COMB SHAPED POLYMER-SALT SYSTEMS: A.C. CONDUCTIVITY AND DIFFERENTIAL SCANNING CALORIMETRY STUDIES.

A thesis submitted to the University of Stirling
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Preface

This thesis is submitted for the degree of
Doctor of Philosophy
at the University of Stirling,
having been submitted for no other degree.
It is a record of research undertaken in the
Department of Chemistry. This work is wholly
original except where due reference is made.

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ABSTRACT

It is anticipated that a polymer electrolyte which exhibits properties superior to those exhibited by polyethylene oxide (PEO) -salt complexes, particularly at low temperatures, would be suitable for use in the development of a solid state cell.

Comb-shaped polymers were used as the host materials in the polymer electrolytes examined in this study. Conductivities were measured as a function of temperature and the levels of conductivity measured for the various amorphous polymer-salt complexes prepared were dependent on the character of the polymeric host, the nature and concentration of the salt dopant and the temperature of examination.

Dissociation of a salt in a polymer resulted in the glass transition temperature (Tg) of the polymeric host increasing. The increase in Tg with salt concentration was measured using differential scanning calorimetry. It was therefore possible to identify salts which generated a great many charge carriers when dissolved in a polymer. Such salts were particularly effective dopants.

Certain polymer-salt complexes examined in this study exhibited higher conductivities at low temperatures than those reported for PEO-salt complexes. These materials were found to have relatively low Tg values when a large number of charge carriers had been generated in the system.

Conductivity-temperature data were linearized using the Vogel-Tammann-Fulcher equation and the configurational entropy model of Adam and Gibbs was used to interpret the conductivity-temperature behaviour in a meaningful manner.

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CHAPTER ONE

INTRODUCTION AND BACKGROUND

For many years research and development in the battery industry has been directed mainly towards improvement of the traditional battery system. There is now an increasing demand for a more sophisticated range of batteries and the advantages of an all solid state cell have been highlighted <1>.

Some years ago, solvent-free alkali metal salt complexes were prepared from polyethylene oxide (PEO) <2>. In these materials the metal ion is solvated, by ether oxygen atoms in the polymer coordinating to it due to the donation of lone pair electrons <3,4>. A favourable polymer salt interaction, allowed the formation of a salt complex in the linear polymer, an effect which had previously been detected by Pedersen <5> and other workers <6,7> in alkali metal-cyclic ether complexes.

These polymer-salt complexes were seen to have the potential to be used as the electrolyte material in an all solid state cell. The light weight, flexibility and ease of fabrication into thin film configurations, were attractive features of the polymeric host and therefore the electrical properties of these materials were fully investigated.

1.1 Electrolyte Theory.

A true solid electrolyte, like an aqueous electrolyte, is a phase which has electric conductance wholly due to ionic motions within the solid lattice. The electronic contribution to the conduction must by definition be negligible. It is the transport of ions which distinguishes electrolytes from electronic conductors, such as metals. In the latter the current is carried entirely by electrons, and this involves no transport of matter <8,9>.

Considering initially aqueous electrolytes, it is known that on addition of an acid, base, or salt to water, a considerable portion becomes spontaneously dissociated into positive and negative ions

$$MA = M^{+} + A^{-} \qquad 1.i.$$

The degree of dissociation(α) is the fraction of the total electrolyte which is split into ions and is almost constant at unity in strong electrolytes, throughout the concentration range. In a weak electrolyte, the proportion of the molecules which dissociate into ions varies with the concentration of the solution, and is considered to approach unity only at infinite dilution.

In the absence of an electric potential, the ions in solution are free to move independently, but during electrical conduction the ions are attracted to the electrode of opposite charge by the applied field. Consequently, the passage of current in an electrolyte is accompanied by a transport of matter due to the motion of positive and negative ions <9>.

The conductivity(σ) of the solid state electrolye is known to be dependent on both the number of charge carriers present and the mobility of the charged species <10,11> since

$$\sigma = \sum_{i} n_{i} z_{i} e \mu_{i} \qquad 1.ii$$

where n_i is the number of ionic carriers, z_i is the valency of the ionic carriers, e is the elementary electric charge and μ_i is the ionic mobility.

For a monovalent salt, on the assumption that the charge carriers in the electrolyte are generated only from the incorporated salt, Equation 1.ii. can be written as follows <11>

$$\sigma = n_+ e\mu_+ + n_- e\mu_- = ne(\mu_+ + \mu_-) \qquad 1.iii.$$

where n_+ and n_- are the number of cations and anions respectively solvated in the system and equal n, and μ_+ and and μ_- are the ionic mobilities of these charged species respectively. The ionic mobility μ is related to the ionic diffusion coefficient D by the Nernst-Einstein equation <11> as shown below.

$$\mu = \frac{zeD}{kT} \qquad 1.iv.$$

where k is the Boltzmann constant.

Assuming that the electronic conductivity is negligible, transport numbers are used to define the fraction of the total ionic current that is carried by a particular ionic species. The cationic transport number(t_+) and the anionic transport number(t_-) should add together to give unity and t_+ and t_- are related to μ and D <12> since

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-} = \frac{D_+}{D_+ + D_-} \qquad 1.v.$$

1.2 Solid State Electrolyte - Design Parameters.

1.2.1 Requirements of the Polymeric Host.

When considering the development of a useful polymeric electrolyte, the number of charge carriers generated in the system and also the mobility of the charge carriers in the system are important features <13>.

To allow the generation of charge carriers, dissolution of the salt in the polymer must occur to produce ions. An effective polymer-salt interaction is therefore essential.

The chemical character and the conformation of the polymer must provide a suitable solvating environment <14> and so a high density of polar groups, with readily available lone pairs must be spaced at regular intervals throughout the polymer molecules.

Since in polymer electrolytes the charge carriers are coupled to a locally fluid matrix <15> the mobility of ions in the complex is dependent on the segmental motions of the polymer molecules <15>. The flexibility of the polymer must therefore be maximized <14,16,17>. This is achieved by using a polymeric host with the glass to rubber transition (see Section 1.4) at as low a temperature as possible <14,18,19>. To avoid interchain interactions, the polymer should also have a low cohesive energy density <16>. It has been established that at all temperatures ionic conduction occurs only in the amorphous phase present in the polymer-salt complex <20>. For a semicrystalline polymer to be useful as the host material in a solid state electrolyte, the amorphous phase must be optimized at as low a temperature as possible. A useful semicrystalline polymeric host must therefore have a low melting temperature(Tm) <14>.

1.2.2 Factors Affecting the Dissolution of a Salt in a Polymer.

1.2.2.1 Properties of the Polymer.

It could be suggested that polyethers in general would show an ability to solvate metal cations since the ether oxygen atoms, which possess lone pair electrons capable of being donated to allow cation coordination, are present in each of the polymer chains. Salts have, in fact, been added to various polyethers and it has been revealed that an optimum spacing between oxygen atoms is required before dissolution of the salt in the polymer occurs <21>.

Of the polyethers studied, PEO and the analogous structure, polypropylene oxide (PPO), which both contain a repeat unit in which two carbon atoms occur between each oxygen atom, showed the greatest ability to solvate metal cations <21>. Polyoxymethylene <21>, polytrimethylene oxide <21> and polytetramethylene oxide <22>, the shorter and longer chain homologues of PEO were unable to solvate metal ions. Polyvinylmethyl ether, an isomer of PPO, was examined in this study <23> and this polymer showed only a limited ability to solvate metal ions.

PEO is a semicrystalline polymer and numerous studies have been carried out on the pure polymer in the crystalline and molten state <24-31>. In the crystal lattice the polymer molecules are present as 7_2 helices, i.e. seven monomeric units turn two times per fibre period <24,28>. In this conformation the methylene groups are on the periphery of the helix and oxygen atoms are clustered inside when viewing along the axis of the molecule. Due to this helical conformation, which the polymer molecules adopt, an exceptional, oxygen rich environment has been created, which effectively solvates metal cations.

PPO can be obtained in a crystalline form <31> but the material can easily be prepared in an amorphous form <21>. The optimum spacing between oxygen atoms is found in PPO which is reflected in the ability of the material to solvate metal cations, however, it has been suggested that ether oxygen solvation of the cations is hindered slightly in PPO due to the presence of the methyl substituent in the repeat unit <21,32>.

A whole range of other polymers containing polar groups have shown the ability to solvate metal cations <13,14,33-36> but these materials have been studied to a much lesser extent than PEO and PPO.

1.2.2.2 Properties of the Salt.

The energy required for ion separation of a salt in the solvating medium is described by

$$\Delta E = \left(\frac{e^2}{4\pi \epsilon_o \epsilon} \right) \left(\frac{1}{r_c + r_a} \right) \qquad 1.vi.$$

where e is the charge on the ion, ϵ_o is the vacuum permittivity, ϵ is the dielectric constant of the solvating medium and r_c and r_a are the ionic radii of the cation and anion respectively <22>. From this equation it can be predicted that as the value $1/(r_c + r_a)$ decreases, the cation counterion interaction decreases and the solvation of the salt in the polymer will be enhanced <22>.

When considering the dissolution of salts in PEO, it has been established that there is a threshold lattice energy for salts containing a particular cation and complex formation occurs only if the added salt has a lattice energy below the threshold value <14>. In general complex formation was favoured when the anions in the salt were large and the lattice energy of the salt was low. It was also noted that as the size of the cation in the salt was increased, the threshold lattice energy was lowered.

1.3 Salt Complexes of PEO and PPO.

Crystalline or amorphous complexes are prepared on addition of salts to PEO. The character of the resultant salt complex can be affected by the method of preparation <37>, the thermal history <38> of the sample and the anion of the incorporated salt <21>, but the inherent character of the material is suggested to be dependent on the size of the cation of the incorporated salt <39>. In general, crystalline complexes can be formed if the cation in the added salt is small enough to reside within the cavity produced by the helical arrangement of the PEO chains. When the cation is too large to fit inside the cavity produced by the helical polymer chains then amorphous salt complexes are formed. In spectroscopic studies it has been revealed that amorphous polymer salt complexes are similar in character to molten PEO <16,39>. Because the open chain polymer is very flexible, it is thought possible that the PEO chain may be able to wrap around several large cations before serious distortion of the polymer chains occurs <39>. If the polyether helical conformation is seriously distorted then the solubility of the salt in the polymer is reduced <39>.

Spectroscopic studies have shown that lithium and sodium salts form predominantly crystalline complexes <16,39,40>

whereas rhubidium and cesium salts result in amorphous complex formation <16,39,41>. Although potassium salts can result in crystalline complexes being formed when added to PEO <16,21>, it has been suggested that the potassium ion may in fact exist outside the helical polymer chain <42> rather than inside the cavity of the polymer.

In addition to alkali metal salts, alkaline earth salts <43-46> and salts based on silver, copper <47>, zinc, lead <44> and mercury <3,4,48> can be dissolved in PEO.

The dissolution of a wide range of salts, including transition metal salts is possible in PPO <49-52>. Complexes prepared from this polymer are amorphous.

1.4 Polymer Property Changes on Salt Dissolution

On addition of a salt to a polymer, any interaction which occurs between the two species, can be detected by examination of certain physical properties of the polymer before and after incorporation of the salt. In addition to changes noted in the specific volume <33,49> and the viscosity <22,33,53-55> of the polymer it is known that the addition of a salt to a polymer can have a profound effect on the temperature of the glass to rubber transition (Tg) <18,45,49-52,56-59>.

In amorphous polymers, below Tg, the free volume or unoccupied space in the polymer, which arises due to inefficient packing of the disordered chains, attains a particular value and remains constant as the temperature is reduced <60>. Alternatively, the configurational entropy of the system is limited at temperatures below Tg <60>.

As the temperature is increased above Tg, the free volume or configurational entropy of the system increases with temperature and with a specific temperature increase above Tg, the polymer will possess a particular free volume or configurational entropy, relative to that present at Tg. This temperature increase is known as the reduced temperature.

Tg is therefore the temperature above which long range segmental motion is possible in the polymer and the material changes from being in a glassy state to a rubber as the temperature is increased <60>. (In the glassy state the polymer chains are frozen in a disordered state and only localized motions are possible within the matrix, i.e. in pendent sidechains or short sections of the backbone.)

At Tg, dramatic changes occur in the physical properties of the polymer, and marked discontinuities can be noted in the specific volume, modulus, heat capacity and refractive index as the polymer changes from the glassy state to the rubber.

The Tg of the polymer is highly dependent on the chemical structure of the material <60>. Non flexible units in the polymer chain, bulky sidegroups, dipole-dipole interactions between adjacent chains or crosslinks between the chains will hinder the movement of the polymer backbone and the Tg will be measured at a high temperature since the temperature at which the Tg occurs reflects the energy required to overcome the rotational barriers in the polymer chain backbone.

The transition from a glass to a rubber is completely reversible in an amorphous polymer but the precise temperature which is measured for Tg is dependent on the experimental method used and the rate of heating or frequency of analysis.

It can be predicted that on addition of a salt to a polymer, an ~~effective~~ interaction between the polymer and the salt will result in the solvation of the metal cations, which will, in effect, stiffen or crosslink the polymer chains. This will be reflected in the Tg of the polymer increasing as the interactions between the polymer and the salt molecules increase.

In almost all of the polymer-salt systems examined, it was reported that interactions occurring between the polymer and the salt resulted in the Tg of the polymer increasing. If no interactions occur between the polymer and salt then the Tg will remain unchanged as the salt concentration is increased in the polymer <33>. The change in Tg can be detected using mechanical <33,49,51,61,62> or dielectric <45,63-69> techniques, however, in this study the extent of the interaction occurring between the polymer and added salt was monitored, using d.s.c. by noting the enhancement of Tg which occurred as the salt concentration in the polymer was increased

1.5 Conductivity Studies in Polymer-Salt Complexes.

1.5.1 Character of the Polymeric Host.

The ionic conductivity of a polymer-salt complex is greatly affected by the structure of the polymer and also the characteristics of the incorporated salt species <13,18,70>.

A great many polymers containing polar groups have shown the ability to solvate metal cations and the electrical properties of such materials have been investigated <13,34-36,57,71-82>. In general, the conductivity levels demonstrated by complexes prepared on addition of salts to polymers including polyethylene sulphide <34>, polyethylene imine <71,72>, polyvinyl fluoride <74,75>, polyethylene adipate <82>, polyethylene succinate <13,80,81> and polyethylene sebacate <13> tended to be significantly lower than the levels observed for PEO or PPO systems.

PEO-alkali metal salt complexes can exhibit conductivity levels of the order of 10^{-3} Scm^{-1} at high temperatures, but at low temperatures the conductivity is of the order of 10^{-6} Scm^{-1} . At low temperatures, the presence of crystalline polymer and/or crystalline complexes can reduce the flexibility of the polymer <2,70,83>, which affects the migration of the mobile charge carriers in the system and can also reduce the number of mobile charge carriers in the system. As the temperature is increased, the conductivity is increased dramatically when the amorphous component in the material is increased, due to the melting of the crystalline phases. The number of mobile charge carriers in the system and the flexibility of the polymer molecules are both increased simultaneously <38> and this results in the dramatic enhancement of the conductivity at Tm. The thermal history of salt complexes prepared from this polymer is therefore of great importance <84>.

Complexes prepared from PPO can exhibit conductivity levels reaching 10^{-5} Scm^{-1} at moderate temperatures when a high molecular weight polymeric host is used <21,85>, which is comparable to the levels measured in PEO complexes. Conductivity levels ranging from 10^{-6} to 10^{-4} Scm^{-1} can be measured at room temperature, however, when examining complexes prepared from low molecular weight PPO oligomers <54,86>.

Since all of the PPO-based complexes are amorphous, no discontinuity is noted in the conductivity as the temperature is increased and the conductivity-temperature behaviour of the PPO based complexes therefore differs from that observed for the PEO based materials.

1.5.2 Conductivity-Temperature Behaviour.

Depending on the character of a polymer-salt complex, various types of conductivity-temperature behaviour can be exhibited.

Complexes which contain crystalline material, throughout the temperature range, can be analysed in terms of the Arrhenius equation <21,70>.

$$\sigma = A \exp\left(\frac{-Ea}{RT}\right) \qquad 1.vii.$$

where Ea is the activation energy of the ion conduction process and R is the gas constant. When log conductivity is plotted as a function of reciprocal temperature for such materials, two intersecting straight lines can be detected. This reflects the transition from a high activation energy process to a low activation energy process at the melting temperature of a crystalline phase in the sample <70,83>.

Some complexes exhibit Arrhenius behaviour at low temperatures but above the melting temperature of the crystalline complex non-Arrhenius behaviour is exhibited <21>. A straight line changes to a curved line in the plot of log conductivity versus reciprocal temperature.

When complexes are totally amorphous at all temperatures, non-Arrhenius behaviour is exhibited throughout the temperature range. Conductivity-temperature data for complexes which do not exhibit Arrhenius behaviour can often be linearized using the Vogel-Tammann-Fulcher equation <21> but at temperatures near to but above Tg, where the free volume or configurational entropy in the system is limited, this equation may not apply <87>.

The empirical Vogel-Tammann-Fulcher (VTF) equation <88-90>, was originally developed to examine the nature of transport proccesses which occur in glass forming liquids, but the concepts and equations have subsequently been applied to fused salt systems (at low temperatures) <91> and concentrated aqueous electrolytes <92-94>, to analyse the transport proccesses occurring in these systems.

The empirical VTF equation describes transport properties $\omega(T)$ where ω represents conductance, viscosity, fluidity, diffusion, mobility and dielectric relaxations, as shown in Equation 1.viii.

$$\omega(T) = A \exp\left(\frac{-B}{T-To}\right) \qquad 1.viii.$$

where A and B are constants characteristic of the transport process under consideration and To is a reference temperature. This equation implies that it is the temperature interval above the temperature To, rather than above 0K, which is of interest to transport. The reference temperature To is often correlated with Tg and the importance of the reduced temperature (T-Tg) on the conductivity of polymer-salt complexes was highlighted by Killis et al. <95>. Alternatively To can be associated with the "ideal glass transition temperature" <96>, which occurs at a temperature below Tg.

Differences which may occur in the conductivity of a range of polymer-salt complexes, under constant reduced temperature conditions, can result from variations in the number of charge carriers in the system or variations in the mobility of the carrier ions. Although the motions of the ions through the polymer are linked to the motions of the polymer chains, the ionic conductivity exhibited by a material is also dependent on the mobility of the mobile ion itself <97>.

1.5.3 Character of the Mobile Charge Carrier.

In early studies carried out on PEO-alkali metal salt complexes, it was reported that these materials were essentially cationic conductors, with the anion immobile in the system <98>. After examining a wide range of polymer-salt complexes, there is now evidence to suggest that, rather than these materials being cationic conductors <11.99,100>, both ions are mobile <37,44,101-109> or the anion is the predominant charge carrier <43,110,111>.

It is essential that the mobile species in these polymer-salt complexes are identified since the occurrence of anionic conductance to any great extent could restrict the use of such materials in the development of an all solid state cell <98,112>.

Some indication as to the nature of the mobile ions can be obtained by examining the conductivity levels exhibited by various polymer-salt complexes prepared from a particular polymeric host, under constant reduced temperature conditions, when the same number of charge carriers have been generated in the materials. Wholly cationic conduction would be suggested if no change in the conductivity occurred as the anion was varied in the salt complexes containing a common cation. Similarly purely anionic conduction would be suggested if the conductivity was unchanged when complexes containing different cations and a common anion were examined.

Direct determination of the character of the mobile species in the polymer-salt complexes is, of course, possible by measurement of the transport numbers <98,111,113-117>.

1.6 Development of a Superior Polymeric Host.

In the anticipation of developing a polymer-salt complex which would exhibit higher levels of conductivity, particularly at room temperature, than is demonstrated by the alkali metal salt complexes of PEO, solid state electrolytes based on network polyethers, polyether block copolymers, and comb-shaped polymers containing ether sidechains have been prepared.

1.6.1 Network Structures.

By introducing light crosslinking into a polymer, the crystalline component in a semicrystatlline complex can be reduced <118>, the mechanical properties of the low Tg polymer used to prepare the complexes are improved, particularly at high temperatures <119> and the formation of crystalline material could be inhibited in potentially crystallizable, amorphous complexes which would enhance the long term storage properties of such materials <120>.

The introduction of crosslinks into a potentially useful linear polymer would therefore serve to enhance the stability of the polymeric host, and in addition, improved conductivity levels could be envisaged due to the increased amorphous content of the sample, by the modification of the useful polymeric host in such a manner.

Extensive crosslinking should be avoided since it would be detrimental to the use of the material as a solid state electrolyte. The Tg of a crosslinked polymer is higher than that of a non-crosslinked material <118> and similar to the effects noted in linear polymers, the Tg would be further enhanced on dissolution of the salt in the polymer <121>. It is therefore important to ensure that the motions of the polymer molecules are not impeded dramatically by the introduction of a high density of crosslinks.

Network polymer-salt complexes based predominantly on PEO and PPO have been extensively studied <11,95,107,119,121-129>, however, marked improvement of the conductivity levels exhibited by the PEO-alkali metal salt complexes was not noted.

1.6.2 Block Copolymers.

Although non-crystallizable liquid electrolytes were prepared from a random copolymer based on EO and PO units <55>, more interesting materials which contained dimethyl siloxane and EO units were prepared by Nagaoka et al.<59>. Complexes prepared from poly(dimethyl siloxane-co-ethylene oxide) exhibited conductivity levels of 1.5×10^{-4} Scm^{-1} at 298K which was a vast improvement on the levels of conductivity exhibited by similar complexes prepared from PEO. The introduction of the siloxane units into

PEO allowed increased carrier mobility in the system, however, it was also suggested that dissolution of the salt in the polymer was suppressed by the siloxane units, which affected the carrier ion generation processes in the complexes.

1.6.3 Comb-Shaped Polymers.

The development of comb-shaped polymers for use as polymeric electrolytes, has focussed on the use of polymer backbones which have low Tg values. These materials are therefore inherently flexible as required for use in solid state electrolytes. To provide a solvating environment, characteristic of the materials which allow efficient solvation of metal cations, EO sidechains have been substituted onto the polymer backbone. The sidechain units hang pendent from the polymer backbone but, provided they are short and flexible, they do not impede the reorientational freedom of the polymer <120>.

One of the most interesting materials to be developed recently is a comb-shaped polymer-salt complex based on a phosphazene mainchain <17-19,130,131>. The phosphazene mainchain (which comprises of alternating phosphorus and nitrogen atoms) is inherently one of the most flexible macromolecular backbones known and exhibits Tg values of 183-193K when small or highly flexible sidegroups are attached. On addition of lithium and silver salts to poly[bis(methoxyethoxyethoxide)phosphazene], i.e. MEEP, conductivity levels two or three orders of magnitude higher than those for PEO complexes were reported <19>. Complexes were also prepared using the salts of divalent and trivalent cations, however, the conductivity levels of the materials decreased as the valency of the cation in the complex increased <18>.

Comb-shaped polymers prepared from a siloxane <132-135> or a methacrylate <58,106,128,136-141> backbone have also been studied. EO sidechains were introduced into the polymers and amorphous materials with Tg values in the range 180-220K can be prepared, provided the sidechain length is short. Crystallinity was detected in polymers containing long EO sidechains and therefore these materials were of less immediate interest. Dissolution of various salts in the amorphous polymers was possible but the salt complexes formed exhibited lower levels of conductivity than observed for complexes prepared from MEEP.

It can therefore be envisaged that by varying the composition of a comb-shaped polymer, a novel structure could be identified, which on doping, would exhibit exceptionally high levels of conductivity at low temperatures.

Since the development of such a polymeric host is of great interest, the aim of this piece of work was to expand the limited study of salt complexes prepared from comb-shaped polymers. A new range of polymeric hosts were therefore prepared, and examined when doped, which were based on either an itaconic acid or a vinyl ether backbone and incorporated either EO or PO sidechains, since these materials were seen to have the potential to be exciting new structures for use in solid state electrolytes, as discussed below.

1.7 Itaconic Acid Comb-Shaped Polymers and Related Structures.

A range of comb-shaped polymers, based on an itaconic acid backbone and containing methoxyterminated EO sidechains, were previously prepared by Ferguson ‹142›. These materials were fully amorphous and had low Tg values. Due to the character of the sidechains in the polymer these materials were potentially capable of solvating metal ions to form polymer-salt complexes. It was therefore of interest to examine the solvating abilities of these polymers and also determine the conductivity levels which could be achieved in any polymer-salt complex prepared.

Since the itaconic acid based comb-shaped polymers can incorporate two sidechains per monomeric unit, unlike the methacrylate systems which contain only one, a higher density of EO sidechains per monomeric segment can be introduced into the polymers based on itaconic acid. It was considered possible that this feature could be advantageous in attempting to develop a polymeric host, for use in a solid state electrolyte, which was significantly superior to PEO, particularly at low temperatures.

In this study, throughout the temperature range, the length of sidechain in the polymeric host and the character of the incorporated salt, were considered of vital importance.

Concentrating initially on complexes prepared from itaconic acid based comb-shaped polymers containing EO sidechains, conductivity levels were examined as a function of increasing sidechain length in the polymeric host and as a function of salt concentration. Changes which occurred when the incorporated salt species was varied were also noted.

Until this study, there were no reports concerned with the preparation of comb-shaped polymers containing PO sidechains and therefore the conductivity levels exhibited by complexes prepared from such materials had not been examined. It was possible that, similar to the effects noted in EO materials, complexes prepared from a comb-shaped polymer containing PO sidechains would exhibit higher levels of conductivity than complexes prepared directly from the linear PPO.

A comb-shaped polymer based on an itaconic acid backbone, and containing PO sidechains was therefore prepared. The conductivity levels exhibited by complexes prepared from this material were measured and compared initially with those reported for PPO based complexes. To consider how the solvating ability of the itaconic acid based polymer was affected by the presence of PO and EO sidechains, and how the character of the sidechain of the polymer affected the conductivity levels which could be achieved, the results obtained for complexes prepared from itaconic acid with PO and EO sidechains were compared.

A comb-shaped polymer containing a vinyl ether backbone and EO sidechains was prepared. The amorphous material had a low Tg and dissolution of various inorganic salts was possible in the flexible structure. The conductivity levels exhibited by salt complexes prepared from this material were of great interest since it was possible to use these results to compare directly the effect of backbone variation and also sidechain density on the conductivity levels exhibited by the comb-shaped polymer-salt complexes.

Poly(vinyl methyl ether) (PVME) is an isomer of PPO. This amorphous polymer has a low Tg and similar to the other polyethers, contains ether oxygen atoms spaced regularly along the polymer chains, however, the ability of this polyether to solvate metal cations has not yet been investigated. The solubility of a range of salts in this polymer was examined in this study and the conductivity levels which could be achieved by polymer-salt complexes prepared were also noted.

The overall aim of this study was therefore to investigate the solvating abilities of a range of comb-shaped polymers containing polyether sidechains and from the results of the conductivity studies carried out on a variety of polymer-salt complexes, prepared from these materials, establish how the character of the polymeric host and the incorporated inorganic salt affected the levels of conductivity which could be achieved by such solid state electrolytes.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES AND SYNTHESIS

2.1 Instrumentation.

2.1.1 Molecular Weight Determination. <143>

Polymeric materials were characterized by determining the number average molecular weight (Mn) using techniques based on the colligative properties of dilute solutions. In this study both vapour pressure osmometry and membrane osmometry were used to determine Mn.

2.1.1.1 Vapour Pressure Osmometry. (v.p.o.)

V.p.o. is a relative technique which relies on instrument calibration using a low molecular weight material of high purity such as benzil or methyl stearate. The technique is based on vapour pressure lowering by a solute and involves the suspension of drops, of a solvent, and a solution, on matched differential thermistors, located in an isothermal chamber of saturated solvent vapour. Isothermal transfer of solvent to the solution occurs due to the concentration gradient. At the solution sensor, owing to the solution's vapour pressure differential, the rate of solvent condensation is greater than the rate of evaporation and the resulting excess heat of condensation causes a temperature increase in the solution and it's sensor. When equilibrium is attained the temperature difference between the two drops (ΔT) is a measure of the vapour pressure lowering by the solute. The two thermistors form part of a Wheatstone's bridge and ΔT for various polymer concentrations (c) is recorded as a difference in resistance (ΔR). The number average molecular weight can be calculated using equation 2.i by extrapolating the data to $c=0$

$$Mn = \frac{K^*}{(\Delta R/c)_{c \to 0}} \qquad 2.i.$$

K^* is a calibration constant, determined in the solvent and at the temperature of operation, by measuring ΔR for solutions of known concentration (c) prepared from standard compounds of known molecular weight. K^* can then be used to evaluate the number average molecular weight of polymeric samples in the range 50-20,000 $gmol^{-1}$ although the upper limit is often practically found to be 15,000 $gmol^{-1}$.

The instrument used in this study was a Hewlett Packard 302B model Vapour Pressure Osmometer. Mn determinations were carried out at 303K using either toluene or methyl ethyl ketone (MEK, butan-2-one) as a solvent. Solutions of benzil (210.23 $gmol^{-1}$) were prepared (4-10 gdm^{-3}) and used to calibrate the instrument. Calibration constants, $K^* = 1.04 \times 10^4$ Vg^{-1} dm^3 and $K^* = 2.8 \times 10^4$ Vg^{-1} dm^3 were found for toluene and MEK respectively. Polymer solutions were prepared in the concentration range 10-50 gdm^{-3} .

2.1.1.2 Membrane Osmometry. (m.o.)

Membrane osmometers are characterized by the use of a semipermeable membrane which is permeable to solvents and other low molecular weight materials but impermeable to macromolecular solutes. Such membranes are used to separate osmometer compartments, where one compartment contains pure solvent and the other a solution of dissolved polymer.

Assuming the hydrostatic pressure is initially equal in the two osmometer compartments, a difference of solvent chemical potential across the membrane causes solvent to diffuse through the membrane into the solution, which reduces the chemical potential difference across the membrane. The pressure reduction required to equalize the chemical potential on both sides of the membrane is the osmotic pressure.

The Van't Hoff law relating osmotic pressure and molecular weight

$$\frac{\pi}{c} = \frac{RT}{Mn} \qquad 2.ii.$$

where R is the gas constant and T is the temperature in Kelvin, is applicable only in solutions which obey ideal conditions i.e. theta solvents. For other solvent conditions it is convenient to express osmotic pressure in a virial (power) series.

$$\pi/c = RT\ (A_1 + A_2c + A_3c^2 + \ldots\ldots) \qquad 2.iii.$$

where $A_1 = 1 / Mn$

The coefficients of the concentration terms are the virial coeffcients. The second virial coefficient A_2 is indicative of the excluded volume of the polymer molecules while it has been shown that the third virial coefficient A_3 may often be set equal to zero.

Calculation of the molecular weight requires the determination of the osmotic pressure at several concentrations (c). By calculating π/c for each solution and plotting π/c against c a straight line should be obtained. With the extrapolation of the data to infinite dilution the Mn can be determined from the intercept.

In this study a Knauer Membrane Osmometer and detecting bridge were used. Measurements were carried out at 306K using MEK as a solvent. Membranes,(Sartorious 11539 50N, regenerated cellulose) were conditioned stepwise to MEK and the instrument was calibrated by the application of a known external pressure. Polymer solutions were prepared (2-10 gdm^{-3}) and introduced into the instrument in the order of increasing concentration. For each solution the pressure change detected by a transducer was displayed as a signal proportional to the pressure change on a chart recorder. Using this instrument, molecular weights greater than 20,000 gmol^{-1} were determined successfully.

2.1.2 Thermal Analysis.

2.1.2.1 Differential Scanning Calorimetry. (d.s.c.)

D.s.c. is a technique used to detect any phenomena that are accompanied by an enthalpic change. Details of the theory and design of differential scanning calorimeters have been desribed by Watson and al. <144> and O'Neil <145>.

D.s.c. is a technique in which the heat flow into or from a sample and an inert reference is measured as a linear function of temperature. In the equipment the heat flow is measured by keeping the sample and the inert reference thermally balanced by changing a current passing through the heaters under the two chambers. The variation in power required to maintain this level during a transition is measured. A signal, (dH/dt) proportional to the power difference is plotted on one axis of an X-Y recorder and temperature is plotted on the other.

The instrument used for analysis in this study was a Perkin

Elmer model D.S.C.-2 equipped with a low temperature mode accessory. Measurement was therefore possible in the temperature range 100-1000K. Operation of the instrument was normally carried out in the sub-ambient mode where dry helium was used as the purge gas and liquid nitrogen was used as the cooling fluid. Analysis of samples in the above-ambient mode was carried out using oxygen-free nitrogen as the purge gas. The scan rate used was 20 $Kmin^{-1}$ for all samples.

The Tg is manifest by a step change or a baseline shift in the output voltage as a function of scanning temperature. It is possible to define Tg as either the temperature of onset of the step change or the midpoint of the resulting inflexion of the recorder trace. In this work the latter was employed. Figure 2.1 demonstrates this.

In the d.s.c., when a sample material is subjected to a linear temperature increase, the rate of heat flow into the sample is proportional to its instantaneous specific heat. The absolute specific heat, Cp(T), can be obtained by measuring this rate of heat flow and comparing it with that for a standard material under the same conditions.

Heat capacities for polymer samples were determined using the following procedure. Isothermal baselines were obtained at the lower and upper temperatures of the scanning range using empty aluminium sample pans. These two isothermal baselines were used to interpolate the reference baseline over the same scanning section. The scan was repeated with a sample of known mass in the sample pan and a trace of dH/dt against time was recorded. The recorder deflection occurred due to the

Figure 2.1. Schematic diagram indicating how the glass transition temperature was determined using d.s.c. analysis.

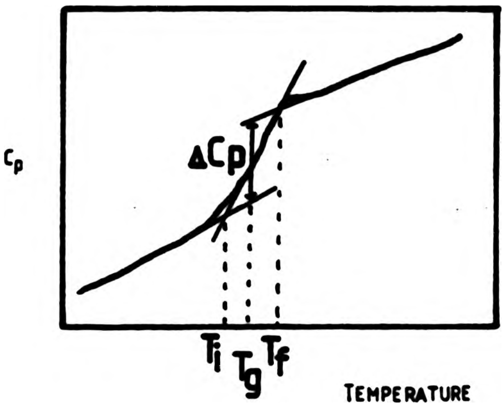
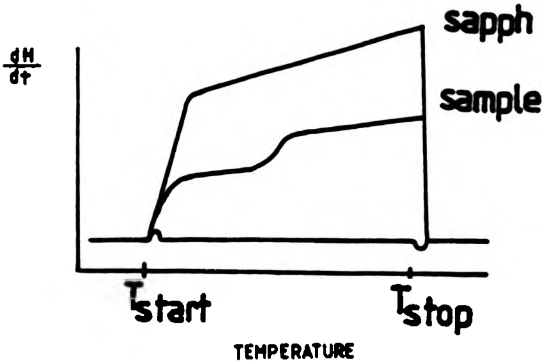


Figure 2.2. Schematic diagram showing the d.s.c. recorder trace obtained during the measurement of the heat capacity change at Tg in a polymeric sample.



absorption of heat by the sample, and thus

$$\Delta H/dt \quad = \quad m\ Cp\ (dT_p/dt) \qquad 2.iv$$

where m is the mass of the sample and dT_p/dt is the programmed rate of temperature increase. The procedure was repeated with a known mass of reference sapphire in the sample pan, the heat capacity of which is well established <146>, and a new trace was recorded. The two ordinate deflections are thus obtained D(sample) and D(sapph) as shown in Figure 2.2. at any chosen temperature which allows determination of the ratio of the Cp values of the sapphire and the sample. Using Equation 2.v. the value of Cp for the sample can be evaluated.

$$Cp(sample) = \frac{D(sample).m(sapph).Cp(sapph)}{D(sapph).m(sample)} \qquad 2.v.$$

Evaluation of Cp(sample) at convenient temperature intervals in the chosen scan range provided Cp versus temperature data. During analysis all data were collected by an Apple II microcomputer system and data processing was carried out using software developed for the purpose, to obtain Cp versus temperature data. The Tg and corresponding step change in specific heat (ΔCp) at the transition were determined from these data.

2.1.2.2. Thermogravimetric Analysis. (t.g.a.)

The modern thermobalance is designed to produce a continuous record of weight loss as a function of temperature. Weight loss can also be measured as a function of time at constant temperature.

In this study a Perkin Elmer Thermogravimetric system model TGS-2 connected to the Perkin Elmer DSC-2 temperature programmer was used. Analysis of the samples was carried out under a nitrogen atmosphere using a heating rate of 20 $Kmin^{-1}$. Results were collected as % wt loss vs temperature.

2.1.2.3 Torsional Braid Analysis. (t.b.a.)

T.b.a. is a technique of thermomechanical analysis developed by Gillham <147>. It is an extension of the torsion pendulum method of analysing materials, which allows investigation of systems which cannot support their own weight. Since the resultant test piece is a composite and not a pure polymer of known dimensions, absolute values cannot be determined during experimentation.

A torsion braid analyzer model 100B, manufactured by Chemical Industries Corporation of New York, which had been modified slightly was used in this work. The frequency of measurement was approximately 1 Hz and and the instrument was capable of operating over the temperature range 83-773 K.

A specimen was prepared by impregnating a multifilament glass braid substrate with a concentrated solution of test material. After complete removal of the solvent, the polymer braid composite was suspended in the sample chamber, which was continually flushed by nitrogen gas. Recording the temperature using an iron-constantan thermocouple, the instrument was cooled by the circulation of nitrogen gas (liquid nitrogen cooled). Data were collected only when the instrument had equilibrated at the low starting temperature. Allowing the temperature of the instrument to increase naturally until 273K, a heater was then used to increase the temperature at a controlled rate of ~2 Kmin^{-1}. Torsional oscillations were initiated every 2.5 minutes during the temperature scan and the output damped sinusoidal waveform was sampled, and collected by an Apple II microcomputer. (The data processing algorithms were fully described previously ‹142›.)

From the data collected the logarithmic decrement (LD) and the relative rigidity ($1/p^2$), which is proportional to the modulus of the polymer glass fibre composite were calculated for each oscillation. The Tg is manifest by a maximum in LD and a large drop in $1/p^2$ as the temperature range is scanned.

2.1.3 Conductivity Instrumentation.

Conductivity measurements were carried out as a function of increasing temperature using a PT1 Digital Conductivity Meter which generated a low power a.c. voltage (~1 volt) at 1.49 kHz.

The conductivity meter operates basically on the Ohm's Law principle

$$I = V / R \qquad 2.vi.$$

where R is the resistance (in ohms), I is the current (in amperes) and V is the electromotive force (emf, in volts). The resistance of the material between the cell plates is proportional to the distance between the plates (l, cm) and inversely proportional to the cross-sectional area (A, cm^2)

of the plates. By introducing a proportionality constant(ρ), the specific resistance of the material, it is possible to write

$$R = \rho \,.\, 1/A \qquad 2.\text{vii.}$$

where ρ has the units ohms-centimetres. The specific conductance or conductivity (σ) of the material is the reciprocal of the specific resistance.

$$\sigma = 1/\rho = 1/R \,.\, 1/A \qquad 2.\text{viii.}$$

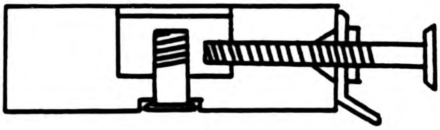
For a given cell the distance between the plates and the crossectional area does not change and a cell constant (C) can be introduced.

$$\sigma = C / R \qquad 2.\text{ix.}$$

Electrode blocks were prepared using an inert insulating material (tuffnall). Silver discs were cut ($\sim 1cm^2$) and silver soldered to a metal block. This complete unit was inserted into the tuffnall block so that the electrode surface was coplanar with the machined surface of the block. A schematic diagram of the half cell block is shown as Figure 2.3. Spacer shims were used to separate a pair of matched electrode blocks by a known distance ($\sim$0.1cm), and the complete cell block arrangement was clamped together firmly during measurements. Using a solution of potassium chloride (1×10^{-3}M, 298K), cell constants of 0.092 and 0.097 were determined for two different cell assemblies used during the study.

In this study the conductivity meter was calibrated regularly using a standard resistance box. The meter compared the resistance of the test sample with the resistance of an

Figure 2.3. Schematic diagram of the half cell block used during conductivity experiments.



accurate resistor in the circuit. The reciprocal resistance of the material was displayed in microsiemen (μS, where siemen is unit corresponding to reciprocal ohm or mho).

A thermostatically controlled oven was used to study the temperature variation on the conductivity of samples. Although the apparatus was equipped with a cooling mode, most conductivities were measured as a function of increasing temperature. A chromel-alumel thermocouple placed in the heating chamber, (with the reference junction at 273K), was used to determine the temperature of the sample during the experiments. After changing the temperature, a chart recorder was used to ensure that the system had stabilized before the temperature and conductance data were collected.

Conductivity measurements were carried out inside a dry box where the atmosphere was continuously circulated over fresh phosphorus pentoxide, using a small compressor. The transfer compartment to the dry box was flushed with a dry nitrogen supply during transfer operations, to maintain anhydrous conditions at all times.

To measure the conductivity of a material, the dry sample was loaded into the cell and rapidly transferred to the dry box. After connecting the cell block to the conductivity meter, the temperature was increased to ~353K for several minutes. The polymer sample was then allowed to cool to room temperature and stabilize overnight. After noting the temperature and conductance of the sample at room temperature, the temperature was increased and the new details were noted after ~1 hour. Data were in general collected from room temperature to ~410 K. Similar principles were applied when collecting data as a function of decreasing temperature.

Using the conductance data in conjunction with the pertinent cell constant for the cell assembly used during the experiment it was possible to calculate the specific conductance or conductivity of the sample using Equation 2.ix.

2.1.4 Spectroscopic Techniques.

^{1}H n.m.r. were recorded on either a Hitachi Perkin Elmer R-24 (60 MHz) or a Perkin Elmer R-32 (90 MHz) spectrometer. Samples were analysed using deuterated chloroform as a solvent and tetramethylsilane (T.M.S.) as the internal standard.

Infrared analysis was carried out using a Perkin Elmer 577 Grating Infrared Spectrometer, a Shimadzu I.R. 435 Infrared Spectrometer or a Perkin Elmer 197 Infrared Spectrometer. Samples were examined as films cast on sodium chloride plates.

2.2 Monomer and Polymer Preparation.

2.2.1 Ethylene Oxide Substituted Itaconic Acid Polymers - PDMEO$_n$I Series.

2.2.1.1 Monomers.

The above diesters were prepared <142> by conventional acid catalysed esterification of itaconic acid in toluene solution using a 3-4 mole excess of predried alcohol.
p-Toluenesulphonic acid was used as a catalyst and a Dean and Stark trap was employed to remove water. The monomethoxy terminated ethyleneglygols (alcohols) were all available as commercial products. The details of the alcohols used in the synthesis of DMEO$_n$I monomers are shown in Table 2.I.

Table 2.I

Details of Alcohols Used in Preparation of Ethylene Oxide Substituted Itaconic Acid Monomers.

n	Alcohol	Supplier	Code
1	2-methoxyethanol	M & B	DMEO1I
2	2-(2-methoxyethoxyethanol)	Aldrich	DMEO2I
3	Triethyleneglycolmonomethylether	Fluka	DMEO3I
5	3,6,9,12,15 –Pentaoxahexadecanol	Aldrich	DMEO5I
* 7	Poly(ethylene glycol methyl ether), MW=350	Aldrich	DPMeG 350I
* 12	Poly(ethylene glycol methyl ether), MW=550	Aldrich	DPMeG 550I

* Values of 'n' for these alcohols are average repeat unit lengths.

Table 2.II

Isolation Procedure for Ethylene Oxide Substituted Itaconic Acid Monomers.

Monomer	Method of Isolation	%Yield
DMEO1I	Distilled 393-397K, 0.1 mmHg.	59
DMEO2I	Distilled 415-419K, 0.01 mmHg.	30
DMEO3I	Pure diester extracted from aqueous solution of crude material using diethyl ether.	40
DMEO5I		30-40
DPMeG 350I	Crude diester dissolved in chloroform and washed with water to remove impurities. Pure material isolated from chloroform.	55
DPMeG 550I		30

Reaction times ranged from 24 hours for the short chain lengths to 2-3 days for the longer homologues. After reaction, the toluene solutes were washed first with aqueous sodium bicarbonate and then with water till the washings were neutral. After drying the toluene over anhydrous magnesium sulphate the crude diesters were obtained by removing the solvent using rotary evaporation. For n=1 and n=2 the pure diester was isolated using vacuum distillation. For all other diesters prepared the isolation procedure involved solvent extraction techniques. The details are shown in Table 2.II.

The pure diester products were characterized using i.r. and n.m.r. techniques and representative spectra are shown in Figures 2.4. and 2.5.

2.2.1.2 Polymerization

All of the polymers were prepared in bulk using the free radical initiator α,α' azo-bis-iso-butyronitrile (AIBN). Initiator was added to a preweighed polymerization flask and monomer was filtered as it was charged into the flask. After determining the weight of the monomer added, the flask was evacuated using a series of freeze thaw cycles and sealed under vacuum. Polymerization details are shown in Table 2.III. All polymeric products were isolated by several reprecipitations of chloroform solutions of the polymer into suitable solvent systems. Details of polymer isolation are shown in Table 2.IV. Ethylene dimethacrylate (Polysciences) was used as a crosslinking agent in some cases. A bulk polymerization was carried out using AIBN as the initiator (0.6 wt%) with crosslinking agent present as 3 wt% with

Table 2.III

Polymerization Conditions Used for
Ethylene Oxide Based Itaconic Acid Monomers

Monomer	wt% AIBN	Polym Temp./K	Time/hours	% Conv.
DMEO1I	0.4	328	43	55
DMEO2I	0.4	328	40	58
DMEO3I	0.4	333	120	53
DMEO5I	0.5	333	120	36
DPMeG 350I	0.1	333	72	32
DPMeG 550I	0.4	328	170	17

Table 2.IV

Isolation and Characterization of
Ethylene Oxide Substituted Itaconic Acid Polymers.

Polymer	Precipitant	10^{-3}Mn/gmol^{-1}	DPn *
PDMEO1I	diethyl ether	86	350
PDMEO2I	diethyl ether	131	392
PDMEO3I	75% diethyl ether/cyclohexane	44	104
PDMEO5I	50% diethyl ether/cyclohexane	90	150
PDPMeG 350I	70% diethyl ether/cyclohexane	37	47
PDPMeG 550I	90% diethyl ether/cyclohexane	28	23

* where DPn = Number average degree of polymerization.

Table 2.V

Details of Propylene Oxide Based Polymers.

