases so will the number of carriers and the ease of activation (as reflected by a reduction of the temperature of onset of conduction). The energy required for conduction remains constant as indicated by a constant slope for the $\log f_{\text{max}}$ vs. $1/T$ plot. In the light of this argument the data obtained from a sample of poly(vinyl alcohol) containing 15 mole % lithium thiocyanate may appear somewhat incongruous. At this concentration of salt the maximum solubility is being approached and most of the available sites are occupied. If conduction is by a hopping process the number of available hopping sites will be greatly reduced and there will be a subsequent increase in the activation energy.

The onset of conduction is so swift that any superimposed relaxation process (as reflected by a step in $\varepsilon'$ data) is obscured. This argument is
Figure 5.15.

Comparison of dielectric and mechanical loss tangent data for Poly(vinyl alcohol) containing Li SCN

a) Dielectric data

b) Dynamic mechanical data
further supported by the log $f_{\text{max}}$ vs. $1/t$ plot for this situation which shows distinct curvature. Williams $^{237}$ has indicated from studies of main chain relaxation processes that increases in activation energies in such transitions give curvature to log $f_{\text{max}}$ vs. $1/T$ plots at low frequencies. The increased order resulting in some areas of the polymer following complexation and a more consistent packing also reduces the number of available complexation sites. The system will require a larger energy input before the required free volume to activate conduction is present. This is reflected as a shift of the $\varepsilon'$ relaxation to higher temperatures.

The complexes can be envisaged as having a schematic structure of a type shown in Figure 5.16.

This behaviour is also demonstrated by other complexes of poly(vinyl alcohol) and metal thiocyanates. A greater perturbation caused by the larger sodium ions results in a down shift of activation energy and an increase in the loss tangent maximum in comparison to the lithium salt. The inclusion of the ammonium cation produces similar dimensional effects but curiously leads to anomalously high values of $\varepsilon'$ and $\varepsilon''$ values in the glassy state. The origin of this effect probably lies in the following explanation. The high values of $\varepsilon'$ and $\varepsilon''$ reflect a subzero °C relaxation process with a loss peak from which the dielectric response never recovers. This implies the presence of a very mobile species. If we consider the ammonium ion then an equilibrium will exist of the type

$$\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + H^+ \quad \text{pK}_a \quad 5.6 \times 10^{-10}$$

In aqueous solutions exchange would normally occur between the ammonium ions and water. In the solid solution in poly(vinyl alcohol) this process is not possible although exchange with hydroxyl groups may occur. Such an exchange process would constitute limited protonic hopping conduction
Schematic representation of hopping conduction in metal salt complexes of Poly(vinyl alcohol)

a) Below Tg (Ions trapped in matrix)

b) T ~ Tg (Free volume sufficient to allow limited ion movement)

c) T > Tg (Sufficient free volume to allow conduction by ion hopping)
requiring a lower free volume for activation. The conduction for ammonium thiocyanate-containing samples will be the result of contributions from protonic and cationic hopping effects.

Connors has shown that conduction effects in poly(ethylene glycol) result in plots of log $\varepsilon''$ vs. log $f$ having linear slope of -1. This observation has subsequently been taken as a good indication of conduction effects in polymers. Dielectric relaxation data for poly(vinyl alcohol) containing metal thiocyanates did not show slope of -1 although in the region of anomalous electrical behaviour log $\varepsilon''$ vs. log $f$ plots were linear. This suggests that the observed effects were the combination of conduction and space charge phenomenon.

Dielectric dispersion data may be represented in the form of Cole-Cole plots the theory for which has been previously discussed in Chapter 2. Examples of such plots are shown in Figures 5.17 and 5.18. The previously described theory for such plots predicts that for a normal relaxation process a semi-circular plot results in which the $\varepsilon'$ axis is cut at two points. It is clearly evident that this simple behaviour is not followed by complexes of poly(vinyl alcohol) containing metal thiocyanates. Serious deviations from the predicted behaviour occur at low frequencies which are manifested as a change of curvature. The studies of Grant suggest that, as borne out by other representations, a conduction process overtakes the normally observed relaxation phenomena observed in the polymer.

The high crystallinity of poly(vinyl alcohol) and the associated problems involved in complexation result in great difficulties in successfully studying the properties of ion containing systems. To gain greater insight into the properties of this type of polymer when complexed it is convenient to study a system in which hydrogen bonding and crystallinity effects are absent but which have a structure similar to poly(vinyl alcohol). For this reason studies have been carried out on a series of poly(alkyl vinyl
Figure 5.17

Cole-Cole representation of dielectric data for Poly(vinyl alcohol) containing 5 mole percent KSCN
Cole-Cole representation of dielectric data for Poly(vinyl alcohol) containing 8 mole percent LiSCN
ethers) of which poly(vinyl alcohol) may be regarded as the parent polymer. Results from these systems will be discussed in the following Chapter.
DISCUSSION OF COMPLEXES OF POLY(ALKYL VINYL ETHERS) AND METAL SALTS

6.1 General Properties of Poly(alkyl vinyl ethers) Containing Metal Salts

It has been shown previously that the addition of metal salts to poly­
(alkyl vinyl ethers) resulted in the formation of a new series of single
phase compounds with properties different from those of the parent polymer. Visually the complexes showed similarities to those of poly(vinyl alcohol) in that they were optically transparent and adopted the colour of the incorporated salt although there was typically a tendency for the formation of an amber colouration from samples containing colourless salts.

Using arguments similar to those proposed in Chapter 5 for poly(vinyl alcohol) complexes it is possible to conclude that any heterogeneities present in the samples were smaller than 2000 Å in size and even in the absence of further direct evidence it is plausible to suggest that incorporation of the salt was on a molecular scale even at higher loadings.

6.2 Glass Transition Behaviour of Poly(alkyl vinyl ethers) Containing Metal Salts

6.2.1 General Comments

The effects of the addition of ions to polymers were extensively reviewed in Chapter 5 where it was shown that three major models have evolved for polymers into which an ionic co-monomer has been introduced. It was also shown that the applicability of these models to systems in which the ion was present as a complexed species was not always ideal. Models were, however, proposed to explain the glass transition temperature data of type I and II complexes of poly(vinyl alcohol).
The assertion that compounds of poly(vinyl alcohol) and metal salts were single phase was based partly upon the observed glass transition behaviour. Similar criteria may be applied to poly(alkyl vinyl ether) systems.

The glass transition temperature profiles shown in Figures 4.30 and 4.36 indicate the relaxation process to be sharp in the homopolymer. Addition of metal salt resulted in an elevation of $T_g$ and an increase in the breadth of the transition although the strength of the process (as defined in Chapter 4) remained essentially unaltered. At higher concentrations of salt the elevation of $T_g$ resulting from unit addition of metal salt decreased and was accompanied by a sharpening of the transition process.