Polymer	Mn/gmol^{-1}	DPn
PPO	993	17
PDPPGI	28000	13

Figure 2.4. Characteristic infrared spectra of EO substituted itaconic acid monomers.
a. DMEO3I
b. DPMeG 350I

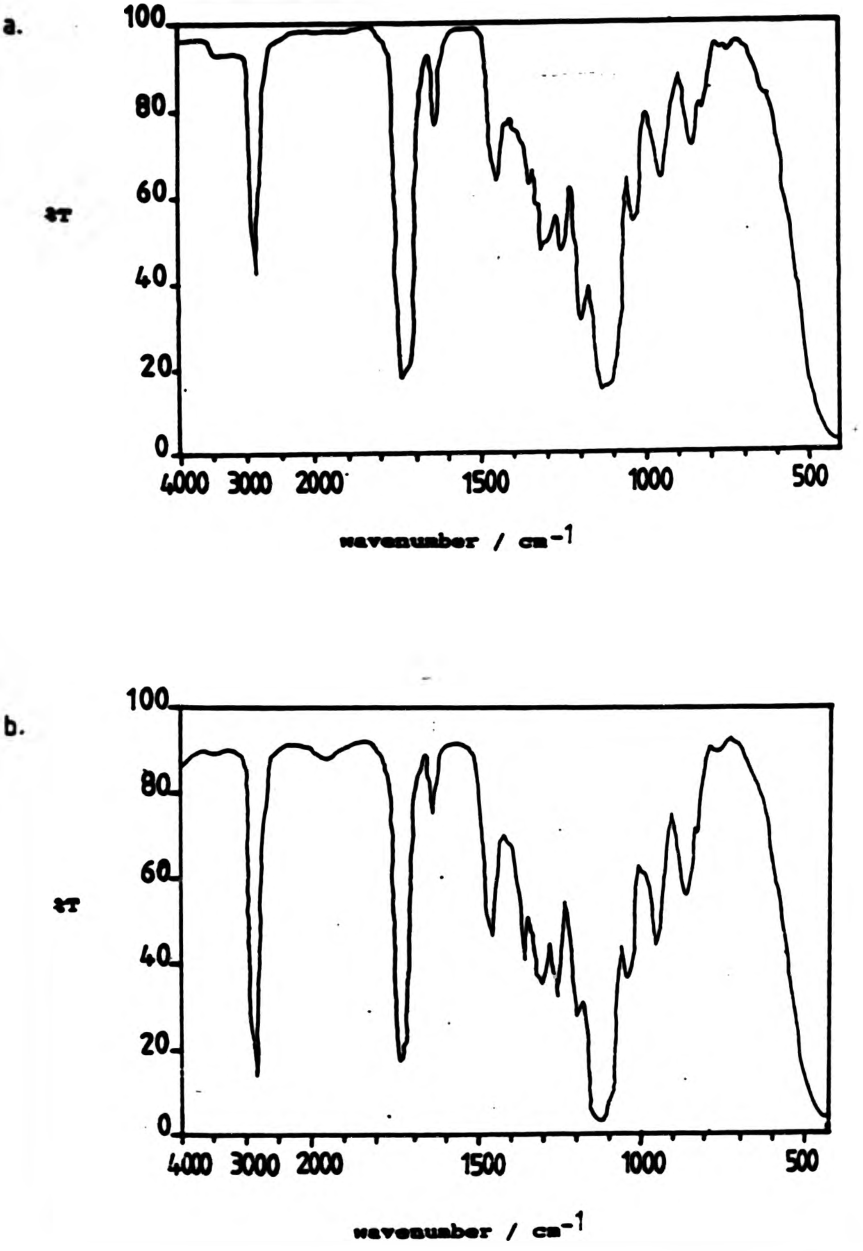
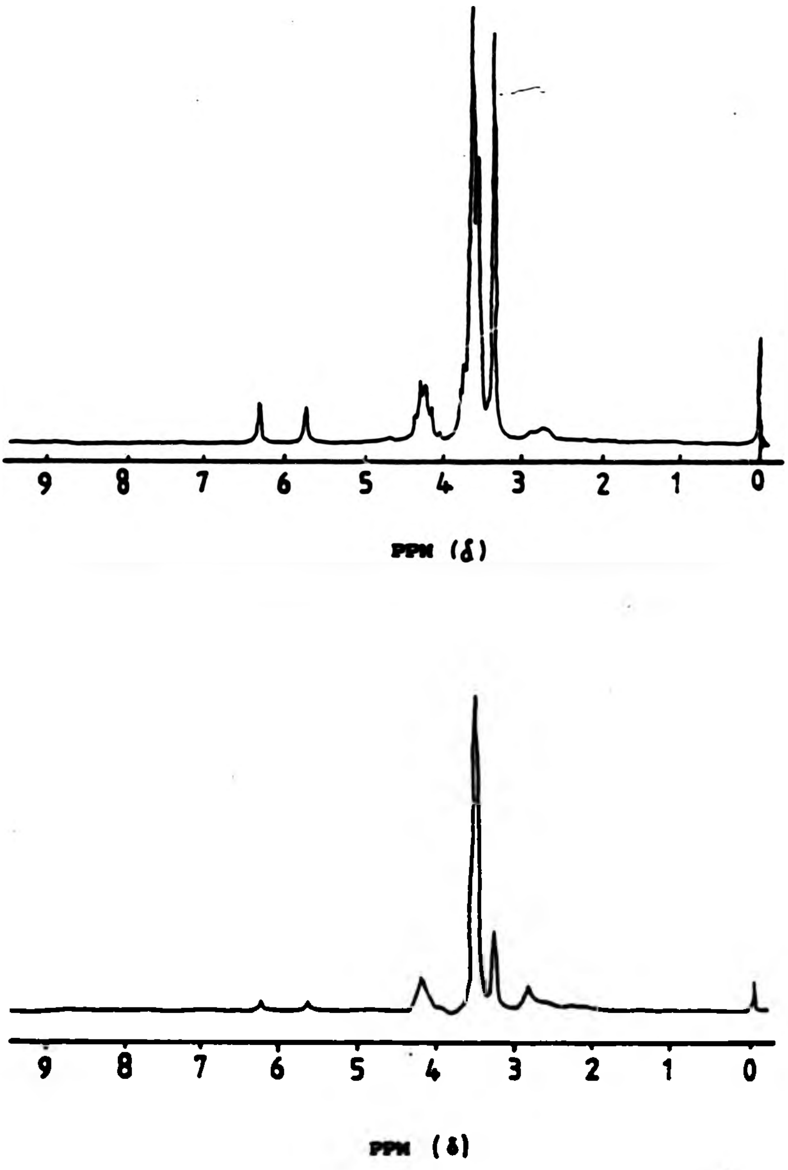


Figure 2.5. Characteristic ^{1}H n.m.r. spectra (60 MHz) of EO substituted itaconic acid monomers.

a. DMEO3I
b. DPMeG 350I



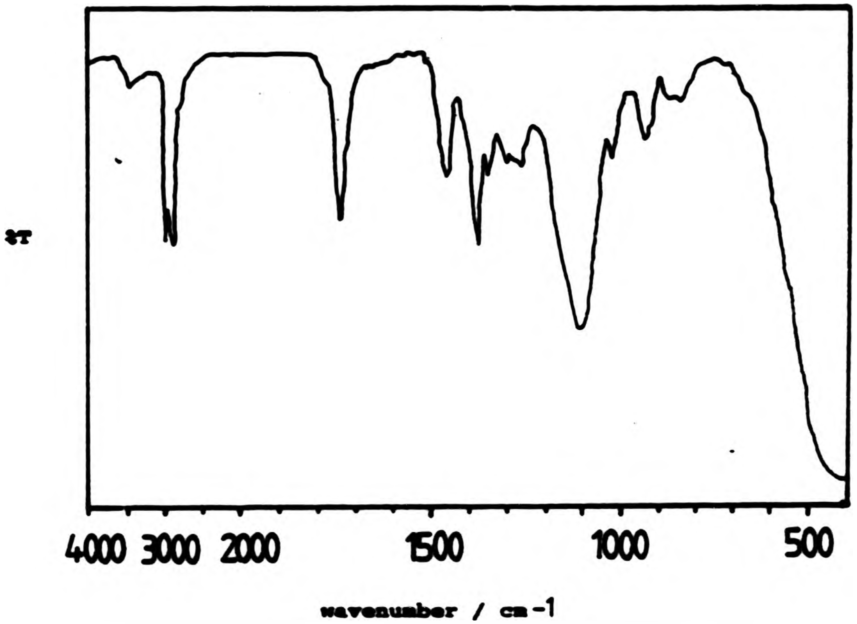
respect to monomer. After a reaction time of 65 hours at 333K the polymerization was terminated and soxholet extraction (chloroform) was used to separate uncrosslinked material from the product gel.

2.2.2 Polypropylene Oxide Substituted Itaconic Acid Polymer - PDPPGI.

Using the same esterification procedure as described in the previous section, a polypropyleneglycol diester of itaconic acid was prepared. Using a 4 mole excess of polypropyleneglycol 1025 (B.D.H.) the reflux was continued for 3-4 days. Toluene was then removed from the flask using rotary evaporation.

Polymerization was carried out in situ by adding AIBN, (~1wt%, assuming that the esterification reaction had produced successfully 60% of the theoretical yield), and the reaction was allowed to continue for 6 days at 343K. The desired polymeric material was isolated by adding the polymerization mixture to hexane. A cloudy solution formed initially and from this a yellow precipitate eventually settled. The precipitate was washed many times with fresh hexane and the viscosity of the material was noted to increase. The viscous liquid product was filtered and dried prior to characterization using i.r. and n.m.r. techniques. Figure 2.6. indicates the absence of monomeric material in the isolated product and the spectrum is consistent with the expected polymeric material.

Figure 2.6. The infrared spectrum of PDFPGI.



Details of the original and final polymeric materials are described in Table 2.V.

2.2.3 Ethylene Oxide Substituted Vinyl Ether Polymer - PVEMEO3.

2.2.3.1 Monomer

Using the method described by Mathias <148> the vinyl ether monomer VEMEO3, with a sidechain three ethylene oxide units long was prepared. Triethyleneglycol monomethyl ether (Fluka, 0.6 mol) was added to a three necked flask, fitted with a gas inlet and outlet and while bubbling nitrogen gas through the alcohol the temperature was raised to 393K. A catalytic amount of potassium metal (0.076 mol) was added to the flask slowly while the nitrogen flow was maintained. The originally clear reaction mixture turned yellow initially and then rapidly to dark brown. The temperature was then increased and allowed to stabilize at 448-458K before the nitrogen flow was replaced by acetylene gas. After bubbling acetylene gas through the solution for 2.5 hours the reaction was stopped when the mixture had solidified. Nitrogen gas was allowed to flush through the system until room temperature had been reached.

The solid reaction mixture dissolved easily in carbon tetrachloride and was washed several times with water to remove unreacted alcohol. On removal of the carbon tetrachloride the crude monomer was obtained (70%). The crude material was vacuum distilled (50%) and the highest boiling fraction only was redistilled under vacuum using a fractionating column. Degradation during distillation was a problem but the pure methoxy terminated triethylene oxide vinyl ether monomer was isolated as a fraction boiling at 331-333K 0.01 mmHg (~10%). I.r. and n.m.r. spectra of the product VEMEO3 are shown in Figures 2.7. and 2.8.

2.2.3.2 Cationic Polymerization of VEMEO3.

The cationic polymerization of VEMEO3 was carried out according to the homopolymerization procedure described by Mathias <148>. The initiator solution was prepared using freshly distilled BF_3-etherate (50μl) and freshly dried and distilled 1,2-dichloroethane (5ml).

Monomer VEMEO3 (3g, 0.016 mol) was added to a septum sealed polymerization flask containing a magnetic stirrer which had been flame dried under vacuum. The system was evacuated using several freeze thaw cycles and nitrogen gas was then introduced into the flask to 1 atmosphere pressure. The polymerization mixture was brought to ice temperature (273K) before initiator solution (50 μl) was added slowly to the stirred monomer using a syringe. The polymerization mixture was stirred continually at 273K and within several hours the viscosity of the mixture had increased to such an extent that stirring was no longer possible. The polymerization mixture was dissolved in chloroform and reprecipitated several times into cyclohexane. The pale yellow polymer (PVEMEO3) was obtained in 80% yield. The i.r. spectrum, indicating the absence of the vinyl group in the material, is shown as Figure 2.9. Using m.o. the molecular weight of the polymer was determined as 30,000 $gmol^{-1}$.

Figure 2.7. The infrared spectrum of VEMEO3

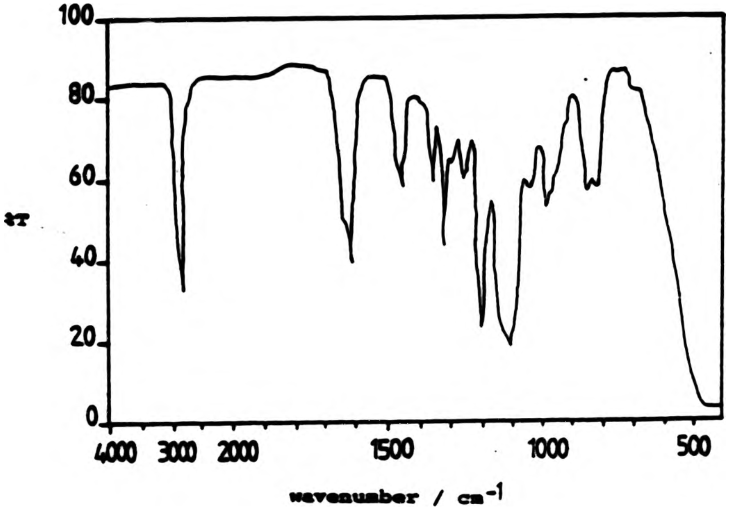


Figure 2.8. The ^1H n.m.r. spectrum (90 MHz) of VEMEO3.

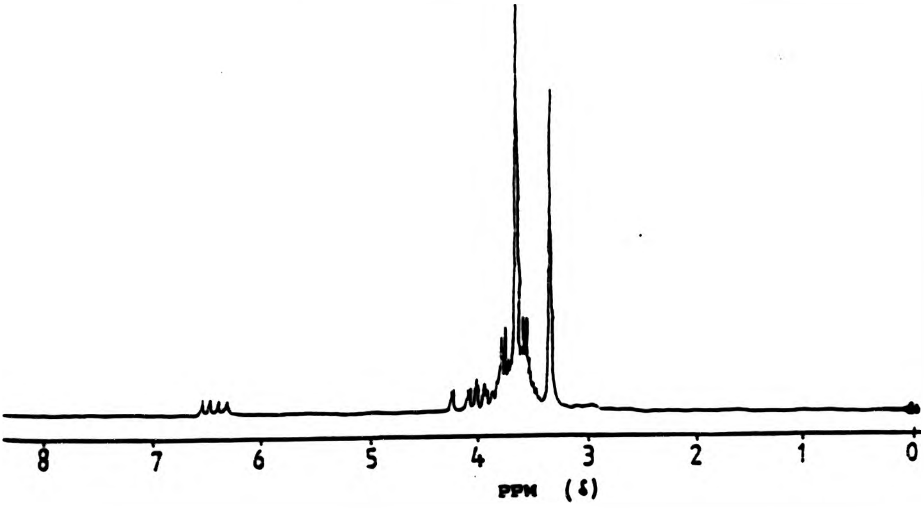
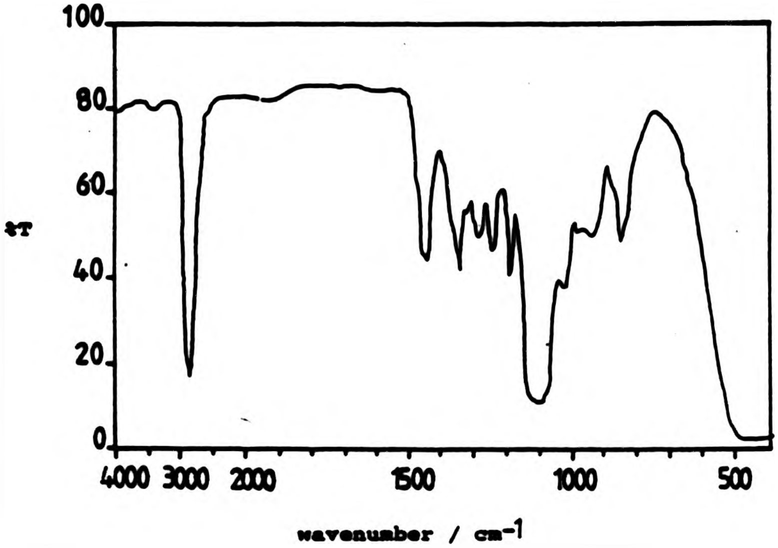


Figure 2.9. The infrared spectrum of PVEMEO3.



2.2.4 Preparation of Poly(vinyl methyl ether) - PVME.

PVME was obtained as a commercial product from Polysciences. Several times, the material was dissolved in acetone and reprecipitated into hexane, before determining the molecular weight of the sample as 27,000 gmol^{-1} , using m.o.

2.2.5 Preparation of an Ionomer.

2.2.5.1 Preparation of Monomethyl Itaconate (MMI).

Monomethyl itaconate is prepared and used in the laboratory regularly <142> using the method initially described by Baker <149>. Itaconic acid (0.5 mol) and acetyl chloride (~2 wt% with respect to itaconic acid) were added to a reaction flask and immersed in a partially heated oil bath. Reactants were brought to reflux rapidly and after stirring for 30 minutes at reflux the excess acetyl chloride and methanol were removed using rotary evaporation. As the residue cooled a white crystalline solid was formed. The material was recrystallized in 70% yield (Tm = 338-340K) from a toluene/hexane mixture at 273K.

2.2.5.2 Copolymerization of DMEO3I and MMI.

Using a bulk, free radical polymerization (AIBN), copolymers based on DMEO3I and MMI were prepared. In an initial copolymerization, a monomer feed of DMEO3I (~70wt%), MMI (~30wt%) and AIBN (0.3wt%), were charged into a flask which was sealed under vacuum after a series of freeze thaw cycles. After 4 hours at 338K the copolymer was isolated by precipitation into 50% diethylether/cyclohexane.

The concentration of MMI present in the copolymer was determined using potentiometric titration. A methanolic solution of the polymer of known concentration was prepared and titrated with sodium hydroxide (0.01M, MeOH). The copolymer composition was found to be 85wt% MMI (94 mol%) at an overall monomer conversion of 25%.

Using this information a series of three copolymers with MMI feed concentrations ranging from 1-9 wt% were prepared. After a polymerization time of 8 hours at 343K the copolymers were reprecipitated from chloroform solutions using 75% diethylether/cyclohexane. The copolymers were analysed as described above and the results are summarized in Table 2.VI.

An ionomer was prepared from copolymer-2 by neutralizing the MMI acid groups present with an equivalent molar amount of sodium hydroxide (0.1M,H_2O). The aqueous solution was stirred for several hours after adding the base and on removal of the solvent the resulting ionomer was thoroughly dried under high vacuum at 333K for 36 hours. The i.r. of the parent copolymer and derived ionomer are shown as Figures 2.10. and 2.11.

2.2.6 Preparation of Polymer-Salt Complexes.

All polymer samples and salts were dried under high vacuum at 333K for at least 3-6 days prior to use and were then stored under anhydrous conditions. Methanol was used as the solvent in the preparation of the polymer-salt complexes. Prior to use this solvent was distilled and stored over activated molecular sieves. Using Karl Fischer titration the

Table 2.VI

Copolymerization of DMEO3I and MMI.

Composition		Copolymer		
		1	2	3
Copolymer Feed	wt% AIBN	0.3	0.3	0.3
	wt% MMI	0.9	3.9	7.9
	mol% MMI	2.7	10.5	20.0
Copolymer Isolated	wt% MMI	12.4	14.8	37.5
	mol% MMI	29.2	33.8	63.7

Table 2.VII

Description of the solvating unit (S) in each polymer used to define the salt concentration in a polymer-salt complex.

Polymer	S	No.per monomer unit	Salt Conc.
PDMEO1I	ethylene oxide	2	$[M^+]/[EO]$
PDMEO2I	ethylene oxide	4	$[M^+]/[EO]$
PDMEO3I	ethylene oxide	6	$[M^+]/[EO]$
PDMEO5I	ethylene oxide	10	$[M^+]/[EO]$
PDPMeG 350I	ethylene oxide	14	$[M^+]/[EO]$
PDPPGI	propylene oxide	34	$[M^+]/[PO]$
PVEMEO3	ethylene oxide	3	$[M^+]/[EO]$
PVME	ether oxygen	1	$[M^+]/[O]$

Figure 2.10. The infrared spectrum of DMEO3I/MMI Copolymer.

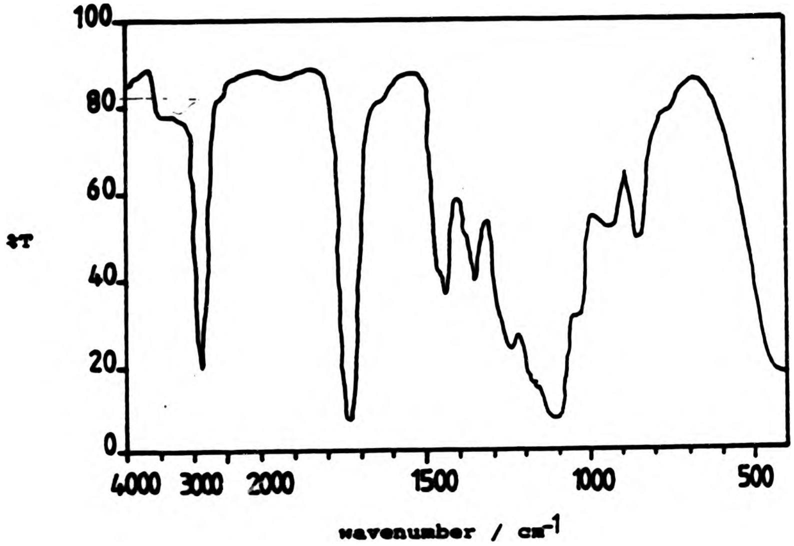
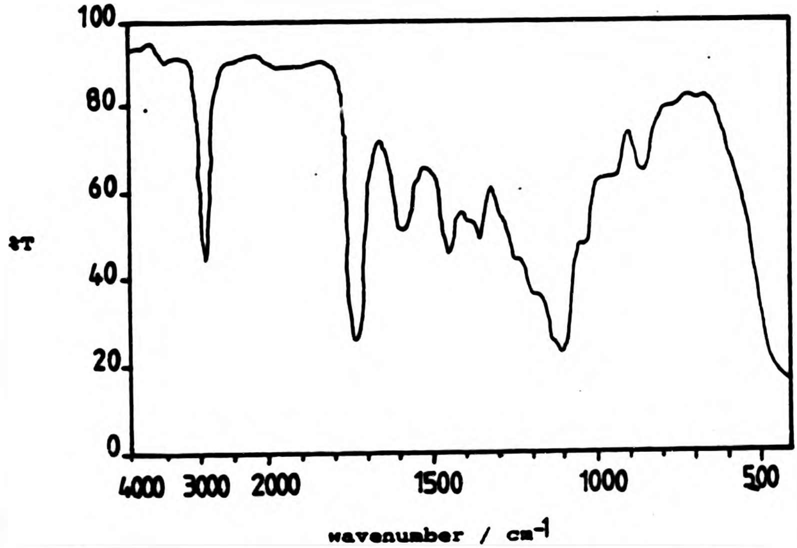


Figure 2.11. The infrared spectrum of DMEO3I/MMI/Na Ionomer.



moisture content of the solvent was determined as <0.1%.

A wide range of polymer-salt complexes were examined in this study and in Table 2.VII., the character of the solvating unit (S) in each of the polymeric hosts is shown. Salt concentrations in the complexes were described using $[M^+]/[S]$, i.e. the number of moles of cations per mole of solvating units. In general, complexes containing salt in the concentration range $[M^+]/[S]=0.0125$ to 0.25 were examined in this study.

A known weight (~0.5g) of dried polymer was added to a flask. A predetermined quantity of salt was weighed out and added to the polymer sample. Dry methanol was added to the flask (~8ml) and the flask was sealed until the mixture had become homogeneous. Solvent was removed by evaporation and after complete loss of solvent all samples were dried under high vacuum at 330-340K for 2-3 days prior to use. All samples were stored in anhydrous conditions and using Karl Fischer titration the moisture content of the dried polymer-salt complex was determined as <0.01%.

Using this technique to prepare the samples it was found that predominantly transparent, homogeneous products were isolated, however, heterogeneous polymer-salt mixtures were obtained on removal of the solvent from a limited number of samples.

CHAPTER THREE

RESULTS AND DISCUSSION

ETHYLENE OXIDE SUBSTITUTED ITACONIC ACID POLYMER-SALT COMPLEXES.

3.1 Examination of the Pure Polymer.

Ethylene oxide (EO) substituted itaconic acid polymers were isolated as transparent materials which ranged from rigid solids through to viscous fluids depending on the length of the pendent chain. The Tg of the material decreased as the sidechain length ~~was~~ increased, as is shown from both the d.s.c. and t.b.a. results displayed in Table 3.I. As the length of the flexible sidechain is extended the backbone of the polymer is increasingly plasticized and this is reflected in the continual lowering of the Tg.

It was shown by Ferguson <142> that a minimum in Tg occurred in such itaconic acid based polymers when the number of atoms in the sidechain (I) was approximately 10, with longer sidechains resulting in an increase in Tg. In this present study it proved possible to synthesize two higher homologues, using heterodisperse, methoxy terminated oligoglycols, corresponding to on average 22 and 37 atoms per sidechain. This corresponds to about 7 and 12 EO units per sidechain respectively. Due, presumably to a distribution of sidechain lengths, the Tg of PDPMeG 350I was even lower than the minimum detected by Ferguson. Incipient crystallinity of the sidechains, which is thought to be the reason for the increasing Tg at longer sidechain length, was only detected (using d.s.c.) in PDPMeG 550I. The oligomeric substituent DPMeG 550I, used as the sidechain for this last polymer is crystalline at room temperature, and so the inherent crystalline nature of the material is not suppressed when it is incorporated onto the itaconic acid backbone.

Examination of the properties of comb-shaped polymers based

Table 3.I

Glass Transition Temperatures measured for ethylene oxide substituted itaconic acid polymers using d.s.c. and t.b.a.

Polymer	I	Tg/K d.s.c.	 t.b.a.
PDMEO1I	4	303.0	300
PDMEO2I	7	252.0	255
PDMEO3I	10	218.5	230
PDMEO5I	16	216.0	-
PDPMeG 350I	22	212.5	-
PDPMeG 550I	37	219.5 [a]	-

[a] Tm at 298K

Table 3.II

Glass Transition Temperatures/K of sodium perchlorate doped ethylene oxide substituted itaconic acid polymers.

$[M^+]/[EO]$	PDMEO1I	PDMEO2I	PDMEO3I	PDMEO5I	PDPMeG 350I
0.0125	303.5	261.0	229.0	224.5	220.5
0.017	-	-	244.0	-	-
0.02	-	-	248.0	229.0	-
0.025	305.5	266.5	252.0	231.0	220.5
0.033	-	-	258.0	-	-
0.05	308.0	275.0	255.5	243.0	236.5
0.067	-	-	265.0	253.0	244.0
0.10	-	-	273.0	-	264.0
0.125	310.0	306.0	288.5	282.5	278.0
0.167	-	-	-	-	285.0
0.2	-	-	305.5	-	292.5
0.25	318.5	334.0	306.5	303.5	293.5

on a siloxane backbone <132-134> or a methacrylate backbone <136,137> revealed that crystallinity could be detected in polymers with sidechains on average 8 EO units long <133,134> or on average 22 EO units long <136>. It has also been suggested, however, that crystallinity only developed on storage of the methacrylate system containing approximately 22 EO units per sidechain <137>.

The isolation of amorphous comb-shaped polymers therefore appears to be greatly dependent on the character of the polymer backbone and also on the thermal history.

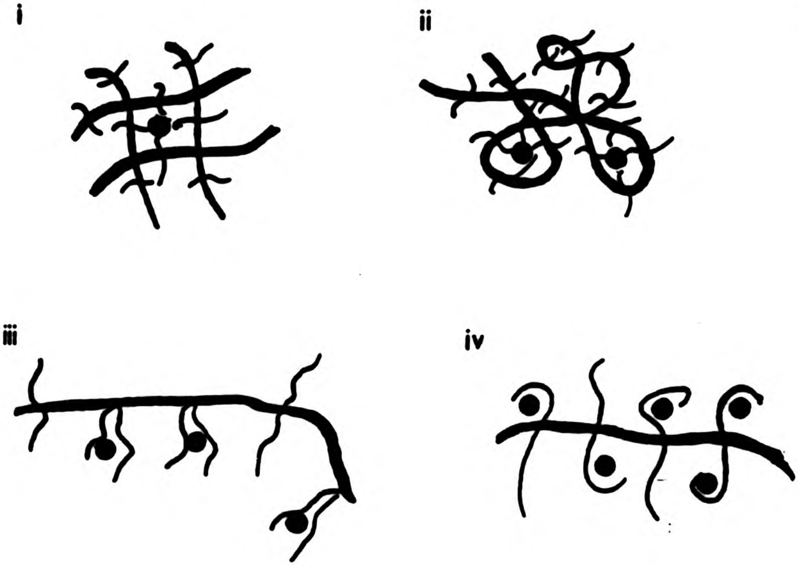
3.2 Polymer-Salt Interaction Geometries Possible in Itaconic Acid Comb-Shaped Polymer-Salt Complexes.

At least four types of polymer-salt interaction geometries can be visualized, as shown in Figure 3.1.

Both intermolecular (i) and intramolecular (ii) crosslinking of the polymer chains is possible or sidechain stiffening (iii and iv) effects could occur. The effect observed depends on whether the cation is coordinated to ether oxygen atoms which are in different polymer molecules (i), or coordination occurs within the same polymer chain (ii). Because the itaconic acid comb-shaped polymers contain two sidechains per monomeric unit intermonomeric sidechain coordination (iii) is possible. Provided the sidechain is long enough, a cation could be coordinated wholly by oxygen atoms within an isolated sidechain (iv).

Each of these coordination processes will result in a loss of flexibility and as the number of ions coordinated by the polymer is increased the extent of crosslinking or sidechain

Figure 3.1. Schematic diagram of the interaction geometries possible in itaconic acid based polymer-salt complexes.



stiffening by the polymer should also increase. At some critical salt concentration, further interaction between the salt and the polymer will not be possible and no further change in the crosslinking or sidechain stiffening effects will be detected.

One method of examining these effects is to record the Tg of the polymer-salt complexes as a function of salt concentration. In this study the measurement of the Tg of the polymer-salt complexes was carried out predominantly using d.s.c. techniques, however, similar behaviour was also determined using t.b.a., as described in Section 9.2.

3.3 Alkali Metal Perchlorate Salt Complexes.

3.3.1 D.S.C. Studies.

In Tables 3.II and 3.III the Tg values determined for complexes formed on addition of various concentrations of both $NaClO_4$ and $LiClO_4$ to the itaconic acid based polymers are shown. The Tg was measured as the concentration of the salt in the complex increased and the enhancement of the Tg (ΔTg) noted for each of the materials is shown graphically in Figures 3.2. and 3.3. The loss of flexibility noted in these polymers on addition of salts will be a result of the cation coordination processes described above.

3.3.1.1 Effect of Sidechain Length Variation.

From Figures 3.2. and 3.3. it is apparent that the relative increase of Tg on addition of salt to PDMEO1I is small even at high concentrations of salt. The slight enhancement of Tg noted, however, does indicate that interaction of the polymer

Table 3.III

Glass Transition Temperatures/K of lithium perchlorate doped ethylene oxide substituted itaconic acid polymers.

[M+]/[EO]	PDMEO1I	PDMEO2I	PDMEO3I	PDPMeG 350I
0.0125	303.5	255.0	230.0	217.5
0.017	-	261.0	240.0	-
0.02	-	-	243.5	-
0.025	-	267.5	246.0	221.5
0.033	307.0	-	-	-
0.05	-	275.0	253.0	232.5
0.067	-	-	256.0	241.5
0.1	-	-	269.5	-
0.125	309.5	296.0	288.0	261.5
0.167	313.0	-	-	-
0.2	-	-	312.5	-
0.25	315.5	323.0	309.0	281.0

Figure 3.2. Plot of ΔTg vs salt concentration for sodium perchlorate complexes of EO substituted itaconic acid polymers.

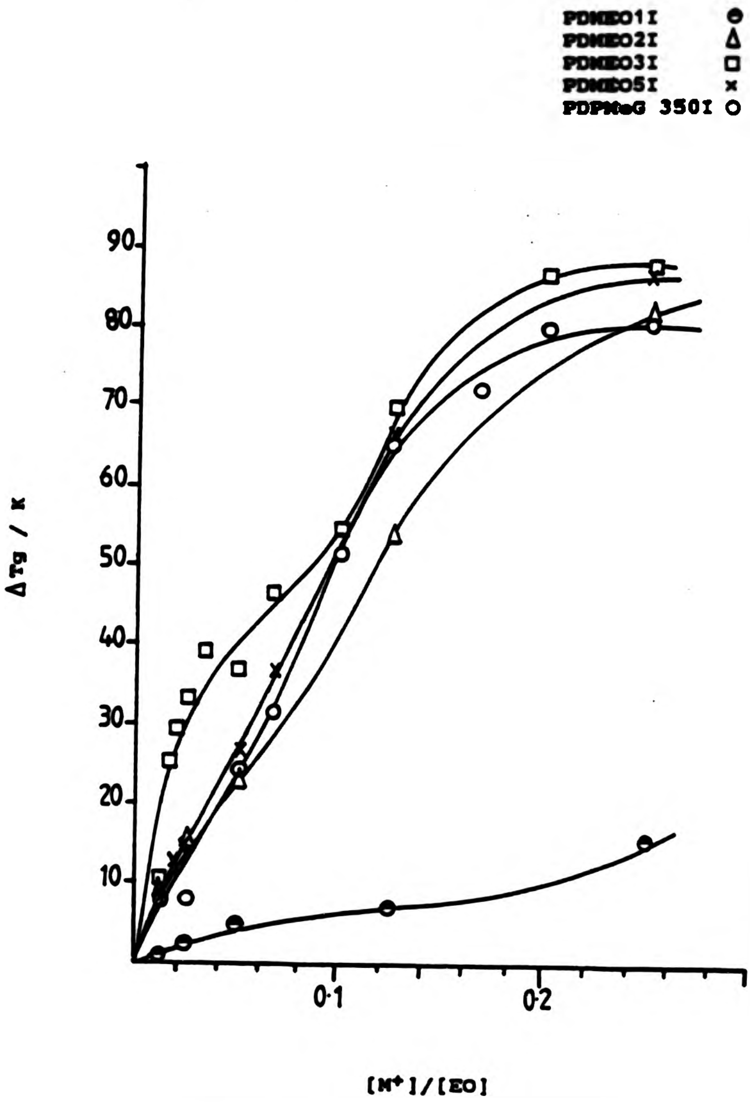
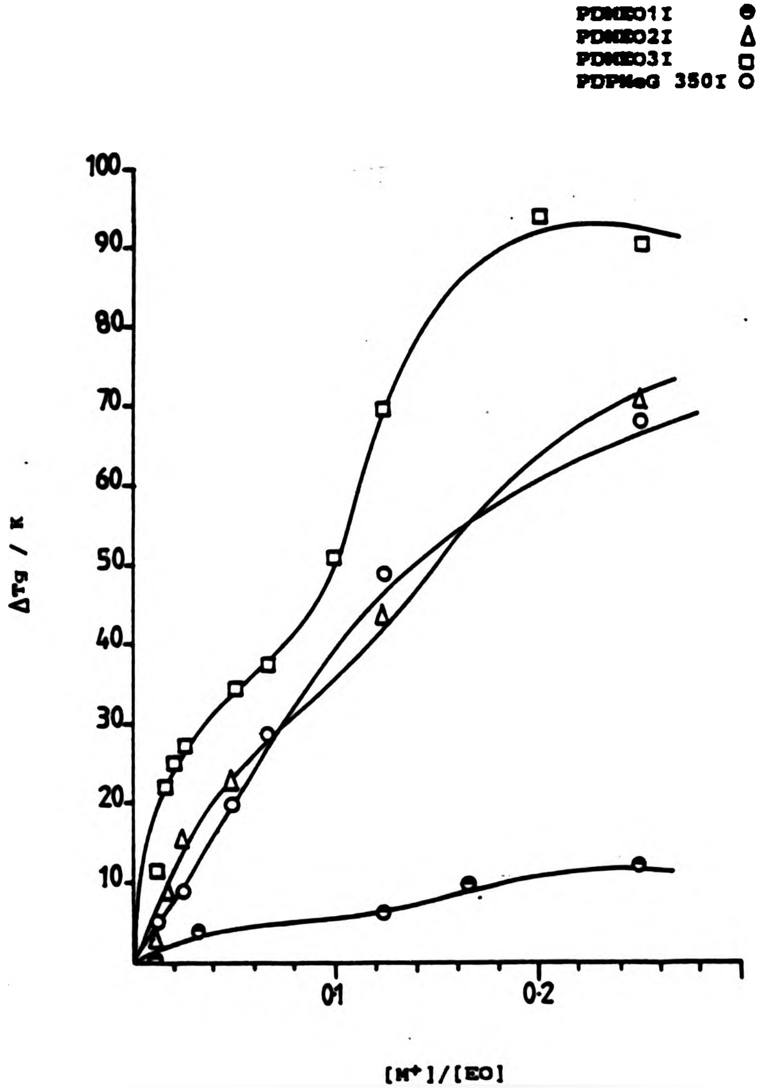


Figure 3.3. Plot of ΔTg vs salt concentration for lithium perchlorate complexes of EO substituted itaconic acid polymers.



and salt has occurred. In this polymer the sidechains are very short (one EO unit) and thus the opportunity for chain stiffening is relatively restricted, irrespective of the type of cation coordination that may occur.

When the EO sidechain is extended by one unit i.e. PDMEO2I the enhancement of Tg with salt concentration is markedly greater. However, at all salt concentrations, the most dramatic increase in Tg with added salt occurs in the polymer with EO sidechains three units long i.e. PDMEO3I. A slightly reduced enhancement of Tg is evident in the complexes prepared from PDMEO5I (in Figure 3.2.), and more markedly PDPMeG 350I (Figures 3.2. and 3.3.), when compared with the enhancement noted in the PDMEO3I complexes.

In undoped PDMEO5I and PDPMeG 350I the polymer backbone is effectively plasticized by the long EO sidechains. On cation coordination these sidechains are considerably stiffened, but the resultant gain in rigidity is apparently not sufficient to fully overcome the inherent flexibility of the sidechain groups, at least in comparison with the effect noted in PDMEO3I.

The resultant Tg of a salt complex prepared from these comb-shaped polymers would therefore appear to be dependent on both the inherent flexibility of the sidechain and also the rigidity that is introduced into the system by the crosslinking and sidechain stiffening effects which occur on coordination of cations.

3.3.1.2 Effect of Salt Concentration.

On addition of salt to each of the polymers a non-linear increase in Tg occurs with increasing salt concentration. At high salt concentrations a plateau value of Tg was observed in some polymer-salt complexes. This effect is indicative of the solubility limit of the salt in the polymer <51>. In the sodium perchlorate complexes of PDMEO3I, PDMEO5I and PDPMeG 350I this solubility limit is reached at a salt concentration of $[M^+]/[EO] = 0.14$. With $LiClO_4$ as a dopant, the solubility limit is observed at the slightly higher salt concentration of $[M^+]/[EO] = 0.17$, but only on addition of the salt to PDMEO3I. For the remaining systems, illustrated in Figures 3.2. and 3.3., plateau conditions are not observed in the concentration range examined.

It can be seen in the complexes prepared on addition of $LiClO_4$ to PDMEO2I, and also complexes prepared from PDMEO3I in particular, that the ΔTg versus salt concentration plot showed a marked inflexion at about $[M^+]/[EO] = 0.1$. This behaviour may be indicative of two overlapping coordination processes occurring simultaneously. At a particular salt concentration it can be suggested that a transition from one dominant coordination process to another may occur. A changeover from a predominantly crosslinking to a predominantly sidechain stiffening (i and ii to iii and iv in Figure 3.1) coordination process can be suggested as the reason for the noted irregular enhancement of Tg with salt concentration exhibited by these complexes.

It is difficult to envisage how it may be confirmed which of these two processes occurs initially at low salt concentration and which occurs on incorporation of high concentrations of salt.

3.3.1.3 Effect of Cation Variation.

The effect of changing the cation in the perchlorate salt from the lithium ion to the sodium ion can also be identified from consideration of Figures 3.2. and 3.3.

In PDMEO1I, independent of whether lithium or sodium perchlorate was added to the material, the increase in Tg with salt concentration was virtually the same. This suggests that solvation of lithium and sodium ions in the polymer was comparable, throughout the salt concentration range.

Addition of $LiClO_4$ to PDMEO2I resulted in the inflexion noted above when the salt concentration approached $[M^+]/[EO] = 0.1$. Similar effects were not apparent in the $NaClO_4$ complexes. The enhancement of Tg noted at salt concentrations below $[M^+]/[EO] = 0.06$ were comparable whereas at higher salt concentrations the Tg enhancement was much more dramatic in the $NaClO_4$ complexes. This could suggest that at high salt concentrations the sodium ions were solvated to a greater extent than the lithium ions, however, the differences noted in the ΔTg versus salt concentration plots may result only from the dominant coordination process in each complex being different at high salt concentrations. It is therefore difficult to compare the extent of solvation of the different ions in these complexes.

On introducing these alkali metal salts into PDMEO3I it was found that, in general, the dissolution of $NaClO_4$ was greater than the dissolution of $LiClO_4$ in the polymer when low concentrations of salt were incorporated. The solubility limit of $NaClO_4$ was reached in the polymer at a lower concentration than noted for $LiClO_4$ and therefore at high salt concentrations ion solvation occurred to a greater extent in the lithium ion complex.

When considering PDPMeG 350I systems, throughout the salt concentration range, but particularly when high concentrations of salt were present in the complex, sodium ions were solvated to a greater extent than lithium ions.

From this d.s.c. study of alkali metal salt complexes it is apparent that:

1. All of the EO substituted itaconic acid polymers have an ability to solvate metal cations.
2. A loss of flexibility is noted in each of the polymeric hosts on dissolution of salt. This effect is increased as the number of cations solvated by the polymer is increased until at the solubility limit of the salt in the polymer no further loss of flexibility occurs.
3. The loss of flexibility noted in the polymer on addition of a particular concentration of salt was dependent on the polymeric host and the cation present in the added salt.
4. As the salt concentration was increased in some polymers there appeared to be a transition from one predominant coordination process to another at a concentration of salt particular to the complex.

3.3.2 Conductivity Studies.

The conductivity levels measured for each of the undoped polymers were less than 10^{-6} Scm^{-1}, throughout the temperature range.

Since each of the polymeric hosts showed the ability to solvate metal cations the conductivities exhibited by the alkali metal perchlorate complexes of these comb-shaped polymers were measured as a function of increasing temperature.

In Figures 3.4. to 3.8. log conductivity-reciprocal temperature data obtained for $NaClO_4$ complexes of each of the polymeric hosts are displayed. In each Figure the conductivities of complexes prepared from one polymer with a particular sidechain length is shown as the concentration of $NaClO_4$ in the complex was varied. From initial examination of the plots it is apparent that the conductivity of a particular complex increases as the temperature is increased but since curved lines were obtained the complexes do not exhibit Arrhenius behaviour in the temperature range examined. It can also be noted that at a particular temperature the most conductive materials are not always the richest in salt.

Many factors are involved in determining the conductivity exhibited by a polymer-salt complex at a particular temperature, and as will be demonstrated, the information gained in the d.s.c. study of these materials is of great relevance.

Figure 3.4. Arrhenius Plot of log conductivity against reciprocal temperature for various sodium perchlorate complexes of PDMEO1I with $[N^+]/[EO]$ ratios of 0.0125 (○), 0.025 (⊘), 0.05 (□), 0.067 (▣), 0.125 (Δ) and 0.25(+).

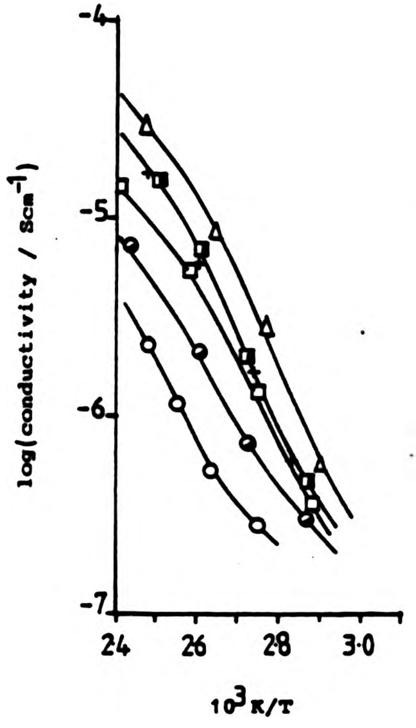


Figure 3.5. Arrhenius Plot of log conductivity against reciprocal temperature for various sodium perchlorate complexes of PDMEO2I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.025 (⊖), 0.05 (□), 0.067 (▣), 0.125 (△) and 0.25(+).

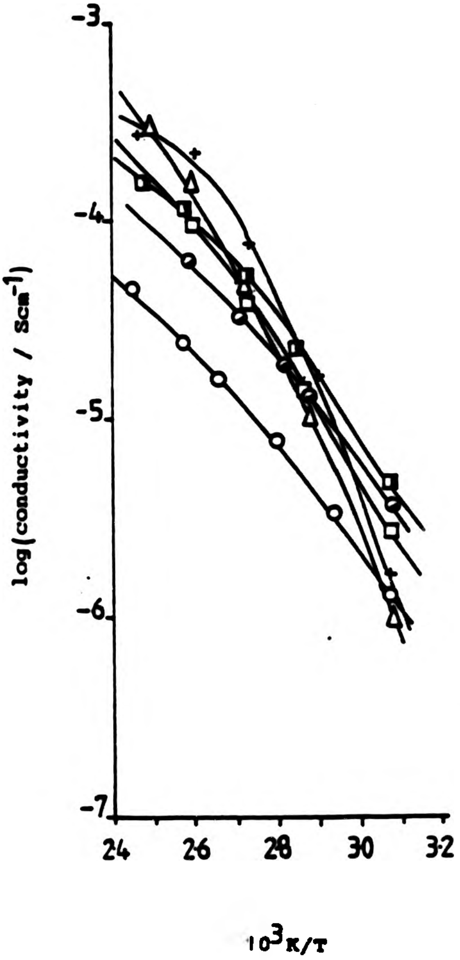


Figure 3.6. Arrhenius Plot of log conductivity against reciprocal temperature for various sodium perchlorate complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.025 (⊘), 0.05 (□), 0.067 (⊠), 0.125 (Δ) and 0.25(+).

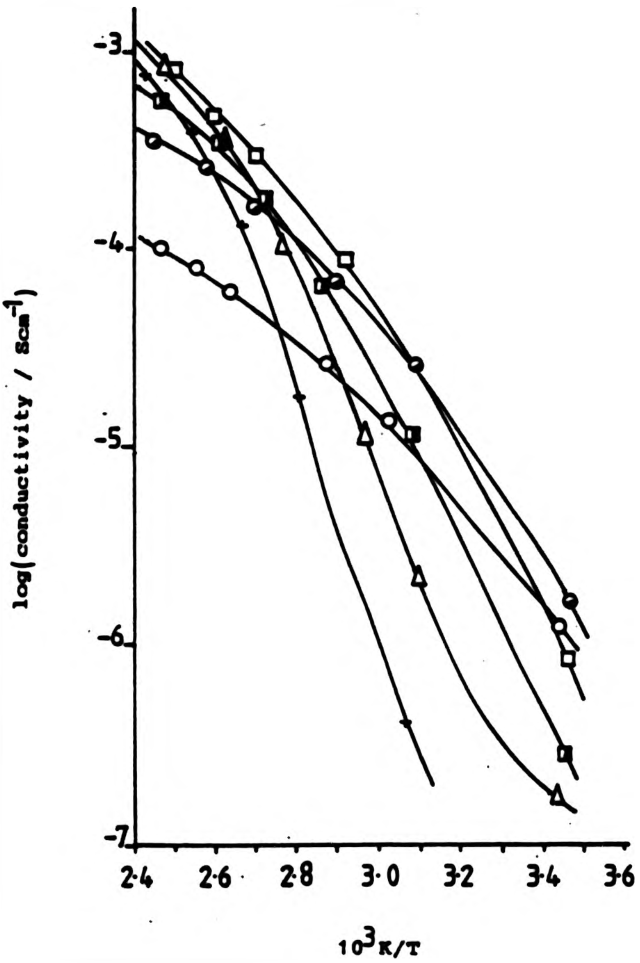


Figure 3.7. Arrhenius Plot of log conductivity against reciprocal temperature for various sodium perchlorate complexes of PDMEO5I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.025 (⊘), 0.05 (□), 0.067 (▣), 0.125 (Δ) and 0.25(+).

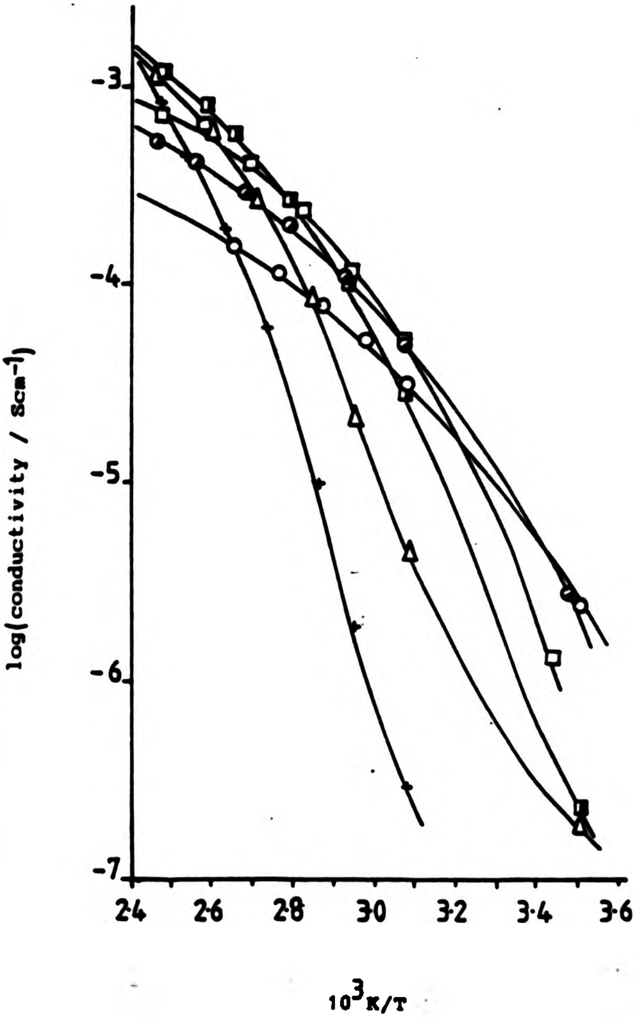
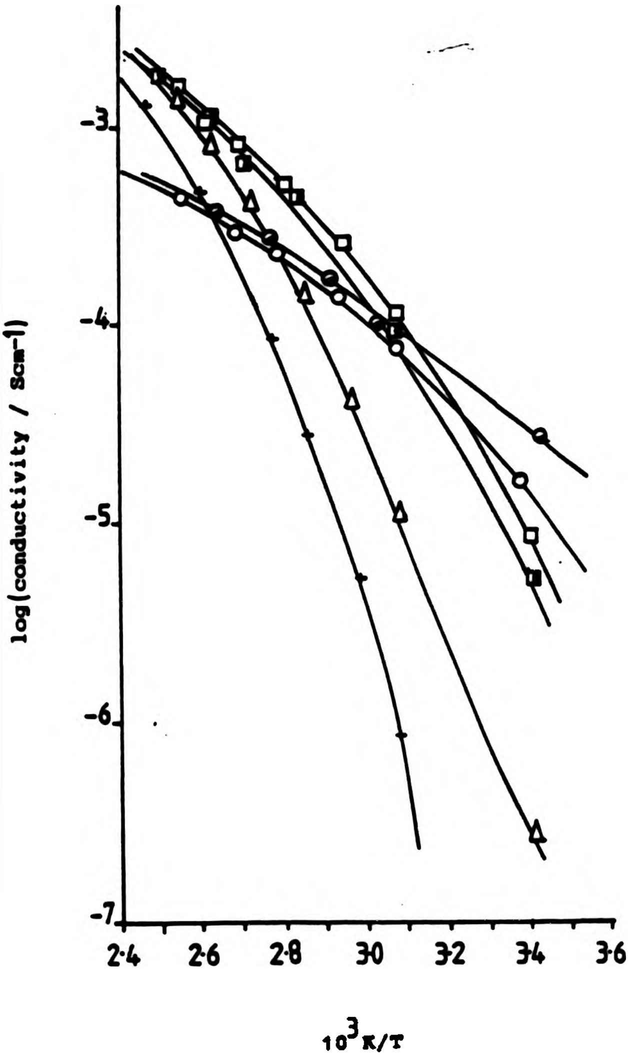


Figure 3.8. Arrhenius Plot of log conductivity against reciprocal temperature for various sodium perchlorate complexes of PDPMeG 350I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.025 (⊘), 0.05 (□), 0.067 (▣), 0.125 (Δ) and 0.25(+).



3.3.2.1 Effect of Increasing Sidechain Length.

In Figure 3.9., the conductivity temperature behaviour is shown for complexes prepared from each of the polymers containing salt at a fixed concentration of $[M^+]/[EO] = 0.125$. The conductivity is increased throughout the temperature range studied as the length of the sidechain in the polymeric host is extended. At high temperatures (~400K), the conductivity observed for the $NaClO_4$ complex prepared from PDPMeG 350I is approximately two orders of magnitude higher than for the complex prepared from PDMEO1I.

Examining the complexes at an isothermal temperature of 403K, where the maximum levels of conductivity were exhibited, as shown in Figure 3.10., the log conductivity is seen to pass through a maximum as the salt concentration in each complex is increased.

Angell and Bressel <92,94> observed similar behaviour in concentrated aqueous electrolytes when examining the conductivity of the materials under isothermal conditions. It was suggested that the conductivity maximum arises naturally from the balancing of carrier density and mobility factors, which may change continually as the salt concentration is varied in the ionic material and it is now believed that similar effects cause the conductivity maximum observed in the polymeric electrolytes <87,150>

In the itaconic acid based systems, a shallow maximum in conductivity occurred at decreasing salt concentrations as the length of the sidechain was extended from one to three EO units long. When longer sidechains were present (PDMEO5I and PDPMeG 350I) the maximum conductivity occurred once again

Figure 3.9. Arrhenius Plot of log conductivity against reciprocal temperature for sodium perchlorate complexes of EO substituted itaconic acid polymers ($[M^+]/[EO] = 0.125$).

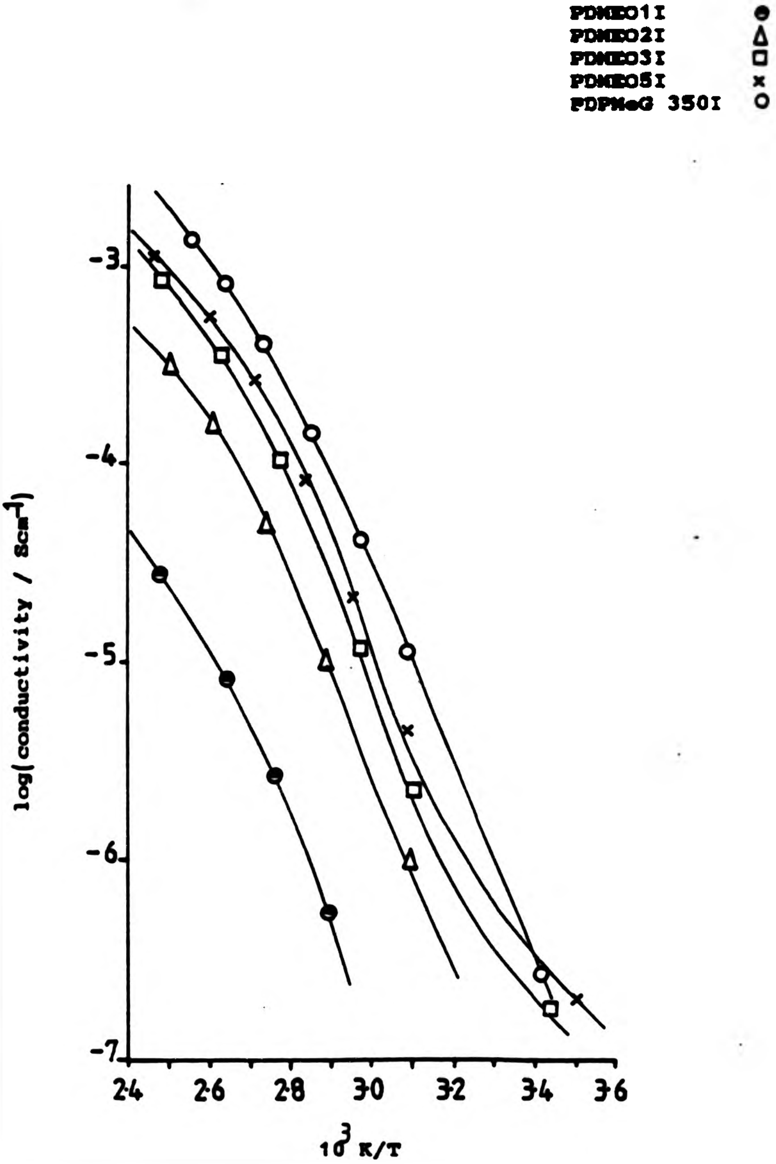
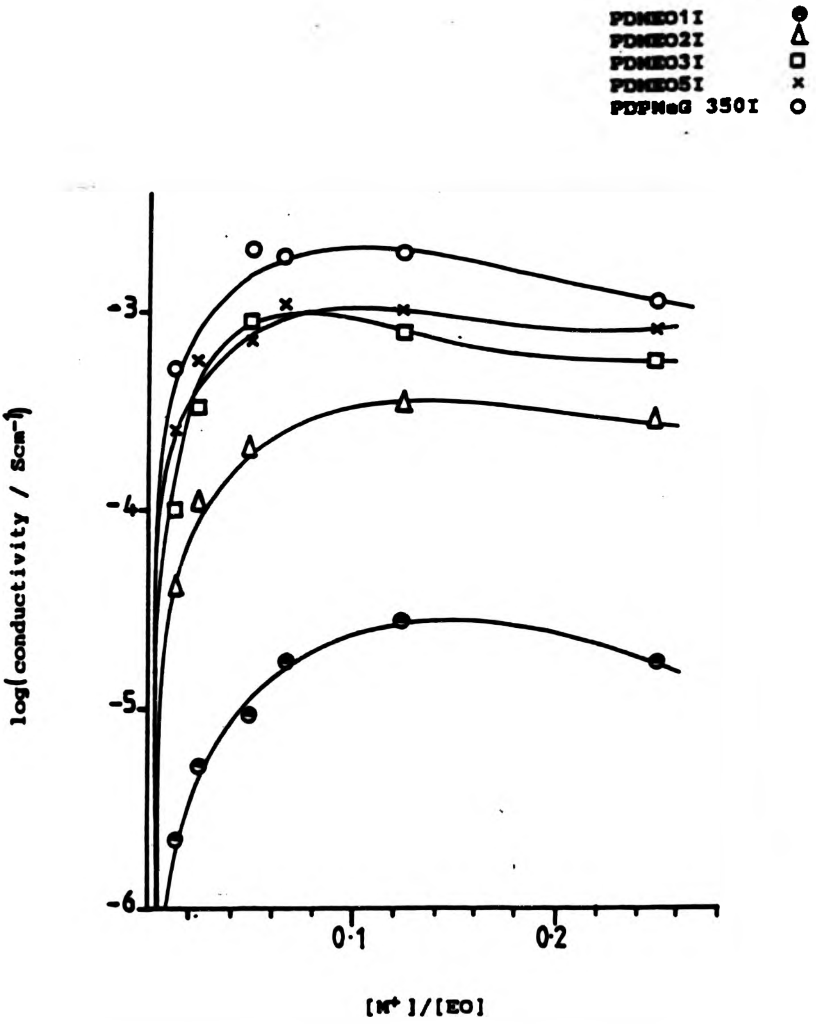


Figure 3.10. Plot of log conductivity against sodium perchlorate concentration for EO substituted itaconic acid polymer-salt complexes examined at an isothermal temperature of 403K.



at increasing concentrations of salt.

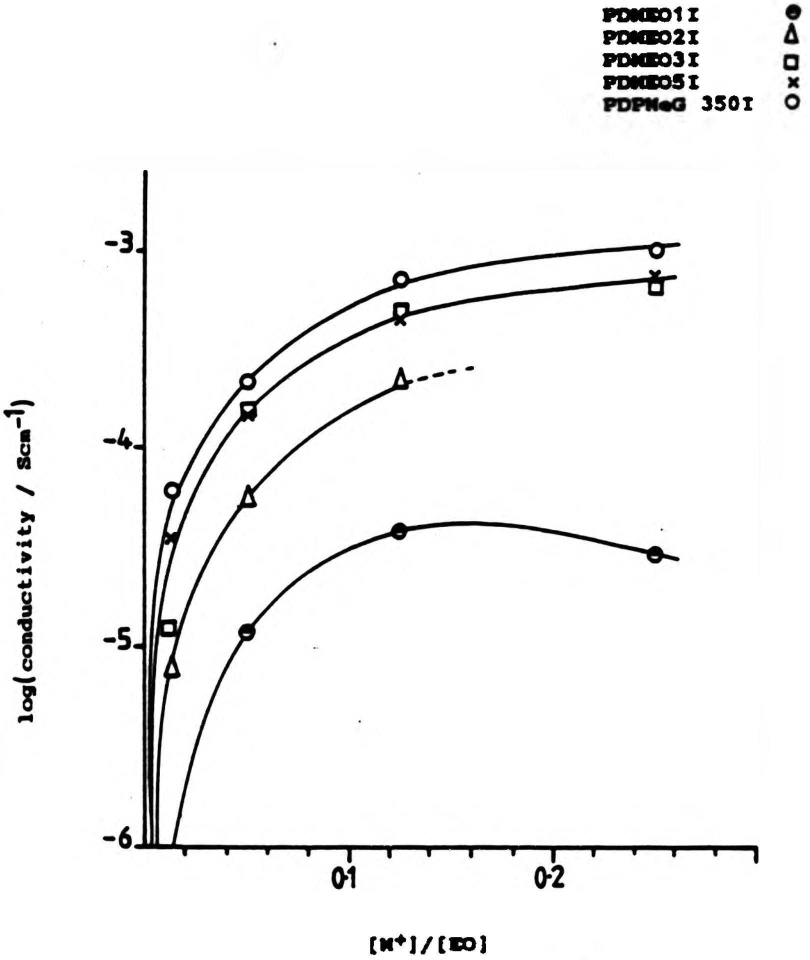
This behaviour agrees well with that reported by Angell <150> who predicted that the maximum in conductivity would move to lower salt concentrations as the dependence of Tg on salt concentration was increased.

In these alkali metal perchlorate complexes, prepared from the itaconic acid based polymers, the materials prepared from PDMEO3I exhibited the most dramatic increase in Tg with salt concentration. Under isothermal conditions, a maximum in conductivity is therefore expected and found at the lowest concentration of salt, in complexes prepared from this polymer.

By examining the complexes under conditions of constant reduced temperature (Tg+100K), it is possible to consider the conductivities exhibited when the mobility of the polymer is the same in each complex. Due to the common salt in the materials, differences which are noted in the conductivity will thus result from the differences in the number of charge carriers in the complex. As shown in Figure 3.11. the conductivity of the complex is increased, particularly at low concentrations of salt, as the length of the sidechain in the polymeric host is extended. This behaviour suggests that dissociation of salt is enhanced, at low concentrations of salt particularly, due to a more efficient polymer-salt interaction, when longer EO sidechains are present in the polymer.

Kobayashi et al. <138> also suggested that dissociation of salt was more extensive in methacrylate polymers containing longer EO sidechains when low concentrations of salt were

Figure 3.11. Plot of log conductivity against sodium perchlorate concentration for EO substituted itaconic acid polymer-salt complexes examined under constant reduced temperature conditions of T-Tg=100K.



present in the complex, however, they were not examining their materials under constant reduced temperature conditions.

The fact that the itaconic acid polymers containing long EO sidechains exhibited the highest levels of conductivity throughout the temperature and salt concentration ranges was highlighted in this area of the study. PDMEO3I and PDPMeG 350I were therefore considered to be of most interest as the host polymers for a potential polymeric electrolyte and so further studies of the itaconic acid comb-shaped polymers concentrated on these material.

3.3.2.2 Effect of Increasing Tg with Salt Concentration.

In Figures 3.12. and 3.13. the conductivities exhibited under isothermal conditions (323, 353 and 403K) for various $NaClO_4$ complexes of PDMEO3I, and PDPMeG 350I respectively are displayed. A maximum conductivity is observed at all temperatures as the salt concentration in each of the complexes is varied, however, as the temperature is increased the maximum in conductivity becomes less pronounced (Figures 3.12 and 3.13). A plateau conductivity value is approached at high concentrations of salt and high temperatures. For a particular polymeric host, the maximum conductivity appears to be exhibited at slightly higher salt concentrations as the isothermal temperature of examination is increased, i.e. optimum levels of conductivity were exhibited by the complexes containing salt at a concentration of $\sim[M^+]/[EO] = 0.04$ at 323K whereas at 403K complexes containing salt at a concentration of $[M^+]/[EO] > 0.06$ exhibited the highest levels of conductivity.

Figure 3.12. Plot of log conductivity against salt concentration for sodium perchlorate complexes of PDMEO3I examined at various isothermal temperatures.

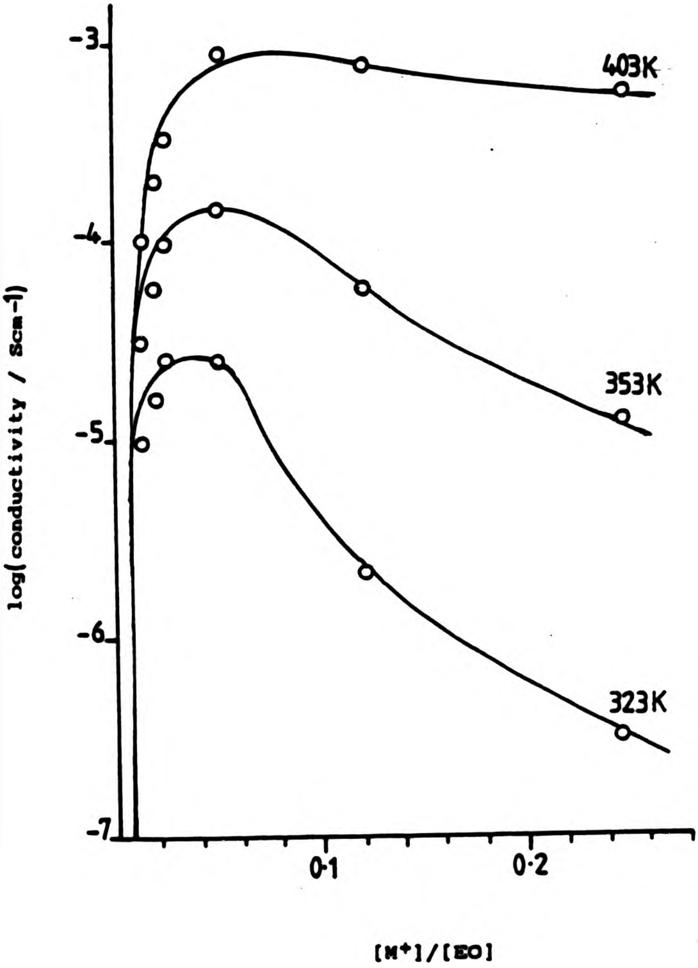
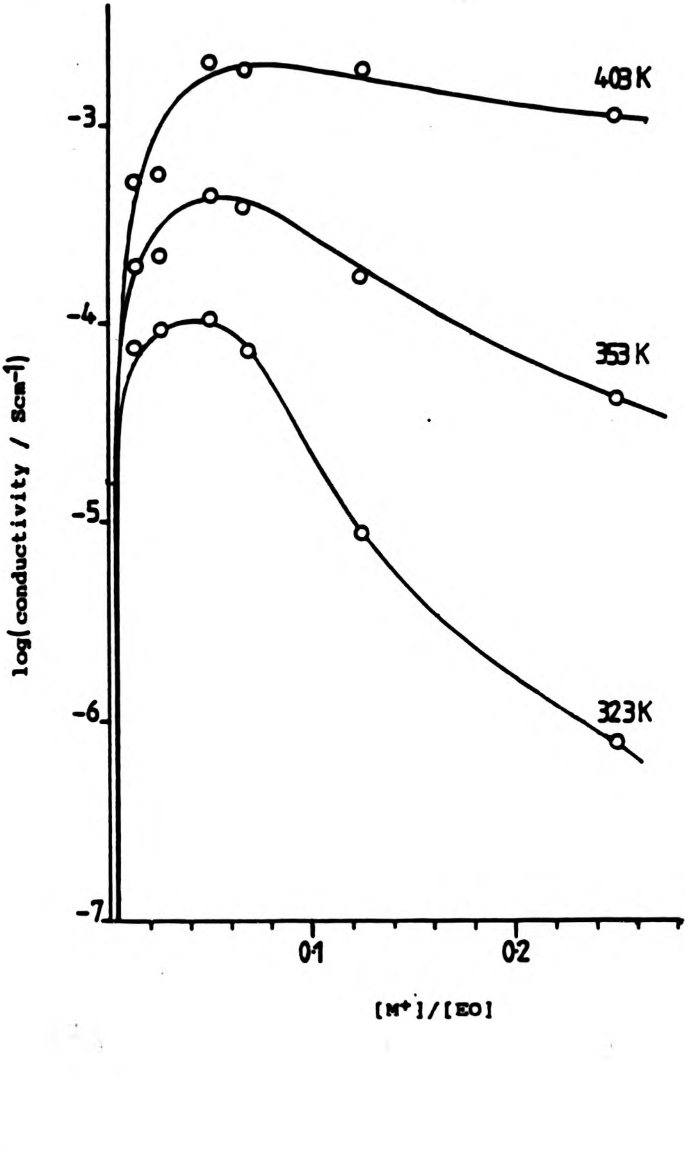


Figure 3.13. Plot of log conductivity against salt concentration for sodium perchlorate complexes of PDPMeG 350I examined at various isothermal temperatures.



It is known that the conductivity of a material is dependent on the number of charge carriers in a system and also the mobility of the charge carriers in the system <10,11>. As the concentration of salt introduced into a polymer was increased, the number of charge carriers produced increased correspondingly, as noted by the loss of flexibility in the polymer. The mobility of the charge carriers in the system is dependent on the flexibility of the polymer chains and therefore the increasing Tg of the polymer, noted as the salt concentration is increased, is an undesirable feature which restricts the ion motion. As the Tg of the complex is increased, higher temperatures must be reached before the polymer chains are suitably mobile to allow high levels of conductivity to occur.

The low levels of conductivity exhibited by materials which contained high concentrations of salt were the result of the complexes having greatly enhanced Tg values compared to those measured when low concentrations of salt were present. In such materials limited polymer chain mobility was possible, particularly at low temperatures.

The effect of changing Tg on the conductivity of the polymer-salt complexes can be eliminated by plotting the observed conductivity of the complexes as a function of reduced temperature. At a particular reduced temperature the complexes are being examined under iso-free volume conditions or conversely under conditions of constant configurational entropy. The mobility of the chains in each polymer-salt complex are therefore the same and provided a common salt species is present when comparing the materials, any differences observed result from differences in the number of charge carriers in the systems. This is of course related to the concentration of salt in the polymer-salt complex.

3.3.2.3 Effect of Increasing Salt Concentration.

In Figures 3.14. and 3.15. the log conductivity of complexes prepared from $NaClO_4$/PDMEO3I and $NaClO_4$/PDPMeG 350I respectively are shown as a function of reduced temperature. In the PDMEO3I complexes, the conductivity increases continually as the salt concentration is increased whereas in the PDPMeG 350I complexes, an increase in conductivity is noted initially, but at high concentrations of salt a plateau conductivity level is reached. This is better demonstrated by examining the conductivity as a function of increasing salt concentration at a particular reduced temperature as shown in Figures 3.16. and 3.17. From these plots it is apparent that initially the conductivity is increased dramatically as the salt concentration is increased, however, at high concentrations of salt, the increase in conductivity with salt concentration is less marked. Above a salt concentration of $[M^+]/[EO] = 0.125$ little enhancement of the conductivity occurs when the materials are examined under constant reduced temperature conditions.

It was proposed by Angell <87,150> that the maximum in conductivity exhibited under isothermal conditions resulted from the balancing of opposing effects resulting from increasing numbers of charge carriers and the loss of flexibility in the polymer as the salt concentration was

Figure 3.14. Plot of log conductivity against reduced temperature for various sodium perchlorate complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.025 (◐), 0.05 (□), 0.125 (Δ) and 0.25 (+).

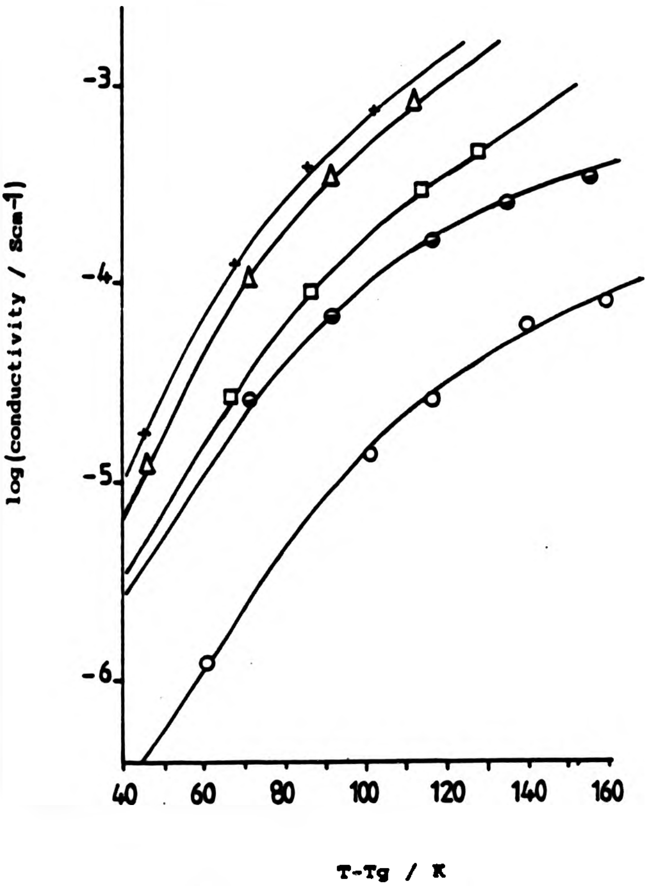


Figure 3.15. Plot of log conductivity against reduced temperature for various sodium perchlorate complexes of PDPMeG 350I. with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).

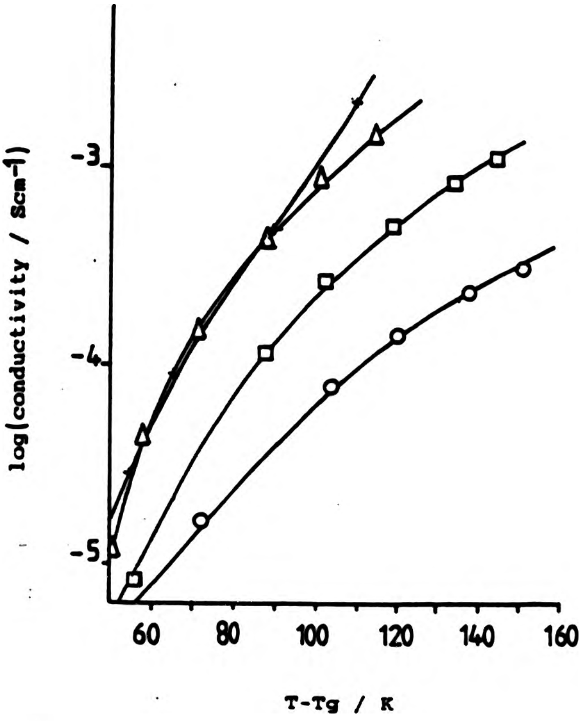


Figure 3.16. Plot of log conductivity against salt concentration for sodium perchlorate complexes of PDMEO3I examined under various constant reduced temperature conditions.

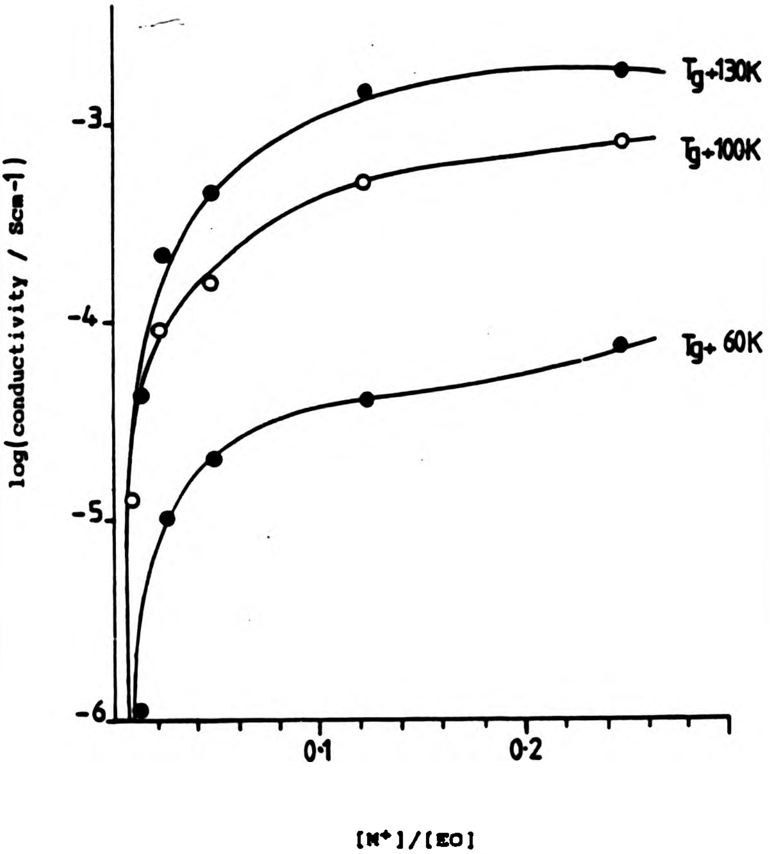
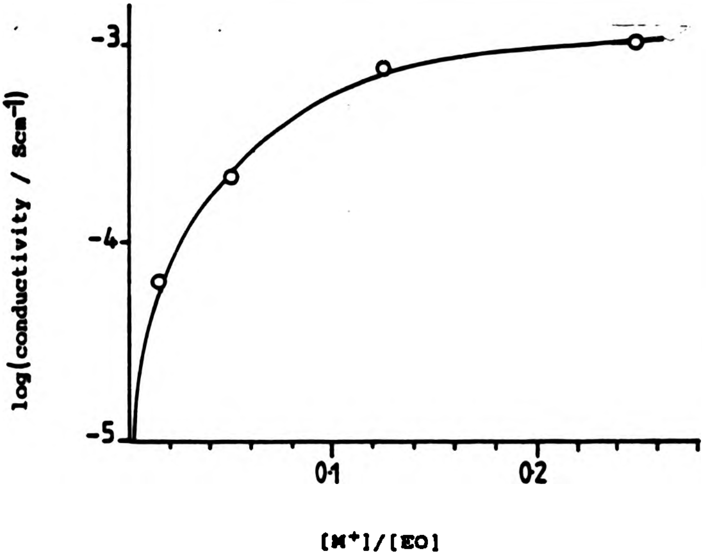


Figure 3.17. Plot of log conductivity against salt concentration for sodium perchlorate complexes of PDPMeG 350I examined under constant reduced temperature conditions of T-Tg=100K.



increased. A continual increase in conductivity as the salt concentration was increased would therefore be expected when the effect of increasing Tg with salt concentration was eliminated, by examining the complexes at a constant reduced temperature.

As noted above, virtually no increase in conductivity with increasing salt concentration was observed above a $NaClO_4$ concentration of $[M^+]:[EO] = 0.125$. At high concentrations of salt the conductivity appears to be restricted. It must be appreciated that the equation presented by Angell was for use in materials which exhibited a linear increase in Tg with salt concentration, however, it is possible that the dramatic effects observed in this study could be the result of the charge carrier concentration or the mobility of the charge carriers being reduced at high concentrations of salt. This could be the result of aggregate ion formation occurring in the complex since large charged clusters are expected to contribute less to the overall conductivity of a system <151>.

3.3.2.4 Effect of Cation Variation.

In Figures 3.18. to 3.20. the conductivity-temperature data exhibited by $LiClO_4$ complexes of PDMEO1I, PDMEO3I and PDPMeG 350I respectively are displayed. Similar to the effects noted in the $NaClO_4$ complexes, it is apparent that throughout the salt concentration and temperature ranges, the conductivities measured for the complexes prepared PDMEO1I are much lower than those found for the complexes prepared from PDMEO3I and PDPMeG 350I.

Concentrating initially on the alkali metal perchlorate

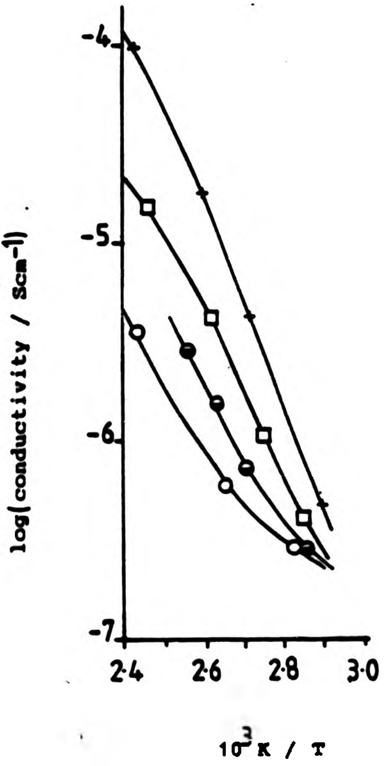


Figure 3.18. Arrhenius Plot of log conductivity against reciprocal temperature for lithium perchlorate complexes of PDMEO1I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.025 (⊖), 0.05 (□) and 0.25 (+).

Figure 3.19. Arrhenius Plot of log conductivity against reciprocal temperature for lithium perchlorate complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.025 (⊖), 0.05 (□), 0.067 (▣), 0.125(Δ) and 0.25 (+).

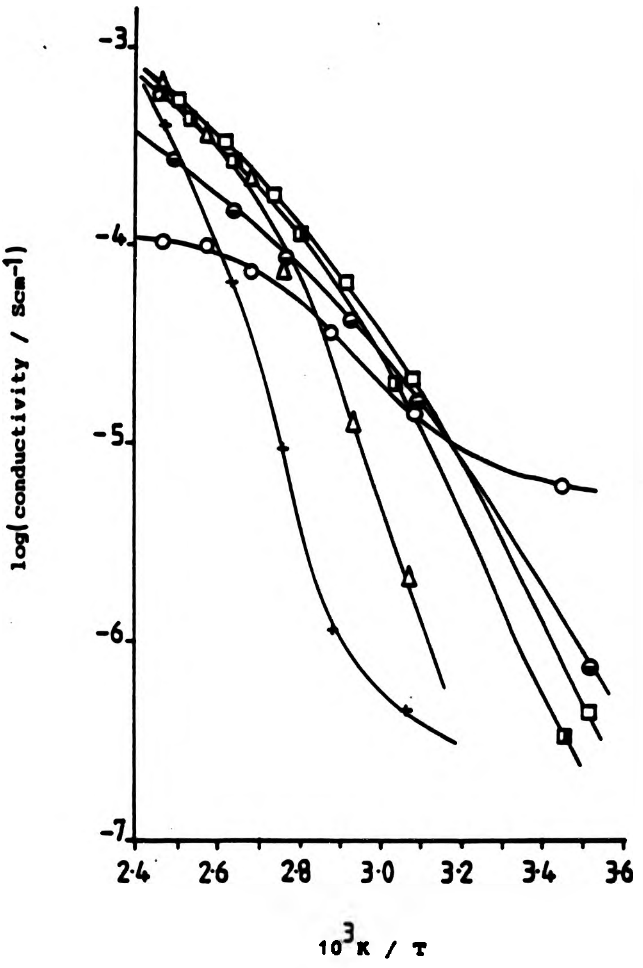
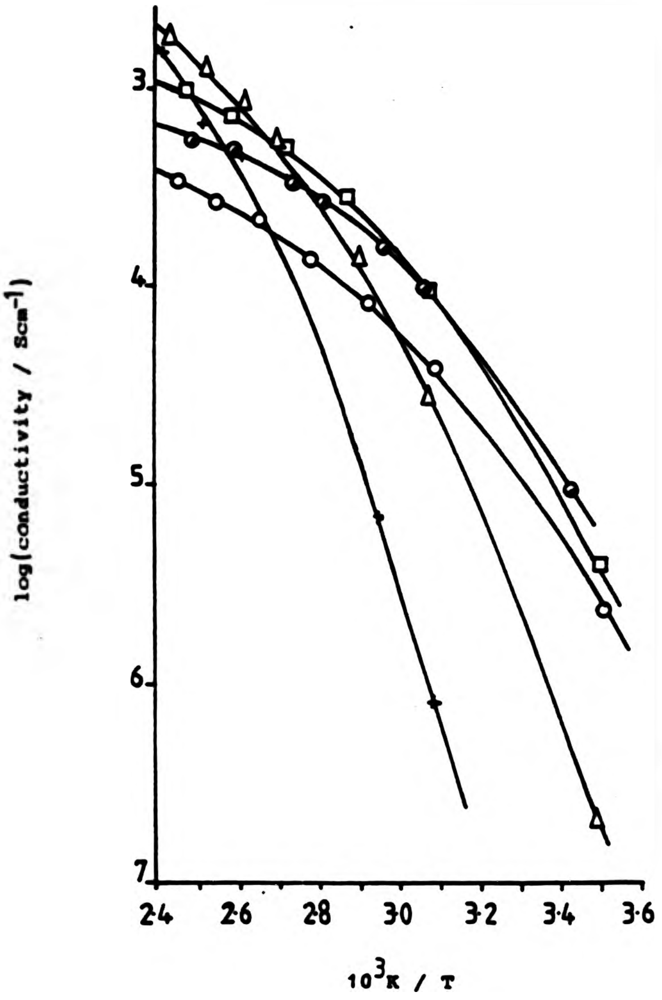


Figure 3.20. Arrhenius Plot of log conductivity against reciprocal temperature for lithium perchlorate complexes of PDPMeG 350I with [M$^+$]/[EO] ratios of 0.0125 (○), 0.025 (⊖), 0.05 (□) and 0.125 (Δ) and 0.25 (+).



complexes of PDMEO3I it is apparent from examination of Figure 3,21. that throughout the salt concentration and temperature ranges, the sodium ion complexes exhibit higher levels of conductivity than the lithium ion complexes. When the complexes were examined under constant reduced temperature conditions as shown in Figure 3.22, it would appear that, when the flexibility of the polymer chains in the complexes are comparable, higher levels of conductivity are exhibited by the sodium ion complexes consistently.

This difference noted under constant reduced temperature conditions is indicative of the number of charge carriers in the complexes or the mobilities of the charge carriers in the complexes varying as the cation in the complex is changed.

It is interesting to note that incorporation of both $LiClO_4$ and $NaClO_4$ into PDMEO3I at a salt concentration of $[M^+]/[EO] = 0.125$ resulted in almost identical enhancement of the Tg of the polymer (Figures 3.2. and 3.3.). This would suggest that at that particular salt concentration solvation of lithium and sodium ions, to produce charge carriers, had occurred to a similar extent. When examining the conductivities of these materials, where the mobility of the polymers are constant, as shown in Figure 3.22, knowing that the carrier ion concentration is constant also, would suggest that the sodium ion is able to move through the polymer with greater ease than the lithium ions.

Such behaviour is also suggested by the complexes containing salt at a concentration of $[M^+]/[EO] = 0.25$. From consideration of the d.s.c. data, more charge carriers were generated in the $LiClO_4$ complex, however, examination of the

Figure 3.21. Plot of log conductivity against salt concentration for alkali metal perchlorate complexes of PDMMO3X examined at various isothermal temperatures.
$NaClO_4$ (○), $LiClO_4$ (□).

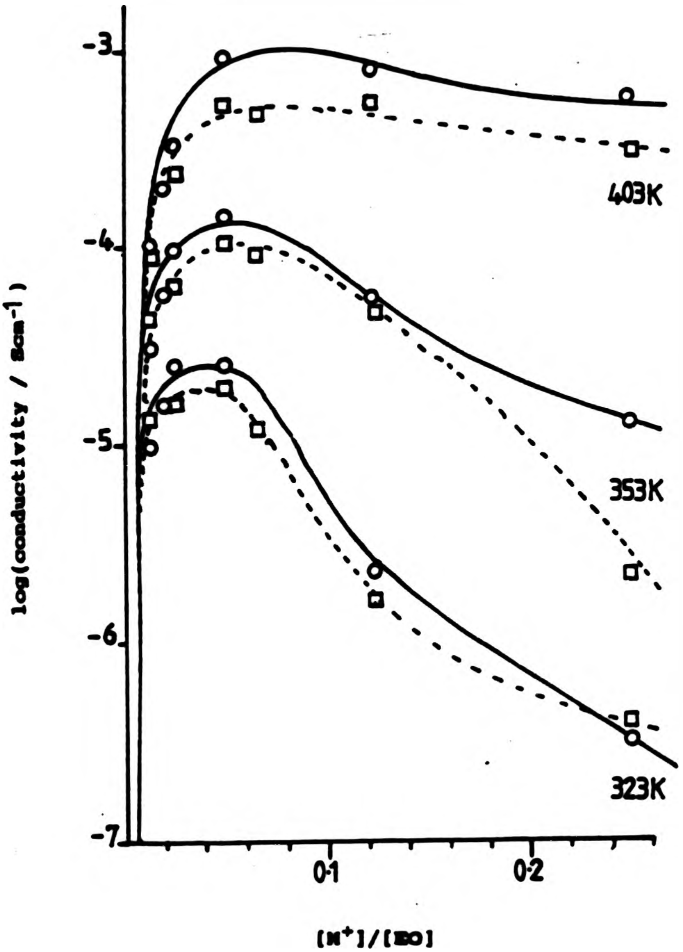
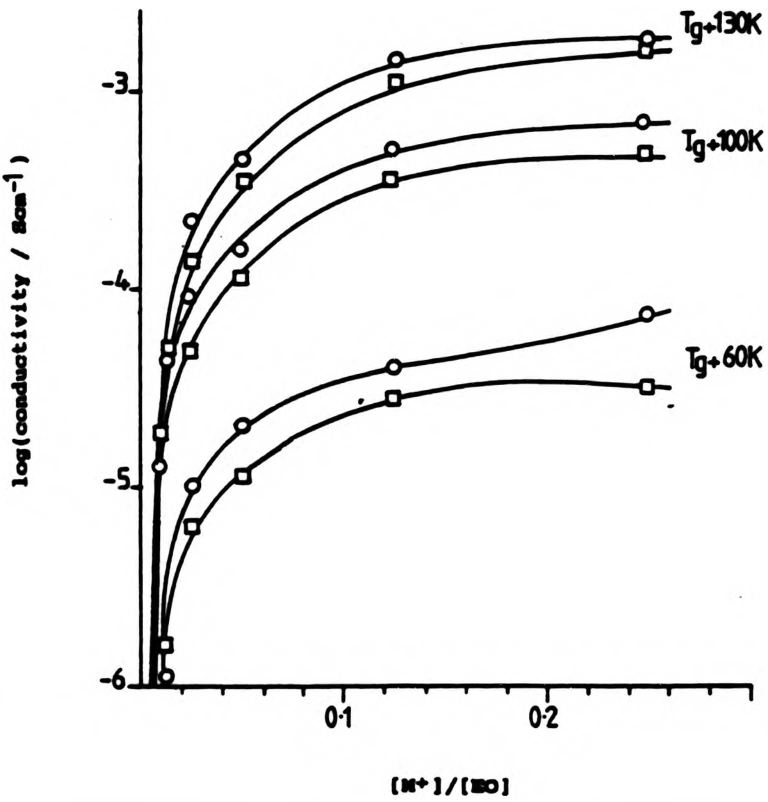


Figure 3.22. Plot of log conductivity against salt concentration for alkali metal perchlorate complexes of PDMEO3I examined under various constant reduced temperature conditions. $NaClO_4$ (○), $LiClO_4$ (□).



conductivities of the materials, under constant reduced temperature conditions revealed that higher levels of conductivity were exhibited by the sodium ion complexes.

In all other complexes, the differences noted in the conductivities could occur as a result of the sodium ion complexes containing more charge carriers than the lithium ion complexes.

From consideration of the behaviour exhibited by the complexes containing salt at a concentration of $[M^+]/[EO] = 0.125$. it can be suggested that purely anionic conduction does not occur in these materials since different levels of conductivity were exhibited by the two complexes containing the same number of charge carriers, at a constant reduced temperature when the anion in the complex was common.

From the information collected so far it is not possible to comment on whether purely cationic conduction occurs in these materials or whether there is evidence to suggest that both ionic species are mobile.

Moving on to consider the alkali metal perchlorate salt complexes of PDPMeG 350I, it was found when examining the materials at various isothermal temperatures, as shown in Figure 3.23., that at low concentrations of salt, the lithium ion complexes exhibited lower levels of conductivity than the sodium ion complexes whereas at high concentrations of salt, both systems exhibited comparable levels of conductivity. This behaviour was noted throughout the temperature range.

When the materials were examined at a constant reduced temperature of 100K, as shown in Figure 3.24., the sodium ion complexes showed higher levels of conductivity than the

Figure 3.23. Plot of log conductivity against salt concentration for alkali metal perchlorate complexes of PDPMeG 350I examined at various isothermal temperatures.
$NaClO_4$ (○), $LiClO_4$ (□).

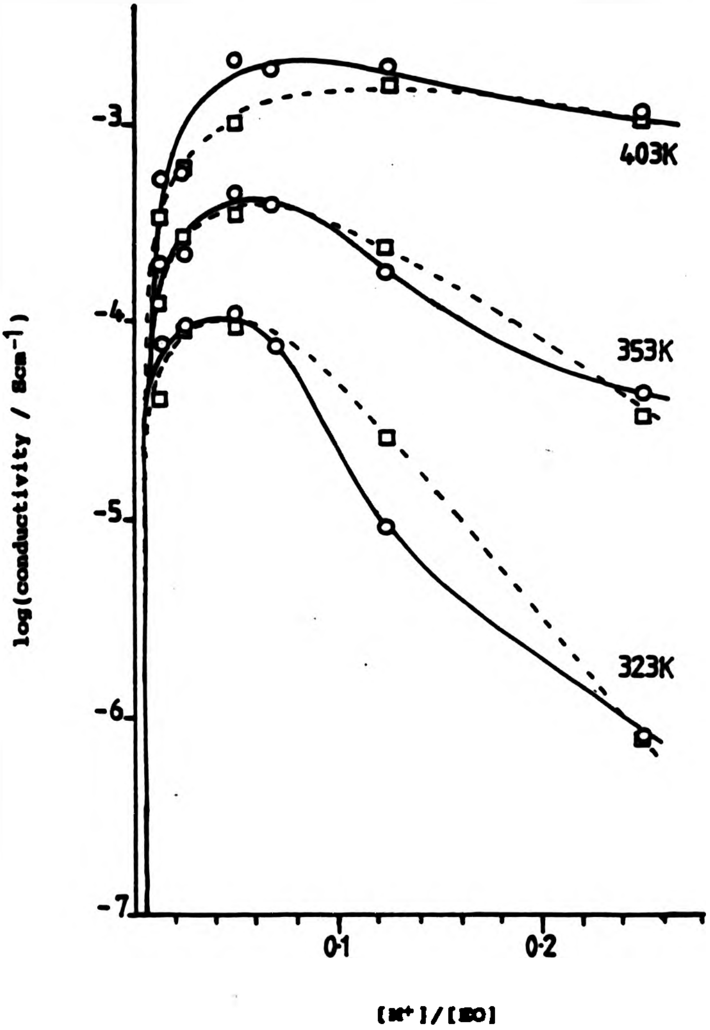
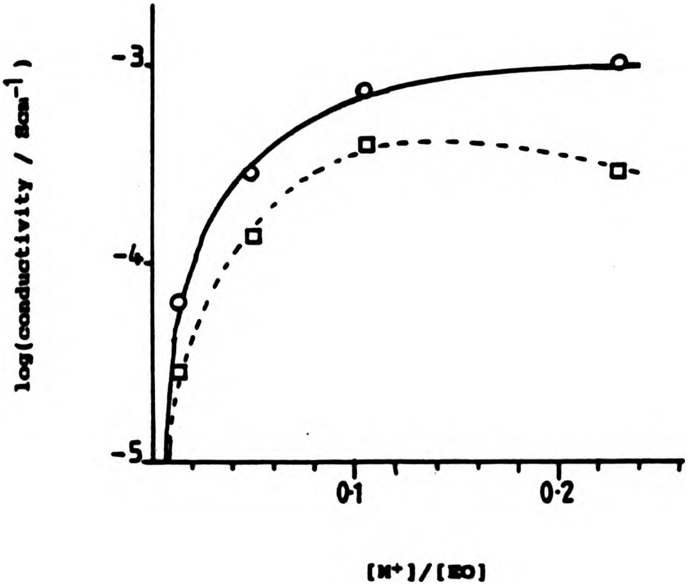


Figure 3.24. Plot of log conductivity against salt concentration for alkali metal perchlorate complexes of PDPMeG 350I examined under constant reduced temperature conditions of T-Tg=100K.
$NaClO_4$ (○), $LiClO_4$ (□).



lithium ion complexes. From the results of the d.s.c. analysis of these materials it was established that generation of ion carriers had occurred to a greater extent in the sodium ion complexes, particularly at high concentrations of salt.

Differences noted in the levels of conductivity measured when different cations were involved in the complex would appear to be the result of the sodium ion complexes containing more charge carriers than the lithium ion complexes. It is still not possible to determine from the information collected whether only the cations or both the cations and the anions in the system are the mobile charge carriers.