The polymer initially consists of essentially ideal monomer sequences having approximately the same relaxation behaviour. The observed glass transition process is narrow and well defined. Addition of salt results in the formation of areas in which complexation has occurred in addition to the undisturbed homopolymer sequences. A copolymer consisting of complexed and uncomplexed sequences is formed which shows a broad spectrum of relaxation times and thus a wide glass transition. At very high salt concentrations approaching the maximum solubility, near homogeneity is restored as the occurrence of uncomplexed polymer sequences is greatly reduced. The results are comparable with those obtained from conventional block and graft copolymers in which broadened glass transitions intermediate between those of the constituent homopolymers have been observed. 217

The glass transition behaviour of poly(alkyl vinyl ethers) differs from that of poly(vinyl alcohol) in that the incorporation of all the investigated salts into the system results in an elevation of $T_g$ to a maximum value followed by a slight depression at very high concentrations as was shown in Figures 4.31 and 4.37. The position of the maximum both in the temperature and concentration plane shows strong dependence upon the nature
of the salt suggesting that the degree of interaction is related to the nature of the salt used.

It was shown previously that complexation of metal salts to poly(vinyl alcohol) took place by partial involvement of the lone pairs on the hydroxyl group oxygen atoms with vacant orbitals of the cationic species. Whilst the bonding in poly(alkyl vinyl ether) systems may not directly correspond to such processes it is valid to state that the arguments presented in Chapter 5 to support the evidence for a single phase model for poly(vinyl alcohol) systems may be equally applied to the alkyl derivatives.

The presence of the alkyl side groups will affect the ease of complexation of poly(alkyl vinyl ethers) and will thus produce profound changes in the physiochemical properties of the system. Steric hindrance effects will reduce the ability of the oxygen atoms to adopt the correct conformations for complexation and the approach of suitable cationic species. Such effects reduce the number of sterically suitable oxygen atoms available on the poly-(alkyl vinyl ether) for donation of electrons. This results in a reduction of salt solubility. In contrast to poly(vinyl alcohol)-metal salt systems the complexation process does not compete with inherent hydrogen bonding.

The interaction of any cationic species with the polymer chain will involve the co-operative action of more than one monomer unit as was previously discussed for complexes of poly(vinyl alcohol) in section 5.2. The initial introduction of salt produces the strongest interactions with the polymer and involves maximum etheral group participation. A copolymer consisting of uncomplexed and complexed monomer sequences results which exhibits a higher $T_g$ than that of the parent polymer. Continued addition of salt can take place with an accompanying elevation of $T_g$ until all available uncomplexed sites are taken. Addition of salt at higher concentrations results in incorporation as a second phase filler with little or no residual effect upon the glass transition temperature. For such an incorporation
mechanism the $T_g$ vs. composition curve would be expected to follow a sigmooidal shape as has been observed with poly(propylene oxide)-zinc chloride composites. The results obtained for poly(alkyl vinyl ethers) containing metal salts were in contrast to that expected for such a process. In Figures 4.31 and 4.37 it was shown that a maximum occurred in the $T_g$ vs. composition curve, the position of which was dependent upon the nature of the salt included. For the inclusion of lithium ions the maxima represent a salt to monomer unit ratio of 1:6, whilst for zinc a value of 1:8 emerges. A model for complexation involving the interaction of the metal cations with the oxygen atoms may be proposed in which the mode of complexation is similar to that described in Chapter 5 for type II complexes involving metal thiocyanates and poly(vinyl alcohol). In such a model formation of cage-like structures analogous in many respects to crown ethers takes place such that the cationic species is shielded from the gegen ion.

The formation of ring-type structures involving several monomer units successfully enables oxygen atoms to partially donate electrons to the metal whilst retaining sufficient conformational flexibility to prevent any one monomer sequence from being highly strained. It is extremely unlikely that any one polymer chain would have sufficient conformational stability to enable it to complex completely. It is therefore suggested that interaction takes place by involvement of more than one polymer chain. Wright, in studies of poly(ethylene oxide)-thiocyanate complexes, proposed similar cyclic structures to explain their observed thermal and electrical behaviour. He suggested that two or three polymer chains could be involved in the complexation process which involved a total of four oxygen atoms. Analogous structures to those of Wright may be proposed for poly(alkyl vinyl ether)-metal salt complexes and some of these are shown in Figure 6.1.

It has been shown previously in this thesis that conventionally interaction involving more than one polymer chain constitutes a crosslink, and
Figure 6.1
Schematic representation of some of the interactions
Poly(alkyl vinyl ethers) with metal salts

a) Single chain interaction

b) Double chain interaction

c) Triple chain interaction
thus would lead to $T_g$ changes greater than those observed. The contribution from each ion-dipole interaction is weak and thus the strength of any cross-links formed is negligible.

In Chapter 5 it was shown that complexation between poly(vinyl alcohol) and zinc chloride took place by formation of chelate ring structures. Using similar arguments it would not therefore seem unreasonable to propose a comparable structure for poly(alkyl vinyl ether) systems. The conformational and steric restraints created by the presence of alkyl groups on the polymer side chains make it difficult, if not impossible, for two neighbouring oxygen atoms to coordinate to one centre. In addition to the restraints set on the polymer if chelate formation took place, it can also be shown from molecular models that serious steric contortion between chlorine atoms and the alkyl groups would occur if tetrahedral coordination occurred. In preference the polymer weakly interacts with the entire zinc chloride species. Formation of a multi-monomer unit cyclic structure totally encompassing the salt molecule can be predicted by analogy with crown ethers.22-30

The incorporation of the ammonium ion leads to curious glass transition data. Whilst the ion could be successfully included into poly(ethyl vinyl ether) as a single phase (as indicated by optical transparency) there was no variation in the glass transition temperature. It is certain that the large dimensions of the ammonium precluded direct coordination and that any interaction was only at a relatively long range. It is likely that only single ion-dipole effects were responsible for the interaction so that only minor changes in mobility of the polymer chain occurred. This effect would result in the negligible variation of glass transition temperature with salt concentration observed.

The glass transition temperature data observed for complexes of poly-(alkyl vinyl ethers) can be reconciled in terms of the stability of the complexes formed. It has been stated previously that incorporation of salt
to form complexed sequences will result in an overall increase in the glass transition temperature for the system. For any such process the $T_g$ vs. composition curve will follow a relationship in which there is initially a rapid rise in $T_g$ with salt inclusion followed by a more gradual elevation as salt-out phenomena occur.

The complex will however also show a second relaxation process which will be associated with the complete breakdown of the complex structure. The position of this process relative to that for the glass transition will depend upon the stability of the complex but under normal circumstances lies above that of the glass transition. The stability of the complex from simple mass activity concepts is expected to follow a relationship of the form $\phi(1 - \phi)$ such that maximum stability occurs when half the available sites are occupied. Thus a generalised scheme of the type shown in Figure 6.2a can be envisaged which describes the thermal transitions of strongly bonded polymer complexes.