From this study of the conductivity behaviour exhibited by the alkali metal perchlorate salt complexes it can be concluded that:

1. The conductivity of the solid state electrolyte is increased throughout the temperature range as the length of the sidechain in the polymeric host is extended.
2. When a particular salt is incorporated at a certain concentration into each of the polymeric host materials, dissociation of the salt occurs to a greater extent as the sidechain length of the polymer is extended.
3. A maximum in conductivity is noted when examining polymer-salt complexes under isothermal conditions. The salt concentration at which the maximum is observed is dependent on the polymeric host, the incorporated salt and the isothermal temperature.

4. The conductivity maximum is believed to occur as a result of the balancing of carrier density and mobility factors in the polymer-salt complex as the salt concentration is increased, however, it was suggested from examination of the materials under constant reduced temperature conditions that the conductivity is lowered at high concentrations of salt due to a reduction in the number of carrier ions or the restricted mobility of the carrier ions.
5. The conductivity of a material increases as the reduced temperature is increased, therefore, as the Tg of a polymer is increased, higher temperatures are required to allow high conductivities to be exhibited.
6. The number of charge carriers in a system is increased as the salt concentration is increased at low concentrations but at high concentrations little enhancement of the number of charge carriers in the system is noted as the salt concentration is increased.
7. Sodium ion complexes exhibit higher levels of conductivity isothermally and under constant reduced temperature conditions than lithium ion complexes when a similar concentration of salt is incorporated into the polymer. This effect occurs predominantly due to the higher number of charge carriers in the sodium ion complexes, however, it has been suggested, by the behaviour observed when examining the complexes under constant reduced temperature

conditions, that the sodium ion may move through the polymer faster than the lithium ions.

8. It is suggested that purely anionic conduction does not occur in these complexes. Further examination is required, however, to establish whether the behaviour of these materials suggests that purely cationic conduction occurs in the systems or whether both ionic species appear to be mobile.

3.4 Effect of Salt Variation on Polymer-Salt Complex Formation and Complex Conductivities.

From the initial d.s.c. and conductivity studies carried out on the EO substituted itaconic acid polymer-salt complexes, it was apparent that all the polymers had the potential to be used as the host materials in solid state electrolytes. The most useful materials, however, appeared to be the salt complexes prepared from the comb-shaped polymers which contained the longer EO sidechains, i.e. PDMEO3I, PDMEO5I and PDPMeG 350I.

To gain more information on the processes of complex formation in the potentially useful materials, the solubilities of a wide range of salts in PDMEO3I, and to a lesser extent in PDPMeG 350I, were investigated. All salts which were capable of dissolving in the polymeric host, to produce ions were of immediate interest and the conductivities of such materials were investigated as a function of temperature and salt concentration to determine the salt properties which allow optimum levels of conductivity to be measured for a particular polymeric host.

3.4.1 PDMEO3I-Salt Complexes.

A wide range of salts were added to PDMEO3I and optical transparency of the material suggested that dissolution of the salt in the polymer had occurred. It was, however, possible that the system was in fact two phase with inert inclusions molecularly dispersed throughout the polymer <51>. In Tables 3.IV. and 3.V. the "apparent homogeneity" of the dried products isolated on addition of various salts to PDMEO3I is described.

Assuming that an enhancement of Tg noted on addition of salt to the polymer reflected the number of ions solvated in the polymer and therefore demonstrated that dissolution of the salt in the polymer had occurred, d.s.c. was used to confirm the presence of ions in the optically transparent materials. The results obtained are shown in Table 3.VI.

3.4.1.1 Alkali Metal Salts.

3.4.1.1.1 Solubility Studies.

Heterogeneous polymer-salt mixtures were obtained on addition of NaCl and NaBr to PDMEO3I. When these materials were examined, the Tg of the doped polymer was almost the same as that measured for the pure polymer which confirmed that dissolution of the salt in the polymer was negligible.

Each of the optically transparent materials demonstrated an increasing enhancement of Tg as the salt concentration was increased, however, the magnitude of the Tg enhancement noted at a particular salt concentration was dependent on the salt incorporated into the complex.

Table 3.IV

"Apparent homogeneity" of PDMEO3I with added Alkali Metal salts.

Anion	Cation			
	Li^+	Na^+	K^+	Cs^+
Cl^-	Yes	No	-	-
Br^-	Yes	No	-	-
I^-	Yes	Yes	No	No
SCN^-	-	Yes	No	-
ClO_4^-	Yes	Yes	-	-
$CF_3SO_3^-$	Yes	Yes	Yes	-
BF_4^-	No	-	-	-

Table 3.V

"Apparent homogeneity" of PDMEO3I with added Non-alkali Metal salts.

Salt	Homogeneous
$AgCF_3SO_3$	Yes
NH_4SCN	No
$Ca(ClO_4)_2$	Yes
$HgCl_2$	No

TABLE 3.VI

Increase in Tg as a function of salt concentration in PDMEO3I-salt complexes.

Salt	[M⁺]/[EO] 0.0125	0.017	0.025	0.05	0.067	0.125	0.25
LiCl	6.0	-	-	14.0	-	26.5	38.5
LiBr	-	-	-	17.5	-	-	-
LiI	13.5	-	-	26.5	-	57.5	81.5
$LiCF_3SO_3$	18.5	-	-	35.0	-	54.0	79.5
$LiClO_4$	11.5	22.0	27.5	34.5	37.5	69.5	90.5
NaCl	-	-	-	6.5	-	-	-
NaBr	-	-	-	5.5	-	-	-
NaI	19.5	20.5	23.0	36.5	56.5	81.5	97.0
$NaCF_3SO_3$	14.5	-	-	38.0	-	61.5	79.5
$NaClO_4$	10.5	25.5	33.5	37.0	46.5	70.0	88.0
KCF_3SO_3	-	-	-	33.0	-	-	-
$AgCF_3SO_3$	9.0	-	14.5	25.5	37.5	53.5	73.5
$Ca(ClO_4)_2$	8.5	-	-	61.5	-	/	/

In general, it was noted that ion solvation occurred to a greater extent when the salt had a relatively low lattice energy and contained large anions such as iodide (I^-), perchlorate (ClO_4^-) and trifluoromethane sulphonate (triflate, $CF_3SO_3^-$). LiCl, a salt which has a small anion and a high lattice energy was dissociated to a much lesser extent in the polymer.

When considering incorporation of alkali metal salts into PDMEO3I, it would appear from the information shown in Table 3.IV., that, similar to the effects noted in the PEO-alkali metal salt complexes, dissolution of the salts in PDMEO3I occurs only if the salt has a lattice energy below a threshold value. Since NaBr and KSCN formed complexes in PEO <14> but were insoluble in PDMEO3I, it would appear that for sodium and potassium salts the threshold lattice energy is lower for PDMEO3I than for PEO.

3.4.1.1.2 Conductivity Studies.

In Figures 3.25. to 3.29. the log conductivity as a function of reciprocal temperature is shown for polymer-salt complexes prepared on addition of a range of lithium and sodium salts to PDMEO3I. Figures 3.6. and 3.19. are also of interest since they describe the conductivity-temperature behaviour of the alkali metal perchlorate complexes. In general it is very apparent that the conductivity behaviour is dependent on the incorporated salt species, the concentration of salt and the temperature of examination.

As described in Chapter 1., the conductivity demonstrated by a material is dependent on the number of ion carriers

Figure 3.25. Arrhenius Plot of log conductivity against reciprocal temperature for various lithium trifluoromethane sulphonate complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).

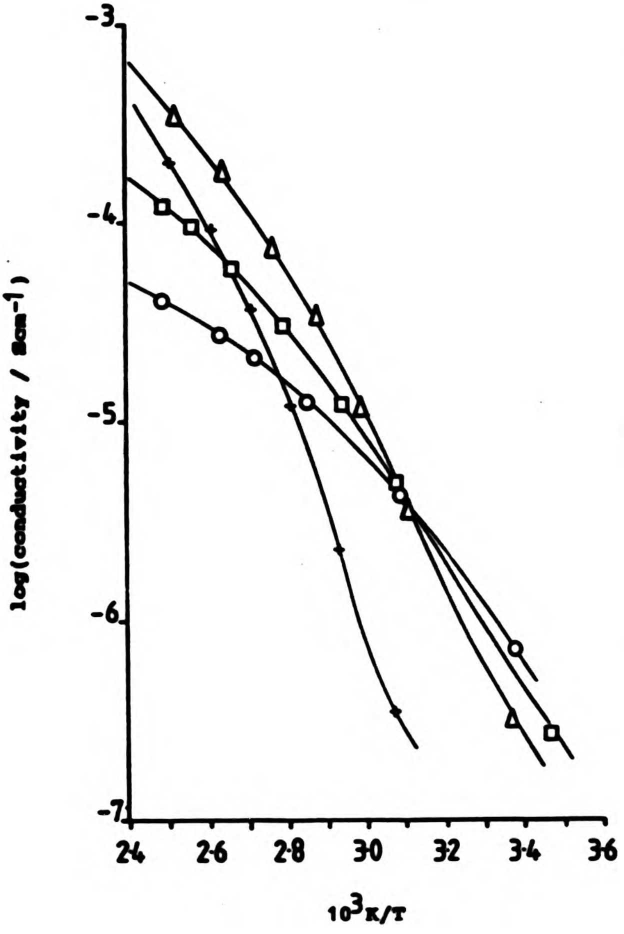


Figure 3.26. Arrhenius Plot of log conductivity against reciprocal temperature for various lithium iodide complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.05 (□), 0.125 (△) and 0.25 (+).

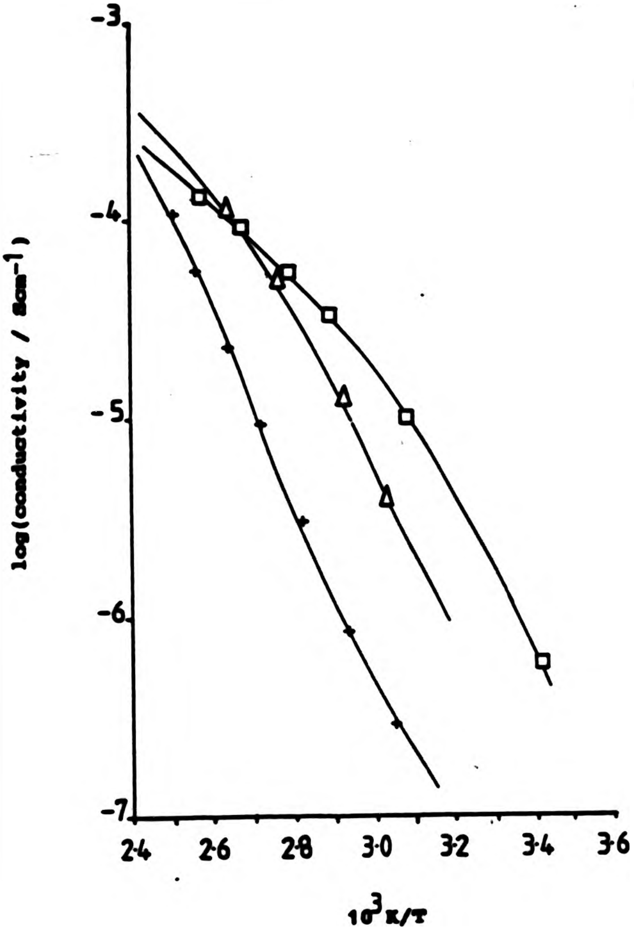


Figure 3.27. Arrhenius Plot of log conductivity against reciprocal temperature for various lithium ~~chloride~~ complexes of PDMEO3I with [M+]/[EO] ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).

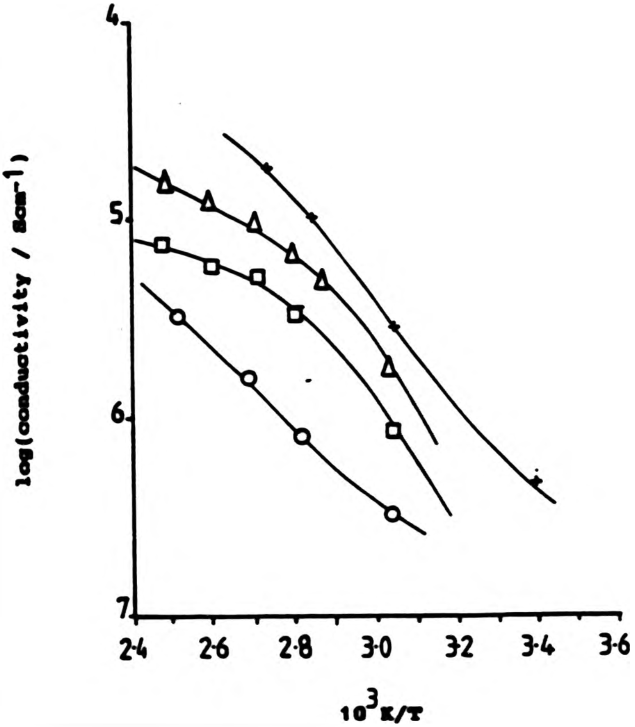


Figure 3.28. Arrhenius Plot of log conductivity against reciprocal temperature for various sodium iodide complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).

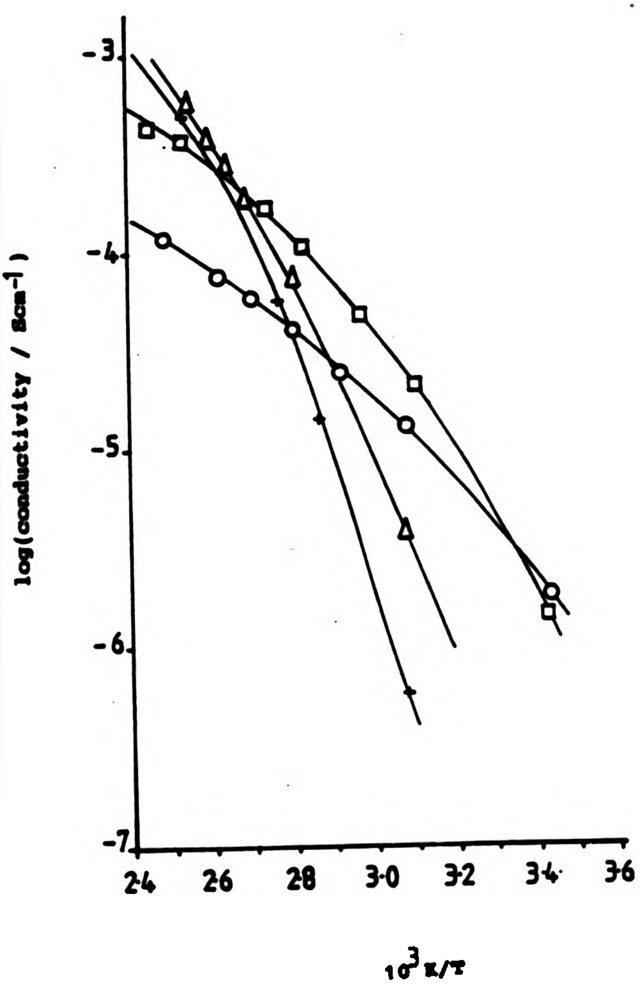
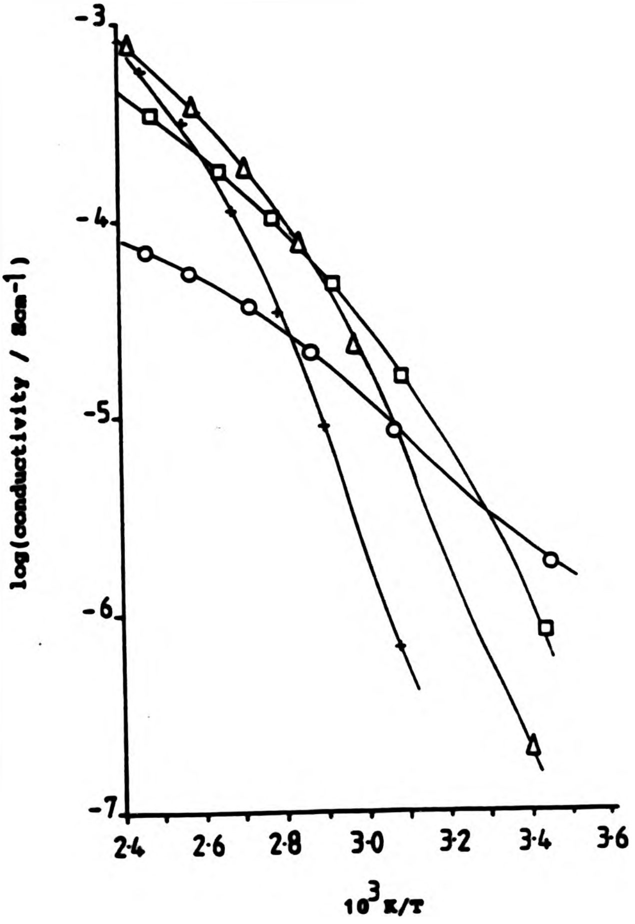


Figure 3.29. Arrhenius Plot of log conductivity against reciprocal temperature for various sodium trifluoromethane sulphonate complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).



present in the system. The dissolution of the salt in the polymer is affected by the ionic radii of the species present in the salt lattice and it has been predicted <22> that as the value of $1/(r_c + r_a)$ decreases the generation of ion carriers in the system will increase, which will increase the conductivity of the material correspondingly.

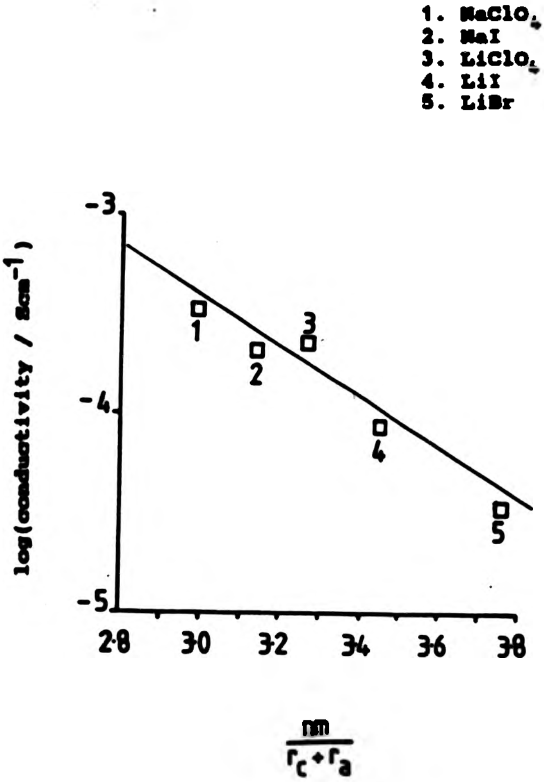
When the complexes prepared from PDMEO3I and the alkali metal salts at a concentration of $[M^+]/[EO] = 0.05$ were examined at a temperature of 373K, the conductivity and the sum of the ionic radii were seen to be related in the manner predicted, as shown in Figure 3.30.

Salts which showed low solubility in the polymer tended to behave irregularly compared to the salts which enhanced the Tg of the polymer dramatically with increasing salt concentration. The latter materials exhibited behaviour such that the conductivity levels increased linearly as the sum of the ionic radii of the salt species was increased. As predicted the complexes prepared from salts which contained large cations and anions tended to show higher levels of conductivity at a particular salt concentration and a particular temperature.

3.4.1.1.2.a Effect of Cation Variation.

It was noted previously (Section 3.3.2.4.) when considering the alkali metal perchlorate salt complexes, that the sodium ion complexes tended to exhibit higher levels of conductivity than the lithium ion complexes. This behaviour appears to be independent of the character of the anion in the salt. When examining the triflate and iodide complexes, as shown in

Figure 3.30. Plot of log conductivity against reciprocal sum of the cationic and anionic radii of alkali metal salts present in complexes prepared from PDMEO3I.
($[M^+]/[EO] = 0.05$, 373K)



Figures 3.31. and 3.32., it was found that when the salt was present in the polymer at a concentration of $[M^+]/[EO] = 0.05$, the sodium ion complexes exhibited higher levels of conductivity, throughout the temperature range. [In the triflate complexes it was suggested that increasing the size of the cation in the complex, by incorporating potassium ions, resulted in a further enhancement of the levels of conductivity exhibited by the materials. Limited data were collected for potassium complexes, however, so this comment is speculative.]

As shown in Figure 3.33., under constant reduced temperature conditions, sodium ion complexes exhibit higher levels of conductivity than the lithium ion complexes. In most materials this is related to the number of charge carriers generated in the sodium ion complexes being greater than the number generated in the lithium ion complexes.

When considering the triflate complexes, containing salt at a concentration of $[M^+]/[EO] = 0.25$, similar numbers of charge carriers were considered to be present in the sodium and lithium ion complexes as shown in Table 3.VI. From the behaviour exhibited at constant reduced temperature conditions it is suggested that purely anionic conduction does not occur in these materials. The sodium ion appears to move through the polymer with greater ease than the lithium ion.

3.4.1.1.2.b Effect of Anion Variation.

Examining the constant reduced temperature conductivity behaviour of PDMEO3I-salt complexes, the conductivity would be expected to increase as the number of charge carriers

Figure 3.31. Arrhenius Plot of log conductivity against reciprocal temperature for various trifluoromethane sulphonate salt complexes of PDMEO3I. ($[M^+]/[EO] = 0.05$)

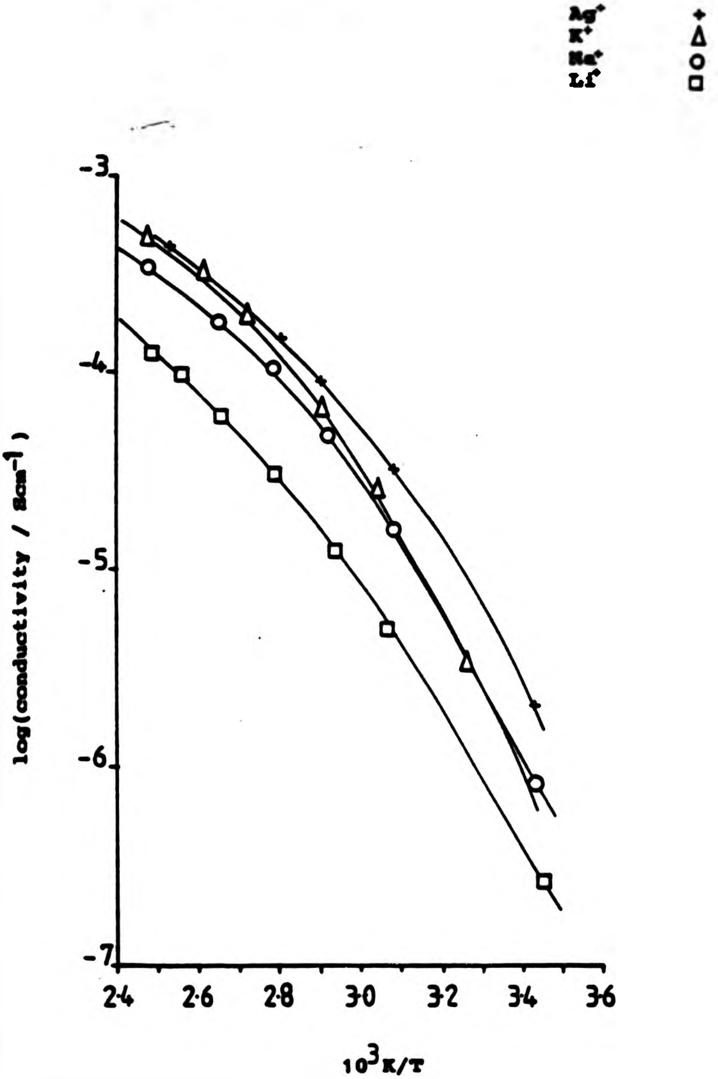


Figure 3.32. Arrhenius Plot of log conductivity against reciprocal temperature for various alkali metal iodide complexes of PDMEO3I. ($[M^+]/[EO] = 0.05$), LiI (□), NaI (○).

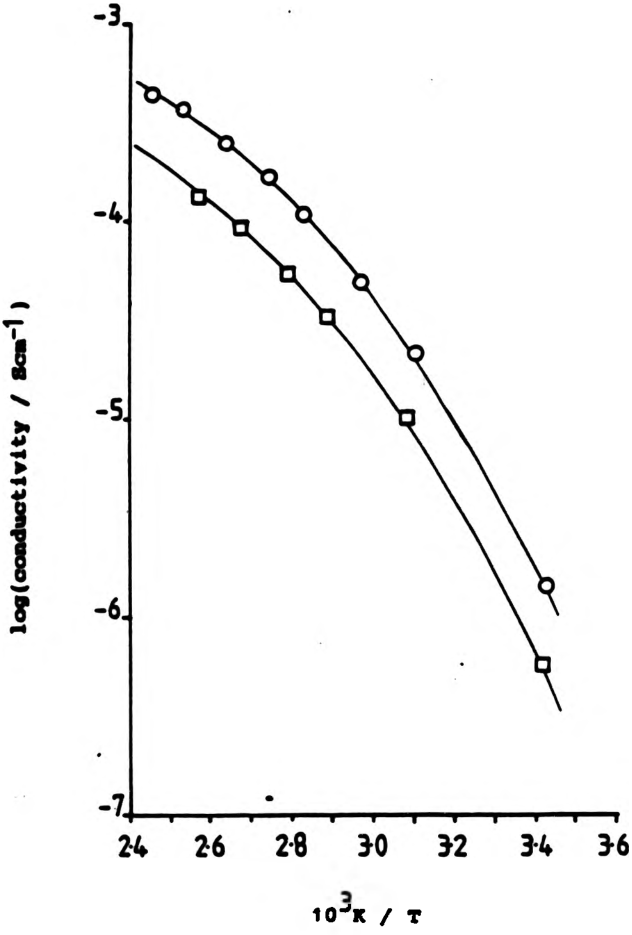
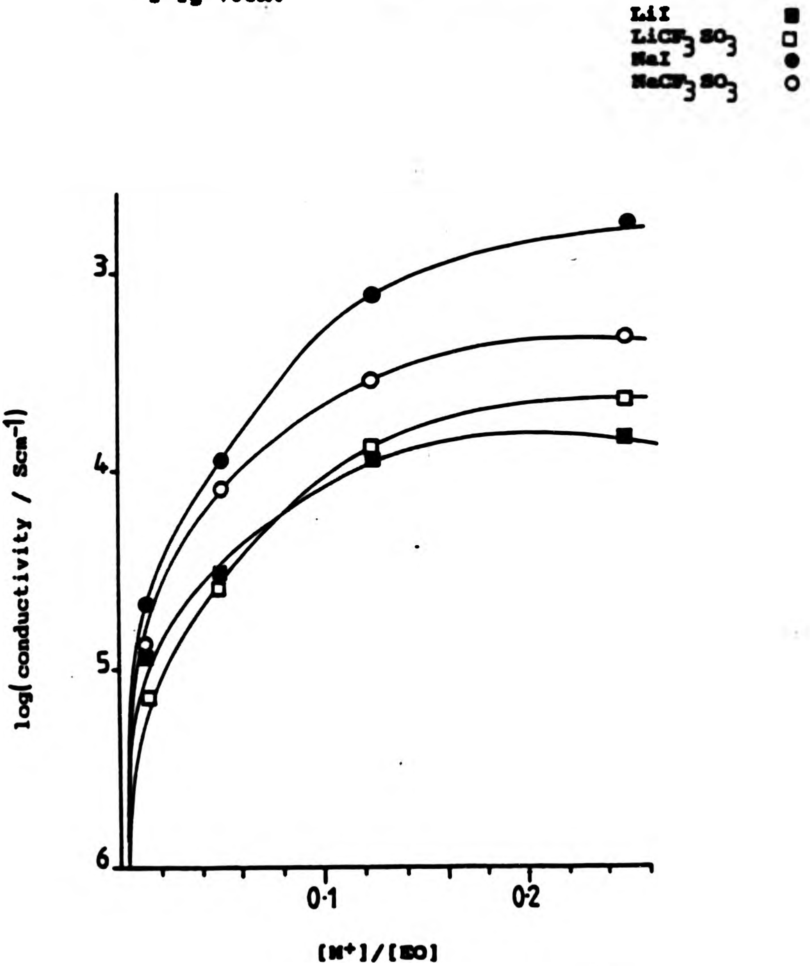


Figure 3.33. Plot of log conductivity against salt concentration for sodium and lithium salt complexes of PCMEEO3I examined under constant reduced temperature conditions of T-Tg=100K.



in the system was increased. In Figures 3.34. and 3.35., the log conductivity as a function of salt concentration, at a reduced temperature of 100K, is displayed for complexes containing lithium and sodium salts respectively.

Comparing these data with the d.s.c. data displayed in Table 3.VI it is apparent that at high concentrations of salt, the conductivity data clearly reflect the increase in charge carriers present in the systems as the anionic radii of the incorporated salt species are increased, particularly when considering the sodium ion complexes.

When considering the materials with a salt concentration of $[M^+]/[EO] = 0.05$ present, however, the iodide complexes in particular appear to show higher conductivity levels than expected from consideration of the estimated number of charge carriers in the systems. Perchlorate complexes also appear to show higher levels of conductivity that expected but to a lesser extent than noted in the iodide complexes.

This behaviour could suggest that the anionic species are mobile in these systems and the extent of anionic conduction detected in these different complexes is dependent on the character of the anion present in the different salts and also the concentration of salt present in the complex.

3.4.1.2 Silver Salt Complexes.

In Figure 3.36. the conductivity-temperature data obtained for PDMEO3I-$AgCF_3SO_3$ complexes containing various concentrations of salt are shown. The magnitude and general trends in conductivity demonstrated by these complexes are

Figure 3.34. Plot of log conductivity against salt concentration for lithium salt complexes of PDMEO3I examined under constant reduced temperature conditions of T-Tg=100K.

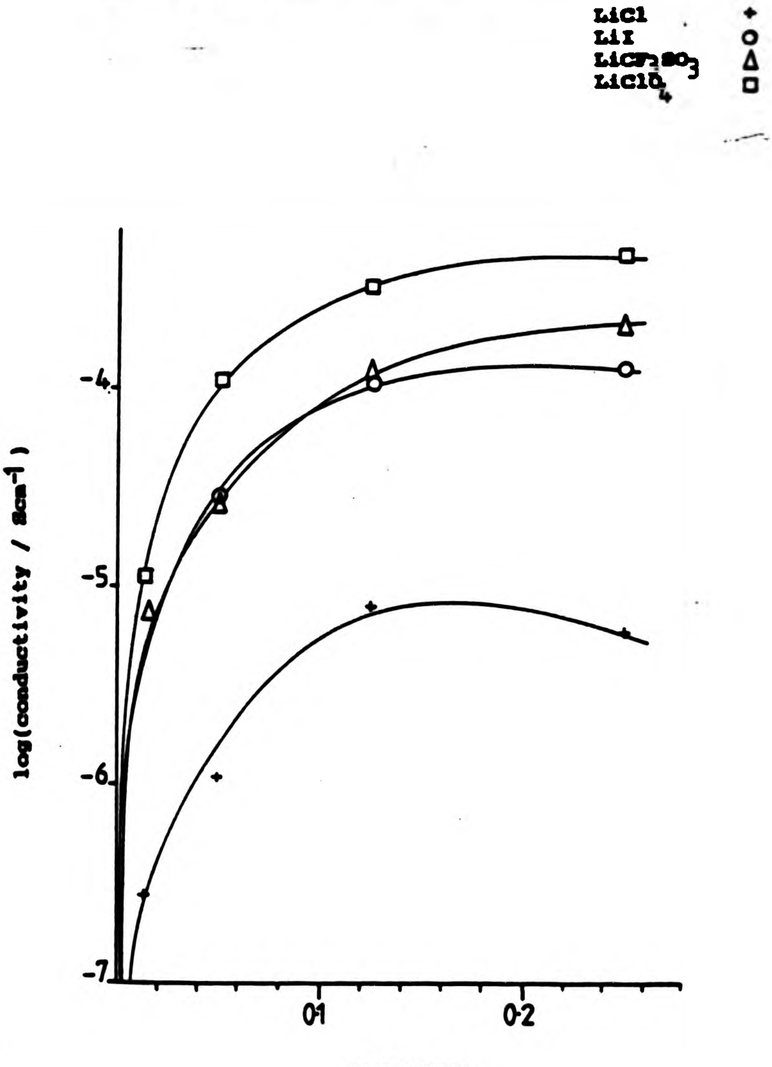


Figure 3.35. Plot of log conductivity against salt concentration for sodium salt complexes of PDMEO3I examined under constant reduced temperature conditions of $T-T_g=100K$.

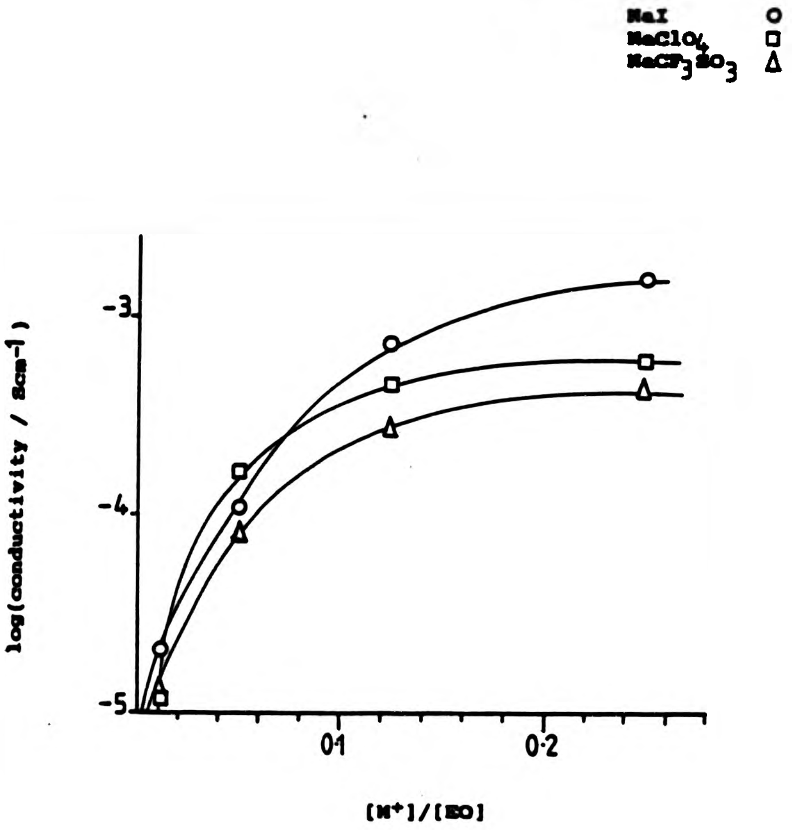
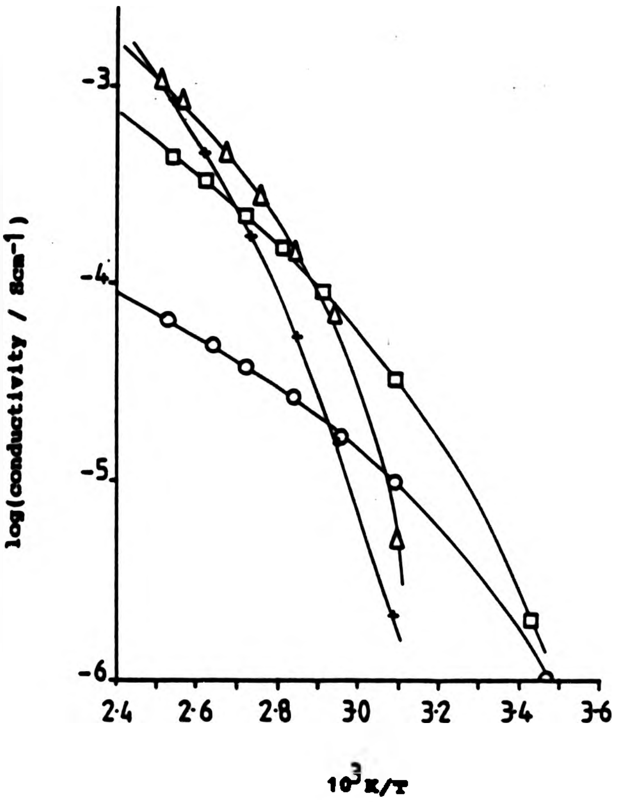


Figure 3.36. Arrhenius Plot of log conductivity against reciprocal temperature for various silver trifluoromethane sulphonate complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).



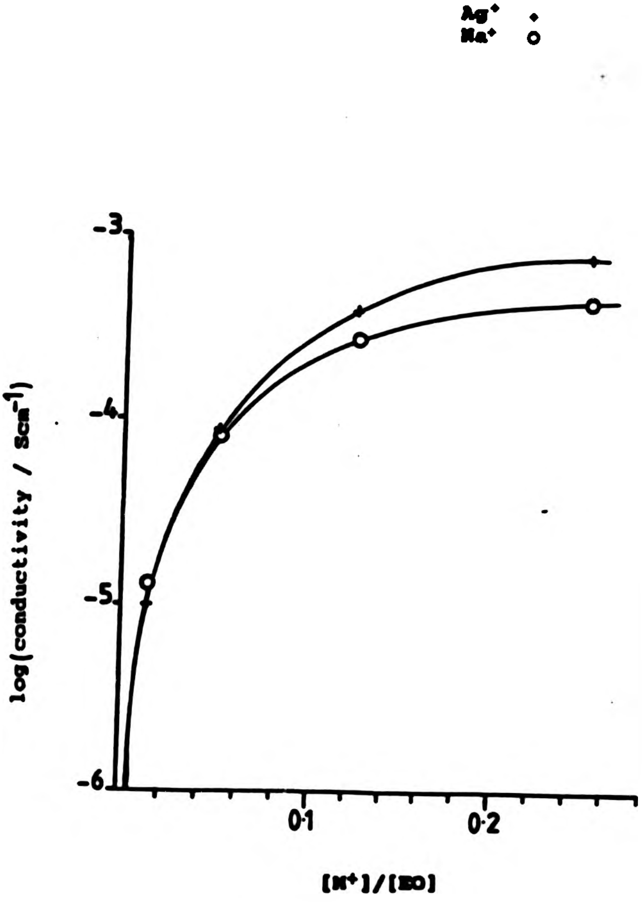
very similar to the behaviour observed for alkali metal salt complexes.

In Figure 3.31. the temperature dependence of the conductivity, at a fixed salt concentration, for triflate complexes in which the cation has been varied is displayed. The conductivity of the silver ion complex is higher than that of the alkali metal salts, throughout the temperature range, but particularly at low temperatures.

Silver ions have an ionic radii which is comparable to the ionic radii of potassium and sodium ions <152>. Since limited data are available for the potassium triflate complexes, the behaviour of the silver and sodium triflate complexes were compared under constant reduced temperatures of 100K, as shown in Figure 3.36a. Similar levels of conductivity were observed for the complexes with a salt concentration of $[M^+]/[EO]$ = 0.05 but at higher salt concentrations the silver ion complexes exhibited higher levels of conductivity.

As shown in Table 3.VI., the enhancement of Tg resulting from ion solvation occurred to a lesser extent, throughout the salt concentration range, when silver ions were introduced rather than sodium ions. The silver ion complex is therefore presumed to contain fewer charge carriers than the sodium ion complex when a particular concentration of salt is incorporated. From this information it can be suggested that silver ions are able to move through the polymer, under constant reduced temperature conditions, with greater ease than the sodium ions.

Figure 3.36a. Plot of log conductivity against salt concentration for sodium and sillver trifluoromethane sulphonate complexes of PDMEO3I examined under constant reduced temperature conditions of T-Tg=100K.



3.4.1.3 Calcium Salt Complexes.

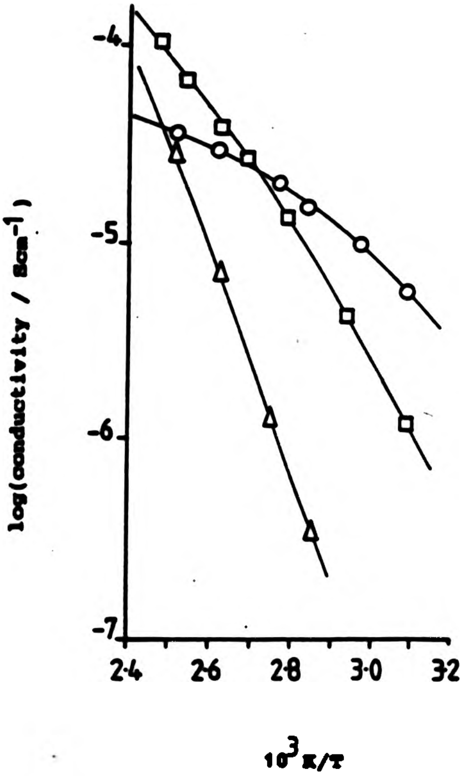
Conductivity results for complexes prepared on addition of $Ca(ClO_4)_2$ to PDMEO3I are shown in Figure 3.37. When the concentration of salt is very low, ($[M^+]/[EO] = 0.0125$) a conductivity of 10^{-5} Scm^{-1} is reached at 336K which is only slightly lower than that observed when similar concentrations of alkali metal perchlorate salts are present in the material. As the concentration of salt in the complex is increased, however, unlike the behaviour demonstrated by the alkali metal perchlorate complexes, little enhancement of the conductivity was observed at high temperatures, while at low temperatures, the conductivity was exceptionally low. At no temperature or salt concentration was a conductivity much greater than 10^{-4} Scm^{-1} recorded.

Conductivity levels of this magnitude are not unexpected, however, when the dramatic increase in Tg, which occurs as the salt concentration in the complex is increased, as shown in Table 3.VI., is considered.

When low concentrations of calcium perchlorate were added to PDMEO3I, the Tg of the polymer was increased in a manner similar to that noted on addition of the alkali metal perchlorate salts to the polymer. At a salt concentration of $[M^+]/[EO] = 0.03$, the enhancement of Tg increased much more dramatically and when salt was present at a concentration corresponding to $[M^+]/[EO] = 0.05$, the enhancement of Tg was much greater than had been observed when a similar concentration of alkali metal perchlorate salt had been incorporated into the polymer.

The addition of calcium perchlorate to PDMEO3I resulted

Figure 3.37. Arrhenius Plot of log conductivity against reciprocal temperature for various calcium perchlorate complexes of PDMEO3I with [M$^+$]/[EO] ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).



in a loss of flexibilty in the polymer which was much more marked than had been noted on dissolution of any other salt in the polymer.

Calcium perchlorate is more soluble in methanol than it is in water <153> and therefore the interaction of the salt with a non-aqueous solvent may be favourable. A favourable polymer-salt interaction would allow the high lattice energy (1958 $kJmol^{-1}$) <154> of $Ca(ClO_4)_2$ to be overcome and dissolution of the salt in the polymer would be possible.

Complete dissociation of the salt to produce Ca^{2+} ions could occur due to the interaction of the polymer and the salt or alternatively partial dissociation to result in the solvation of $Ca(ClO_4)^+$ ions is possible.

The solvation of Ca^{2+} ions would be expected to occur from a polymer-salt interaction geometry similar to that occurring to allow solvation of alkali metal ions. Since the coordinating interaction geometry of the polymer chains, required to allow solvation of the $CaClO_4^+$ species could be slightly different from that required to allow solvation of the alkali metal ions, the changes which would be observed in the Tg of the polymer on solvation of the $CaClO_4^+$ species are more difficult to assess.

Due to the dramatic increase in Tg noted at low concentrations of salt, it can be assumed that solvation of either of the species described above has occurred to produce ions in the polymer on addition of $Ca(ClO_4)_2$.

Although the conductivities observed for the calcium perchlorate complexes were low when considered as a function of increasing temperature, examining the complexes under conditions of constant reduced temperature, when the salt was present at a concentration of $[M^+]/[EO] = 0.05$, the conductivity of the material was only slightly lower than that observed for the sodium perchlorate complex examined under similar conditions, as shown in Figure 3.38.

It is difficult to rationalize this behaviour with no firm evidence as to the character of the ions present in the polymer-salt complex or perhaps, more importantly, knowing whether the main charge carrier in the system is cationic or anionic. From the information available it is only possible to speculate on the reasons for the observed behaviour.

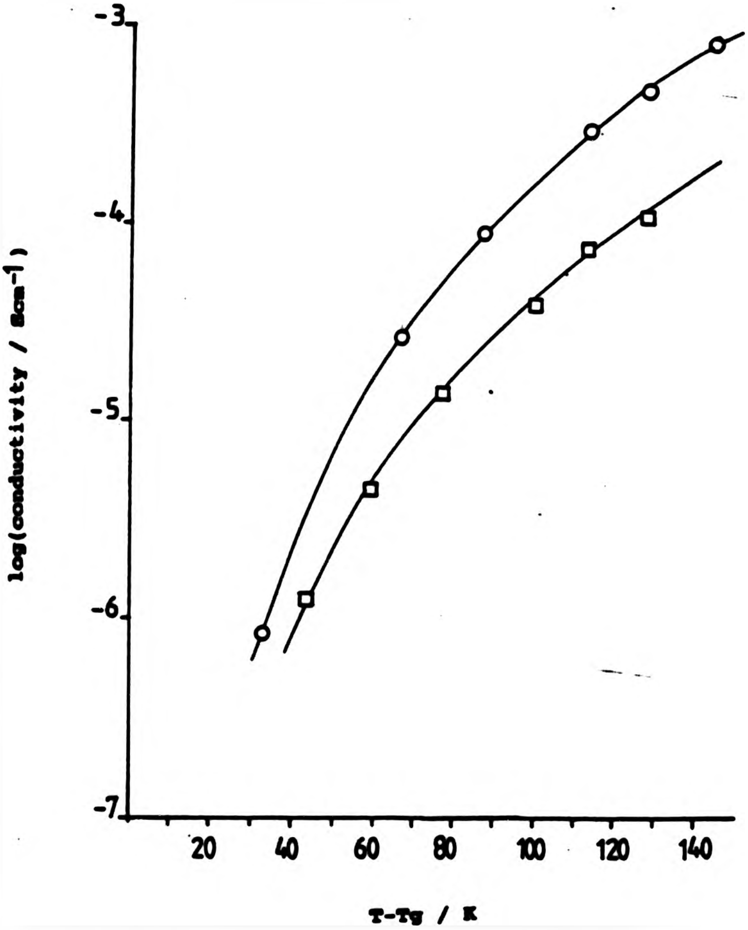
Purely anionic conduction is not suggested unless the dissolution of calcium perchlorate generated fewer charge carriers than the dissolution of the alkali metal perchlorate salt in the polymer. If the perchlorate ion is the predominant charge carrier then the behaviour observed could result from the solvation of $CaClO_4^+$ with dissociation of the salt producing limited mobile anions, compared to those generated in the alkali metal salt complex, but the crosslinking or sidechain stiffening effects in the polymer being more dramatic than those observed in the alkali metal salt complexes.

If the divalent salt complex incorporates Ca^{2+} ions then the mobility of the Ca^{2+} ion is required to be much lower than the mobility of the Na^+ ion, if cation conduction occurs predominantly, since it is assumed that solvation of this species occurred to a much greater extent to produce the observed dramatic increase in Tg.

The behaviour could also be explained if $CaClO_4^+$

Figure 3.38. Plot of log conductivity against reduced temperature for sodium (○) and calcium (□) perchlorate complexes of PDMEO3I.

$[M^+]/[EO]=0.05$



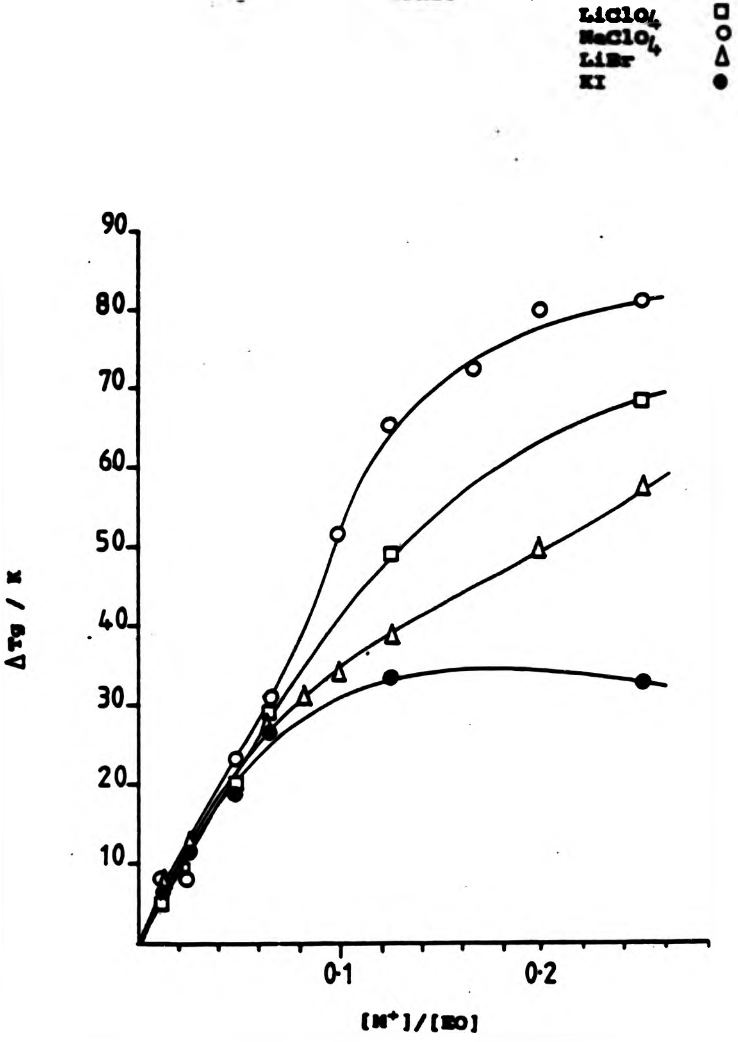
was the predominant charge carrier. The migration of this ion could be expected to be low compared to that of a monovalent alkali metal cation since large ions are expected to contribute less to the conductivity of a system <155>. The coordination geometry of this species could be expected to be different to those considered possible in the complexes prepared from alkali metal salts and the coordination interchange processes required for ion transport through the polymer would also be restricted by the bulk of the ion.

3.4.2 PDPMeG 350I Salt Complexes.

The ΔTg of complexes prepared from alkali metal salts and PDPMeG 350I as a function of salt concentration are illustrated in Figure 3.39. Homogeneous polymer-salt complexes were obtained throughout the salt concentration range on addition of the various lithium and sodium salts investigated. On addition of the potassium salt, KI, optically transparent materials were obtained only on addition of low concentrations of salt. Heterogeneous polymer-salt mixtures were isolated when high concentrations of KI were introduced into the polymer.

The greatest enhancements of Tg were noted on addition of sodium and lithium perchlorate to the polymer and therefore the most effective polymer-salt interaction occurred to produce ions in these complexes. LiBr is a salt with a higher lattice energy than the perchlorate salts and the extent of dissociation of this salt in the polymer is seen to be correspondingly smaller. On introducing KI into the polymer, the initial enhancement of the Tg, noted in Figure 3.39.,

Figure 3.39. Plot of ΔTg vs salt concentration for various salt complexes of PEPMeG 350I.



reflects the solvation of the metal cations by the sidechains in the polymer, however, at a relatively low concentration of salt, the solubility limit of the salt in the polymer is reached. Increasing the salt concentration beyond $[M^+]/[EO]$ = 0.125, no further enhancement of Tg is noted, and the excess salt forms a visible second phase in the polymer. It has been suggested that distortion of a flexible EO chain can occur to allow solvation of large cations, however, the solubility of the salt in the polymer is reduced <39>. In PDPMeG 350I, it would appear that solvation of both lithium and sodium ions can occur relatively easily but the system is less capable of solvating potassium ions without disrupting the natural conformation of the sidechains of the polymer. This salt, KI, therefore has a limited solubility range in the polymer.

In addition to the conductivity-temperature data collected for the alkali metal perchlorate salt complexes of this polymer (Figures 3.8. and 3.20) the conductivity-temperature data were also collected for the LiBr complexes, as shown in Figure 3.40.

3.4.2.1 Effect of Anion Variation.

In Figure 3.41. log conductivities are shown for various $LiClO_4$ and LiBr complexes, as a function of salt concentration at the isothermal temperatures of 323 and 403K. Higher levels of conductivity were exhibited by complexes containing perchlorate anions, however, it is more instructive to consider the materials at a constant reduced temperature of 100K, as shown in Figure 3.42, where the different enhancement of Tg noted on addition of the different salts to the polymer is

Figure 3.40. Arrhenius Plot of log conductivity against reciprocal temperature for various lithium bromide complexes of PDPMaS 350X with $[M^+]/[EO]$ ratios of 0.0125(○), 0.025 (⊖), 0.067 (⊡), 0.125 (Δ) and 0.25 (+).

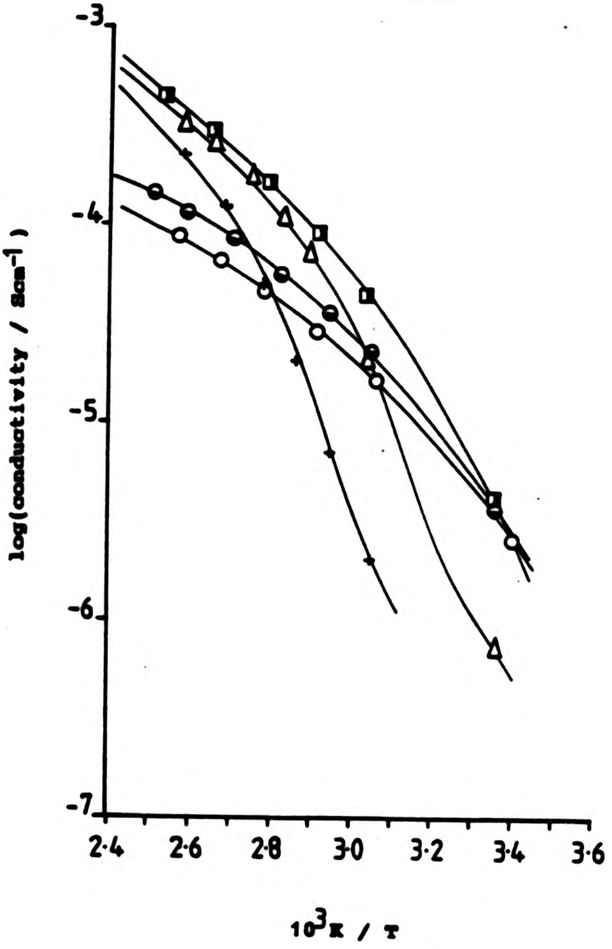


Figure 3.41. Plot of log conductivity against salt concentration for lithium salt complexes of PDPMeG 350I examined at various isothermal temperatures.

$LiClO_4$ □
LiBr Δ

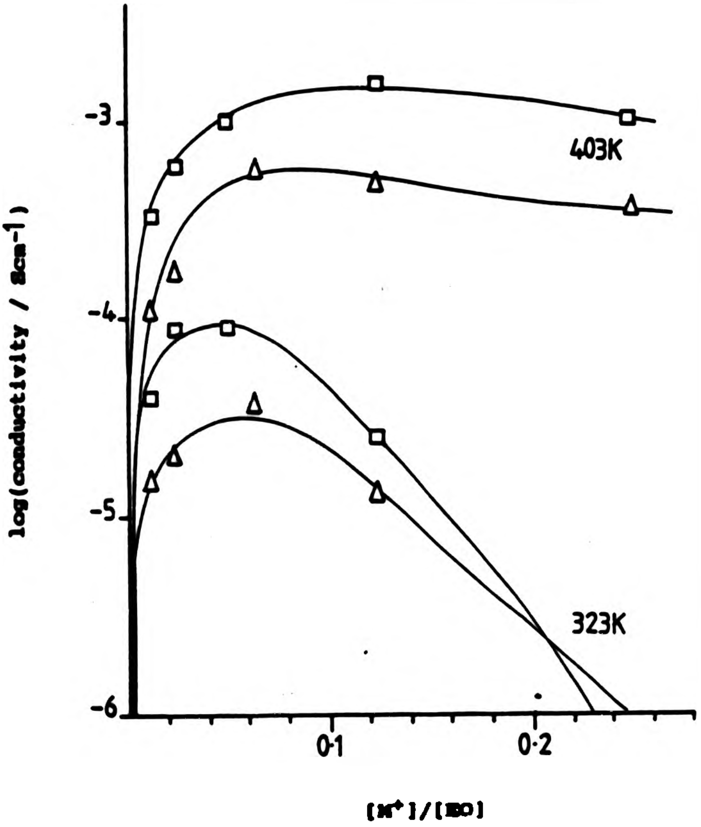
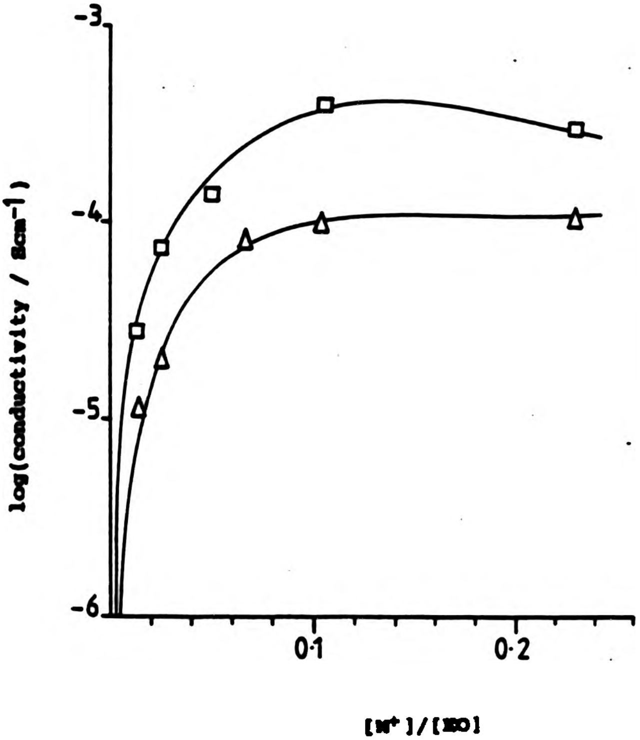


Figure 3.42. Plot of log conductivity against salt concentration for lithium salt complexes of PDPMeG 350I examined under constant reduced temperature conditions of T-Tg=100K.

LiClO$_4$ □
LiBr Δ



taken into account. The enhancement of Tg which occurred on addition of each salt to the polymer is shown in Figure 3.39.

As shown in Figure 3.42., throughout the salt concentration range, the perchlorate complexes exhibited higher levels of conductivity at a reduced temperature of 100K. Particularly at high salt concentrations, the differences noted in the conductivities measured for the different materials can be attributed to the higher number of charge carriers generated in the perchlorate system on dissolution of the salts in the polymer.

The effect of cation variation in this system was discussed previously in Section 3.3.2.4.

From the results of this study it can be concluded that:

1. Optical clarity of a polymer-salt complex suggests that dissolution of a salt in a polymer has occurred to produce ions, however, further examination of the material, e.g. using d.s.c. techniques, is required to determine the extent of cation solvation in the system.
2. The extent of the dissociation of a salt in a polymer is dependent on the cation, but influenced to a greater extent by the anion in the salt.
3. Dissociation of an alkali metal salt in a polymer appears to occur if the salt has a lattice energy below a threshold value. The threshold lattice energy is particular to salts containing a particular cation and as the size of the cation is increased the threshold lattice energy is reduced.

4. For alkali metal salt complexes, the threshold lattice energy for sodium and potassium ion solvation appears to be lower for PDMEO3I than for PEO.

5. In general, dissociation of a salt in a polymer occurs to a greater extent if the salt contains a large anion and the lattice energy of the salt is low.

6. In addition to certain alkali metal salts, these polymeric materials have shown the ability to solvate certain non-alkali metal salts.

7. Conductivity behaviour demonstrated by a polymer-salt complex is dependent on the incorporated salt species, the concentration of salt in the complex and the temperature of examination.

8. If solubility of an alkali-metal salt in a polymer is high, the conductivity of the complex tends to increase as the value $1/(r_c+r_a)$, determined for different alkali metal salts, is decreased.

9. It would appear that as the cation in alkali metal salts, containing a common anion, increases in size, conductivity levels exhibited by the materials are also increased. In most materials this was the result of differences in the number of charge carriers in the system but from limited information available it was suggested that the migration of sodium ions through the polymers, under constant reduced temperature conditions, occurred with greater ease than the migration of lithium ions.

10. In general, salts containing large anions generate more charge carriers in a system and therefore exhibit higher levels of conductivity, however, it was also suggested that under constant reduced temperature conditions, iodide and perchlorate salt complexes, containing a common cation, exhibited higher levels of conductivity than expected from consideration of the number of charge carriers in the system. Anionic conduction may therefore be an important feature of some polymer-salt complexes.

11. It was previously established that purely anionic conduction does not occur in these materials. There is now evidence to suggest that, depending on the anion present in a polymer-salt complex, both ionic species are mobile in the system rather than the cations only. The measurement of transport numbers for the systems is required, however, to establish to what extent anion migration occurs in each system.

CHAPTER FOUR

PROPYLENE OXIDE SUBSTITUTED ITACONIC ACID POLYMER-SALT COMPLEXES.

4.1 Examination of the Undoped Polymer.

The propylene oxide (PO) substituted itaconic acid polymer, PDPPGI, was isolated as a pale brown, viscous fluid. Unlike the other polymeric host materials examined in this study, the sidechains of the polymer were hydroxy terminated rather than methoxy terminated. The polymer was totally amorphous and using d.s.c. the Tg was determined at 220.5K. The Tg of this polymer containing on average 17 PO units per sidechain was comparable to that measured for the EO substituted itaconic acid polymer containing 3 EO units per sidechain, i.e.PDMEO3I.

4.2 Polymer-Salt Complexes Prepared from PDPPGI.

4.2.1 D.S.C. Studies.

In Table 4.I. the Tg values determined at a range of salt concentrations are shown for complexes containing a variety of salts. The enhancement of Tg (ΔTg) noted at a particular salt concentration is shown graphically for each of the materials in Figure 4.1.

In general it was found that a non-linear increase in Tg occurred as the salt concentration in the polymer was increased and, similar to the effect noted on addition of metal halides to PPO <51,52>, the magnitude of the enhancement of Tg, and the salt concentration at which the Tg reached a plateau value, was dependent on the character of the incorporated salt.

Moacanin and Cuddihy <49> carried out one of the earliest studies of polymer-salt complexes and they noted that on addition of 25 wt% lithium perchlorate to PPO 2025, a shift in Tg from 203 to 313K was noted, i.e. ΔTg = 110K, but on

Table 4.I

Glass Transition Temperatures/K measured for various PDPPGI-Salt Complexes.

	$[M^+]/[PO]$					
Salt	0.0125	0.025	0.05	0.067	0.125	0.25
$LiClO_4$	229.0	236.0	248.5	259.5	283.0	295.0
$NaClO_4$	224.0	233.0	254.5	-	290.5	310.0
LiCl	225.0	-	228.0	228.0	227.5	229.0
$ZnCl_2$	227.0	232.5	245.0	-	262.0	274.5

Table 4.II

Conductivities of various Propylene Oxide Based Polymer-salt Complexes.

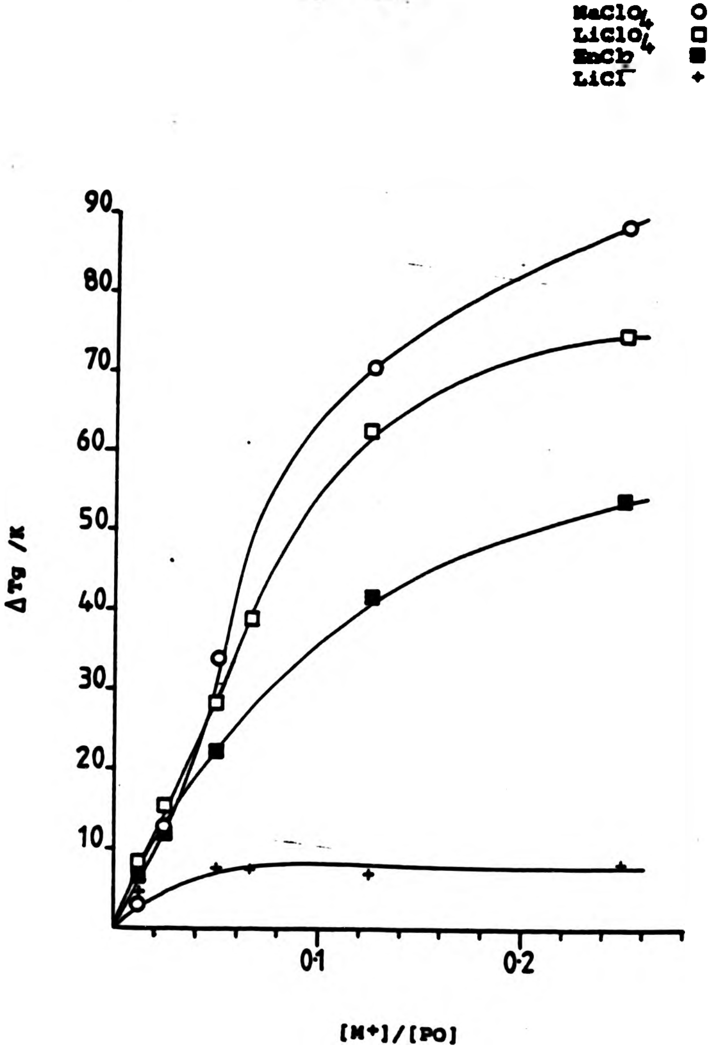
Polymer	Salt	$[M^+]/[PO]$	T/K ($\sigma=10^{-5}$ Scm^{-1})	T/K ($\sigma=10^{-4}$ Scm^{-1})
Linear PPO(a)				
PPO 420	$LiClO_4$	0.125	298	-
PPO 10^5 (b)	$LiCF_3SO_3$	0.11	328	368
Network PPO(c)				
PPO triol 750	$LiCl0_4$	0.05	338	383
PPO triol 3000	$LiClO_4$	0.042	343	-
Comb-Shaped				
PDPPGI	$LiClO_4$	0.0125	344	-
PDPPGI	$LiClO_4$	0.05	322	361
PDPPGI	$LiClO_4$	0.125	344	371

[a] See Ref ‹86›

[b] See Ref ‹85›

[c] See Ref ‹12›

Figure 4.1. Plot of ΔT_g vs salt concentration for various salt complexes of PDPPGI.



addition of similar concentrations of the salt to high molecular weight polymer the increase in Tg was less dramatic. On addition of ca. 30 wt% lithium perchlorate to PDPPGI, i.e. $[M^+]/[PO] = 0.25$, a Tg of 74.5K was noted.

Since the increase in Tg noted on addition of a salt to a polymer is dependent on both the inherent flexibility of the polymer and the loss of flexibility that occurs on addition of the salt to a particular polymer, it is not possible to comment further on the relative dissociation of lithium perchlorate in the various polymers.

From Figure 4.1. it would appear that the interaction of the polymer chains with LiCl is limited. This agrees well with the results presented by James <51,52> who reported that LiCl was insoluble in PPO.

When considering the alkali metal perchlorate complexes of PDPPGI, it is evident that $LiClO_4$ enhanced the Tg of the polymer to a greater extent than $NaClO_4$ at very low salt concentrations while at salt concentrations greater than $[M^+]/[PO] = 0.04$, $NaClO_4$ interacted with the polymer to a greater extent.

On addition of the transition metal salt, $ZnCl_2$, to PDPPGI the Tg of the polymer was enhanced by 55 degrees when salt was incorporated at a concentration of $[M^+]/[PO] = 0.25$. On addition of this salt to PPO <51,52>, a considerable enhancement of Tg was also noted, however, it was suggested that coordination of two ether oxygen atoms directly to the $ZnCl_2$ molecule is possible, to form, in particular, a five membered chelate ring <51>. The formation of this intramolecular chelate ring would result in a loss of flexibility in the sidechains of the polymer without solvated ions being produced. It is therefore difficult to establish, from the d.s.c. data obtained, the extent of ion solvation which has occurred in the PDPPGI-$ZnCl_2$ complex.

Zinc chloride has an extremely high lattice energy (2690 $kJmol^{-1}$) <154>, however, coordination of a third oxygen atom to the dopant would result in the partial dissociation of the salt to produce $ZnCl^+$ and Cl^- ions and solvation of Zn^{2+} ions could also be possible if further polymer-salt interactions occurred.

In general it was found that the interaction of polymer with the salt followed the trend:

$$LiCl < ZnCl_2 < LiClO_4 < NaClO_4$$

Using a non-linear least squares analysis, with no constraints, it was found in this work that the ΔTg versus salt concentration data collected for the $NaClO_4$, $LiClO_4$ and $ZnCl_2$ complexes could be described well, but not perfectly, when the cation solvation in the polymer was considered to be a simple equilibrium of the type shown below <156>.

$$P + MX \rightleftharpoons PM^+ + X^-$$

where P is the polymer, which can be regarded as the number of oxygen sites available for cation coordination, PM^+ is the solvated cation and MX is the alkali metal salt.

[Due to the initial polymer-salt interaction which is believed to occur in the $ZnCl_2$ complexes, the expression above describes the behaviour in these complexes only on coordination of more than two oxygen atoms per salt molecule. LiCl complexes were not analysed using this method.]

It was established in this computer study that dissociation of the salt in each of the complexes was incomplete. $NaClO_4$ was dissociated to the greatest extent in PDPPGI, while $LiClO_4$ was dissociated to a greater extent than $ZnCl_2$. In each of these systems, however, the degree of ionization of the salt in the polymer decreased from >50% to <20% as the concentration of salt in the polymer was increased. This demonstrates that a greater percentage of the incorporated salt remains undissociated in the polymer as the salt concentration in the polymer is increased. Visually, heterogeneity of the materials was not detected.

4.2.2 Conductivity Studies.

It has been suggested that polyethers show relatively high intrinsic conductivities due to an ionic mechanism in which protons are removed from the polymer chains due to the interaction of nearby ether oxygen atoms <157>. As a result of local segmental motions of the polymer chains the protons continually interact with different oxygen atoms and are transported through the polymer.

Due to the presence of the hydroxyl endgroup in the sidechains of PDPPGI, it was considered possible that proton conduction occurring in the material may have complicated the analysis of the conductivity data obtained for the polymer-salt complexes. Since the conductivity for pure PDPPGI was measured at less than 10^{-6} Scm^{-1} throughout the temperature range it was assumed that if proton conduction was occurring in the polymer, it was of a magnitude too small to be detected. All changes noted in the conductivities of the polymer, on addition of a salt were considered to be the result of dissociation of the salt occurring in the polymer, due to the solvation of the cation by the PO sidechain, to produce charge carriers.

Log conductivity-reciprocal temperature data are shown for complexes containing $LiClO_4$, $NaClO_4$, LiCl and $ZnCl_2$ in Figures 4.2. to 4.5. respectively. In each Figure, complexes containing various concentrations of salt have been examined and the conductivity was seen to increase as the temperature was increased. Non-Arrhenius behaviour is exhibited by all the materials.

In Figure 4.6. the levels of conductivity exhibited by each of the polymer-salt complexes are displayed as a function of salt concentration at an isothermal temperature of 403K. Very similar behaviour was exhibited by the alkali metal perchlorate salt complexes. An optimum conductivity of $\sim 5.6\times10^{-4}$ Scm^{-1} was achieved in each system when the polymer incorporated salt at a concentration of $[M^+]/[PO] = 0.09$. In the $ZnCl_2$ complexes, $\sim 5\times10^{-5}$ Scm^{-1} was the maximum conductivity reached and this was noted when the polymer incorporated salt at a concentration of $[M^+]/[PO] = 0.13$. In the LiCl complexes the conductivity reached a plateau value of 1×10^{-5} Scm^{-1} at a concentration of $[M^+]/[PO] = 0.06$.

Concentrating on the $LiClO_4$ complexes it was noted that the maximum in conductivity moved to higher salt concentrations as the isothermal temperature was increased, as shown in Figure 4.7. Unlike the effect noted in the EO materials discussed previously, the maximum in conductivity was pronounced even at high temperatures.

Figure 4.2. Arrhenius plot of log conductivity against reciprocal temperature for various lithium perchlorate complexes of PDPPGI with $[M^+]/[PO]$ ratios of 0.0125 (○), 0.025 (⊖), 0.05 (□), 0.067 (▣), 0.125 (Δ) and 0.25 (+).

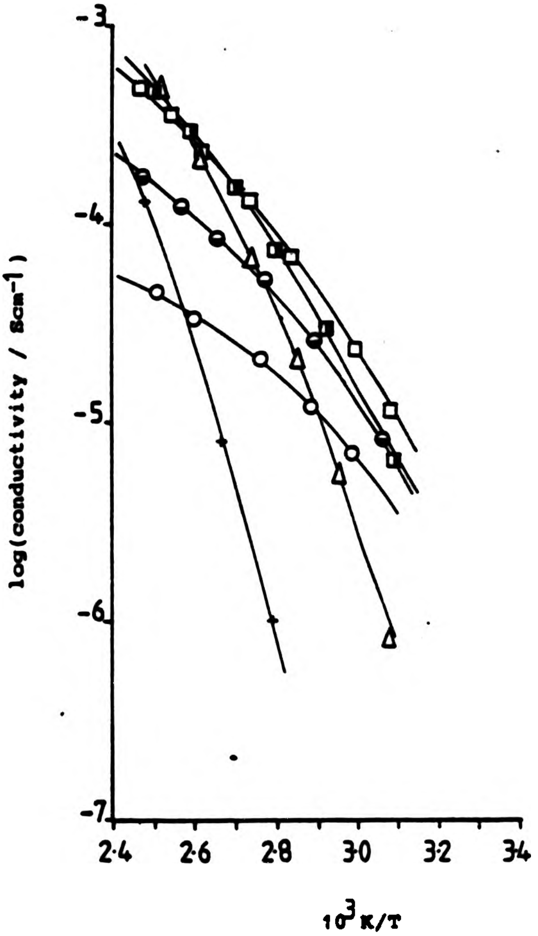


Figure 4.3. Arrhenius plot of log conductivity against reciprocal temperature for various sodium perchlorate complexes of PDPPGI with $[M^+]/[PO]$ ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).

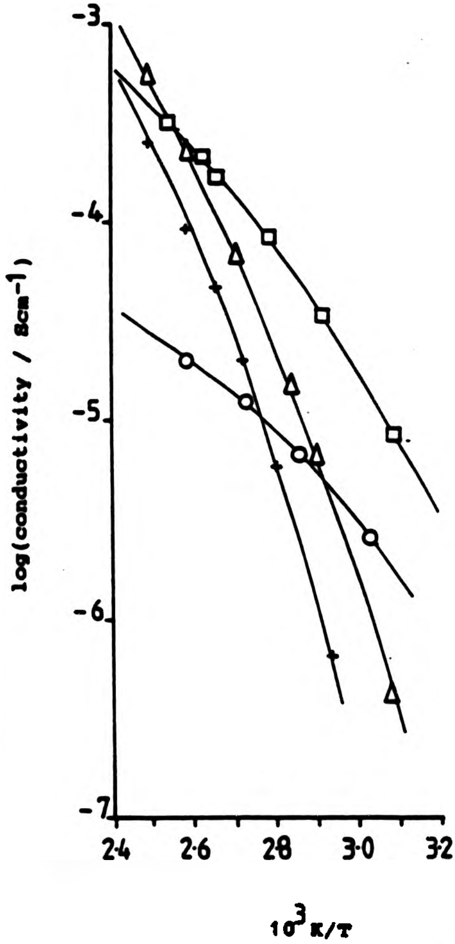


Figure 4.4. Arrhenius plot of log conductivity against reciprocal temperature for various lithium chloride complexes of PDPPGI with $[M^+]/[PO]$ ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).

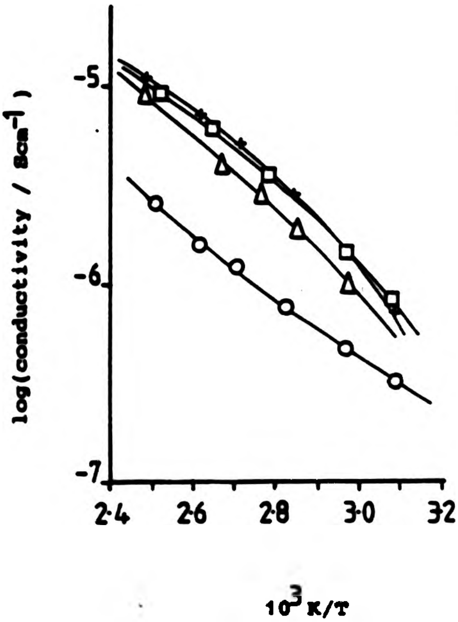


Figure 4.5. Arrhenius plot of log conductivity against reciprocal temperature for various zinc chloride complexes of PDPPGI with [M$^+$]/[PO] ratios of 0.0125 (○), 0.05 (□), 0.125 (Δ) and 0.25 (+).

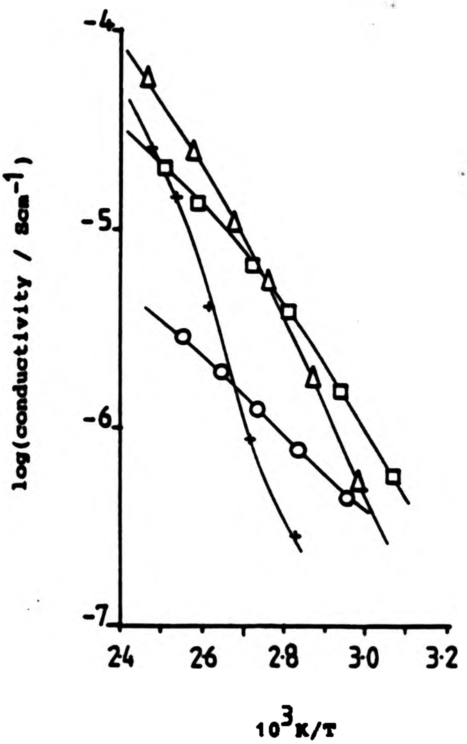


Figure 4.6. Plot of log conductivity against salt concentration for various salt complexes of PDPPGI examined at an isothermal temperature of 403K.

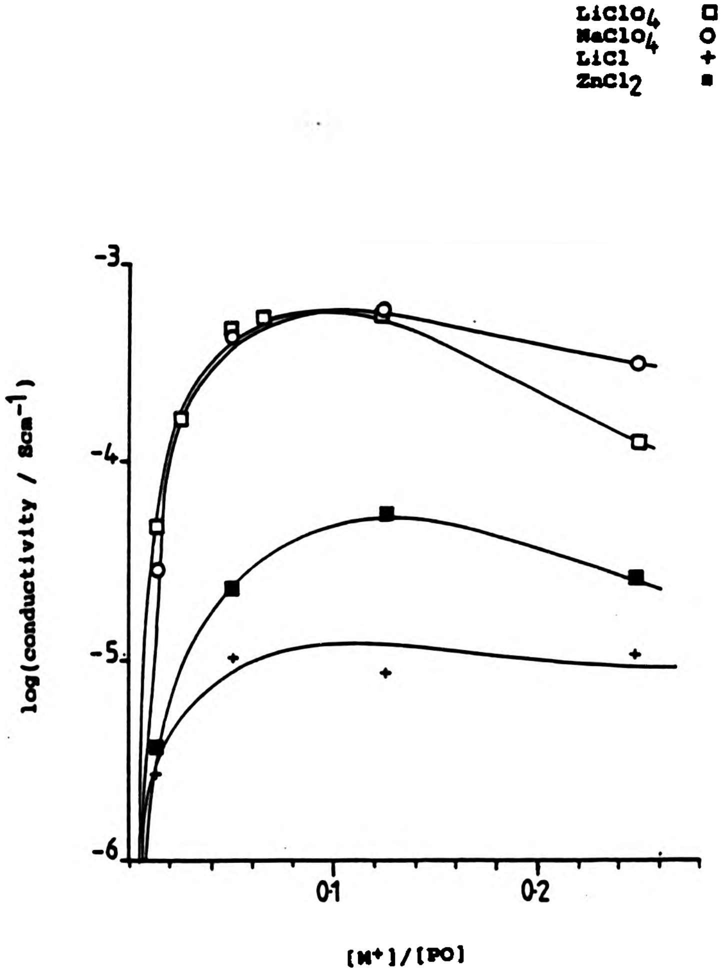
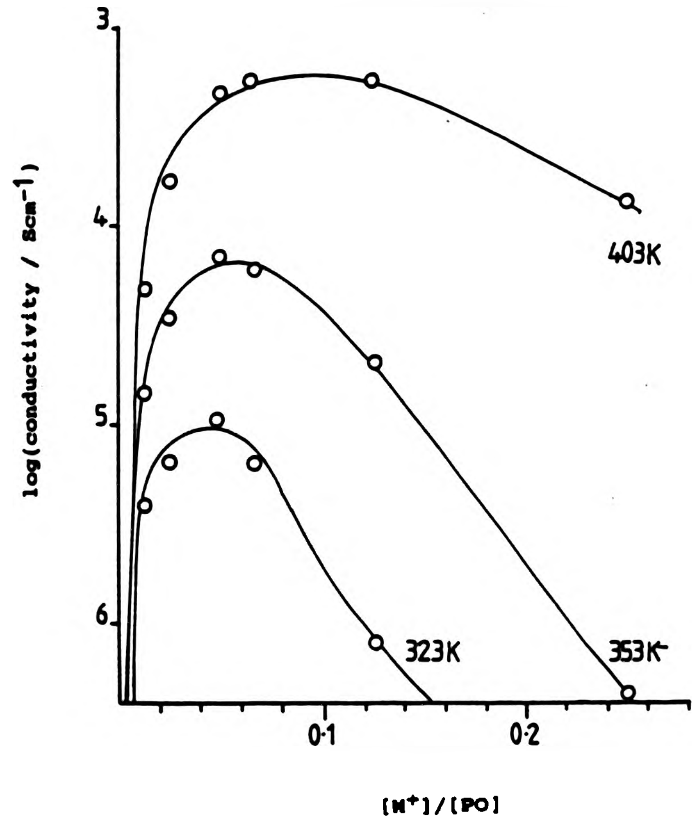


Figure 4.7. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PDPPGI examined at various isothermal temperatures.



Under constant reduced temperature conditions, a maximum in conductivity was found in the material containing salt at a concentration of $[M^+]/[PO] = 0.125$ at all reduced temperatures, as shown in Figure 4.8. This would suggest that, similar to the effects described in Section 3.3.2.3, the conductivity is relatively low at high concentration of salt due to the number of charge carriers in the system decreasing or the charge carriers migrating through the system with less ease. The increased amounts of undissociated salt, present when high concentrations of salt are incorporated into the complex, or the formation of ion aggregates <151>, could explain this drop in conductivity, apparent even at high temperatures, in PDPPGI complexes containing high concentrations of salt.

As the temperature is increased relatively more salt can be incorporated into a polymer before the conductivity is reduced by the restictions described above and therefore this can explain why the maximum in conductivity moves to higher salt concentrations as the isothermal temperature of examination is increased as shown in Figure 4.7.

When examining complexes containing different salts at a constant reduced temperature of 100K, as shown in Figure 4.9., it is evident that in all complexes the increase in conductivity with increasing salt concentration is less pronounced at high concentrations of salt. This effect is less marked in $NaClO_4$ and LiCl complexes compared to the effect noted in the $LiClO_4$ and $ZnCl_2$ complexes.

As the concentration of salt increased in the $NaClO_4$ and LiCl complexes the conductivity reaches a plateau value rather

Figure 4.8. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PDPPGI examined under various constant reduced temperature conditions.

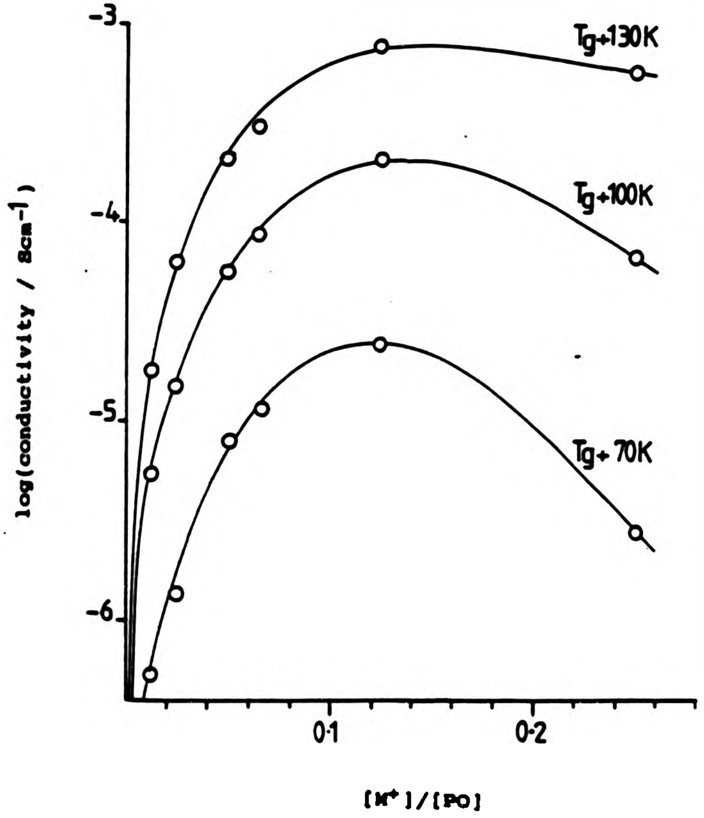
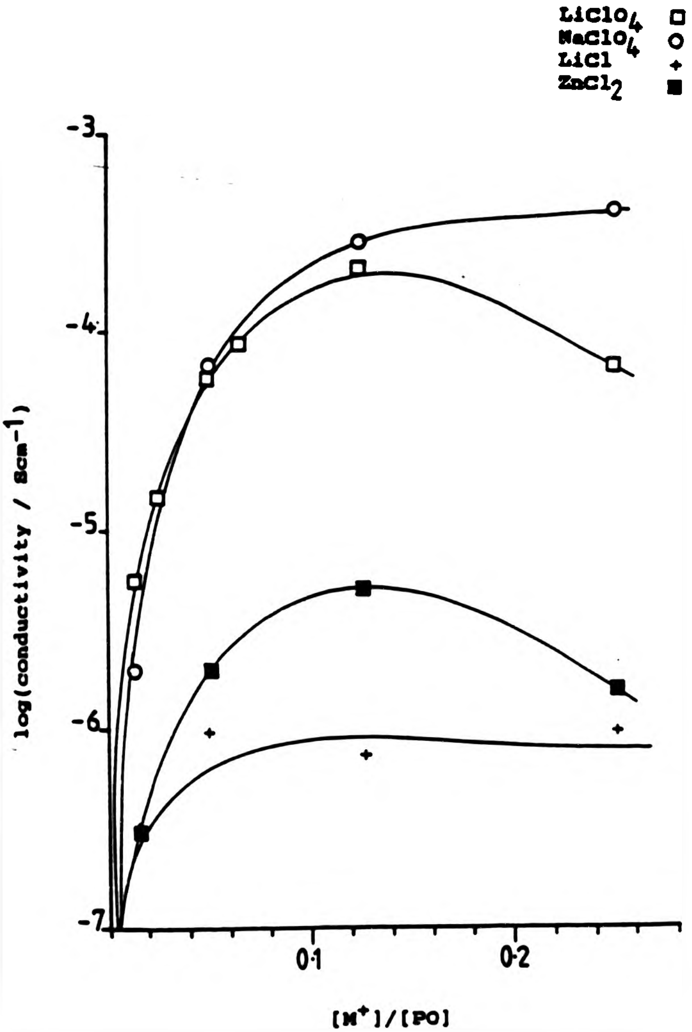


Figure 4.9. Plot of log conductivity against salt concentration for various salt complexes of PDFPGI examined under constant reduced temperature conditions of $T-T_g=100K$.



than decreasing dramatically which would suggest that the reduction in the number of charge carriers or the mobility of the charge carriers is less significant in these materials.

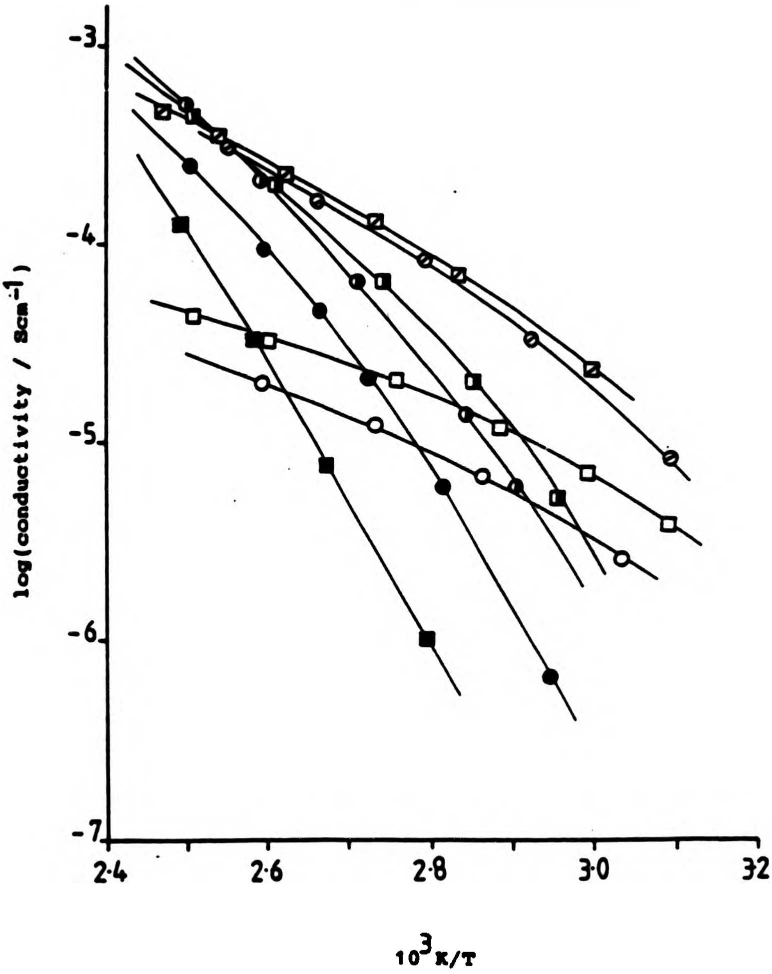
4.2.2.1 Effect of Cation Variation.

In general lithium ion complexes exhibited higher levels of conductivity than sodium ion complexes when comparing the Arrhenius plots of the conductivity-temperature data for these materials, as shown in Figure 4.10., however, examining the materials at a constant reduced temperature, as shown in Figure 4.9, the sodium ion complexes exhibited the highest levels of conductivity, throughout the salt concentration range. In the d.s.c. study of these materials, as shown in Figure 4.1. it was established that a greater number of charge carriers were present in the sodium ion complexes than in the lithium ion complexes and this is the predominant reason for the former systems exhibiting higher levels of conductivity under constant reduced temperature conditions.

Lithium perchlorate enhanced the Tg of the polymer to a lesser extent than sodium perchlorate at any particular salt concentration. The polymer chains are therefore more mobile, at any particular temperature, in the lithium ion complexes. Since fewer charge carriers were generated on addition of the lithium salt to PDPPGI, to rationalize the fact that the lithium complexes exhibited higher levels of conductivity at any particular temperature it must be concluded that in PDPPGI, the lithium ions are able to move through the system with greater ease than the sodium ions. The greater flexibility of the polymer chains, at any particular

Figure 4.10. Arrhenius plot of log conductivity against reciprocal temperature for various alkali metal perchlorate complexes of PDPPGI with $[M^+]/[PO]$ ratios of 0.0125 (□),.0.05 (▨), 0.125 (◧) and 0.25 (■).

NaClO$_4$ ○
LiClO$_4$ □



temperature in the lithium ion complexes, is probably the main reason for the lithium ion complexes having the higher conductivities. This behaviour would also suggest that in the PDPPGI systems, the predominant charge carrier is the cation.

4.2.2.2 Effect of Anion Variation.

Examination of the conductivity of the complexes containing a common cation, under constant reduced temperature conditions should reflect any differences in the number of charge carriers in the system. The conductivities of lithium ion complexes under constant reduced temperature conditions are shown in Figure 4.9. Since the dissociation of $LiClO_4$ in PDPPGI was much greater than the dissociation of LiCl in the polymer, the higher levels of conductivity exhibited by the former systems reflects the greater number of charge carriers present.

Of course, if anion conduction does occur in these materials, then the relative mobilities of the different anions present in the systems could also contribute to the differences noted in the conductivities of the materials.

$ZnCl_2$ can interact with the polymer in the absence of ionization. The extent of charge carrier generation in the system is therefore difficult to determine from the d.s.c. study made of the materials. Examining the $ZnCl_2$ complexes under constant reduced temperature conditions it is apparent that conductivity levels lower than exhibited by the alkali metal perchlorate complexes, but higher than observed for the LiCl complexes were observed for the materials. From this information it would appear that ion generation occurred to some extent in the complex. The conductivity, however, could be the result of predominantly cationic or predominantly anionic migration resulting from the transport of Cl^- ions, Zn^{2+} ions or $ZnCl^+$ ions through the polymer. Due to the size of the $ZnCl^+$ ion, this species would be expected to migrate through the polymer relatively slowly <155>, however, transport numbers must be determined for these systems before further comment is possible on the transport processes in these complexes.

4.2.2.3 Effect of Sidechain Variation.

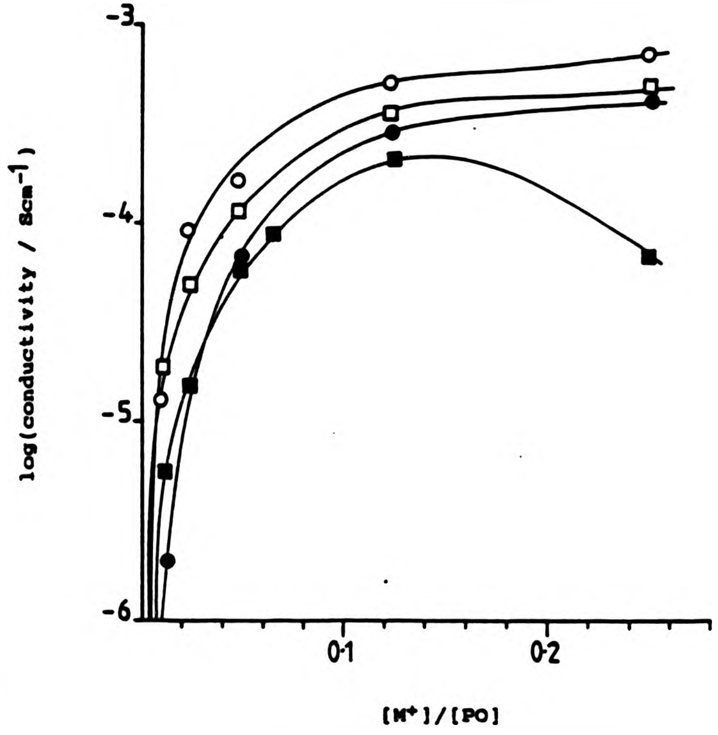
When comparing the Arrhenius plots of the conductivity-temperature data obtained for the alkali metal perchlorate salt complexes of PDMEO3I and PDPPGI as shown in Figures 3.6., 3.19., 4.2., and 4.3., it is apparent that higher levels of conductivity are exhibited by the complexes prepared from PDMEO3I. The data are perhaps easier to assess if the complexes are examined under constant reduced temperature conditions as shown in Figure 4.11.

PDMEO3I would appear to be a better polymeric host for use in a solid state electrolyte than PDPPGI since a greater number of charge carriers have been generated in the EO system. The sidechains in PDPPGI are very much longer than the sidechains in PDMEO3I but the complexes prepared from the former polymer exhibited much lower levels of conductivity, throughout the salt concentration and temperature ranges.

The inherent flexibilities of the two undoped polymers were comparable, however, it is possible that the character of the sidechain in the material is vitally important. It has been

Figure 4.11. Plot of log conductivity against salt concentration for alkali metal perchlorate complexes of PDPPGI and PDMEO3I examined under constant reduced temperature conditions of T-Tg=100K.

	$NaClO_4$	$LiClO_4$
PDPPGI	●	■
PDMEO3I	○	□



suggested that the methyl substituent present in a PO unit inhibits the coordinating ability of the ether oxygen atom <21,32> and therefore restricts solvation of metal cations and the transport of metal cations through the material. It would appear that the lower levels of conductivity observed for the PDPPGI complexes are the result of fewer charge carriers being generated in the system and also the mobility of the ions in the system being lower than in the PDMEO3I complexes. The solvating environment provided by each of the polymers can be compared by considering Figure 4.12. where models representative of each of the sidechains are shown.