If the interactions between the individual dipoles of the monomer units and the metal cations are weak the stability of the complex formed is markedly reduced, and thus the temperature at which complete breakdown occurs is similarly lowered until the $T_{\text{breakdown}}$ curve can cross the $T_g$ elevation plot. This situation is illustrated in Figure 6.2b. For concentrations of salt greater than those present at the point of intersection of the two lines breakdown of the complex will occur at a lower temperature than the projected glass transition for the complex. Thus the latter relaxation process will coincide with $T_{\text{breakdown}}$. The resulting $T_g$ vs. composition curve will be a composite of the two processes following whichever is lower in temperature.

The model proposed in Figure 6.2b corresponds to the situation in which complexation between poly(alkyl vinyl ethers) and lithium thiocyanate or zinc chloride occurs.
Figure 6.2

Relationship between $T_g$ and $T_{breakdown}$ for high and low stability complexes

a) High stability complex ($T_g < T_{breakdown}$)

b) Low stability complex ($T_g \approx T_{breakdown}$)
6.2.2 The Effect of Polymer Side Chain Dimensions

The glass transition data presented in the previous section reflected the influence of the cationic species upon the strength and nature of the resulting interaction. At this point it is relevant to discuss the influence of the dimensions of the ether group.

Poly(alkyl vinyl ethers) have been studied by several workers\textsuperscript{137,157} and have been shown to exhibit curious glass transition behaviour. In Chapter 2 it was shown that the dimensions of the side group on a polymer chain can have a strong influence upon the glass transition temperature. The effect was demonstrated by comparison of polyethylene ($T_g$ -120°C) with polypropylene ($T_g$ -20°C) and polystyrene ($T_g$ +100°C). Using this example it would be expected that poly(alkyl vinyl ethers) having successively longer alkyl groups would show a progressive rise in $T_g$. In reality it has been observed\textsuperscript{239} that the $\alpha$ relaxation process is first shifted down the temperature scale then increased again. The effect was interpreted in terms of initial internal plasticisation effects which increase free volume and thus depress $T_g$. Increasing the length of the alkyl chain above 5 carbon units results in crystallisation of the side chain which form a physical crosslink between the main chains.

The ability of the etheral oxygen to complex to the cationic species would be expected to be strongly influenced by the steric constraints set by the side chain. As the length of alkyl chain increases it will become progressively more difficult for the alkoxyl groups to successfully adopt the correct conformations for complexation. The increasing hydrophobic nature of the side group will also strongly influence the compatibility of the polymer with the salt and thus its ability to form a complex. This hypothesis is borne out by the observation that no complexes could be successfully prepared from poly(isobutyl vinyl ether). The spatial arrangement of the methyl groups on this latter polymer creates additional
restraints for complexing seriously hindering the approach of incoming ionic species.

As steric restraints to complexation increase a gradual decrease in the strength of bonding is reflected by a reduction of the magnitude of the $T_g$ change for a given salt concentration. This effect has not been observed over the limited range of specimens available for analysis and in reality observations indicate that the reverse may be true for methyl and ethyl derivatives. This somewhat surprising result may be interpreted simply in terms of the models previously proposed. The methyl-containing polymer will be subjected to fewer steric restraints to complexing as a result of the presence of the small -CH$_3$ group. For a given interaction it is likely that the deformation required to encompass a cation completely can be met by a single chain. The ethyl-containing polymer will be subjected to more steric restraints. It is unlikely that the necessary conformation could be met with the same number of oxygen-containing groups or that it could be met solely by a single chain. The involvement of a greater number of monomer sequences with each cation leads to a more dramatic effect upon the glass transition temperature.

6.3 Glass Transition Temperature Studies of Poly(propylene sulphide) Containing Metal Salts

The glass transition behaviour of poly(propylene sulphide) remains ill investigated due to the relative obscurity of the polymer. The addition of metal salts to poly(propylene sulphide) resulted in behaviour analogous to that observed for samples of poly(alkyl vinyl ethers) containing ammonium thiocyanate. Though the addition of salt to the polymer produced optically transparent specimens there was no observed change in the glass transition temperature over that of the homopolymer. The presence of optical transparency suggests homogeneity between the polymer and the salt and indicates
that incorporation of the salt as a second phase component is unlikely. It is proposed that interaction between the salt and the polymer is weak and consists of dipole-ion interactions involving only single sulphur atoms with any given salt molecule. The resulting compound analogous to those observed between poly(ethyl vinyl ether) and ammonium thiocyanate are in contrast to those observed from poly(propylene oxide) and metal salts as reported by Wetton and James. The differences arise from the lower comparative donor capability and hence reduced complex stability of the sulphur atom.

6.4 Dielectric Dispersion Studies of Poly(alkyl vinyl ethers) Containing Metal Salts

The dielectric properties of poly(alkyl vinyl ethers) have been studied in the region of the $\alpha$ relaxation by several workers and have been reviewed by McCrum et al. and Hedvig. Most extensively investigated has been poly(ethyl vinyl ether) by Wetton and Wolf. Würstlin has studied poly(methyl vinyl ether). In the former studies a single broad relaxation peak was observed with $\tan \delta_{\text{max}} = 45^\circ$ at $2 \times 10^6$ Hz, whilst for the second polymer the relaxation peak was centred around $37^\circ$ at $2 \times 10^6$ Hz and $-15^\circ$C at 50 Hz. The results obtained in the present studies are in broad agreement with those of previous workers with broad relaxation peaks centred around $0^\circ$ and $-10^\circ$C at $1500$ Hz respectively.

The internal plasticisation effect described previously for poly(alkyl vinyl ethers) was not reflected in the dielectric data although Thurn and Wolf have shown the effect in mechanical data. Mechanical and dielectric relaxation behaviour are frequently comparable in the $\alpha$ relaxation zone but as shown in Chapter 5 for poly(vinyl alcohol)-metal salt complexes this is not always true. It has been shown that the dielectric relaxations of poly(alkyl vinyl ethers) are elevated above those of the mechanical processes and have been shown to be independent of side chain length. This
observation can be reconciled if the dielectric relaxation process is regarded as representing the motion of the polar C-O dipoles which are directly linked to the side chain whilst the mechanical \( \gamma \) transition represents larger scale chain motions.

No evidence was found for the existence of the \( \beta \) and \( \gamma \) relaxation processes at \(-50^\circ\) and \(-85^\circ\) for poly(methyl vinyl ether) and \(-45^\circ\) and \(-90^\circ\) for poly(ethyl vinyl ether) as reported by Schmeider and Wolf\(^{244}\) and Schell\(^{239}\) from mechanical measurements. The \( \beta \) relaxation has been attributed to the rotation of side groups and thus should be absent in the dielectric spectrum since rotation takes place around the C-O bond and does not contribute to polarisation. An inductive effect results in the alkyl group exhibiting a polarity which can be reflected as a dielectric loss peak as observed for poly(n-butyl vinyl ether) by Schell\(^{239}\).