4.2.2.4 Comparison of PDPPGI-Salt Complexes With PPO-Salt Complexes.

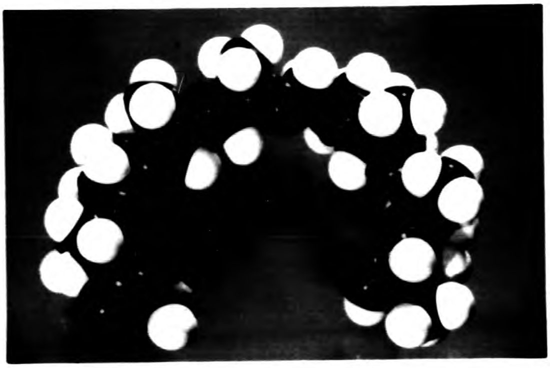
In Table 4.II. the conductivity levels demonstrated by lithium ion complexes of PDPPGI have been compared with the lithium ion complexes prepared from both linear and network PPO. In general it is evident that the conductivity levels demonstrated by complexes prepared from PDPPGI are lower than those demonstrated by complexes prepared from linear PPO, however, the conductivity levels found for the former materials are markedly higher than those exhibited by complexes prepared from crosslinked PPO. [The crosslinked materials have the possible advantage of being more mechanically stable than the PDPPGI complexes, particularly at higher temperatures, as outlined in Chapter 1.]

It is worth noting, with reference to Table 4.II that higher conductivity levels were exhibited by complexes prepared from oligomeric PPO, rather than high molecular

Figure 4.12. Models depicting the solvating environment created in the polyether sidechains of itaconic acid comb-shaped polymers.
a. ethylene oxide sidechain.
b. propylene oxide sidechain.

a.

b.



weight PPO. It is therefore possible that significantly higher levels of conductivity, than observed for these PDPPGI complexes, could be achieved if much shorter PO sidechains were introduced into the itaconic acid comb-shaped polymer and complexes were prepared from this material. The resultant Tg of the new PO substituted material would, of course, be an important factor which would have to be taken into account.

From this study of PO substituted itaconic acid salt complexes it was concluded that:

1. PDPPGI was capable of dissolving certain alkali metal salts and also the transition metal salt $ZnCl_2$. The extent of the polymer-salt interaction which occurred on addition of the salt to the polymer was reflected in the increasing enhancement of Tg noted as the salt concentration in the polymer was increased.
2. Dissociation of the salt was incomplete in all polymer-salt complexes and as the salt concentration was increased in the polymer the degree of dissociation of the salt decreased.
3. Sodium perchlorate was dissociated to a greater extent than lithium perchlorate or zinc chloride in the polymer, throughout the salt concentration range. This effect was apparent when comparing the conductivities exhibited by the alkali metal perchlorate complexes under constant reduced temperature conditions but in general, throughout the temperature and salt concentration ranges the lithium ion complexes exhibited higher levels of conductivity than the sodium ion complexes.

4. PDPPGI complexes show lower levels of conductivity than measured for complexes prepared from PDMEO3I, when both the salt and the salt concentration in the complexes were comparable.
5. PDPPGI complexes appear to exhibit lower levels of conductivity than complexes prepared from linear PPO, however, they show higher levels of conductivity than reported for complexes prepared from crosslinked PPO.

CHAPTER FIVE

ETHYLENE OXIDE SUBSTITUTED VINYL ETHER POLYMER-SALT COMPLEXES.

5.1 Examination of the Pure Polymer.

The vinyl ether based comb-branched polymer containing sidechains 3 EO units long, PVEMEO3, was isolated as a pale yellow material which was totally amorphous. Using d.s.c. the Tg of the material was determined at 206.5K.

When comparing the undoped polymers containing methoxy terminated sidechains 3 EO units long, i.e. PVEMEO3 and PDMEO3I, it would appear that the comb-branched polymer based on a vinyl ether backbone and containing only one sidechain per monomeric unit, is inherently more flexible than PDMEO3I which is based on the itaconic acid backbone and contains two sidechains per monomeric unit.

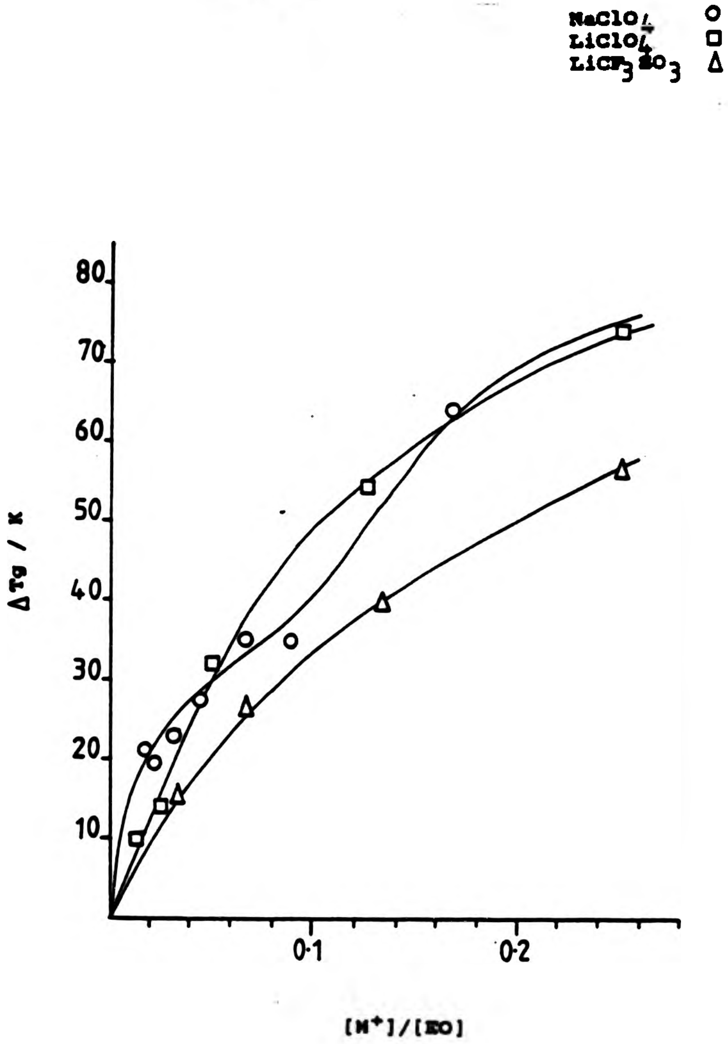
5.2 Alkali Metal Salt Complexes.

5.2.1 D.S.C Studies.

In Figure 5.1 the ΔTg of various polymer-salt complexes is described as a function of salt concentration. A non-linear increase in Tg is noted as the salt concentration in each complex is increased. On addition of sodium perchlorate to the polymer, an inflexion is noted in the plot of ΔTg versus salt concentration, similar to the effect observed on addition of various salts to PDMEO3I. This behaviour was thought to be the result of a transition from one predominant coordination process to another occurring as the salt concentration was increased in the polymer.

In PVEMEO3, $NaClO_4$ and $LiClO_4$ increased the Tg of the polymer to the greatest extent and when a salt concentration corresponding to $[M^+]/[EO] = 0.25$ was present in the polymer the Tg was increased by 74 K. $LiCF_3SO_3$ enhanced the Tg to a

Figure 5.1. Plot of ΔT_g vs salt concentration for various salt complexes prepared from PVEMEO3.



lesser extent, throughout the salt concentration range.

As shown in Figure 3.3 . the PDMEO3I complexes containing $LiClO_4$ at a concentration of $[M^+]/[EO] = 0.25$ showed a ΔTg of 90.5K while a similar concentration of $NaClO_4$ enhanced the Tg of PDMEO3I by 88K, as shown in Figure 3.2. The addition of alkali metal perchlorate salts to each of the polymeric hosts, has resulted in a greater loss of flexibility in the PDMEO3I system compared to that which occurred in the PVEMEO3 based materials. Since the enhancement of Tg, noted on addition of a salt to a polymer, at a particular salt concentration is dependent on both the inherent flexibility of the polymer and the loss of flexibility observed in the polymer due to the polymer-salt interactions, it is not possible to comment further on the relative dissociation of the salt in the polymers.

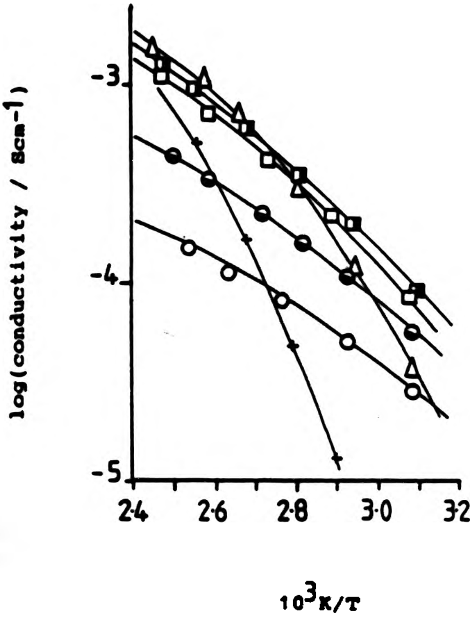
5.2.2 Conductivity Studies.

The conductivity of the parent polymer was measured as less than 10^{-6} Scm^{-1} throughout the temperature range. On addition of $LiClO_4$ to the polymer, marked enhancements in the conductivity were noted due to the generation of charge carriers which had occurred in the system on dissociation of the salt.

In Figure 5.2. the log conductivities of $LiClO_4$-PVEMEO3 complexes, containing various concentrations of salt, are plotted against reciprocal temperature. Curved lines were obtained and therefore the conductivity-temperature data can not be interpreted using an Arrhenius analysis.

In general, conductivities in excess of 10^{-4} Scm^{-1} were

Figure 5.2. Arrhenius plot of log conductivity against reciprocal temperature for lithium perchlorate complexes of PVEMEO3 with $[M^+]/[EO]$ ratios of 0.0125 (○), 0.025 (⊖), 0.05 (□), 0.067 (▣), 0.125 (Δ) and 0.25 (+).



observed for all complexes throughout the temperature range but at high temperatures, conductivities approaching 1.6×10^{-3} Scm^{-1} were measured for some complexes.

The conductivities of the complexes were examined isothermally as a function of salt concentraion and in Figure 5.3 the data are displayed graphically for temperatures of 323, 353 and 403K. At 323K the maximum conductivity measured was 10^{-4} Scm^{-1} when the complex contained $LiClO_4$ at a concentration of $[M^+]/[EO] = 0.06$. As the temperature was increased, the maximum in the conductivity became less pronounced and also occurred at higher salt concentrations. At 403K the maximum conductivity of approximately 1.5×10^{-3} Scm^{-1} was observed for complexes containing salt at a concentration of $[M^+]/[EO] = 0.11$. On examining the complexes under a constant reduced temperature of 100K, a maximum in conductivity was noted when salt concentrations in the complex corresponded to $[M^+]/[EO] = 0.125$, as shown in Figure 5.4. It is therefore suggested that in this polymer, when high concentrations of salt are present, even at high temperatures the conductivities of the materials are lowered due to fewer charge carriers existing in the system or the mobility of the charge carriers being restricted.

5.2.3 Comparison of $LiClO_4$ Complexes of PVEMEO3 and PDMEO3I.

When comparing the Arrhenius plots of the conductivity-temperature data collected for the $LiClO_4$ complexes of PVEMEO3 and PDMEO3I, (Figures 3.19. and 5.2.) it is apparent that throughout the temperature and salt

Figure 5.3. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PVEMEO3 examined at various isothermal temperatures.

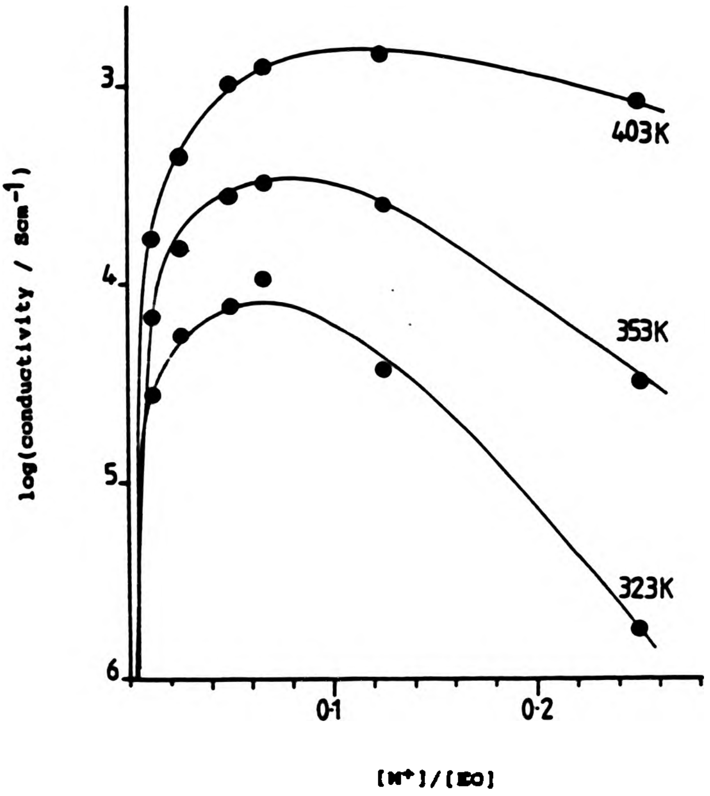
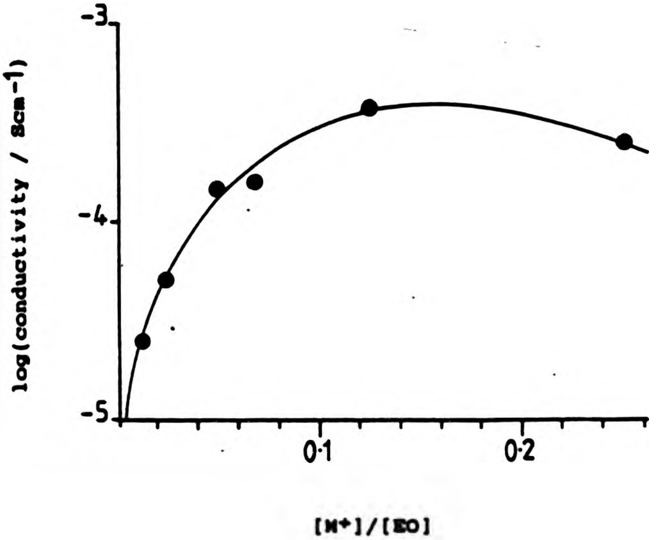


Figure 5.4. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PVEMEO3 examined under constant reduced temperature conditions of T-Tg=100K.



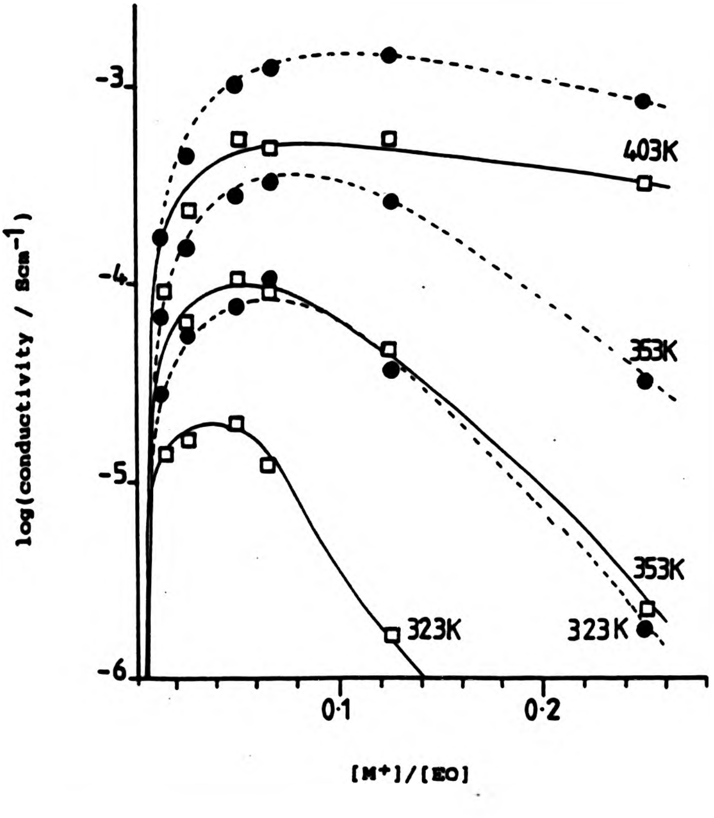
concentration ranges, higher levels of conductivity were measured for the PVEMEO3 complexes. The differences in the conductivities are more apparent from consideration of Figure 5.5. where the materials are compared under several isothermal conditions.

Undoped PVEMEO3 has a lower Tg than pure PDMEO3I and on addition of lithium perchlorate to PVEMEO3, the Tg of the polymer was enhanced to a much lesser extent than noted on addition of the salt to PDMEO3I. In the PVEMEO3 complexes the polymer chains are therefore much more flexible than in the PDMEO3I complexes, at any temperature.

The materials were compared under a constant reduced temperature of 100K, as shown in Figure 5.6. and with the exception of the complexes containing salt at a concentration of $[M^+]/[EO] = 0.25$, the conductivities exhibited by the materials prepared from PVEMEO3 and PDMEO3I are only marginally different, throughout the salt concentration range. This would suggest that the number of charge carriers is comparable in each system. Higher conductivities are therefore measured for the PVEMEO3 complexes as a result of the solvated cations enhancing the Tg of the polymer to a lesser extent than in the PDMEO3I complexes. At any temperature, the greater mobility of the polymer chains in the PVEMEO3 complexes resulted in the complexes prepared from that polymer exhibiting higher levels of conductivity than the PDMEO3I complexes, throughout the salt concentration range.

Under constant reduced temperature conditions the number of charge carriers generated in PDPMeG 350I on addition of $LiClO_4$ is comparable to those generated in the PDMEO3I and PVEMEO3

Figure 5.5. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PVEMEO3 (●) and PDMEO3I (□) examined at various isothermal temperatures.



complexes, as shown in Figure 5.6.

Undoped PDPMeG 350I has a lower Tg than that measured for PDMEO3I but higher than the Tg measured for PVEMEO3. The increases in Tg, noted on incorporation of $LiClO_4$ into PDPMeG 350I were much smaller than those noted on addition of the salt to PDMEO3I and it has been established that, under isothermal conditions, the conductivity levels demonstrated by $LiClO_4$ complexes of PVEMEO3 and PDPMeG 350I are comparable, as shown in Figure 5.7.

PVEMEO3 therefore appears to resemble PDPMeG 350I to a greater extent than it resembles PDMEO3I, when comparing the behaviour of the materials for use as the polymeric host in a solid state electrolyte.

From examination of Figure 5.6., where the reduced temperature conductivities of the lithium perchlorate complexes of PDMEO3I, PDPMeG 350I and PVEMEO3 are shown as a function of salt concentration, it is apparent that the conductivity of each complex falls on a common value at a reduced temperature of 100K, when the complexes contain salt at a concentration of $[M^+]/[EO] = 0.125$.

In Figure 5.8. the log conductivity, as a function of reduced temperature, has been plotted for complexes containing salt at a concentration of $[M^+]/[EO] = 0.125$ prepared from each of the three polymers discussed above. Throughout the reduced temperature range, the conductivity values exhibited by each of the three materials fall on a common line. At this particular salt concentration, when the mobilities of the polymer chains in each of the complexes are the same, and a common salt is present, the conductivity-temperature relation

Figure 5.6. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PVMMEO3 (●), PDMEO3I (□) and PDPMeG 350I (○) examined under constant reduced temperature conditions of $T-T_g = 100K$.

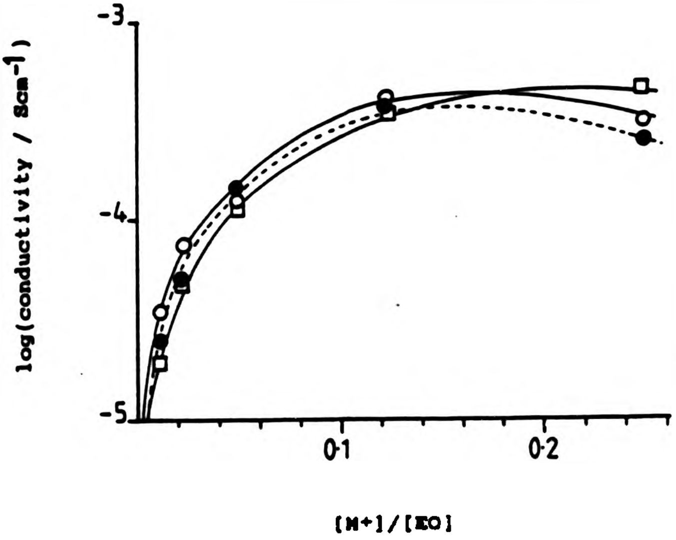


Figure 5.7. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PVEMEO3 (●) and PDPMeG 350I (○) examined at various isothermal temperatures.

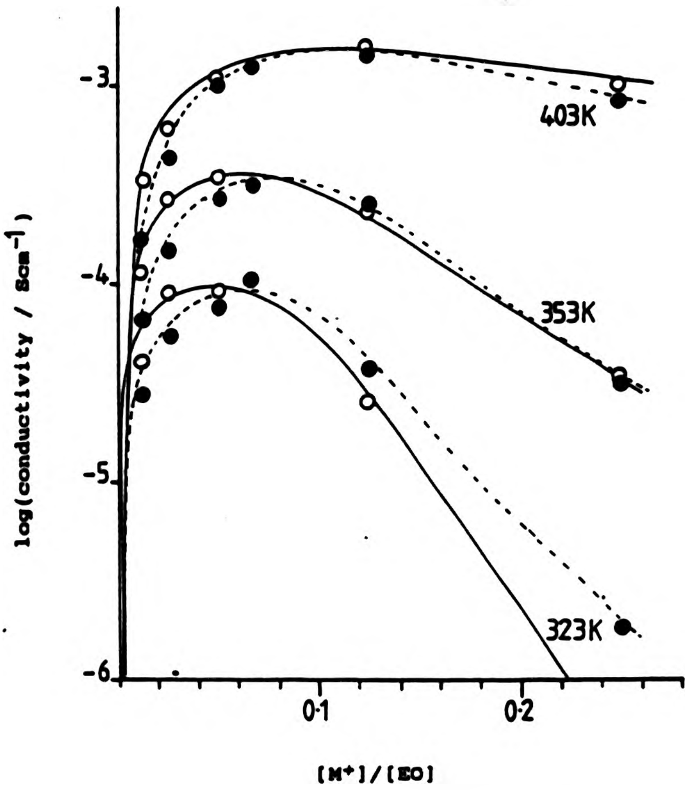
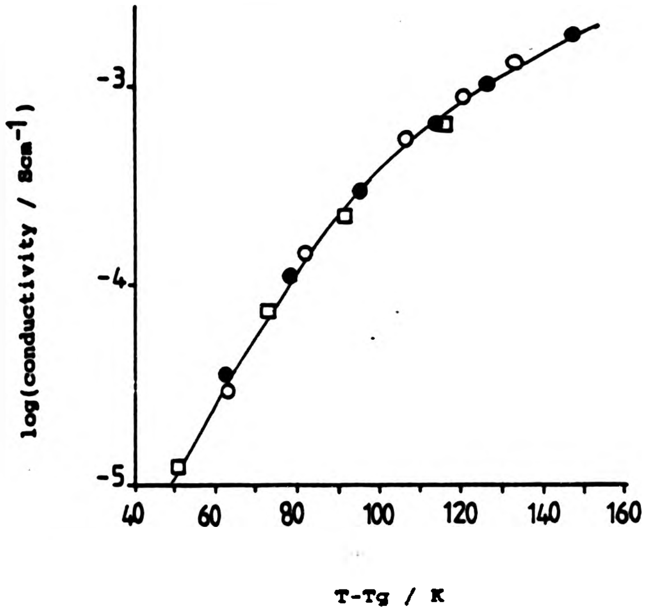


Figure 5.8. Plot of log conductivity against reduced temperature for lithium perchlorate complexes of PVEMEO3 (●), PDMEO3I (□) and PDPMeG 350I (○).
$([M^+]/[EO] = 0.125)$



exhibited by PVEMEO3, PDMEO3I and PDPMeG 350I is identical.

From this study of the salt complexes prepared from PVEMEO3, it was established that:

1. PVEMEO3 is capable of dissolving alkali metal salts and the enhancement of Tg noted in the polymer on addition of salt was lower than that observed when similar concentrations of the same salt were added to PDMEO3I.
2. From the conductivity study it was established that under constant reduced temperature conditions, the conductivity levels observed for complexes containing lithium perchlorate at a concentration of $[M^+]/[EO] = 0.125$, prepared from PVEMEO3, PDMEO3I and PDPMeG 350I were comparable. This suggested that a similar number of charge carriers had been generated on introducing the salt into each of the polymeric hosts.
3. When comparing the conductivities exhibited by $LiClO_4$ complexes of PVEMEO3 and PDMEO3I, containing the same concentration of salt, at a particular temperature, higher conductivities are observed for the PVEMEO3 complexes, as a result of the polymer chains in the complex having a greater segmental mobility than the chains in the PDMEO3I complex.
4. The lithium perchlorate complexes of PVEMEO3 exhibit conductivity temperature behaviour which is comparable to the behaviour exhibited by $LiClO_4$ complexes of PDPMeG 350I.

5. The comb-branched polymer prepared from a vinyl ether backbone and containing EO sidechains 3 units long appears to be a more useful polymeric host than the comb-branched polymer prepared from the itaconic acid backbone which contains EO sidechains 3 units long. Comparable conductivities are exhibited by the complexes prepared from polymers based on an itaconic acid backbone if the sidechains incorprated into the polymer are on average 7 EO units long.

CHAPTER SIX

POLY(VINYL METHYL ETHER) SALT COMPLEXES

6.1 Examination of the Pure Polymer.

Poly(vinyl methyl ether)(PVME) is an isomer of PPO and therefore contains ether oxygen atoms which may be capable of interacting with cations of an added salt to form polymer-salt complexes.

The undoped polymer is totally amorphous and using d.s.c. the Tg was measured at 255.5 K. When comparing this material with the itaconic acid based comb-shaped polymers, PVME and PDMEO2I have similar Tg values and therefore the inherent flexibility of the polymer chains in each material is comparable.

6.2 D.S.C. Studies.

Optically transparent products formed on addition of salts to PVME suggested the dissolution of the salt in the polymer. In Table 6.I, the "apparent homogeneity" or optical transparency of the materials formed on addition of various salts to PVME is described. PVME appeared to be capable of solvating only lithium ions although it was difficult to establish whether $NaClO_4$ was dissolved in the polymer or not.

D.s.c. was therefore used to examine the Tg of materials containing salt at a concentration of $[M^+]/[O] = 0.05$ and the Tg values determined are shown in Table 6.II. It is confirmed from the d.s.c. study that only lithium salts are solvated to any great extent in PVME <23>. Since LiCl is reported to be soluble in PEO <14>, the threshold lattice energy for complex formation using salts with a lithium cation is lower for PVME than for PEO.

Table 6.I

"Apparent Homogeneity" of PVME containing Alkali Metal Salts

Anion	Cation		
	Li^+	Na^+	K^+
Cl^-	No	No	No
I^-	Yes	No	No
ClO_4^-	Yes	?	-
$CF_3SO_3^-$	Yes	No	No
BF_4^-	Yes	-	-

Table 6.II

Glass Transition Temperatures/K of materials formed on addition of various salts to PVME ($[M^+]/[O] = 0.05$).

Anion	Cation		
	Li^+	Na^+	K^+
Cl^-	257.5	256.5	259.0
I^-	274.5	256.5	258.0
ClO_4^-	277.5	258.5	---
$CF_3SO_3^-$	270.0	260.5	256.5
BF_4^-	267.0	---	---

The enhancement of Tg noted in the complexes containing lithium salts will probably result from crosslinking interaction processes occurring on solvation of the metal cations in the polymer. This will reduce the flexibility of the polymer and increase the Tg. The ΔTg values noted for several salt complexes as a function of increasing salt concentration are shown in Figure 6.1. It is apparent that $LiClO_4$ increased the Tg of the polymer by 60 degrees when the complex contained salt at a concentration of $[M^+]/[O] = 0.25$. $LiCF_3SO_3$ enhanced the Tg of the polymer to a lesser extent throughout the salt concentration range while $NaClO_4$ increased the Tg of the polymer by only 6 degrees when high concentrations of salt had been incorporated.

6.3 Conductivity Studies.

The undoped polymer exhibited levels of conductivity lower than 10^{-6} Scm^{-1}, throughout the temperature range. In general, conductivity levels higher than measured for the undoped polymer were determined for the polymer-salt complexes containing lithium salts, but only at temperatures greater than 360K.

The conductivity levels demonstrated by complexes containing various concentrations of $LiClO_4$ are shown in Figure 6.2. When log conductivity was plotted as a function of reciprocal temperature, straight lines were obtained and therefore the conductivity-temperature behaviour of these materials can be examined using an Arrhenius analysis. Arrhenius behaviour was not observed for any of the other polymer-salt complexes examined in this study.

Figure 6.1. Plot of ΔT_g vs salt concentration for materials prepared on addition of various alkali metal salts to PVME.

$LiClO_4$ □
$LiCF_3SO_3$ Δ
$NaClO_4$ ○

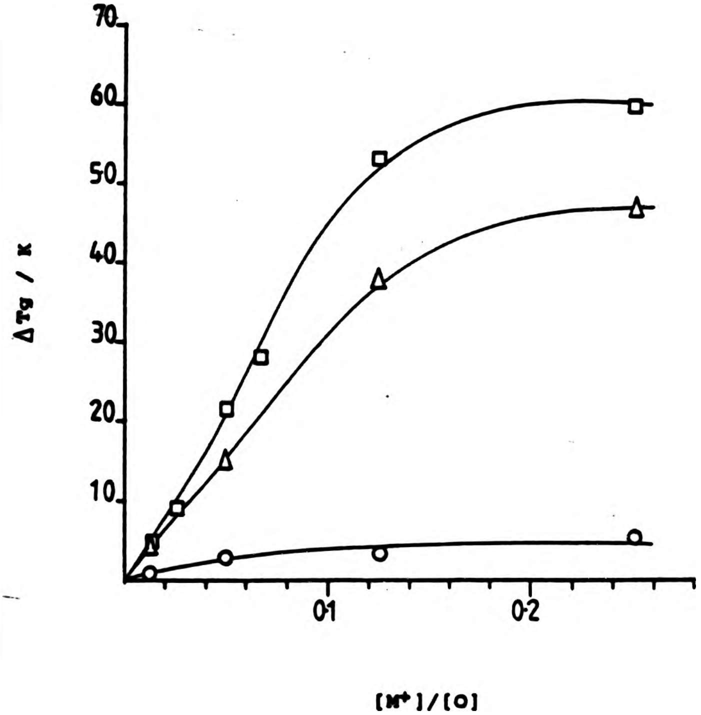
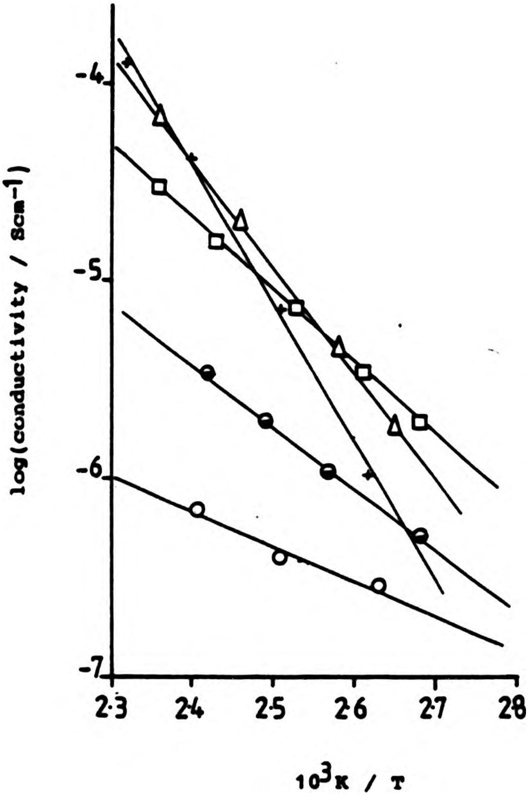


Figure 6.2. Arrhenius plot of log conductivity against reciprocal temperature for various lithium perchlorate complexes of PVME with $[M^+]/[O]$ ratios of 0.0125 (○), 0.025 (⊖), 0.05 (□), 0.125 (Δ) and 0.25 (+).



As the concentration of salt in the complex was increased from $[M^+]/[O] = 0.0125$ to 0.25., the activation energy for the ion conduction process increased correspondingly from approximately 34 $kJmol^{-1}$ to 134 $kJmol^{-1}$. This indicates that increasing the salt concentration reduces the flexibility of the polymer chains, which inhibits the motion of ions through the system.

As shown in Figure 6.3., a plateau conductivity level of $1.6x10^{-5}$ Scm^{-1} was observed for complexes containing $LiClO_4$ at concentrations in excess of $[M^+]/[O] = 0.11$ when the complexes were examined at a constant temperature of 403K.

Examination of the complexes 100K above the Tg of the materials indicated that the number of charge carriers in the systems increased continually as the concentration of salt in the complex increased. The dramatic incease in conductivity noted initially was not continued throughout the salt concentration range as shown in Figure 6.4. Examination of the complexes under constant reduced temperature conditions would suggest that when high concentrations of salt are present in the polymer, the conductivity is lower than expected from consideration of the equation presented by Angell <87,150> and therefore the number of charge carriers in the system must be reduced or the ions must exhibit reduced mobilities when the concentraion of salt in the complex is high.

When considering the $LiClO_4$-PVME complexes, which exhibited the highest levels of conductivity, throughout the salt concentration and temperature ranges, it was possible to achieve conductivity levels of 10^{-4} Scm^{-1} at 430K, when the concentration of salt in the complex was $[M^+]/[O] = 0.25$.

Figure 6.3. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PVME examined at an isothermal temperature of 403K.

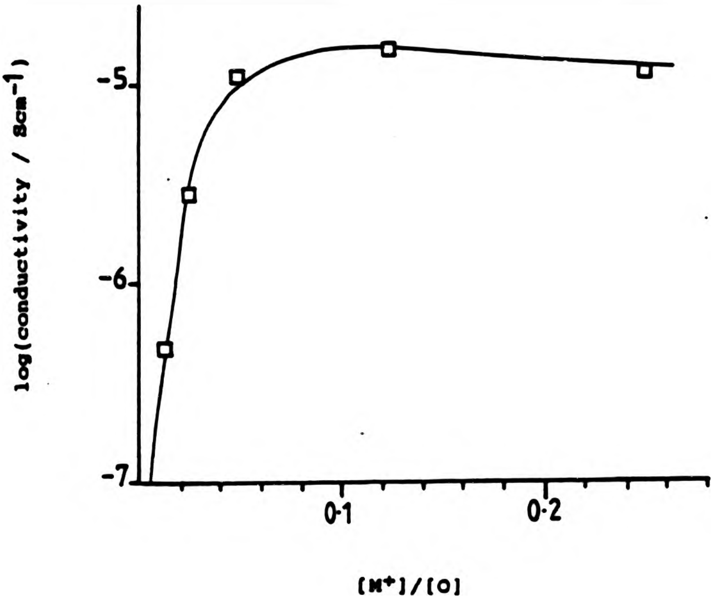
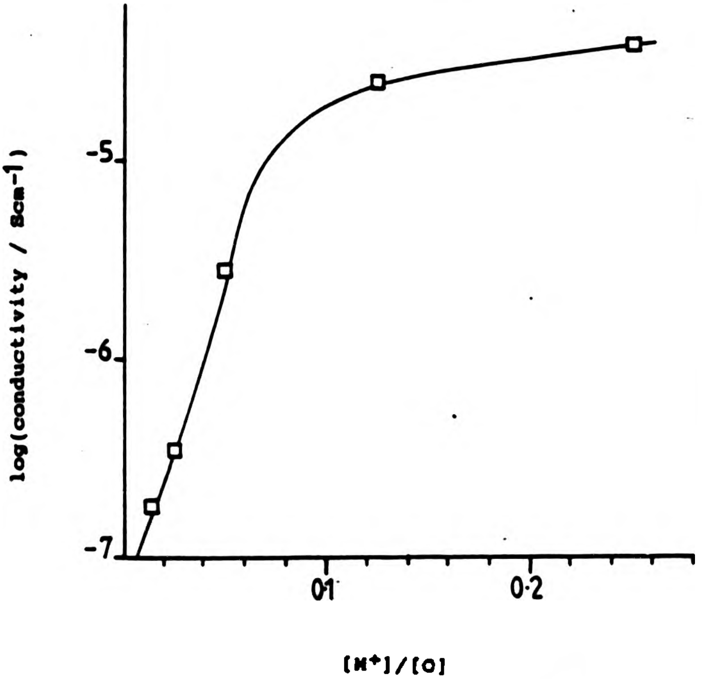


Figure 6.4. Plot of log conductivity against salt concentration for lithium perchlorate complexes of PVME examined at a constant reduced temperature of T-Tg=100K.



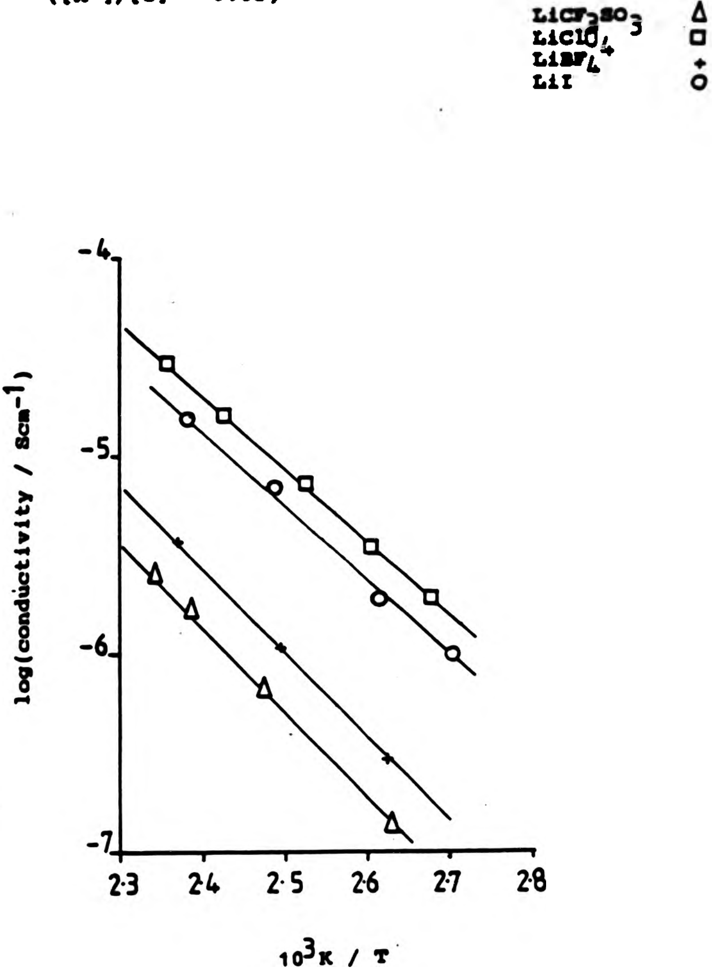
In Figure 6.5. log conductivity is shown against 1/T for complexes containing different lithium salts at a concentration of $[M^+]/[O] = 0.05$. The dissociation of each of these salts occurred to a different extent in the polymer, as described in the d.s.c. study, and therefore the levels of conductivity exhibited by the materials reflects the variation in the number of charge carriers in the systems predominantly. In the Figure the slopes of each of the plots were comparable, independent of the incorporated salt and an average value of ~64 $kJmol^{-1}$ was calculated for the activation energies.

It was established previously that a polymer suitable for use in solid state electrolyte applications must incorporate a high density of polar groups with readily available lone pairs, positioned with an optimum spacing between each, along the polymer chain.

From consideration of Figure 6.6., it is possible to compare the chemical environment provided by polymers based on PEO, PPO and PVME. PVME has a hydrocarbon backbone and the ether oxygen atoms are present in the sidechain of the structure, unlike PPO where the oxygen atoms occur regularly in the backbone of the polymer. From the information gained in this study it is apparent that the presence of the oxygen atoms in the sidechains of PVME do not provide the optimum spacing between polar groups, which is required for effective polymer-salt interactions, on addition of salts to the polymer.

In PVME, a more open structure is adopted by the polymer due to the position of the methyl groups at close proximity to the polymer backbone. In this polymer only extremely small

Figure 6.5. Arrhenius plot of log conductivity against reciprocal temperature for various lithium salt complexes of PVME. ($[M^+]/[O] = 0.05$)



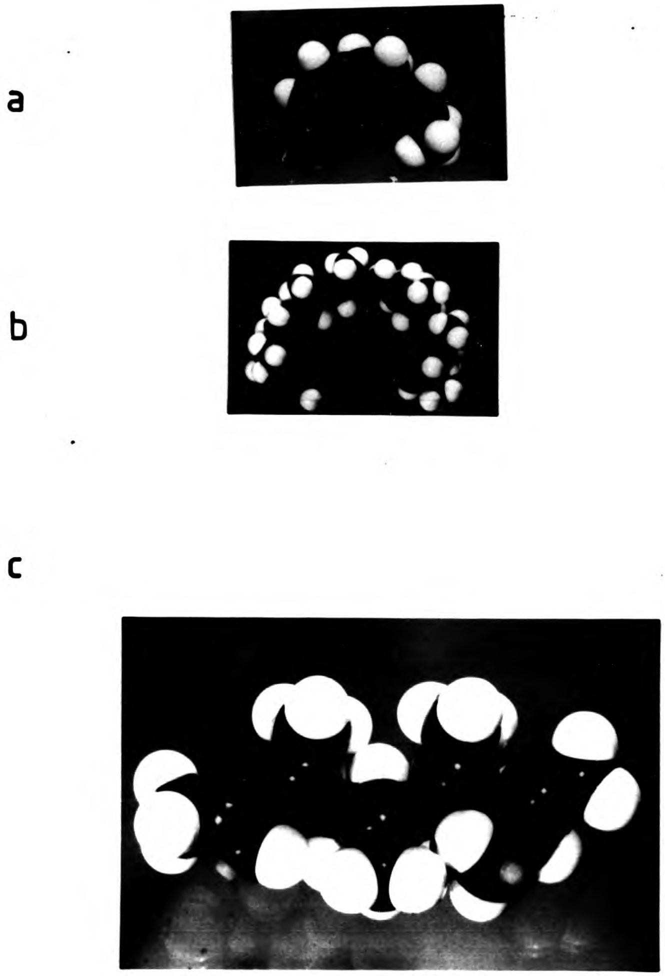


Figure 6.6. Models demonstrating the solvating environment present in materials containing
a. ethylene oxide sidechains,
b. propylene oxide sidechain
and also that present in
c. poly(vinyl methyl ether).

sections of the chain can be oriented in such a way that an oxygen-rich environment can be formed, unlike the conformations which can be adopted by polymers incoporating EO or PO units, where even small sections of the polymer chains provide an oxygen-rich environment, as a result of all oxygen atoms being oriented towards the interior of a helix.

Both the solvation of cations and the transport of the ions through the polymer appears to be restricted in PVME due to the poor solvating environment provided by the open chain polymer structure. This is reflected in the low conductivity levels observed for the complexes prepared from this polymer.

From the information gained in this study it would appear unlikely that conductivity levels comparable to those demonstrated in EO- or PO- based polymer-salt complexes could ever be achieved, when using PVME as the host polymer in a solid state electrolyte.

CHAPTER SEVEN

THEORETICAL TREATMENT OF CONDUCTIVITY-TEMPERATURE DATA.

7.1 Conductivity-Temperature Data.

Curved lines were obtained when log conductivity was plotted against reciprocal temperature for complexes prepared from itaconic acid and vinyl ether based comb-shaped polymers. These complexes therefore do not exhibit conductivity-temperature behaviour which can be analyzed in terms of the Arrhenius Equation. Materials which do not exhibit Arrhenius conductivity-temperature behaviour can be examined using the Vogel-Tammann-Fulcher (VTF) equation in the form

$$\sigma = A'T^{-1/2}\exp\left(\frac{-B}{T - To}\right) \qquad 7.i.$$

where A' and B are constants and To is a reference temperature.

7.1.1 Analysis Using Experimentally Determined Reference Temperatures.

Tg has been identified as the reference temperature when analysing the conductivity-temperature data of polymer-salt complexes using the VTF equation <119,135>. In this study the Tg values, determined for a polymer-salt complex, prepared from a particular polymeric host, increased as the salt concentration in the polymer increased. It was therefore possible to identify two reference temperatures which could be employed in Equation 7.i, to analyse the data in terms of the VTF equation, one representative of the undoped polymeric host, and another representative of the doped polymer samples. The conductivity-temperature data obtained for various characteristic salt complexes, prepared from each of the polymeric hosts, were therefore examined initially using experimentally measured (d.s.c.) reference temperatures.

Method 1: $\log(\sigma T^{1/2})$ was plotted against reciprocal T-Tg where Tg is particular to each polymer-salt complex.

Method 2: $\log(\sigma T^{1/2})$ was plotted against reciprocal $T-Tg_o$ where Tg_o is the temperature measured for the undoped polymer and was therefore unchanged when considering salt complexes prepared from a particular polymeric host.

The slopes of the straight lines obtained when plotting the conductivity-temperature data in the forms described above, corresponds to the constant, B, in Equation 7.i., with units of temperature in Kelvin. B has been assumed representative of an activation energy (Ea') in many studies <71,119,127,135> and Ea' values in the range 3-10 kJmol^{-1} have been reported previously in the study of polymeric electrolytes.

Using methods 1 and 2, linearization of the conductivity-temperature data was possible for all salt complexes prepared from the itaconic acid or vinyl ether based comb-shaped polymers. In Table 7.I. the values of the constant B, determined from the slope of the linearized data and also Ea' values calculated directly from the B values, are displayed for representative salt complexes prepared from each of the polymeric hosts.

It has been pointed out that discrepencies can arise in the values obtained from the VTF analysis as a result of the choice of reference temperature used in Equation 7.i. <129>. In this study, it was noted that Ea' values increased as the reference temperature employed in Equation 7.i. was lowered

Table 7.I

Values of B and Ea' determined from the VTF equation using method 1 (*) and method 2 (**).

Polymer-Salt Complex			B/K		Ea'/kJmol^{-1}	
Polymer	Salt	$[M^+]/[S]$	*	**	*	**
PDMEO1I	NaClO$_4$	0.05	136	155	2.6	3.0
PDMEO2I	NaClO$_4$	0.05	163	238	3.1	4.6
PDMEO3I	NaClO$_4$	0.0125	222	258	4.2	4.9
	NaClO$_4$	0.05	213	349	4.1	6.7
	NaClO$_4$	0.125	186	609	3.6	11.7
	NaClO$_4$	0.25	160	764	3.1	14.6
	LiClO$_4$	0.0125	196	229	3.8	4.4
	LiClO$_4$	0.05	189	362	3.6	6.9
	LiClO$_4$	0.125	188	615	3.6	11.8
	LiClO$_4$	0.25	181	1020	3.4	19.5
PDMEO5I	NaClO$_4$	0.05	212	328	4.0	6.3
PDPMeG 350I	NaClO$_4$	0.05	231	332	4.4	6.4
PDPPGI	LiClO$_4$	0.0125	235	268	4.5	5.1
	LiClO$_4$	0.05	259	405	5.0	7.8
	LiClO$_4$	0.125	212	710	4.1	13.6
	LiClO$_4$	0.25	325	974	6.2	18.6
	NaClO$_4$	0.0125	268	287	5.1	5.5
	NaClO$_4$	0.05	200	381	3.8	7.3
	NaClO$_4$	0.125	208	788	4.0	15.1
	NaClO$_4$	0.25	222	813	4.2	15.6
	ZnCl$_2$	0.0125	290	322	5.6	6.2
	ZnCl$_2$	0.05	269	410	5.2	7.9
	ZnCl$_2$	0.125	335	633	6.4	12.1
	ZnCl$_2$	0.25	541	1040	10.4	19.9
	LiCl	0.0125	235	224	4.5	4.3
	LiCl	0.05	252	286	4.8	5.5
	LiCl	0.125	289	306	5.5	5.9
	LiCl	0.25	256	295	4.9	5.6
PVEMEO3	LiClO$_4$	0.0125	199	239	3.8	4.6
	LiClO$_4$	0.05	209	343	4.0	6.6
	LiClO$_4$	0.125	194	505	3.7	9.7
	LiClO$_4$	0.25	248	933	4.7	17.9

[a] S is the solvating unit particular to each polymer, as described in Section 2.2.6.

from Tg to Tg_0. The magnitude of the differences in the results, noted on changing the polymeric host, the incorporated salt or the concentration of salt in the complex, were dependent on whether Tg or Tg_0 was used as the reference temperature and changes in B and Ea' were of a smaller magnitude when the data were obtained using method 1 rather than method 2. In general, B and Ea' increased as the salt concentration in the complex increased. B ranged from 136-541 K and Ea'was calculated as 2.6-10.4 $kJmol^{-1}$ using method 1. Using method 2, values in the range 155-1040 K and 3.0-19.9 $kJmol^{-1}$ were determined for B and Ea' respectively.

Although Ea' values were obtained using both methods, method 1, in particular, produced Ea' values which were of comparable magnitude to those reported by other workers. The results obtained from this part of the study are not of particular interest since the reference temperature employed in Equation 7.i. had been approximated using an experimentally determined Tg value, rather than a reference temperature which had been identified from the conductivity-temperature data directly. The use of such a predetermined reference temperature forces an additional unwarrented constraint upon the values of the VTF parameters obtained via this technique. A more acceptable method of analysis which does not prejudge the outcome would be to perform a direct nonlinear least squares analysis on the original data.

7.1.2 Nonlinear Least Squares Analysis.

To determine the best fit of the conductivity-temperature data to the VTF equation, a nonlinear least squares analysis was carried out where no assumptions were made. The resulting values of ln A, B and To are displayed in Table 7.II for a range of salt complexes prepared from the itaconic acid and vinyl ether based polymers.

Using the nonlinear least squares analysis the value of B ranged from 581 to 2975 K, depending on the host polymer, the incorporated salt and the concentration of salt. The value of B increased as the concentration of salt in the polymer increased.

The To values determined using this method increased as the concentration of salt in the polymer increased, however, in all complexes To was found to be lower than the Tg values which had been measured experimentally.

In the EO substituted itaconic acid polymer-salt complexes To has values ranging from 5-130 K below the experimental Tg determined for each complex but in the complexes prepared from PDPPGI and PVEMEO3, To was evaluated consistently at temperatures 40-50 degrees below the Tg of the complex.

The fact that To values were predominantly 40-50 degrees below Tg in these polymer-salt complexes is of great interest since this would suggest that the non-linear least squares analysis of the conductivity-temperature data has identified the "ideal glass transition temperature" of Gibbs and DiMarzio ‹158› as being more or less the same as the reference temperature, To, in the VTF equation. This ideal glass transition temperature, T_2, where the configurational entropy of a system vanishes, is defined as being a temperature 50 degrees below Tg.

Table 7.II

Best fit parameters from nonlinear least squares analysis of conductivity data.

Polymer	Salt	$[M^+]/[S]$	LnA	B/K	To/K	Tg-To/K
PDMEO1I	$NaClO_4$	0.05	-1.92	1092	237.3	70.5
	$NaClO_4$	0.125	-1.29	935	251.5	58.5
	$NaClO_4$	0.25	0.72	1595	221.0	97.5
	$LiClO_4$	0.05	2.87	2390	187.6	120.5
	$LiClO_4$	0.25	6.89	2975	184.8	130.5
PDMEO2I	$NaClO_4$	0.0125	-0.96	1330	186.4	74.5
	$NaClO_4$	0.05	0.28	1166	209.3	65.5
	$NaClO_4$	0.125	2.77	1386	221.4	85.0
	$NaClO_4$	0.25	-0.87	581	261.4	72.5
PDMEO3I	$NaClO_4$	0.0125	2.38	794	195.7	33.5
	$NaClO_4$	0.05	1.31	1090	201.7	54.0
	$NaClO_4$	0.125	2.64	1127	233.3	55.0
	$NaClO_4$	0.25	3.48	1278	241.0	65.5
	$LiClO_4$	0.0125	-2.92	590	212.5	17.5
	$LiClO_4$	0.05	2.10	1423	180.9	72.0
	$LiClO_4$	0.125	1.98	1061	236.3	51.5
	$LiClO_4$	0.25	4.66	1646	239.7	69.5
PDMEO5I	$NaClO_4$	0.0125	2.17	613	207.1	17.5
	$NaClO_4$	0.05	-0.11	735	217.4	25.5
	$NaClO_4$	0.25	3.39	1115	255.5	48.0
PDPMeG 350I	$NaClO_4$	0.0125	-1.69	563	209.0	11.5
	$NaClO_4$	0.05	0.61	748	213.7	23.0
	$NaClO_4$	0.125	2.97	1039	233.4	44.5
	$NaClO_4$	0.25	4.18	1287	239.0	54.5
	$LiClO_4$	0.0125	-1.89	591	212.6	5.0
	$LiClO_4$	0.05	0.62	607	217.4	15.0
	$LiClO_4$	0.125	2.50	1140	210.0	51.5
	$LiClO_4$	0.25	3.58	1255	238.4	42.0
PDPPGI	$LiClO_4$	0.0125	-2.46	954	187.3	41.5
	$LiClO_4$	0.05	1.32	1204	201.5	47.0
	$LiClO_4$	0.125	3.56	1302	234.5	48.5
	$LiClO_4$	0.25	5.84	1801	250.3	44.5
	$NaClO_4$	0.05	0.86	1082	213.4	41.0
	$NaClO_4$	0.125	5.29	1728	223.2	67.5
	$ZnCl_2$	0.125	1.17	1546	214.7	47.5
PVEMEO3	$LiClO_4$	0.0125	-2.13	747	188.0	28.5
	$LiClO_4$	0.05	0.45	884	197.9	40.5
	$LiClO_4$	0.125	1.96	1012	214.5	46.0
	$LiClO_4$	0.25	4.47	1440	232.4	48.0

---

[a] S is the solvating unit particular to each polymer, as described in Section 2.2.6.

Although reference temperatures have been identified at Tg <119,135> and at various temperature below Tg <39,71,127,129,150>, it would appear from this study <96> that the reference temperature which is consistently identified is the ideal glass transition temperature, T_2, where the configurational entropy of a system is reduced to zero, as has been reported by other workers <21,98>.

7.1.3 Interpretation of the VTF Analysis Using a Theoretical Model.

Although conductivity-temperature data collected for a material can be linearized using the VTF equation, the equation is empirical and a theoretical model must be used in conjunction with the equation to allow the values derived from the expression to be interpreted in a meaningful manner.

Severe limitations have impeded any simple understanding of the conductivity-temperature behaviour of many polymer-salt complexes. Some polymer-salt complexes are composed of various crystalline phases and therefore their thermal behaviour reflects phase melting and ionic flow among phases as well as ion transport itself <83,159-161>. Ion pairing can occur in polymer-salt complexes and this leads to variations in the charge carrier concentration and also to effects resulting from multiple ion formation <69,162,163>. The VTF equation interprets the conductivity-temperature behaviour of many polymer-salt complexes in terms of the motions of polymer molecules which participate in complexation. Although the elementary processes of ion migration are not emphasised in this particular approach, it should be recognised that such fundamental ion migration processes are of great importance in the overall ion transport process <97>.

Many types of materials demonstrate transport behaviour which can be analysed in terms of the VTF equation, however, the theoretical model that is suitable for use in the interpretation of the data is determined by the character and the physical properties of the material under investigation.

When considering the interpretation of the parameters derived from the application of the VTF equation to the conductivity-temperature data of polymer electrolytes, both free volume and configurational entropy models have been employed.

The free volume model proposed by Cohen and Turnbull <164,165,166> was designed for hard sphere monomeric liquids and the diffusion process in this model was assumed to occur by jumps of molecular dimension. The importance of the free volume theory in the study of polymer electrolytes was highlighted in the work presented by several workers <11,61,112,132>, however, the model was originally proposed for use in the study of rigid molecules, and not for the treatment of complex flexible units such as polymer chains. More elaborate "free volume" models have been proposed <97>, but as the theory is extended, these models becomes less attractive as a result of their complexity, and they also begin to resemble the configurational entropy model proposed by Adam and Gibbs <167>.

In an early publication <158>, Gibbs and DiMarzio identified a second order transition at a temperature, T_2, where the configurational entropy, S, of a system is zero. It was established that since relaxation times characterizing viscoelastic and dielectric responses become very long as T_2 is approached from above, the glass transition temperature, Tg, is the experimental manifestation of the second order transition T_2. At temperatures well above T_2 polymer molecules do not prefer any one particular conformation and there are many ways that the polymer molecules can be packed together in the bulk phase. As the polymer is cooled, the molecules have less energy and two processes occur, i.e. low energy molecular conformations begin to predominate and the volume decreases. As a result of this, the number of ways that the molecules can be packed into the bulk phase is reduced. At T_2 the system remains in one of its configurations of lowest permissible energy i.e. the "ground state" of amorphous packing and the free energy barrier resisting flow of a system from one of these states (configurations) to another is very high in the neigbourhood of and at all temperatures below T_2. The configurational entropy plays a central role in the theory of Gibbs and coworkers since it is simply related to the number of configurations, W, available to the polymer molecule as the temperature is varied.

In a later publication, Adam and Gibbs <167> discussed the temperature dependence of cooperative relaxation properties in glass forming liquids and it is the theory given in this reference which is of particular relevance when considering the interpretation of the VTF equation in terms of the configurational entropy model.

In this study, it was reported that the temperature dependent relaxation times in dynamic mechanical or dielectric experiments in liquids were determined by the probability of cooperative rearrangements. To study these transition probabilities, a cooperatively rearranging region was defined as a subsystem of the sample which upon sufficient fluctuation in enthalpy, was able to rearrange into another configuration, independently of its environment.

The number of molecules (or monomeric segments, in the case of polymers) in such a cooperatively rearranging region was denoted by z, and in the treatment, the probability of a cooperative rearrangement occurring in a fixed subsystem was considered to be a function of the size, z.

The subsystems were then directed into one of two classes: (a) 'n' subsystems which resided in states which allowed a cooperative rearrangement and (b) N-n subsystems that were in states not allowing a transition under isobaric and isothermal conditions.

The cooperative transition probability W(T) is proportional to n/N and it can be shown that <167> :-

$$W(T) = A \exp\left[\frac{-z\,\Delta u}{kT}\right] \qquad 7.ii.$$

where k is the Boltzmann constant and Δu is the potential energy barrier hindering the cooperative rearrangement per monomeric segment.

There is a lower limit (z^*) to the size of the cooperative region that is taken into account by expressing the average transition probability in the form

$$\bar{W}(T) = \bar{A} \exp\left[\frac{-z^*\,\Delta u}{kT}\right] \qquad 7.iii.$$

This expression states that the overwhelming majority of transitions are undergone by regions whose size differs negligibly from the smallest size, z^*, that permits a transition at all. It is an expression of the fact that the transition of these smallest cooperative regions involves the smallest number, z^*, of monomer units, surmounting essentially simultaneously, the individual barriers restricting their arrangement.

The temperature dependence of the critical size was then defined. The critical size, z^*, of the cooperative region, containing a critical number of monomer segments, could be expressed in terms of the molar configurational entropy (Sc) of the macroscopic system using

$$z^* = \frac{N\, sc^*}{Sc} \qquad 7.iv.$$

where sc^* is the critical configurational entropy representative of the critical cooperatively rearranging group, which contains a critical number of monomeric segments.

Inserting this expression into Equation 7.iii it is possible to write

$$\bar{W}(T) = \bar{A}\ \exp\left[\frac{-\Delta u\ sc^*}{kT\ Sc}\right] \qquad 7.v.$$

It has been shown that sc^* can be approximated by k ln(2), and from the thermodynamic definition of entropy it is possible to write

$$Sc(T) - Sc(To) = \int_{To}^{T} \frac{\Delta Cp}{T}\, dT \qquad 7.vi.$$

where ΔCp is the molar heat capacity difference between the liquid and the glass, noting of course, that the configurational entropy vanishes at T_0.

Adam and Gibbs assumed ΔCp to be independent of temperature, however, the temperature dependence of the configurational entropy is much better described by

$$\Delta Cp = \frac{Y}{T} \qquad 7.vii.$$

where Y is a constant <39,97>. It is then possible to express Equation 7.v. in the form

$$\bar{W}(T) = \lambda \exp\left[\frac{-\Delta u \ln(2) To}{Y (T - To)}\right] \qquad 7.viii.$$

where the constant Y is defined by ΔCp Tg.

When written in this form the equation is recognizable as being comparable to the VTF equation <39,83> as shown in Equation 7.1. where

$$B = \frac{\Delta u \ln(2) To}{\Delta Cp\ Tg} \qquad 7.ix.$$

The configurational entropy model, as described above, is a more realistic approach than the original free volume model for use in polymeric systems since it is more probable that transport in the polymer systems will occur by cooperative rearrangements, rather than by the hole-to-hole jumping motions, which are implied by the use of the free volume model. It is important to stress once again, however, that the configurational entropy model describes the properties of the polymer in the salt complex but does not describe fully the ionic conductivity.

In this study, results obtained from the VTF analysis of the conductivity-temperature data of various polymer-salt complexes were interpreted in terms of the configurational entropy model. To evaluate Δu, the free energy barrier per mole of monomer segments, which impedes rearrangement of the critical rearranging group. Equation 7.x. is used and values for B, Tg, To and the molar heat capacity change at Tg, characteristic of each system, were required.

$$\Delta u = \frac{\Delta Cp\ Tg\ B}{\ln(2)\ To} \qquad 7.x.$$

The value of the molar heat capacity change ΔCp which was used in the case of comb-branched polymers required some consideration.

In the configurational entropy model, the probability of a transition occurring in a cooperatively rearranging region was dependent on the size of the region, z^*, where z was assumed to be the number of monomeric segments in the cooperative region. The cooperative region was therefore considered to be composed of at least one complete monomeric unit. Δu is representative of the free energy per mole of monomer units required to allow a rearrangement and therefore the use of the monomeric unit in the calculation of the molar quantities ΔCp and Δu is evident.

The molar heat capacity change, ΔCp, can be easily calculated for a linear polymer, however, when considering the application of the configurational entropy model to the comb-shaped polymers, relevant to this study, the definition of the basic unit representative of a monomeric segment required for the calculation of the ΔCp is less apparent.

The monomeric units in these comb-shaped polymers are extremely large and it is unreasonable to consider the possibility of a complete monomeric unit acting as the basic structural unit involved in defining the critical size of the cooperatively rearranging region. It was therefore essential to identify a more realistic "basic unit" for use in evaluating the molar ΔCp, required to calculate Δu.

An "equivalent monomeric unit" was established in this study which was considered representative of the basic unit in these comb-shaped polymers. Depending on the character of the sidechain in the polymer an EO or PO unit was considered representative of a monomeric segment of the material, however, to account for the itaconic acid or vinyl ether backbones and the methoxy terminal groups in the materials, an additional factor was incorporated. Details of the "equivalent monomeric unit" used for each polymeric host are described fully in Appendix A and are summarized in Table 7.III.

Experimentally, ΔCp per gram was evaluated for a range of polymer-salt complexes. These values were corrected to account for the salt that had been present in the complex sample examined and the Cp(corr) values were then converted to molar ΔCp values using the molecular weight of the "equivalent monomeric unit" particular to the polymer under consideration, as described above.

In Table 7.IV. the molar ΔCp values determined for the range of polymer-salt complexes examined are displayed. It is apparent that the values reported for the PDPPGI based materials are slightly different to those reported previously <96>. In the initial report, ΔCp values had been based on the PO monomeric unit rather than the "equivalent monomeric unit", an initial approximation which was appropriate since 95% of PDPPGI comprises of PO sidechain units. The values reported previously are therefore slightly lower than those presented

Table 7.III

Molar Mass of the "Equivalent monomeric unit" for Various Polymers.

Polymer	Molar Mass/$g mol^{-1}$
PDMEO3I	70.3
PDPPGI	61.2
PVEMEO3	47.5

Table 7.IV

Heat capacity measurements in polymer-salt complexes.

Polymer-salt Complex			ΔCp(comp)	ΔCp(corr)	ΔCp
Polymer	Salt	$[M^+]/[S]$	$/Jg^{-1} K^{-1}$	$/Jg^{-1} K^{-1}$	$/J mol^{-1} K^{-1}$
PDMEO3I	$NaClO_4$	0.0125	0.59	0.60	42.2
	$NaClO_4$	0.05	0.56	0.61	42.8
	$NaClO_4$	0.125	0.57	0.69	48.5
	$NaClO_4$	0.25	0.55	0.78	54.8
PPO 1025	---	---	0.51	0.51	29.6
PDPPGI	---	---	0.50	0.50	30.6
	$LiClO_4$	0.0125	0.46	0.47	28.8
	$LiClO_4$	0.05	0.47	0.51	31.2
	$LiClO_4$	0.125	0.50	0.61	37.3
	$LiClO_4$	0.25	0.47	0.67	41.0
	$NaClO_4$	0.05	0.51	0.56	34.3
	$NaClO_4$	0.125	0.52	0.65	39.8
	$ZnCl_2$	0.125	0.44	0.56	34.3
PVEMEO3	$LiClO_4$	0.0125	0.51	0.52	24.7
	$LiClO_4$	0.05	0.54	0.59	28.0
	$LiClO_4$	0.125	0.51	0.62	29.4
	$LiClO_4$	0.25	0.44	0.62	29.4

here. It is accepted now that the values presented here are more characteristic of the system.

It is apparent from Table 7.IV. that molar ΔCp values increase as the salt concentration in the polymer is increased. The values were also noted to be dependent on the polymeric host and the incorporated salt.

Using the molar ΔCp values displayed in Table 7.IV. and the To and B values displayed in Table 7.II. it was possible to evaluate Δu, using Equation 7.x. The relevant parameters required to evaluate Δu and the Δu values obtained are displayed in Table 7.V.

Δu, the free energy barrier to rearrangement per mole of "monomer segments", increased as the concentration of salt in the polymer increased. This suggested that intermolecular interactions increased in the polymers as the salt concentration was increased which resulted in higher energies being required to allow rearrangement of the "monomeric units" in the polymers.

When comparing the Δu values calculated for the different polymer systems, it was suggested that group rearrangement was easier in the vinyl ether based polymers than in the itaconic acid based polymers.

In general Δu values were an order of magnitude higher, i.e. 30-129 $kJmol^{-1}$, than the apparent activation energy Ea' values, i.e. 2-20 $kJmol^{-1}$, determined directly from the slope, B, of the linearized conductivity-temperature data, as discussed in section 7.1.

Table 7.V

Configurational Entropy Model Parameters.

Polymer	Salt	$[M^+]/[S]$	B /K	ΔCp /$Jmol^{-1}K^{-1}$	Tg /K	To /K	Δu $kJmol^{-1}$
PDMEO3I	$NaClO_4$	0.0125	794	42.2	229.0	195.7	56.6
		0.05	1090	42.4	255.5	201.7	84.1
		0.125	1127	48.5	288.5	233.3	97.5
		0.25	1278	54.8	306.5	241.0	128.5
PDPPGI	$LiClO_4$	0.0125	954	28.8	229.0	187.3	48.0
		0.05	1204	31.2	248.5	201.5	66.8
		0.125	1302	37.3	283.0	234.5	84.6
		0.25	1801	41.0	295.0	250.3	125.7
	$NaClO_4$	0.05	1082	34.3	254.5	213.4	63.9
		0.125	1728	39.8	290.5	223.2	129.2
	$ZnCl_2$	0.125	1546	34.3	262.0	214.7	93.4
PVEMEO3	$LiClO_4$	0.0125	747	24.7	216.5	188.0	30.7
		0.05	884	28.0	238.5	197.9	43.0
		0.125	1012	29.4	260.5	214.5	52.1
		0.25	1440	29.4	280.5	232.4	73.7

It is encouraging to note, however, that activation energies (Ea), estimated using linear portions of the Arrhenius plots of the conductivity data, are of comparable magnitude to the Δu values calculated using the configurational entropy model. When Ea was estimated for a high and a low temperature region of the plot, for a particular complex, the Δu values calculated tended to lie intermediate between the two estimated Ea values. The relevant Ea values and the temperature ranges over which they were estimated are displayed in Table 7.VI.

When considering the use of the configurational entropy model, in conjunction with the VTF equation, as applied in this study, several comments should be noted.

1. The "equivalent monomeric unit" established in this study may not be an ideal choice of "monomeric segment" for use in the theory, however, it does seem a more acceptable basic structural unit than the complete monomeric unit which is extremely large. It would seem important that the character of the "monomeric segment" is identified for comb-shaped polymers in general since it is apparent that the molar ΔCp and therefore the Δu values calculated can vary dramatically depending on the choice of the "monomeric segment" for the system.

2. Although the Δu values determined from the application of the configurational entropy model are purely representative of the polymer chains in the complex, it is apparent that the information gained concerning the system, Δu, is meaningful and further expansion of the theory could possibly allow information concerning the ion transport processes in the system to be collected.

Table 7.VI

Arrhenius Activation Energies estimated for various Polymer-Salt Complexes.

Polymer	Salt	[M+]/[S]	Temp. Range/K	Ea/kJ mol^{-1}
PDMEO3I	$NaClO_4$	0.0125	333 - 400	26
		0.05	333 - 400	46
		0.125	322 - 357	100
		0.125	357 - 400	59
		0.25	322 - 370	122
		0.25	370 - 400	64
PDPPGI	$LiClO_4$	0.0125	322 - 357	49
		0.0125	357 - 400	30
		0.05	320 - 360	60
		0.05	360 - 400	39
		0.125	320 - 360	122
		0.125	360 - 400	62
		0.25	360 - 400	128
	$NaClO_4$	0.05	320 - 360	64
		0.05	360 - 400	39
		0.125	320 - 360	121
		0.125	360 - 400	84
	$ZnCl_2$	0.125	320 - 360	74
		0.125	360 - 400	96
PVEMEO3	$LiClO_4$	0.0125	320 - 400	25
		0.05	320 - 360	43
		0.05	360 - 400	28
		0.125	320 - 360	62
		0.125	360 - 400	27
		0.25	320 - 400	86

3. To encourage further use of the configurational entropy model in the full characterization of solid state electrolytes, it is worth noting that it is considered unwise to associate the slope of the linearized conductivity-temperature data, B, identified in the VTF equation, directly, with a real activation energy <97>.

CHAPTER EIGHT

MISCELLANEOUS CONDUCTIVITY STUDIES

8.1 Effect of Crosslinking.

In Figures 8.1 and 8.2, log conductivity as a function of reciprocal temperature is shown for polymer-salt complexes prepared from crosslinked (XL) and non-crosslinked PDMEO3I. Complexes containing $NaClO_4$ and $LiClO_4$ were examined containing salt at concentrations of $[M^+]/[EO] = 0.05$ and 0.125. Complexes prepared from crosslinked PDPMeG 350I, were also examined and the conductivity-temperature data obtained for these materials are shown in Figure 8.3. In Table 8.I. a summary of the conductivity behaviour exhibited by the various systems allows easy comparison of the network and comb branch structures.

In this study it was found that compared with the conductivity levels determined for the non-crosslinked materials, reduced conductivity levels were observed for the network polymer-salt complexes. The magnitude of the differences observed when comparing the network and non-crosslinked materials was dependent on the concentration of salt in the complex and also the temperature of examination.

In PDMEO3I complexes the network materials exhibited conductivity levels ranging from 28% to 68% of the conductivities observed for the non-crosslinked polymer, when complexes were examined at the same temperature and incorporating similar concentrations of salt. Similarly in PDPMeG 350I complexes, the crosslinked samples exhibited conductivities ranging from 9% to 69% of that demonstrated by the non-crosslinked materials.

Table 8.I

Effect of crosslinking on the conductivity of a polymer-salt complex.

a) Temperature = 353K.

Polymer	Salt	$[M^+]/[EO]$	$10^5\sigma$ /Scm^{-1}	%(a)	$\Delta T/K$(b)
PDMEO3I	$LiClO_4$	0.05	10.96	--	--
PDMEO3I XL	$LiClO_4$	0.05	3.09	28	25
PDMEO3I	$LiClO_4$	0.125	4.17	--	--
PDMEO3I XL	$LiClO_4$	0.125	2.14	51	8
PDMEO3I	$NaClO_4$	0.05	15.85	--	--
PDMEO3I XL	$NaClO_4$	0.05	5.75	36	17
PDPMeG 350I	$LiClO_4$	0.05	33.88	--	--
PDPMeG 350I XL	$LiClO_4$	0.05	10.00	29	29
PDPMeG 350I	$LiClO_4$	0.125	23.98	--	--
PDPMeG 350I XL	$LiClO_4$	0.125	2.14	9	30

b) Temperature = 403K.

Polymer	Salt	$[M^+]/[EO]$	$10^4\sigma$ /Scm	%(a)	T/K(b)
PDMEO3I	$LiClO_4$	0.05	5.75	--	--
PDMEO3I XL	$LiClO_4$	0.05	2.57	45	30
PDMEO3I	$LiClO_4$	0.125	6.02	--	--
PDMEO3I XL	$LiClO_4$	0.125	4.07	68	12
PDMEO3I	$NaClO_4$	0.05	8.51	--	--
PDMEO3I XL	$NaClO_4$	0.05	3.46	41	30
PDPMeG 350I	$LiClO_4$	0.05	10.00	--	--
PDPMeG 350I XL	$LiClO_4$	0.05	6.92	69	22
PDPMeG 350I	$LiClO_4$	0.125	15.85	--	--
PDPMeG 350I XL	$LiClO_4$	0.125	3.63	23	42

[a] The percentage quoted above describes the level of the conductivity exhibited by the crosslinked materials (assuming the non-crosslinked materials exhibited 100% conductivity) and NOT the percentage loss noted in the conductivity.

[b] Crosslinked system at the specified temperature is used as the reference.

Figure 8.1. **Arrhenius** plot of log conductivity against reciprocal temperature for alkali metal perchlorate complexes prepared from PDMEO3I and also from crosslinked PDMEO3I. ($[M^+]/[EO] = 0.05$)

	$NaClO_4$	$LiClO_4$
PDMEO3I	○	☐
PDMEO3I (XL)	●	■

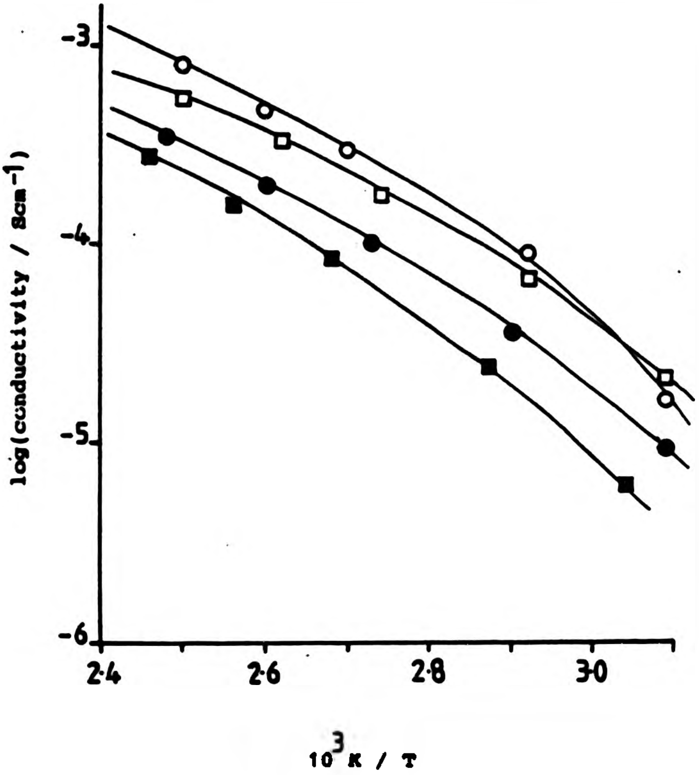


Figure 8.2. Arrhenius plot of log conductivity against reciprocal temperature for lithium perchlorate complexes prepared from PDMEO3I (□) and also crosslinked PDMEO3I (■).
$([M^+]/[EO] = 0.125)$

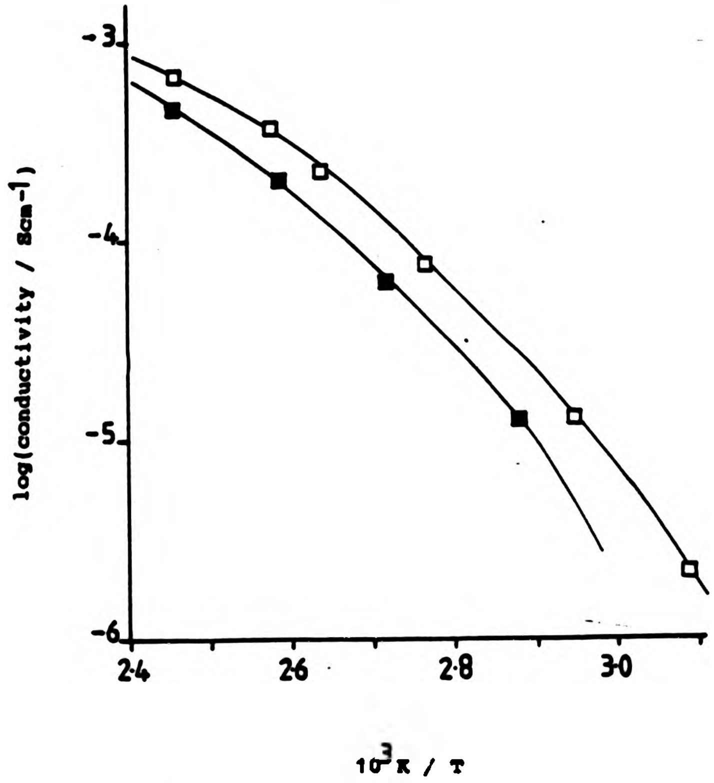
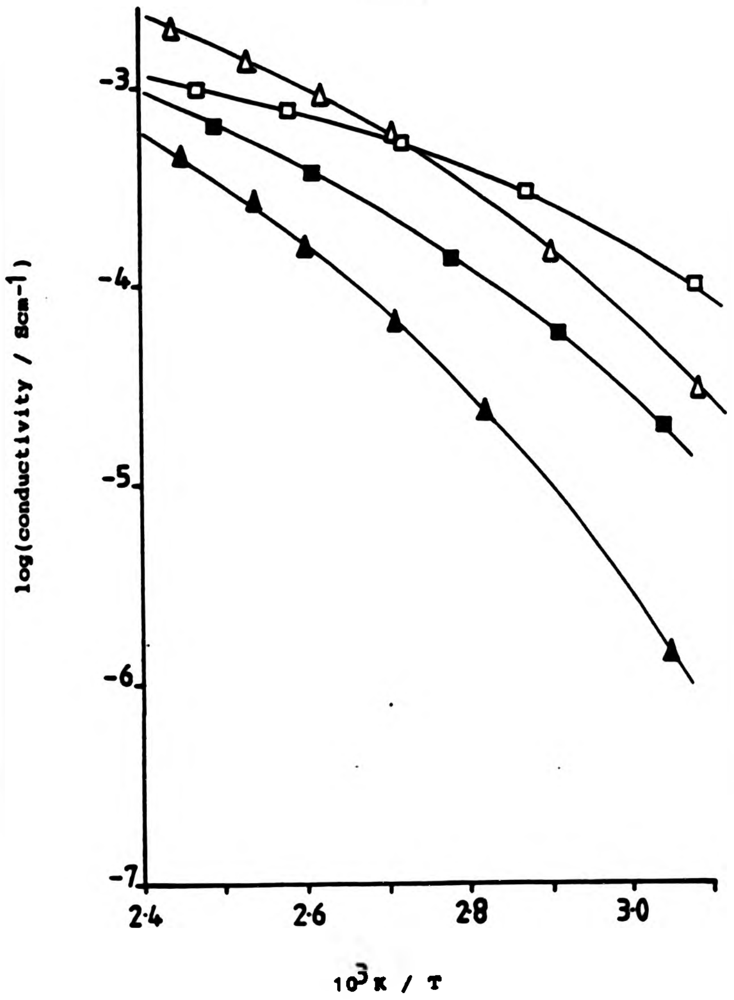


Figure 8.3. Arrhenius plot of log conductivity against reciprocal temperature for lithium perchlorate complexes prepared from PDPMeG 350I (□) and also from crosslinked PDPMeG 350I (■). with $[M^+]/[EO]$ ratios of 0.05 (□) and 0.125 (Δ).



Although the conductivities would appear to have been dramatically reduced by crosslinking the polymer, these percentages quoted above are misleading since it is possible for a drop of 2-3 orders of magnitude to occur when reducing the temperature by approximately 80 degrees. The reduced conductivity observed on crosslinking the material is therefore relatively small compared with the effect noted on temperature variation.

By comparing the temperatures at which complexes prepared from crosslinked and non-crosslinked polymers exhibit a particular level of conductivity (when the salt and salt concentration are the same) the effect of crosslinking on the conductivity of a system can be assessed in a more meaningful manner. A non-crosslinked material exhibits a particular conductivity at a lower temperature than a crosslinked system. The noted difference in temperature (ΔT) reflects how dramatically the crosslinking has affected the conductivity of the complex. Such data are displayed in Table 8.I. In the PDMEO3I complex containing $LiClO_4$ at a concentration of $[M^+]/[EO] = 0.125$, the conductivity exhibited by the crosslinked system at 353K was measured for the non-crosslinked polymer-salt complex at a temperature 8 degrees lower. In general ΔT was found to be of the order of 30 degrees for most materials but in the PDPMeG 350I complexes with a salt concentration of $[M^+]/[EO] = 0.125$ ΔT was found to be greater than 30 degrees.

This would suggest that the degree of crosslinking employed in this study does not greatly affect the conductivities of the polymer-salt complexes in most systems. The effect of crosslinking on the conductivity of a material is dependent on the polymer involved, the concentration of salt in the network structure and the temperature of operation. The effect of crosslinking on the conductivity of a material is obviously dependent on the crosslink density, however, this variable parameter was not investigated in this study.

As shown in Table 8.II., the Tg values determined for the undoped polymers and also the polymer-salt complexes were higher in the crosslinked materials. Since it is known that the conductivity of the polymer-salt complex is greatly influenced by the inherent flexibility of the system, which is reflected in the Tg value, the reduced conductivity levels observed in the crosslinked systems, which have higher Tg values, are not unexpected.

8.2 Effect of Moisture.

To study the effect of moisture on the physical properties of a material and its conductivity a polymer-salt complex was prepared from PDMEO3I and sodium perchlorate at a concentration of $[M^+]/[EO] = 0.125$. After thoroughly drying the material, samples were prepared in which the moisture content was varied. Before measuring the conductivity levels exhibited by each of the test samples, the Tg values were determined using d.s.c. and the moisture content was determined using t.g.a. All results were compared with a control complex which had been stored under anhydrous conditions prior to examination.

Table 8.II

DSC determined Tg values for polymer-salt complexes prepared from both (a) non-crosslinked and (b) crosslinked polymers.

Polymer	Salt	$[M^+]/[EO]$	Tg/K^a	Tg/K^b	ΔTg/K
PDMEO3I	----	---	218.5	229.5	11.0
PDMEO3I	$NaClO_4$	0.05	255.5	261.5	6.0
PDMEO3I	$LiClO_4$	0.05	253.0	266.5	13.5
PDMEO3I	$LiClO_4$	0.125	288.0	297.0	9.0
PDPMeG 350I	----	---	212.5	229.0	16.5
PDPMeG 350I	$LiClO_4$	0.05	232.5	256.5	24.0
PDPMeG 350I	$LiClO_4$	0.125	261.5	281.0	19.5

In Figure 8.4., the Tg of the sample is shown as a function of the wt% moisture determined. The extent of plasticization, ΔTg, resulting from the presence of the moisture is also shown. As the moisture content in the complex increased, the Tg values decrease in a sigmoidal manner almost to the value measured for the undoped polymer. In Figure 8.5. the log conductivity is plotted against reciprocal temperature for complexes containing various amounts of moisture. It is apparent that the conductivity-temperature behaviour demonstrated by the polymer-salt complex does not change, throughout the temperature range, as the moisture content is increased, however, greatly enhanced conductivites are observed in the presence of even small amounts of moisture. At room temperature the conductivity of the complex was enhanced by two orders of magnitude when 7.5 wt% moisture was present in the material.

Similar effects were observed by other workers <168> when predried films of PEO-salt complexes were exposed to controlled humid atmospheres. The enhanced conductivity observed for "wet" polymer-salt complexes can be explained by considering the characteristics of the material which would be altered on introducing moisture into the system. As was observed in Figure 8.4 the Tg of the polymer-salt complex is reduced due to the moisture plasticising the material which results in the system being more flexible at a particular temperature than a fully dried complex. The viscosity of the material is reduced which allows easier passage of an ion through the system. When present in high concentrations, water will increase the dielectric constant of the solvating medium

Figure 8.4. Effect of Moisture on the Tg of a PDMEO3I/NaClO$_4$ complex with a salt concentration of $[M^+]/[EO] = 0.125$
a. Plot of Tg against wt% H_2O.
b. Plot of ΔTg against wt% H_2O.

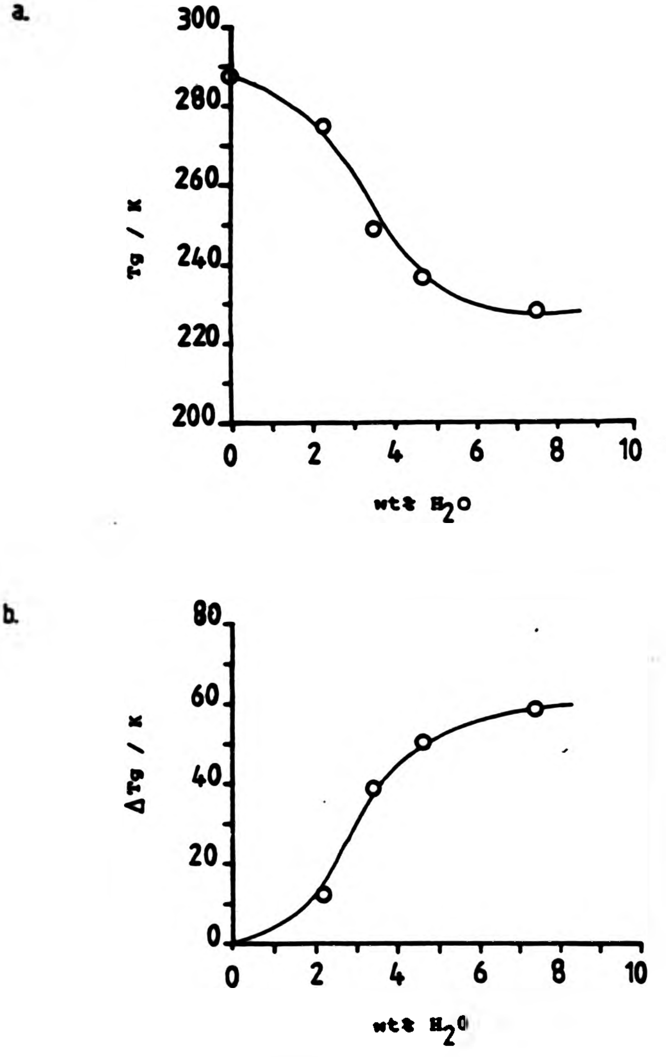
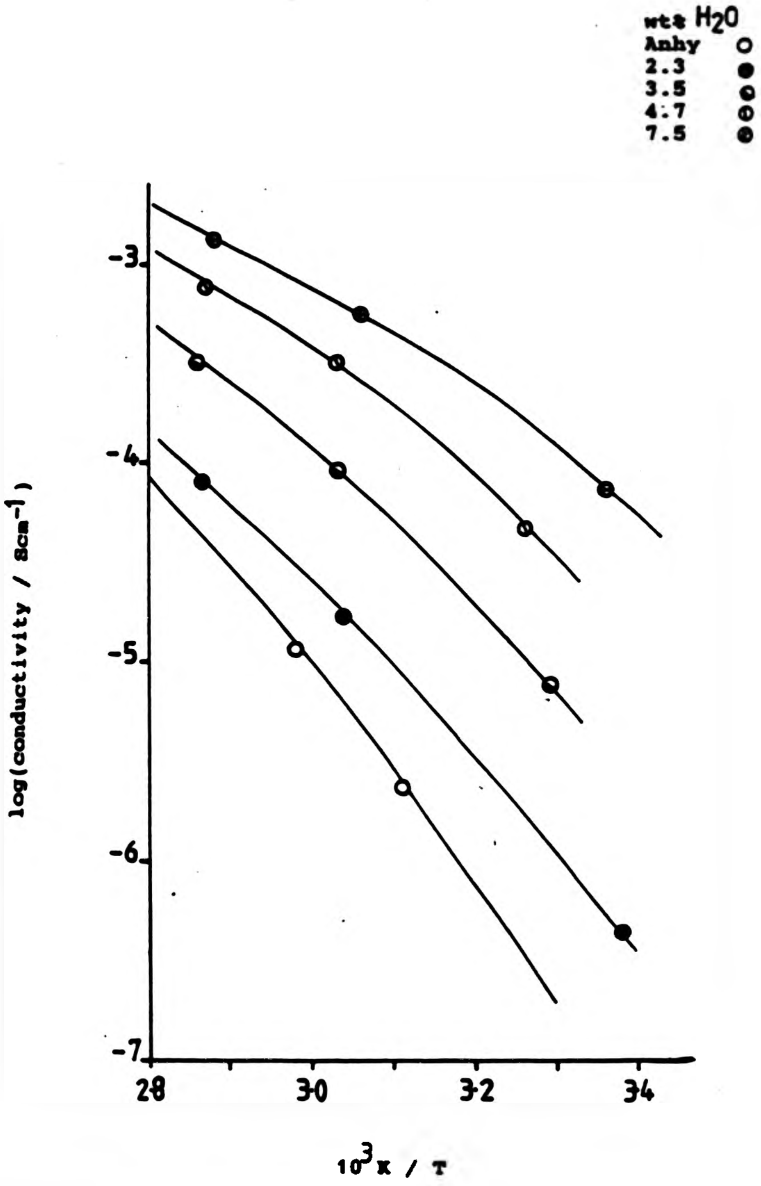


Figure 8.5. Arrhenius plot of log conductivity against reciprocal temperature for a sodium perchlorate complex of PDMEO3I ([M+]/[EO] = 0.125) incorporating various amounts of moisture.



and allow increased dissociation of the salt while at low concentrations the H_2O molecules themselves may dissociate to enhance the charge carrier concentration <169>.

Although Armstrong and Clarke <170> observed enhanced conductivity levels in a predried sample which had been exposed to a humid atmosphere under non-controlled conditions, the conductivity of the sample was reduced when the polymer-salt complex was exposed to trace amounts of moisture absorbed from a controlled humid atmosphere. Wiesmuller and Nicolson <171> also noted that on introducing small amounts of moisture into a polymer-salt complex, the conductivity was not enhanced and they suggested that the initial portion of moisture absorbed was utilized in hydrating the salt present in the complex. On hydration of the salt the coordination of the cation by the ether oxygen atoms would be hindered and therefore the motion of the ion through the system would be restricted. Since the effect of relatively high concentrations of moisture (2.3 wt% - 7.5 wt%) on the conductivity of the polymer-salt complex was examined in this study, the effects noted by workers <170,171> on addition of trace amounts of moisture to PEO salt complexes, where negligible changes or lowering of the conductivity of the material was observed, were not detected.

8.3 Conductivity Studies in an Ionomer Based on PDMEO3I.

It is possible to prepare ion containing polymers which are described as polyelectrolytes, ionomers or ionenes depending on the character and concentration of the ionic moieties involved. In these materials the ionic groups are part of the polymer <172>. Ion containing polymers are generally referred to as polyelectrolytes when they carry sufficient charge to be soluble in water, and ionomers when the concentration of charge is too low to induce water solubility. Ionenes are polyquaternary ammonium compounds with the ammonium ion integral in the backbone of the polymer. Similar to the effect observed in the polymer-salt complexes, the Tg of an ion containing polymer increases as the number of ionic groups in the system increases <173,174>.

Conductivity studies have been carried out on polyelectrolytes <175> and also on ionomers <106>. In these materials the current is carried by a known charge carrier since one of the ionic moieties is bound to the polymer backbone and is therefore immobile. It was found in the study of the polyelectrolytes that the anhydrous materials had a conductivity as low as 10^{-14} Scm^{-1}. Extensive ion pairing and ion clustering, which in effect crosslinked the materials, resulted in these extremely low conductivities. It was found, however, that enhanced conductivity levels could be achieved by introducing polyethylene glycol into the systems. In the ionomer prepared by Kobayashi, conductivity levels of $2x10^{-7}$ Scm^{-1} were reported.

In this study an ionomer was prepared from DMEO3I and MMI. Sodium ions were present at a concentration corresponding to $[M^+]/[EO] = 0.083$ and no Tg was determined for the ionomer below 390K. Degradation of the materials occurred at higher temperatures.

In this material the cation is the only potentially mobile ion since the anionic moieties are fixed to the polymer backbone. Throughout the temperature range conductivities of less than 10^{-6} Scm^{-1} were measured for the ionomer. This would suggest that ion transport, if occurring in the system is of much lower magnitude than that observed on addition of salts to PDMEO3I, systems in which both the cation and the anion are free to move.

From a study of materials such as described here, important information concerning the nature of the charge carrier in polymer-salt complexes can be gained. Since in this system the anion is immobile, and extremely low conductivity levels are observed throughout the temperature range, it could be suggested that the anion is the main charge carrier in the polymer-salt complexes prepared from PDMEO3I. This would support the theories of several groups of workers <43,110,111>, who consider the anion to be the main charge carrier in polymer electrolytes, an approach which is becoming increasingly more attractive to investigators trying to explain the conductivity behaviour observed in polymer-salt complexes.

From this limited study of a polymeric system containing only one mobile species, some interesting factors should be brought to attention.

1. It is well known that the introduction of ionic moieties into a polymeric backbone, to form an ionomer results in an increase in the Tg of the polymer <173,174>. Knowing that a low Tg material is preferable for ion transport in polymer-salt complexes it is possible that the Tg of the material is too high to allow appreciable ion transport to occur through the polymer at reasonable temperatures.

2. It is also possible that dissociation of the salt may be limited due to the salt having a high dissociation energy. This was suggested as a possible explanation for the low levels of conductivity observed in the lithium methacrylate-co-oligo(oxyethylene) copolymer studied by Kobayashi <106>. The number of possible charge carriers generated in the ionomer could therefore be low.

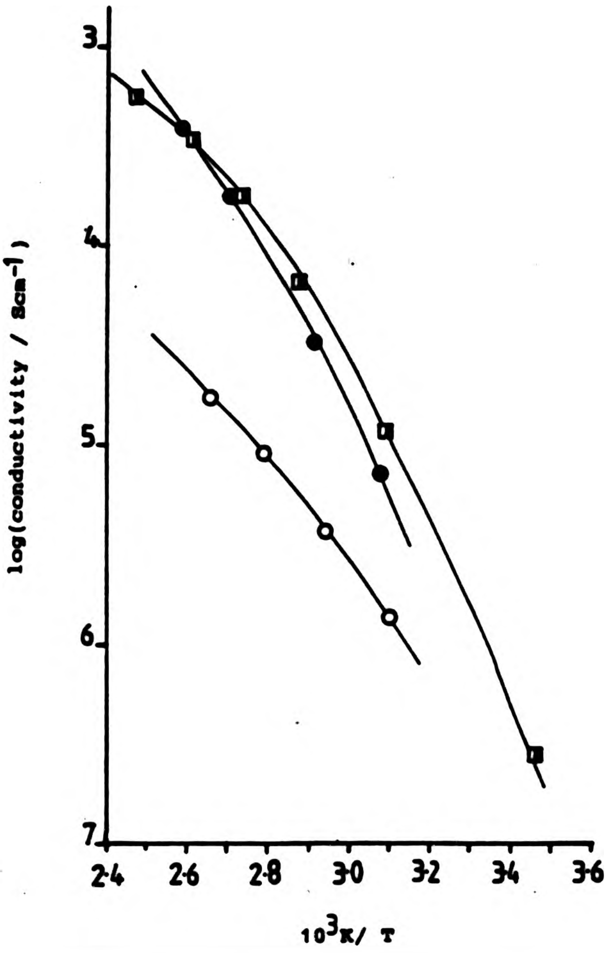
3.The interaction of the ionic groups with EO units present in the sidechains of the DMEO3I segments of the copolymer could be hindered due to the ionic moieties existing in close proximity to the polymer backbone. This would not encourage dissociation of the salt, a feature which requires the solvation of the cations by the oxygen rich environment of the polymeric host. Charge carrier generation would once again be restricted in the system.

Each of these features must be examined in detail before it is possible to declare that ion transport in the ionomer is negligible as a result of the immobilization of the anion.