Figure 6.3 shows the frequency-temperature plot for the \( \alpha \) relaxation. It can be seen that the location remains essentially linear even at low temperatures, suggesting that the activation energy of the system remains essentially constant although as reported previously wholly amorphous polymers typically show curvature in the frequency location plots for main chain relaxations\(^{237}\).

It is possible to calculate the activation energy of the \( \alpha \) relaxation from Figure 6.2 using the relationship

\[
\frac{d}{d} \left[ \frac{\log f}{1/T} \right] = -\frac{\Delta E}{2.303 R}
\]

The value of 171 kJ mol\(^{-1}\) indicates, together with evidence presented by Williams\(^{237,137}\), that the process is cooperative and that the \( \alpha \) relaxation process is related to the glass transition of the poly(alkyl vinyl ethers).

The dielectric data may be replotted in terms of the previously discussed Cole-Davidson plot and shown in Figures 6.4 and 6.5. It can be
Figure 6.3

Frequency-temperature plane location (based on $\tan \delta$ data) for the $\alpha$ relaxation of some Poly(alkyl vinyl ethers)

- Poly(methyl vinyl ether)
- Poly(ethyl vinyl ether)

\[ \log_{10} f \] vs. \[ \frac{1}{T} \times 10^9 \text{(K)} \]
Cole Cole representation of dielectric data for Poly(ethyl vinyl ether)
Figure 6.5

Cole Cole representation of dielectric data for
Poly(methyl vinyl ether)
seen that a good fit is obtained and using the procedure outlined in section 2.2.2 values of $\gamma$ have been determined as 0.36 and 0.44 respectively for the methyl and ethyl polymers.

Figures 4.32 and 4.38 show the dielectric permittivity data for poly-(ethyl vinyl ether) and poly(methyl vinyl ether) containing various quantities of zinc chloride in the temperature plane and measured at 1500 Hz. The introduction of even small quantities of salt results in a dramatic change in the dielectric permittivity data in the region of the $\alpha$ relaxation of the homopolymer.

Initial addition of salt to the polymer produces a shift of the $\alpha$ relaxation to higher temperatures paralleling the observed differential thermal analysis data. The effect is manifested as a shift in position of the step in $\varepsilon'$ to higher temperatures accompanied by an associated increase in the strength of relaxation. With increasing salt content the strength of the relaxation continues to increase whilst the position on the temperature axis begins to decrease following the pattern set by calorimetry data. The plateau region in $\varepsilon'$ data following the $\alpha'$ relaxation was found to decrease and the rapid increase in dielectric constant marking the end of this process was found to shift rapidly down the temperature scale.

Similar trends to those observed in the storage component data were observed in the loss component $\varepsilon''$. The broad absorption associated with the relaxation of the homopolymer was initially shifted to higher temperatures by the addition of salt. The relaxation process grew in magnitude but was not as well defined as in the homopolymer, being seen as a shoulder on the side of a rapidly developing strong $\alpha'$ process. At salt concentrations of greater than $\gamma \approx 10$ mole % both processes were obscured and replaced by a rapid monotonic increase in $\varepsilon''$ with temperature.

Figures 4.33 and 4.39 illustrated comparable data for the same polymer systems containing lithium thiocyanate. Similar trends to those previously
discussed were observed in both $\varepsilon''$ and $\varepsilon'$ but it is notable that for comparable salt concentrations the effects of the latter salt were less dramatic.

It has been shown previously that the metal salt complexes of poly-(alkyl vinyl ethers) and poly(vinyl alcohol) may be regarded as consisting of coordinated and uncoordinated units. Only one $T_g$ process was observed: by differential thermal analysis, it is however possible for each segment to exhibit its own dielectric relaxation associated with its glass transition process. MacKnight et al. observed this effect in dynamic mechanical analysis of poly(2,6-dimethyl phenylene ether)-polystyrene blends. Although partial mixing took place two distinct phases remained in all mixtures, each exhibiting characteristic relaxation processes. Differential thermal analysis of the same systems had revealed only a single relaxation, highlighting the necessity to choose the correct measurement technique when investigating molecular relaxation processes.

It is not surprising that the relaxation processes of coordinated and uncoordinated segments of the polymer chain are not revealed by dielectric analysis. James has shown that at low concentration of salts in poly(propylene oxide) relaxation processes attributable to the $\alpha$ relaxation of coordinated and uncoordinated segments were present in the dielectric spectrum. The $\alpha$ relaxation of uncoordinated units was shown to be related to the glass transition process of the original homopolymer by comparison of the activation energies determined from the slope of the frequency location plot.

The observation of only a single relaxation process in poly(alkyl vinyl ethers)-metal salt complexes even at low salt loadings suggests that the extent of interaction is great even at these concentrations and that larger monomer sequences may be involved in complexation. The increase in strength of the $\alpha'$ relaxation associated with the complexed units with increasing salt content reflects the increased number of coordinated segments.
The observation of the shift of the \( \alpha \) relaxation to higher temperatures with addition of salt indicates the onset of molecular mixing. It has been observed\(^{127} \) that polymer blends may exhibit two \( T_g \)s corresponding to each of the components which broaden and move closer together. Comparable phenomena may occur in poly(alkyl vinyl ether)-metal salt complexes although it is clearly not evident from the data presented. The temperature location of the two processes may however be so close that they cannot be resolved by dielectric spectroscopy.

The absence of clearly defined relaxation processes precluded the calculation of activation energies from either \( \varepsilon'' \) or \( \tan \delta \) data since it was not possible to construct frequency location plots from the observed permittivity data.

Original studies of poly(alkyl vinyl ethers) containing metal salts were prompted by the previously described observations of poly(vinyl alcohol). The presence of crystallinity in the latter polymer made it impossible to assess the contributions of individual species to the polymer systems and thus it was desirable to study systems in which these were not present. Poly(alkyl vinyl ethers), a group of compounds related to poly(vinyl alcohol) were the obvious choice and whilst thermal data has borne out many of the proposals made for the latter polymer, it is clear that the dielectric data when presented conventionally provides little useful information.

6.5 Dielectric Modulus or Inverse Permittivity Representation of Data

In studies of the dielectric properties of alumino silicate glasses by Moynihan et al.\(^{130} \), conductive processes distorted the dielectric spectrum to the extent that no useful information could be obtained. Using the concept of the interrelation of compliance and modulus terms the dielectric inverse permittivity or dielectric modulus was derived, as discussed in Chapter 2. The technique was subsequently successfully applied to polymeric
species in which there was appreciable conduction by North et al. 131

Dielectric modulus data has been obtained for poly(alkyl vinyl ethers) containing metal salts and has been shown in Figures 4.34, 4.35, 4.40 and 4.41. Inspection of these figures reveals several trends absent in conventional representations. The real part of dielectric modulus $M'$ shows little strength in the homopolymer but is greatly enhanced with addition of salt. For samples of polymer containing metal salt the real part of the modulus underwent a step change in the relaxation region. The magnitude of the relaxation remained essentially constant with increasing salt concentration although it was shifted down in temperature. For all samples except those of the poly-(methyl vinyl ether)-lithium thiocyanate system the step in $M'$ encompassed two relaxation processes. The lower temperature relaxation increased in magnitude with increasing salt content at the expense of a higher temperature process. Samples of poly(methyl vinyl ether) containing lithium thiocyanate exhibited a single broad step change in $M'$.

The loss component data complemented the storage component results. In all samples except those of the poly(methyl vinyl ether)-lithium thiocyanate there evolved two loss peaks. The first of these two peaks showed essentially constant strength but was shifted down in temperature on increasing salt concentration. The second or higher temperature relaxation was initially well defined but was rapidly shifted down the temperature scale to become a shoulder on the side of the first peak as salt content was increased. Associated with this shift there was a decrease in the breadth of the transition, an observation thought to be indicative of changes in the homogeneity of the states formed. In common with storage component data, loss component data for poly(methyl vinyl ether) containing lithium thiocyanate was characterised by a single broad relaxation process which decreased in breadth with increasing salt content.

Figures 6.6 and 6.7 show the frequency location plots for the relaxation
Frequency-temperature plane location (based on M" data) for the low temperature relaxation of Poly(methyl vinyl ether) Zinc Chloride complexes.
Figure 6.7

Frequency-temperature plane location (based on $M^*$ data) for the high temperature relaxation of Poly(methyl vinyl ether)-Zinc Chloride complexes.
processes illustrated in section 4.4 isolating both low and high temperature processes where possible. Comparison of the data with conventional dielectric permittivity data indicates that the lower temperature process has constant activation energy comparable to that for the glass transition or relaxation of the homopolymers. The position of the location plot was shifted along the temperature scale with salt concentration but remained above that of the homopolymer. Data for the second or higher temperature relaxation process is less well documented since especially at high frequencies the relaxation peak rapidly degenerated to a mere shoulder on the side of the low temperature process. The frequency location plots for this process showed slightly lower activation energy as calculated by equation (6.1) being approximately 130 kJ mol\(^{-1}\).

The position of both the \(\alpha\) and \(\alpha'\) relaxations in the dielectric modulus data did not parallel the DTA data and it is believed that neither is simply associated with the glass transition of the complex.

The dielectric modulus data may be presented in the form of Cole-Cole diagrams as discussed previously in Chapter 2. Typical plots constructed from data taken at different temperatures are shown in Figures 6.8 and 6.9. It is evident that \(M''\) attains a non-zero value at low temperature which results in a distortion of the curve. This suggests that two distinct but overlapping relaxation processes are taking place. Their presence precludes useful interpretation of these representations.

6.6 Molecular Interpretation of the Observed Dielectric Permittivity and Glass Transition Data and Calculated Dielectric Modulus Data

The published dielectric data for ion-containing polymers has been essentially concerned with ionomeric systems\(^{18,21}\) and in particular ethylene-methacrylic acid copolymers and their salts.\(^{246}\) No relaxations of the type or magnitude of those observed for poly(alkyl vinyl ethers) were reported.
Complex plane representation of dielectric modulus data for Poly(ethyl vinyl ether) containing 15 mole percent Li SCN.
Figure 6.9
Complex plane representation of dielectric modulus data for Poly(methyl vinyl ether) containing 5 mole percent ZnCl₂.
Phillips, Emerson and MacKnight\textsuperscript{247} studied the dielectric properties of poly(ethylene) modified by the addition of phosphoric acid sidegroups. An additional dielectric dispersion considerably larger than the other relaxations was observed which showed dependence upon the concentration of phosphoric acid side groups. The relaxation moved to lower temperatures with increased phosphoric acid concentration and showed an activation energy independent of the number of side groups. There was, however, a broadening in the distribution of relaxation times with temperature. The results were interpreted in terms of Maxwell-Wagner-Sillars interfacial polarization based upon a microphase separated system. The presence of a peak in $\varepsilon''$ and a plateau in $\varepsilon'$ indicated that this process could not entirely explain the results.

The effects of M.W.S.-type polarization have been discussed in section 2.2.6. It was shown that a prerequisite for such behaviour is the presence of a heterogeneous system. The data obtained from glass transition temperature measurements and by visual inspection of samples of poly(alkyl vinyl ethers) containing metal salts have indicated the complexes to be single phase. The molecular dispersion of salt up to concentrations of 20 mole % suggests that conventional M.W.S. behaviour was not possible.

Pohl\textsuperscript{167,168} observed high dielectric constants for molecules having a high degree of conjugation which he attributed to hyper-electronic polarization. The effect, which was described in section 2.2.8, is unlikely to occur in samples of poly(alkyl vinyl ethers) containing metal salts since no evidence of unsaturation or conjugation was present.

The existence of bound salt molecules on the polymer suggests that application of the Schwarz model\textsuperscript{164,165} previously discussed in Chapter 2 could be made. For Schwarz behaviour to occur there must exist a system in which mobile ions are electrostatically bound to immobile counterions but are isolated from other similar areas. Both a chelate polymer complex and
a crown ether type complex fulfil the requirements for this model since in each the immobile cations are isolated from each other by virtue of their association with the polymer chain. If either of the observed relaxations are analogous to a Schwarz process then the thiocyanate or halide counterion would have to be locally mobile around the cation. Such mobility is unlikely because of the stereochemistry of the complex formed and the steric restraints thus introduced.

It is thought that the low temperature relaxation process represents the local scale rotation of backbone C-C bonds within sequences of associated monomer units as previously described in Chapter 5. For such a process an equilibrium of the type shown schematically in Figure 6.10 results.

In this simplified form species A represents a state in which a sequence of etheral oxygens is fully associated with a cation. At $T_g$ the main chain is able to distort slightly such that contributions from peripheral oxygens decrease at one end of the sequence whilst increasing at the other. Species B and C of Figure 6.10 represent the extremes of this effect and it can be seen that it is possible for the ionic species to move to an adjacent uncoordinated sequence. Such a process would eventually lead to conduction through the polymer by an ion transport mechanism. At temperatures close to $T_g$ the movement would not be by a definite hopping process but rather a gradual unravelling/entwining action.

Movement of this type with its associated equilibrium is only possible at temperatures above $T_g$ because of the fast segmental motions required of the polymer chain. The formation of species B and C does not necessarily involve only one chain and interaction with adjacent chains are possible. The activation energy of such a process will depend only upon the cooperative movement of the backbone required. Such a process is characterised by a small distribution of relaxation times and an essentially constant activation energy. As the concentration of salt increases the number of associated
Figure 6.10

Schematic representation of the equilibrium present in metal salt complexes of Poly(alkyl vinyl ethers)
species will increase and it would be expected that such a process would require less free volume change to activate it as reflected by a shift down the temperature scale. These assertions are verified by experimental observations of the frequency location plots which show constant energy of activation with increasing salt content.

The second observed process is thought to represent the total disruption of the polymer complex and the onset of thermally stimulated conduction in the system on a large scale. At low concentrations of salt a series of well defined sequences having good thermal stability will exist and these will require a higher activation temperature to supply the necessary free volume for disruption of the complex. At increased salt concentrations the number of vacant sites and uncoordinated sequences is reduced and there is a shift of the process to lower temperatures. There will exist an ideal salt concentration at which there are sufficient vacant sites to accommodate the movement of the ions and maximum conduction is observed. At concentrations of salt above this level the formation of non-stoichiometric species may take place in addition to the onset of competition for vacant sites by cations. This effect leads to further reduction of the activation temperature for both processes and a reduction in overall conductivity.

The two observed relaxation processes represent the extremes of the transitions taking place in poly(alkyl vinyl ether)-metal salt systems. They are characterised at each concentration by two transition temperatures which can be designated $T_\alpha$ for the lower and $T_{dec}$ for the upper process. Figure 6.11 shows dielectric loss modulus data for poly(methyl vinyl ether)-zinc chloride blends. The curves have been arbitrarily displaced vertically for clarity. The data displayed in this way clearly shows the evolution of these new transitions from the simple glass transition relaxation of the homopolymer. Taking the peak maxima positions it was possible to show the data in the form of a plot of position of relaxation maximum vs. wt. percent
Figure 6.11

Dielectric loss modulus data for Poly(methyl vinyl ether) containing various concentrations of \( \text{Zn Cl}_2 \)
composition. This is shown for the same data in Figure 6.12. This type of representation bears similarities to the time-temperature transition approach which Gilham has applied to thermosetting systems. Using similar criteria a generalised phase diagram may be constructed as shown in Figure 6.13. The structure of this diagram is the result of several competing effects. Of particular interest is the composite line which constitutes the lower transition (T\(T_a\)). At low concentrations of salt the position of the transition is governed by the elevation of T\(_g\) resulting from reduced backbone movement through complexation. At higher concentrations of salt the effects of stability of the complex become evident. Comparison of the T\(_\alpha\) data in Figure 6.12 with the experimental DSC data shown in Figure 4.37 reveals a similar pattern of behaviour by both techniques of measurement. This indicates that both measurements reflect the same local mode movements of the backbone which were outlined in section 6.2.1.

The upper line of Figure 6.13 represents the onset of essentially free movement of ions through the polymer. At an infinitely low concentration of salt this should extrapolate to an infinitely high temperature. In practice there will be a finite value for the breakdown and it is likely that this curve may show a peaking effect. At high salt concentrations the line adopts a position approximately parallel to the T\(\alpha\) curve but at an elevated temperature. This trend reflects the finite number of vacant sites in the polymer and the additional thermal energy required to activate full conduction over that for the local scale motion.

The absence of the presence of T\(_{dec}\) data in DTA measurements is consistent with the transition being associated only with electrical perturbations of the polymer molecules.

Using the above generalised theory and phase diagram the dielectric data obtained from poly(methyl vinyl ether)-lithium thiocyanate complexes may appear incongruous. This system exhibited a transition process which
Figure 6.12

Position of observed dielectric modulus maxima ($M_{\text{max}}$) in temperature plane for Poly(methyl vinyl ether) Zinc Chloride complexes.
Figure 6.13

Idealised phase diagram for the behavior of metal salt complexes of Poly(alkyl vinyl ethers)

Complete breakdown of polymer complex
Free ion movement in matrix

Polymer complex in rubbery state partial ion movement

Polymer complex in glassy state

Temperature

Concentration of salt (wrt moles of monomer)
involved only a single broad peak at low concentrations. At high concentrations sharpening of the transition was observed. It is proposed that this broad peak was in reality an unresolved doublet and was the result of the two relaxation processes being close together. The effect is shown schematically in Figure 6.14.

![Diagram showing the relationship between $T_{\alpha}$ and $T_{\text{dec}}$ for Poly(methyl vinyl ether) Lithium Thiocyanate complexes.](image)

The decrease in breadth of the peak at high concentrations reflects a shift of $T_{\text{dec}}$ towards $T_{\alpha}$ with increasing concentration of hopping species.

Poly(ethyl vinyl ether) containing lithium thiocyanate does not show the same behaviour, but as expected exhibits a double relaxation process. The involvement of more than one chain with any associating cationic species as a result of steric restraints results in a higher proportional value of $T_{\text{dec}}$. The larger difference between $T_{\text{dec}}$ and $T_{\alpha}$ can be resolved by dielectric spectroscopy.

The DTA data observed for complexes of poly(ethyl vinyl ether) and ammonium thiocyanate can also be reconciled using this approach. For such
a system binding is weak and thus the position of $T_\alpha$ is little above that of the homopolymer. If binding is weak then both $T_\alpha$ and $T_{dec}$ may be below the $T_g$ of the homopolymer such that from DTA measurements only the glass transition of the homopolymer can be seen. The effect is shown schematically in Figure 6.15.

Figure 6.15

Relationship between $T_\alpha$ and $T_{dec}$ for complexes of poly(alkyl vinyl ethers) in which interaction is weak
CHAPTER 7

CONCLUSIONS

7.1 General Aspects

The studies presented in this thesis have illustrated the preparation of a series of compounds between poly(alkyl vinyl ethers) and related polymers and metal halides or thiocyanates. The complexes formed were optically transparent and remained thermoplastic to reasonably high salt loadings. Complexes formed from poly(vinyl alcohol) or poly(ethyl vinyl ether) were tough materials being readily moulded by conventional techniques at temperatures above their glass transition. All the experimental evidence obtained from these complexes has indicated that the inclusion of salt is as a single phase and not as a conventional second phase filler. The experimental studies have also indicated that the mode of interaction is dependent both upon the nature of the salt and of the polymer.

7.2 Poly(vinyl alcohol) Complexes

Poly(vinyl alcohol) forms two types of molecularly dispersed compounds which both show well defined but occasionally protracted glass transitions by D.T.A.

The first type of complex was formed by the addition of transition metal chlorides and was characterised by a \( T_g \) elevated over that of the parent polymer. The elevation was dependent both upon the type and amount of salt incorporated, but for a given salt followed a slight sigmoidal relationship.

The second type of complex was formed by the addition of the thiocyanates of Group I metals. This type of complex was characterised by a linear
depression of $T_g$ by up to $50^\circ C$ with increasing salt concentration. In common with complexes in which $T_g$ was elevated these compounds exhibited a dependence both upon the type and concentration of salt incorporated.

The glass transition data has indicated that a necessary requirement for complexation of both types was a molecular dispersion of salt in the polymer. In the absence of strong interactions a two phase system consisting of a crystalline salt phase within the polymer matrix is energetically more favourable than the single phase system. Evidence to support the assertion of incorporation of salt as a single phase interacted with the polymer chain has been obtained from other experimental techniques.

Small Angle X-Ray Scattering indicated the absence of scattering from large scale heterogeneities and confirmed that inclusion of salt was as a single phase and not as isolated crystallites. No evidence of ion clustering as has been observed from ionomeric systems was obtained. This further confirmed the assertion of molecular mixing of salt and polymer.

Wide Angle X-Ray Scattering indicated that at limited concentrations at least the inclusion of metal salt was molecular. At very high salt concentrations peaks attributable to salt crystallites were observed indicating that the solubility limit of the salt had been exceeded. WAXS data indicated a systematic reduction of crystallinity with increasing salt content up to the maximum solubility limit. Evidence was also obtained to suggest that the inclusion of small ions such as lithium was not restricted to amorphous regions but could occur in crystalline segments without major disruption of the unit cell.

Dynamic mechanical thermal analysis produced results which for the most part paralleled those obtained by differential thermal analysis.

Complexes formed from transition metals and poly(vinyl alcohol) exhibited a relaxation process associated with the glass transition. The
loss tangent peak was shifted to higher temperatures with increasing salt concentration and was accompanied by an increase in magnitude and a sharpening of the peak. The change in modulus in passing from the glassy to rubbery state was similarly increased in magnitude and the breadth reduced. The results were indicative of a reduction of crystallinity in the polymer as reflected by an increase in the importance of the glass transition process. The shift of the relaxation to different temperatures reflected the variation of chain mobility resulting from interaction of the polymer with the salt molecules. Calculations of the activation energy for the glass transition process further exemplified this argument.

Complexes formed by Group I metal thiocyanates and poly(vinyl alcohol) exhibited similar trends in their mechanical behaviour to those observed from differential thermal analysis. The significance of the glass transition process became greater with increasing salt concentration and was reflected as a shift of relaxation to lower temperatures with an increase in magnitude and reduction of breadth of both the loss tangent peak and the step change of modulus. The increase in magnitude of the tan \( \delta \) peak was inversely related to the radius of the cation, suggesting that the strength of the complexes formed was similarly dependent.

The incorporation of lithium thiocyanate produced results inconsistent with those obtained from other salts. The relaxation process remained relatively broad and showed a strength lower than that expected. The observation reflected the preferential inclusion of the small lithium cation into crystalline segments of the polymer with only minor effect upon the glass transition.

Dielectric dispersion measurements of the poly(vinyl alcohol)-thiocyanate complexes revealed data which contrasted with that of previous techniques. A new relaxation not previously measured in the polymer and designated \( \alpha' \) was observed. The position of the relaxation did not bear
any simple relationship to that of the glass transition. Values of
dielectric constant and loss were very high and were dependent both upon
the nature and concentration of salt incorporated. It has been proposed
that the $\alpha'$ process represents local relaxation of hydroxyl groups. The
rearrangement of hydroxyl groups is sufficient to activate ionic diffusion,
a process manifest as conduction effects present in the polymer at higher
temperatures.

Models have been proposed which are consistent with the observed results
for both types of complex. For compounds involving transition metal halides
a system in which coordination of two adjacent hydroxyl oxygen atoms on the
polymer backbone to the metal salt has been proposed. This process creates
six-member chelate rings formed from two oxygen atoms, three carbon atoms
and a single metal atom which have good stability. The resulting system
could be considered as a copolymer consisting of chelated and unchelated
monomer units and thus application of conventional copolymer relationships
were made. Although the presence of hydrogen bonded and non-hydrogen bonded
sequences further complicate the model, good approximations of the $T_g$ of
the fully coordinated species could be made.

Calculations and experimental evidence indicated the complexation pro-
cess to be essentially intramolecular with negligible contributions from
intermolecular species. Evidence was present in experimental data to
suggest that at high salt concentrations where chelate formation was not
possible single oxygen coordination could take place.

The inclusion of salts having a high oxygen coordination number such
as copper II compounds presented the possibility of simultaneous intra- and
inter-molecular coordination. Experimental evidence suggested that full
intermolecular coordination did not take place and that solvent was
frequently an integral part of these complexes.
For compounds containing thiocyanates the mode of interaction proposed is weaker and for any given salt involves more monomer units. It is proposed that a number of adjacent monomer units coordinate weakly to the cationic species forming a cage around it. The cage has dimensions just sufficient to accommodate the ionic diameter of the metal. As the ionic radius of the metal increases a greater number of monomer units are involved and thus there is a lower solubility limit. The range varies from four monomer units for the small lithium cation to a sequence of six monomer units for large cations such as ammonium. In common with the model proposed for compounds containing transition metal chlorides it is possible that contributions from intermolecularly coordinated species may be present as a result of the severe conformational restraints enforced on the chain by any complexation process. The experimental evidence suggested that contributions from such species were negligible.

It is proposed that the overall reduction of $T_g$ by the addition of metal thiocyanates to poly(vinyl alcohol) is the result of a net reduction of chain stiffness caused by hydrogen bond disruption effects outweighing complexation effects.

7.3 Poly(alkyl vinyl ether) Complexes

Complexes have been shown to be formed between various metal salts and poly(alkyl vinyl ethers) having a short side chain alkyl group. The steric restraints caused by the presence of the alkyl side chain were such that there were dramatic effects upon the ability of the polymers to form complexes. The effect was observable even between the methyl and ethyl analogues and attempts to synthesise complexes from poly(iso-butyl vinyl ether) were totally unsuccessful because of the large steric restraints involved.
The molecularly dispersed complexes were amorphous and showed well defined glass transitions by differential thermal analysis. $T_g$ was elevated over that of the homopolymer by up to $40^\circ$C. The elevation was dependent both upon the amount and nature of the salt incorporated for any given polymer. The elevation rose to a maximum and then at higher salt concentrations began to fall as the maximum soluble limit was approached.

In common with the results obtained from poly(vinyl alcohol) containing metal salts the glass transition data obtained from poly(alkyl vinyl ethers) indicated that a necessary requirement for $T_g$ elevation was a molecular dispersion of salt in the polymer and that these features were both indicative of interaction between the metal salt and the polymer.

The glass transition behaviour of poly(alkyl vinyl ethers) containing metal salts has been interpreted in terms of the stability of the complex formed. It has been proposed that the stability of a polymer complex will follow a Gaussian relationship with concentration of salt showing a maximum value when half the available sites for complexation are occupied. Under normal circumstances it has been proposed that this curve will lie well above that of $T_g$ elevation resulting from complexation.

For complexes of poly(alkyl vinyl ethers) with metal salts the two curves lay in the same temperature range and intersect at high salt loadings. It has been proposed that the observed $T_g$ versus composition curve represents a combination of the two aforementioned processes. The downturn in $T_g$ elevation at high salt loadings has been shown to reflect the importance of the breakdown process in these regions.

A model has been proposed for the structure of poly(alkyl vinyl ether)-metal complexes which is similar to that adopted by poly(vinyl alcohol)-metal thiocyanate complexes. Greater steric restraints are involved with complexation of poly(alkyl vinyl ethers) and thus a larger number of monomer sequences are involved with each cation. Steric restraints pre-
vented formation of chelate type complexes with even strong acceptors such as zinc chloride. The latter compound was also incorporated in the form of an encapsulating ring structure.

The degree of contortion required of each monomer sequence to effect complexation increases as the length of the side chain increases. It has been proposed that contributions from intermolecularly bonded species may become more significant as this parameter increases. Since the overall strength of the complexation process is weak it has been postulated that the contribution from such effects are negligible and that there is little residual effect upon $T_g$.

Dielectric dispersion measurements of poly(alkyl vinyl ether)-metal salt complexes revealed data which was difficult to interpret because of the onset of conduction effects. Mathematical treatment of the results produced data in the form of the inverse dielectric permittivity or dielectric modulus.

From data in this form several clear patterns emerged. A new relaxation process not previously observed in the parent polymer and designated $(T'_{\text{dec}})$ was observed. The position of this relaxation did not bear any simple relationship to that of the glass transition temperature but was superimposed upon a second lower temperature process designated $(\Gamma_\alpha)$. Both processes were elevated over that of the homopolymer, their position showing a strong dependence upon the concentration of salt present. The lower temperature process followed a concentration dependence similar to that of the glass transition data.

Models have been proposed to explain the observed data in terms of a relaxation process which initiates conduction in the system. It has been proposed that the lower temperature process represents local small scale electrical perturbations of the polymer backbone and is the composite curve
formed by $T_g$ elevation and stability phenomena. The second or higher temperature process has been proposed as representing the large scale disruption of polymer complexes such that full scale ionic conduction can take place.

The conduction of electricity is dependent upon the concentration of hopping ions and of available sites. It has been shown to reach a maximum at an ideal salt concentration beyond which competition for sites results and an overall loss of conductivity.

In one series of specimens produced from the addition of lithium thiocyanate to poly(methyl vinyl ether) the two relaxation processes were shown to be too close on a thermal scale to be resolved.

Taking data from the above representation and applying a principle similar to time temperature transformation a general relationship was derived for the formation of complexes and was resolved into the form of a generalised phase diagram.

The principle of the phase diagram was successfully applied to ammonium thiocyanate-poly(ethyl vinyl ether) complexes and to those of poly(propylene sulphide) containing metal salt. In these systems inclusion of salt was as a single phase but resulted in a negligible effect upon the glass transition. It has been proposed that in such systems interactions are very weak and involve only single dipole-ion interactions. There is little reduction of chain mobility and in the dielectric spectrum breakdown of the complex occurs at temperatures close to the glass transition for the parent polymer.
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APPENDIX A

Calculation of the Mass Absorption Coefficient of a Structural Unit

The method of calculating \( \mu/e \) follows the procedure of Alexander.\textsuperscript{191}

Considering a structural unit containing \( C_i \) atoms/ions of species \( i \) such that the atomic weight of each species is \( A_i \) and the mass absorption coefficient of each species is \( \langle \mu/e \rangle_i \). Numerical values of \( \langle \mu/e \rangle_i \) are given in.

The weight fraction \( w_i \) of each species in the unit of composition is given by:

\[
W_i = \frac{C_i A_i}{\sum_i C_i A_i}
\]  \hspace{1cm} A.1

and the mass absorption coefficient of the structural unit is given by

\[
\langle \mu/e \rangle = \sum_i w_i \langle \mu/e \rangle_i
\]  \hspace{1cm} A.2

For the poly(vinyl alcohol)-zinc chloride sample the structural unit contains C, H, O, Zn\(^+\) and Cl\(^-\) species. There will be 3 carbon atoms, 6 hydrogen and two oxygen atoms per structural unit although the number of Zn\(^+\) and Cl\(^-\) ions will depend on the mole fraction of zinc chloride present.
APPENDIX B

Some Physical and Thermochemical Properties of
Inorganic and Organic Compounds^1

Selected Bond Lengths^1

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<th>Bond</th>
<th>In</th>
<th>Bondlength/nm</th>
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Selected Atomic and Ionic Radii

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<th>R_{cov}/nm</th>
<th>R_i/nm</th>
<th>R_+/nm</th>
<th>N_p</th>
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<tr>
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<td>0.116</td>
<td>0.076  (2+) 0.064 (3+)</td>
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<td></td>
</tr>
<tr>
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<td>0.116</td>
<td>0.074  (2+) 0.063 (3+)</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
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<td>0.115</td>
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<td></td>
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<tr>
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\( R_m \) = radius of atom or metal in non-ionic solid

\( R_{\text{cov}} \) = covalent radius of atom

\( R_i \) = radius of ion in inert gas configuration - figures in brackets give charge state

\( R_{\pm} \) = other important ionic radii - figures in brackets give charge state

\( N_p \) = Pauling electronegativity index.

APPENDIX C

Main Characteristics of the Infra Red Spectrum of Poly(vinyl alcohol) with Probable Assignments

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<th>Wavenumber</th>
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<th>Assignment</th>
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<td>O-H stretch</td>
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<td>C-H stretch</td>
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<tr>
<td>2910</td>
<td>strong</td>
<td>C-H stretch</td>
</tr>
<tr>
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<td>shoulder</td>
<td>C-H stretch</td>
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<td>1446</td>
<td>strong</td>
<td>O-H, C-H bend</td>
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<td>strong</td>
<td>CH₂ bend</td>
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<tr>
<td>1376</td>
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<td>CH₂ wag</td>
</tr>
<tr>
<td>1326</td>
<td>medium</td>
<td>CH-CH bend</td>
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<tr>
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<td>weak</td>
<td>C-H bend</td>
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<tr>
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<td>weak</td>
<td>C-H wag</td>
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<tr>
<td>1215</td>
<td>v weak</td>
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<td>C-C-C-O stretch</td>
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<tr>
<td>640</td>
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<td>O-H twist</td>
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</table>