As shown in Figure 8.6., on addition of an unknown concentration of $NaClO_4$ to the ionomer it was found that a conductivity of $3.6x10^{-5}$ Scm^{-1} could be obtained at ~400K, which although not high compared with the polymer-salt complexes examined in other areas of this study, does demonstrate that enhanced conductivity levels, compared to those measured for the ionomer can be obtained at reasonable temperatures when free ions are present in the system. Similar effects were observed on addition of $NaClO_4$ ($[M^+]/[EO]$ = 0.083) to the parent copolymer, also shown in Figure 8.6., where conductivity levels comparable to those demonstrated by

Figure 8.6. Arrhenius plot of log conductivity against reciprocal temperature for various sodium ion containing materials.

PDMEO3I + $NaClO_4$ $[M^+]/[EO]=0.067$ ▣
Copolymer + $NaClO_4$ $[M^+]/[EO]=0.083$ ●
Ionomer + $NaClO_4$ $[M^+]/[EO]=$? ○



pure PDMEO3I containing $NaClO_4$, at a similar concentration were observed. This again demonstrates that when salt is added to the copolymer, provided ions are produced, the polymeric environment is conducive to ion transport, appreciating of course that the Tg of the copolymer is lower than that of the ionomer.

Taking this additional information into account, both the use of a stronger acidic function in the copolymer, to allow enhanced salt dissociation e.g. SO_3H, CF_3SO_3H and/or the displacement of the ionic moiety away from the polymeric backbone by the use of a spacer unit (preferably EO based), to allow a more efficient interaction of the ionic groups with the EO sidechains of the DMEO3I units must be investigated in this system before comment is possible on whether the predominant charge carrier is anionic or cationic in EO based polymer-salt complexes.

8.4 Hysteresis Effects.

As demonstrated in Figures 8.7. and 8.8., hysteresis was not observed, when examining the conductivity behaviour of these amorphous polymer-salt complexes as a function of increasing and decreasing temperature. Hysteresis is an effect which is common in the conductivity behaviour of complexes prepared from PEO <70,83>.

Figure 8.7. Arrhenius plot of log conductivity against reciprocal temperature for a lithium perchlorate complex of PDMEO3I ($[M^+]/[EO] = 0.125$). Data collected during increasing (○) and decreasing (●) temperature variation in the temperature cycle.

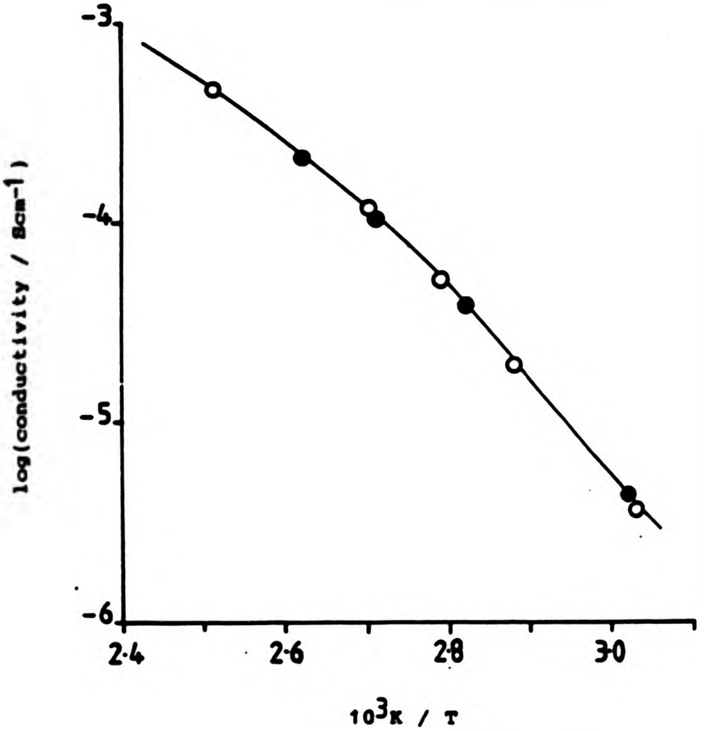
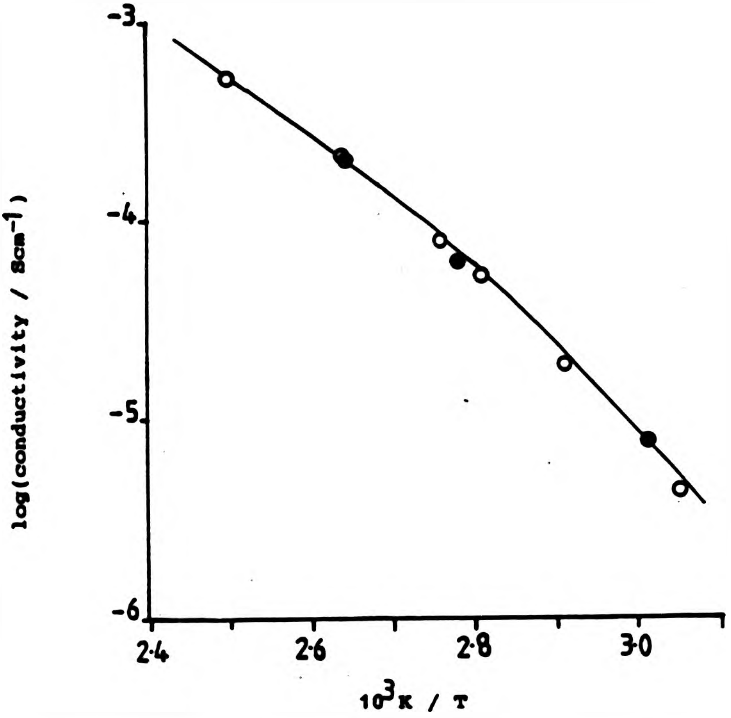


Figure 8.8. Arrhenius plot of log conductivity against reciprocal temperature for a sodium iodide complex of PDMEO3I ($[M^+]/[EO] = 0.125$). Data collected during increasing (○) and decreasing (●) temperature variation in the temperature cycle.



CHAPTER NINE

MISCELLANEOUS STUDIES OF POLYMER-SALT COMPLEXES

9.1 Stability Studies.

T.g.a. was used to examine the thermal stability of a representative polymer-salt complex, based on PDMEO3I and containing $NaClO_4$ at a concentration of $[M^+]/[EO] = 0.125$. A significant weight loss occurred at 470K, which represented the onset of thermal degradation, with complete degradation of the material occurring at 570K. Temperatures in excess of 410K were thus not used during the subsequent conductivity studies of all polymer-salt complexes. This is well within the thermal stability range of the materials.

Using t.g.a., it was also possible to establish that both the undoped polymers and polymer-salt complexes prepared from these materials had a great ability to absorb moisture. The undoped polymers were capable of absorbing ca. 2 wt% moisture on exposure to a humid atmosphere. If the salts incorporated into the complexes were also hygroscopic, eg perchlorate salts, then the ability of the doped polymer to absorb moisture was greatly enhanced. A complex prepared from PDMEO3I, containing $NaClO_4$ at a concentration corresponding to $[M^+]/[EO] = 0.25$, absorbed ~10 wt% moisture on exposure of the sample to a non-controlled humid atmosphere for 12 hours.

The absorption and desorption of moisture by the polymers and polymer-salt complexes appeared to be a reversible process, nevertheless, all samples were carefully prepared and stored under anhydrous conditions.

9.2 Mechanical Relaxations in Polymers and Polymer-Salt Complexes.

The mechanical properties of EO substituted itaconic acid polymers were previously studied <142>. Three relaxation processes were determined. The γ relaxation occurring at 130K was found to be the result of synchronous rotation about C-C and C-O bonds in the sidechain of the polymers. There was evidence of a small relaxation located at 210K which was believed to involve motions of the ester group in the polymer sidechain. This was denoted the β relaxation process. The α loss peak assigned to the relaxation occurring at the highest temperature, at a given frequency, is described as the glass to rubber transition.

In Figures 9.1., 9.2. and 9.3. the logarithmic decrement (LD) as a function of temperature is shown for undoped polymers and $NaClO_4$ complexes prepared from PDMEO1I, PDMEO2I and PDMEO3I respectively. In each figure the mechanical loss spectra were all plotted on the same scale, but the spectra were vertically displaced as the salt concentration in the complex was increased. In these spectra the α loss peak and the γ loss peak were easily identified, however, the β relaxation was not observed.

On addition of $NaClO_4$ to PDMEO1I the α loss peak occurred at virtually the same temperature in the undoped polymer and throughout the salt concentration range in the complexes. In undoped PDMEO2I and PDMEO3I, on extension of the flexible sidechain, the backbone is plasticized and the α relaxation occurs at lower temperatures in these polymers, as explained in Section 3.1. On addition of salt to the polymers, an

Figure 9.1. Plot of logarithmic decrement (LD) versus temperature for undoped PDMEO1I (1) and various sodium perchlorate complexes of PDMEO1I with [M+]/[EO] ratios of 0.02 (2), 0.125 (3), 0.25 (4) and 0.5 (5).

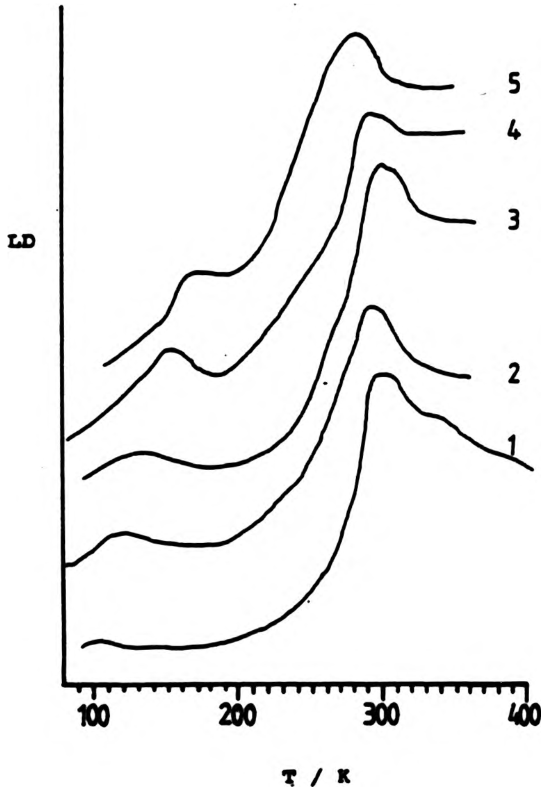


Figure 9.2. Plot of logarithmic decrement (LD) versus temperature for undoped PDMEO2I (1) and various sodium perchlorate complexes of PDMEO2I with $[\mathrm{M}^+]/[\mathrm{EO}]$ ratios of 0.0125 (2), 0.05 (3), 0.125 (4) and 0.25 (5).

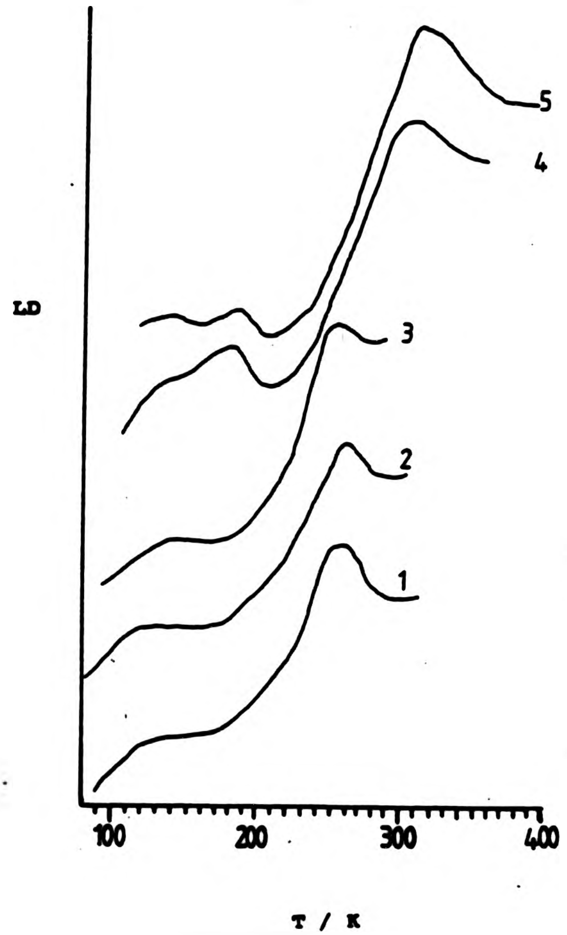
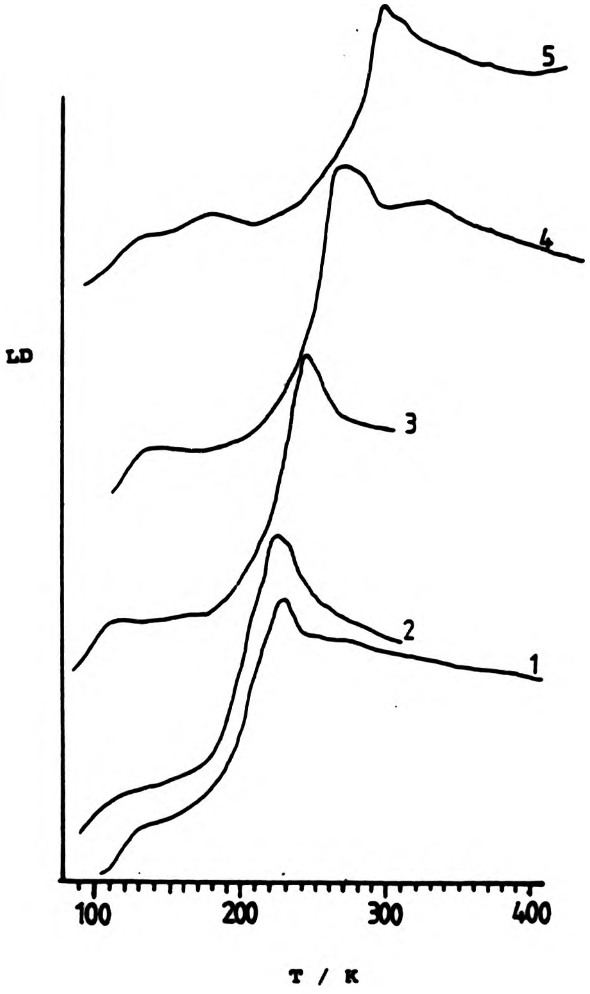


Figure 9.3. Plot of logarithmic decrement (LD) versus temperature for undoped PDMEO3I (1) and various sodium perchlorate complexes of PDMEO3I with $[M^+]/[EO]$ ratios of 0.0125 (2), 0.025 (3), 0.25 (4) and 0.5 (5).



elevation of the temperature of the α process is noted as the salt concentration is increased. This is the result of crosslinking and sidechain stiffening effects, discussed previously, hindering the motions of the polymer backbone. The increase in energy required to allow cooperative motions to occur within the polymer as the salt concentration is increased is reflected in the movement of the α relaxation to higher temperatures.

Sub-glass transition relaxations are observed in all of the polymer-salt complexes. In PDMEO1I-$NaClO_4$ complexes a progressive increase in the γ relaxation temperature from 100 to 170K occurred as the salt concentration was increased. This relaxation is the result of cooperative motion of three to four atoms in the polymer sidechain. As the salt concentration is increased, the extent of the interaction between the salt and the polymer is increased and higher energy is required to allow the motion of the coordinated units within the polymer. The transitions therefore move to higher temperatures.

In complexes based on PDMEO2I and PDMEO3I broad relaxations were observed at ~130K when low concentrations of salt were present. At high concentrations of salt, however, two relaxations were distinguishable, corresponding to the relaxation of non-coordinated (130K) and coordinated (<180K) sections of the sidechains. The relaxation corresponding to the motion of the coordinated sections of the sidechain increases with increasing ion solvation. As this relaxation moves to higher temperature the relaxation stationary at 130K can be identified more easily.

From this limited study of the mechanical relaxations occurring in these polymer salt complexes it would appear that a loss of flexibility in the sidechain of the polymer can be detected using t.b.a. techniques. It seems possible to distinguish between the coordinated and non-coordinated sections of the chains. A much more detailed study of the materials is required, however, before the mechanical relaxations will be fully characterized.

9.3 Infrared Studies.

From examination of Table 9.I. where the i.r. absorption frequencies of amorphous PEO <27> and PDMEO3I are shown, it is apparent that features characteristic of molten PEO occur in the spectrum of PDMEO3I. In Figure 9.4. the i.r. spectra obtained for undoped PDMEO3I and also the $LiClO_4$ and NaI complexes ($[M^+]/[EO] = 0.125$) of this polymer are shown.

Studying crystalline PEO, Davidson <25> concluded that the $-O-CH_2-CH_2-O-$ unit in the polymer occurred predominantly in a gauche conformation due to the presence of two strong bands in the i.r. spectrum, one occurring at approximately 880 and the other at 944 cm^{-1}. In the molten state, broadening of the i.r. absorption bands occurs and molecules are able to adopt a trans conformation. For a trans symmetry of the EO unit one strong rocking absorption is expected at approximately 773 cm^{-1} and a weak feature is expected at 992 cm^{-1}. Predominant signals characteristic of a trans conformation are present at 1322 and 1012 cm^{-1} in PEO-salt complexes <16>.

Since the CH_2- rocking modes in the 700-1000 cm^{-1} region are particularly sensitive to conformation <16>, this region

Table 9.I

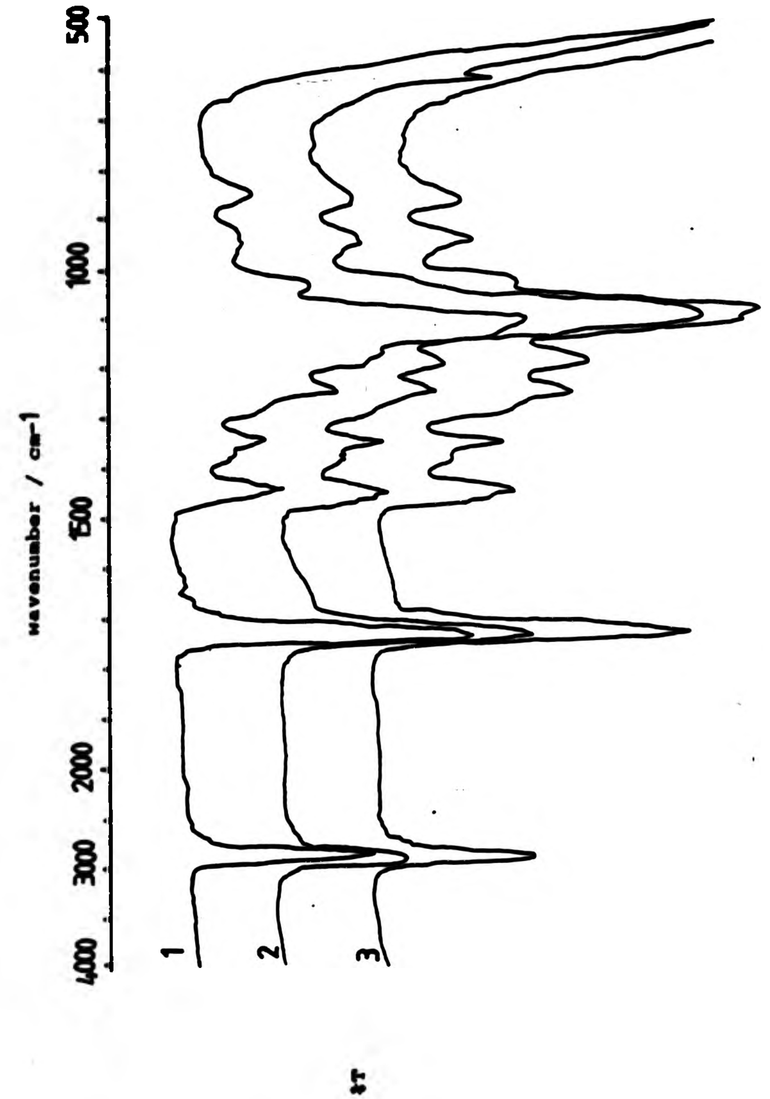
Infrared absorption assignments for (a) molten PEO and (b) PDMEO3I.

PEO Wavenumber /cm^{-1}	PEO assignment	PDMEO3I Wavenumber /cm^{-1}	PDMEO3I assignment
2930 sh	CH_2 str. anti		
2865 s	CH_2 str. sym	2860 s	CH_2 str.
2730 sh			
		1740 s	C=O str.
1485 sh	CH_2 sc. (t)		
1460 m	CH_2 sc. (g)	1450 m	CH_2 sc.
1352 m	CH_2 w. (g)	1350 m	
1326 w	CH_2 w. (t)		
1296 m	CH_2 tw.		
1249 m		1250 m	CH_2 sc.
		1170 sh	
1140 sh	CH_2 r.	1130 sh	C-O-C str. anti
1107 s	C-O, C-C str.	1105 s	C-O-C str. sym
1038 m		1030 m	
992 w	C-O, C-C str. and CH_2 r.(t)	985 sh	CH_2 r.(t)
		963 m	CH_2 r.(g)
945 m	C-C str. CH r.(g)	940 m	
915 sh	C-O, C-C str. and CH_2 r.(g)		
855 m	C-O str, CH_2 r.	853 m	CH_2 r.(g)
810 sh	C-O str, CH_2 r.(g)		
		750 w	CH_2 r.(t)

a. Ref 27

str. = stretch, sc. = scissor/bend, w. = wag, tw. = twist, r. = rock, g = gauche, t = trans.

Figure 9.4. Infrared spectrum of PDMEO3I (1) and the spectra obtained for lithium perchlorate (2) and sodium iodide (3) complexes prepared from the polymer with $[M^+]/[EO]$ ratios of 0.125.



was examined in detail and the spectra of undoped PDMEO3I and a $LiClO_4$ complex ($[M^+]/[EO] = 0.25$) were compared. Details of the spectra shown in Figure 9.5. are described in the inset in Table 9.II.

[In Figures 9.4. to 9.9. the spectra have been displaced vertically (%T) to allow easy comparison of spectra.]

In pure PDMEO3I, absorptions occurring at 853 and 940 cm^{-1} would suggest that predominantly gauche conformations of the $-O-CH_2-CH_2-O-$ unit are present, however, extremely weak bands at 750 and 985 cm^{-1} suggest that some trans conformations may also be present in the polymer. On addition of $LiClO_4$ to the polymer, small changes in the frequency range 700-1000 cm^{-1} are noted. This would suggest that only minor changes in the conformation of the polymer occurred on addition of salt. In addition, no absorptions were detected at 1322 or 1012 cm^{-1} in the spectrum of the complex.

On coordination of alkali metal cations to the polar groups in the polymer sidechains, the largest changes in the i.r. spectrum would be expected to occur in the vibrational modes due to oxygen containing functional units. The i.r. absorptions of carbonyl and ether groups in the polymer were therefore examined in detail. Representative i.r. spectra for both of these absorptions are shown in Figure 9.6. for the $LiClO_4$ complexes containing various concentrations of salt. In Figure 9.7. the ether absorptions in complexes containing NaI are shown as the salt concentration is increased and in Table 9.III. the changes in absorption frequencies occurring in PDMEO3I on addition of $LiClO_4$ are described for both the carbonyl and ether functional groups.

Table 9.II

Infrared absorption frequencies in PDMEO3I and in the lithium perchlorate and sodium iodide complexes.

Polymer PDMEO3I wavenumber/cm^{-1}	Complex $[M^+]/[EO]$=0.125 (0.25)[a] Lithium perchlorate wavenumber/cm^{-1}	[a]	Sodium iodide wavenumber/cm^{-1}
2860	2918		2900
1740	1737		1735
1450	1467		1450
1350	1366		1350
1250	1250		1250
1170	1195		1190
1130			1110
1105	1100		1080
1030		965	1020
985		950	
963		935	
940	949	870	940
853	867	838	860
750	748		750

[a] Inset corresponding to Figure 9.5.

Table 9.III

Changes in the carbonyl and ether absorption frequencies of PDMEO3I on addition of lithium perchlorate.

Polymer-Salt Complex $[M^+]/[EO]$	Carbonyl v wavenumber/	dv cm^{-1}	Ether v wavenumber/	dv cm^{-1}
0	1740.2	---	1108.4	---
0.0125	------	---	1108.2	0.2
0.05	1738.0	2.2	1103.0	5.4
0.125	1736.9	3.3	1099.7	8.7
0.25	1736.7	3.5	1102.1	6.3
0.25	1731.0	9.2	1086.5	21.5
0.5	1736.2	4.0	1100.9	7.5
0.5	1730.5	9.7	1091.1	17.3

Figure 9.5. Infrared spectra (700-1000 cm^{-1}) of PDMEO3I (1) and the lithium perchlorate (2) complex prepared from the polymer. $[M^+]/[EO]$ ratio of 0.125.

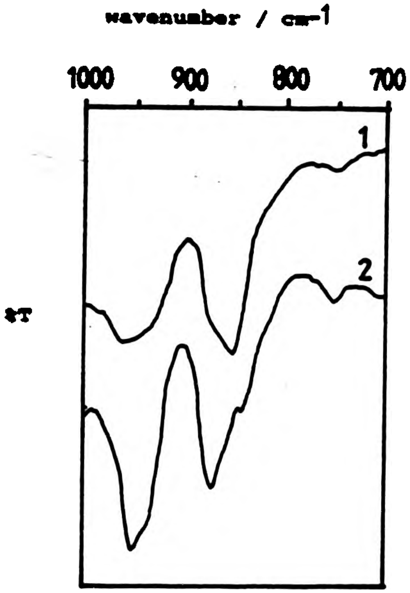


Figure 9.6. Carbonyl and ether absorptions in the infrared spectra of PDMEO3I (1) and various lithium perchlorate complexes prepared from the polymer with $[M^+]/[EO]$ ratios of 0.0125 (2), 0.05 (3), 0.125 (4), 0.25 (5) and 0.25 (6).

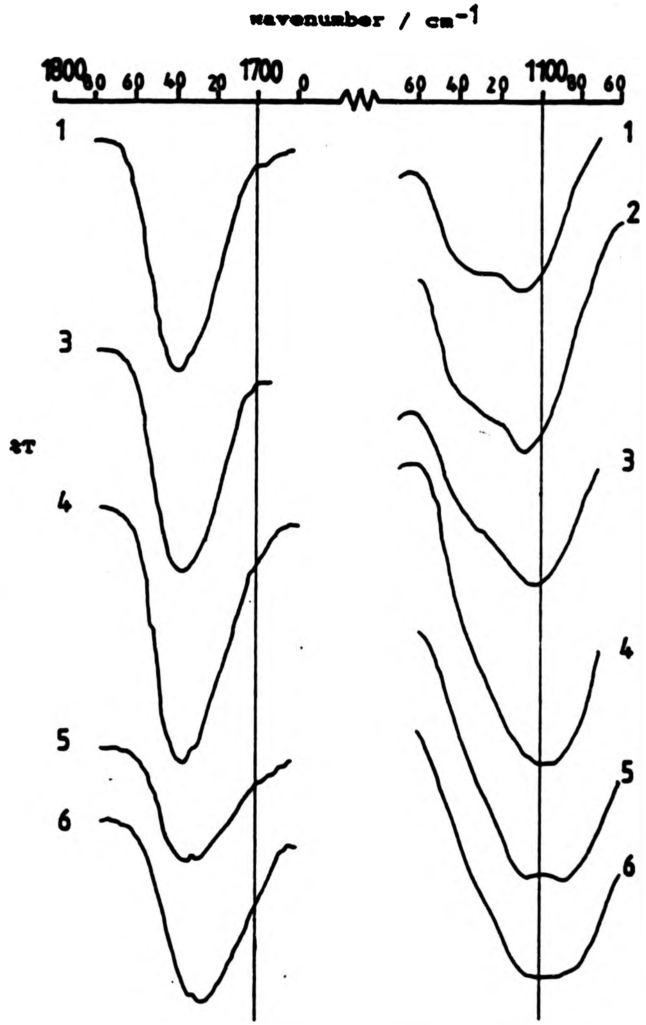
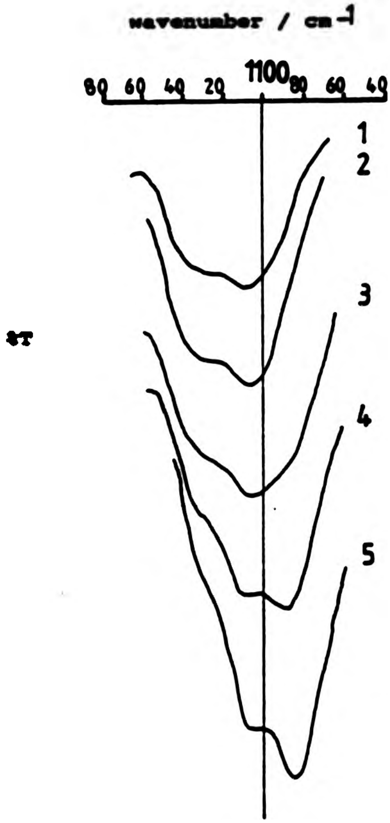


Figure 9.7. Ether absorptions in the infrared spectra of PDMEO3X (1) and various sodium iodide complexes prepared from the polymer with $[M^+]/[EO]$ ratios of 0.0125 (2), 0.067 (3), 0.125 (4) and 0.25 (5).



As the concentration of both $LiClO_4$ and NaI in the complex is increased, the i.r. absorption band characteristic of the ether oxygen group moves continually to lower frequencies. This is indicative of the decreased bond order in the group occurring as a result of the solvation of the salt by the polymer sidechains. The shifts in the ether frequencies are larger than those associated with the carbonyl frequency which would indicate that coordination of the cation occurs predominantly through the ether group. There is, however, a small movement to lower frequency apparent in the carbonyl signal which suggests that the carbonyl bond energy is also reduced due to the interaction of this group with the cation of the added salt.

On addition of NaCl and KI to PDMEO3I non-homogeneous polymer-salt mixtures were formed. When the spectra of these mixtures were examined no change in the ether absorption band was apparent when comparing the undoped polymer and the mixtures in which the salt concentration corresponded to $[M^+]/[EO] = 0.05$, as shown in Figure 9.8.

Interactions between the polymer and salt can be detected using i.r. techniques, however, such interactions were not observed in non-homogeneous polymer-salt mixtures. The magnitude of the shift in the spectrum of the polymer is therefore dependent upon the salt, the concentration of the salt in the complex and the extent of dissociation of the salt in the polymer. Similar effects were observed in the i.r. spectra of complexes prepared from PDPPGI, as shown in Figure 9.9 and Table 9.IV.

Figure 9.8. Ether absorptions in the infrared spectra of PDMEO3I (1) and sodium chloride (2) and potassium iodide (3) complexes prepared from the polymer with $[M^+]/[EO]$ ratios of 0.05.

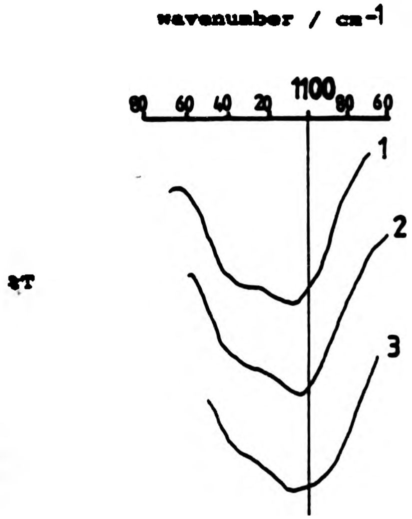
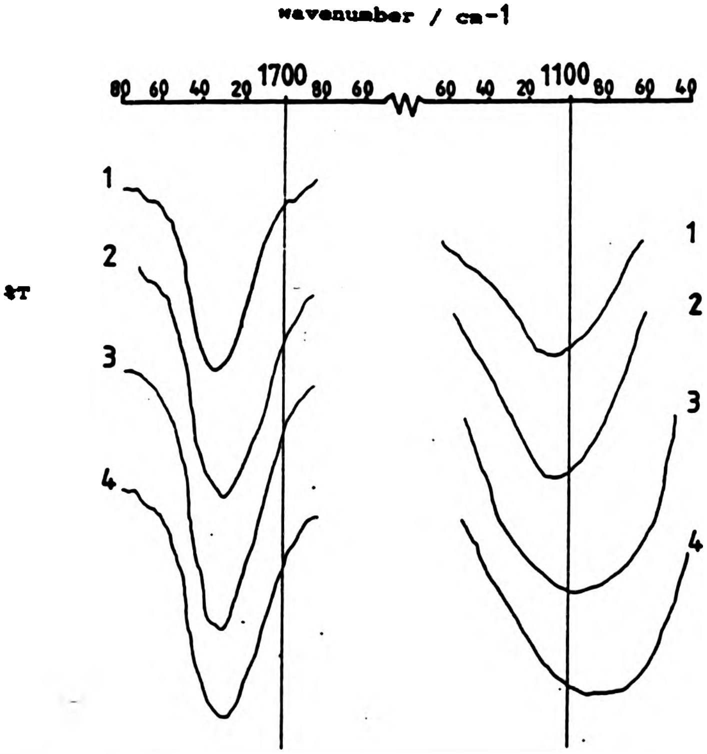


Table 9.IV

Changes in the carbonyl and ether absorption frequencies of PDPPGI on addition of lithium perchlorate.

Polymer-Salt Complex	Carbonyl		Ether	
	ν	$d\nu$	ν	$d\nu$
$[M^+]/[EO]$	wavenumber/	cm^{-1}	wavenumber/	cm^{-1}
0	1735.6	---	1107.8	---
0.025	1734.6	1.0	1105.8	2.0
0.125	1730.6	5.0	1094.7	13.1
0.25	1729.7	6.5	1083.4	24.4

Figure 9.9. Carbonyl and ether absorptions in the infrared spectra of PDPPGI (1) and various lithium perchlorate complexes prepared from the polymer with $[M^+]/[PO]$ ratios of 0.025 (2), 0.125 (3) and 0.25 (4).



CHAPTER TEN

CONCLUSIONS

Research teams throughout the world are now actively involved in studying different aspects of PEO-salt complexes. It has been shown that the levels of conductivity exhibited by a salt complex prepared from polyethylene oxide based materials depends on the character of the polymeric host, the character and concentration of salt in the complex and the temperature of measurement.

10.1 Influence of the Polymeric Host.

It has been shown in this study, that comb-branched polymers can be synthesized which have properties similar to those characteristic of PEO, and amorphous complexes can be prepared on addition of inorganic salts to these materials. Furthermore, the low temperature conductivities measured for certain comb-shaped polymer-salt complexes were higher than those reported for PEO-salt complexes.

Unfortunately, when PVME salt complexes were investigated, it was found that only at temperatures greater than 360K were levels of conductivity higher than measured for undoped PVME achieved in PVME-lithium salt complexes. Conductivity levels above 10^{-5} Scm^{-1} were not attained in these materials therefore the use of PVME as the host material in a polymeric electrolyte would appear to be unlikely. .

In salt complexes prepared from the itaconate comb-branched polymers, it was found that systems prepared from the polymer with EO sidechains demonstrated higher levels of conductivity than similar materials prepared from the polymer with PO sidechains when the inherent flexibility of each polymeric host was the same.

In salt complexes prepared from EO substituted itaconic acid polymers, the conductivity determined for systems containing the same salt and concentration of salt increased as the length of the sidechain in the polymeric host was extended from one to (on average) seven EO units.

Throughout the temperature range, alkali metal perchlorate complexes prepared from PDMEO1I, PDMEO2I, PDMEO3I, and PDMEO5I, exhibited levels of conductivity no higher than those reported for lithium salt complexes of PEO. Similar complexes prepared from PDPMeG 350I, are significantly more interesting. At high temperatures the conductivity levels measured for salt complexes prepared from PDPMeG 350I (and also those prepared from PDMEO3I and PDMEO5I) were comparable to those reported for PEO-salt complexes, however, at low temperatures the levels of conductivity measured when low concentrations of salt (particularly sodium perchlorate) were incorporated into PDPMeG 350I were dramatically higher than those reported for PEO systems. Since one desirable feature which is sought after when attempting to prepare salt complexes from novel polymeric materials is high levels of conductivity at low temperatures, the salt complexes prepared from PDPMeG 350I would appear to be worthy of more detailed examination.

Methacrylate and itaconate comb-shaped polymers have similar Tg values when EO sidechains of a particular length are incorporated into each system. This is true even though twice as many sidechain groups are present per monomeric unit in the itaconate system than in the methacrylate system. Since the itaconate and methacrylate polymers containing on average 7 EO units per sidechain exhibit comparable levels of conductivity at moderate temperatures when similar concentrations of lithium salt have been added to the polymer, it can be suggested that the conductivity exhibited by the doped system is influenced predominantly by the inherent flexibility of the backbone of the polymer, i.e. the Tg of the amorphous material. Flexible sidechains in a comb-shaped polymer plasticize the backbone but changing the density of flexible sidechains in a comb-shaped polymer does not appear to alter the Tg of the polymer or the electrical properties of complexes prepared from the material.

The importance of using comb-shaped polymers with low glass transition temperatures when trying to identify a polymer with superior electrical properties to those exhibited by PEO was highlighted in the study of the lithium perchlorate complexes prepared from PVEMEO3. Although only studied to a limited extent here, these materials have shown the potential to be extremely useful low temperature solid state electrolytes.

PVEMEO3 is inherently more flexible than the comb-shaped polymers prepared from itaconic acid. Particularly at low temperatures, levels of conductivity two orders of magnitude higher than measured for most itaconic acid based polymer-salt complexes could be achieved in some lithium salt complexes prepared from PVEMEO3. This is obviously the result of the polymeric host having an extremely low glass transition temperature. The conductivity levels exhibited by complexes prepared from PVEMEO3 are higher than those demonstrated by similar complexes prepared from PDMEO3I, a polymer which has a higher density of sidechains per monomeric unit (3 EO units long). These conductivities are also better than those exhibited by the complexes prepared from the methacrylate polymers with 7 EO units per sidechain. Moreover, the conductivity levels of PVEMEO3-$LiClO_4$ complexes are comparable with those for salt complexes prepared from PDPMeG 350I; a polymer which has a higher density of sidechains per monomeric unit and also much longer EO sidechains than those present in PVEMEO3.

The lithium perchlorate complexes prepared from PVEMEO3 (and PDPMeG 350I) exhibit electrical properties superior to the salt complexes prepared from methacrylate comb-shaped polymers but inferior to those demonstrated by salt complexes prepared from the siloxane or phosphazene based comb-shaped polymers. Bearing in mind the fact that levels of conductivity achieved in complexes prepared from itaconate polymers were enhanced as the length of the sidechain was extended from 3 to on average 7 EO units long, it can be envisaged that on extending the length of the sidechain in PVEMEO3 from 3 to on average 7 EO units (or possibly to even greater lengths) the levels of conductivity demonstrated by salt complexes prepared from this new material might be comparable or higher than those reported for siloxane or MEEP comb-shaped polymer-salt complexes.

It is essential that these materials are studied in more detail, since it is highly likely that the development of a range of polymers modelled on PVEMEO3 would allow a polymeric material to be prepared which, when doped, would have low temperature conductivities that would be far superior to those attainable for PEO host-based salt-complexes.

10.2 The Influence of the Nature of the Salt Dopant.

The conductivity exhibited by a polymer-salt complex is dependent on the number of charge carriers generated in the system on introducing salt into the polymer. The Tg of a polymer is increased as the number of charge carriers in the system is increased. By considering the increase in Tg which occurs as a function of salt concentration, salts which are highly dissociated within a polymer can be easily identified.

The increase in Tg which occurs in different polymers when a particular salt is added is dependent on both the inherent flexibility of the polymer and also on the loss in flexibility in the system as charge carriers are generated and sidechain stiffening or crosslinking effects occur. It is therefore impossible to compare the extent of polymer-salt interactions occurring in different polymers, when a common salt has been added at a particular concentration, from consideration of the Tg behaviour of the materials only. More information concerning the relative dissociation of a salt in various polymers can be gained if the conductivities of the materials are also taken into account.

Alkali metal salts which incorporated large anions with relatively low lattice energies were found to dissociate to a much greater extent in various polymers than salts with high lattice energies. Alkali metal perchlorate salt complexes exhibited higher levels of conductivity than complexes which contained most other salts. Alkaline earth, non-alkali metal and transition metal salts could be dissolved in the itaconic acid based comb-branched polymers, whereas PVME was only capable of dissolving lithium salts.

10.3 The Influence of Salt Dopant Concentration.

It has been noted in the literature that, in general, isothermal conductivity measurements carried out over a range of dopant concentrations show that the conductivity passes through a maximum as the dopant concentration in the host polymer is increased. This phenomenon was previously attributed to a balancing of effects i.e. an increase in the charge carrier concentration contrasted with a loss of flexibility in the system.

The conductivity behaviour exhibited by polymer-salt complexes examined in this study appeared to be slightly more complex since the conductivity either passed through a maximum or reached a plateau level as the salt concentration was increased (under constant reduced temperature conditions). It was established that the dissociation of various salts in PDPPGI was incomplete in all polymer-salt complexes, and also that the degree of dissociation decreased as the salt concentration in the complex increased. It can be suggested that the behaviour exhibited in these materials under constant reduced temperature conditions occurs as a result of the ion migration in the system being suppressed when high concentrations of salt are present in the complex. This could occur as a result of large quanties of molecularly dispersed salt blocking the ion conduction pathways or alternatively ionic aggregates could form in the system when the concentration of charge carriers is high enough. The ionic mobility of such aggregates would obviously be lower than the ionic mobility of the individual anions and cations. Either one of those conditions would result in conductivity levels falling when high concentrations of salt are present in the polymer-salt complexes.

10.4 The Influence of Temperature.

In all polymer-salt complexes prepared from itaconate and vinyl ether comb-shaped polymers, it was noted that the conductivity increased nonlinearly as the temperature was raised. In this study, the configurational entropy model was used in conjunction with the Vogel-Tammann-Fulcher (VTF) equation to interpret the conductivity-temperature data for some polymer-salt complexes. Furthermore, the information gained from this approach was felt to be of some theoretical importance.

The VTF reference temperature was consistently found to be some fifty degrees below the glass transition temperature of the polymer-salt complex. This reference temperature would therefore appear to coincide with the "ideal glass transition temperature" of Gibbs and DiMarzio, where the configurational entropy of a system vanishes to zero. It was possible to calculate Δu from this configurational entropy model for various polymer-salt complexes, and it was established that the free energy barrier per mole of "monomeric segments" which restrict rotation about limited sequences of a polymer chain increased with the salt concentration in the complex.

The application of the configurational entropy model to the conductivity-temperature data obtained for a polymer-salt complex is by no means a new idea. However, it should be noted that the Δu values presented in this study for various polymer-salt complexes are possibly the first to be reported. At present, the mechanism of ion migration in PEO-salt complexes is still very much under investigation.

Notwithstanding the fact that comb-shaped polymers are difficult to characterize fully in terms of the configurational entropy model, it could be envisaged that useful information could still be obtained by the application of this methodology to simpler amorphous polymer-salt complexes. Such information should then allow the microscopic ion transport mechanism in polymer-salt complexes to be more clearly defined.

10.5 Nature of the Charge Carrier.

In general, the nature of the predominant charge carrier in polymer-salt complexes is still the subject of much speculation. The nature of the predominant charge carrier in a polymeric electrolyte is of prime importance and complete understanding of the processes occurring in polymer-salt complexes is impossible when no details are available concerning this. In the current work, there was some evidence which suggested that both the cation and the anion are mobile in polymer-salt complexes.

More information could be gained concerning the character of the main charge carrier in polymer-salt complexes by extending the study of ionomers; this topic was considered only briefly in this study.

The need for transport numbers to be measured for complexes prepared from the comb-shaped polymers was apparent throughout this study. The possible importance of this type of measurement was particularly highlighted when complexes prepared from calcium perchlorate and zinc chloride were studied.

10.6 Other Features of Importance.

Comb-shaped polymers are obviously interesting materials and it has been shown in this study that new materials can be prepared, which when doped with inorganic salts, are capable of exhibiting conductivity levels superior to those reported for salt complexes prepared from PEO, particularly at low temperatures.

In addition to being able to exhibit high conductivities, a polymer-salt complex which would be a suitable alternative to a PEO-salt complex for use in a solid state cell would require excellent mechanical stability. In this study it was found that introducing a low density of crosslinks into a polymeric host allows a polymer-salt complex to be prepared which exhibits levels of conductivity which were not significantly lower than those measured for the non-croslinked material. Furthermore, the material was obviously more mechanically stable.

A more detailed study of network materials could be undertaken and ideally, crosslinked systems could be prepared which would be more robust than the complexes prepared from the non-crosslinked low Tg comb-branched polymer examined in this study. If the crosslink density was tightly controlled then the conductivities could also be optimized so that acceptable levels could be attained.

10.7 Variation of Conductivity with Frequency.

The conductivities exhibited by the polymer-salt complexes studied in this work, were all determined as a function of increasing temperature at a constant frequency of 1.49 kHz.

However, conductivity measurements can also be carried out as a function of frequency. This additional aspect of the work would be of great interest and could either be carried out on:- (1) a wide range of comb-shaped polymer-salt complexes to collect detailed information describing how the conductivity of a polymer-salt complex is affected by frequency variation, or (2) a single comb-branched polymer-salt complex. This would permit the effects of both temperature variation and frequency variation on the conductivity of a polymer-salt complex to be compared directly.

10.8 Final Conclusion(s).

Although the study of the electrical properties of comb-shaped polymer-salt complexes was initiated only fairly recently, it has already been established that these materials demonstrate many interesting features which could be developed further to allow the preparation of materials exhibiting exceptionally high levels of conductivity at low temperatures.

The ultimate goals in this area of research are the development of a single material which is both highly conductive at low temperatures, and which also possesses suitable electrochemical, mechanical and thermal stability over long periods of time. Notwithstanding the above mentioned goals, it is vital, from an purely academic point of view, that a wide range of materials (such as those investigated in this study) are continually prepared and characterized as fully as possible.

Polyethylene oxide-salt complexes have been under contiuous investigation for nearly 20 years, and, at present certain aspects of these materials are still not fully appreciated. It would be hoped that by studying the electrical properties of many different polymer-salt complexes using a wide range of techniques, much of the speculation which has been noted throughout the duration of this work will finally be resolved. When the mechanism of ion transportation, the nature of the charge carrier(s) and the processes involved in charge carrier generation in polymer-salt complexes are fully understood, it will be possible to predict the electrical properties of a given polymer-salt system, and furthermore, it should also be possible to prepare polymer-salt complexes which would suitable for use as the electrolyte material in solid state cells with relatively greater ease than is currently possible.

REFERENCES

1. Vincent, C.A., Bonino, F., Lazzari, M., Scrosati, B., 'Modern Batteries, An Introduction to Electrochemical Power Sources.', Arnold, London (1984).
2. Fenton, D.E., Parker, J.M., Wright, P.V., Polymer <u>14</u>, 589 (1973).
3. Iwamoto, R., Sailo, Y., Ishihara, H., Tadokoro, H., J. Polym. Sci. A-2 <u>6</u>, 1509 (1968).
4. Yokoyama, M., Ishihara, H., Iwamoto, R., Tadokoro, H., Macromolecules <u>2</u>, 184 (1969).
5. Pedersen, C.J., J. Am. Chem. Soc. <u>89</u>, 7017 (1967).
6. Fenton, D.E., Mercer, M., Poonia, N.S., Truter, M.R., J.C.S. Chem. Comm. p66 (1972).
7. Dale, J., Kristiansen, P.O., Acta. Chem. Scand. <u>26</u>, 1471 (1972).
8. Castellan, G.W.,'Physical Chemistry', Addison Wesley, California, p577 (1964).
9. Gladstone, S., 'Textbook of Physical Chemistry', Macmillan and Co., London, p884 (1962).
10. Watanabe, M., Sanui, K., Ogata, N., Inoue, F., Kobayashi, T., Ohtaki, K., Polymer J. <u>17</u> , 549 (1985).
11. Watanabe, M., Sanui, K., Ogata N., Kobayashi, T., Ohtaki, Z., J. Appl. Phys. <u>57</u>, 123 (1985).
12. Watanabe, M., Ogata, N., 'Polymer Electrolyte Reviews 1', Ed. MacCallum, J.R., Vincent, C.A., Elsevier Applied Science Publishers, Essex, p39 (1987).
13. Watanabe, M., Rikukawa, M., Sanui, K., Ogata, N., Macromolecules <u>19</u>, 188 (1986).

14. Shriver, D.F., Papke, B.L., Ratner, M.A., Dupon, R., Wong, T., Brodwin, M., Solid State Ionics 5, 83 (1981).

15. Ratner, M.A., Acc. Chem. Res. 15, 355 (1982).

16. Papke, B.L., Ratner, M.A., Shriver, D.F., J. Phys. Chem. Solids. 42, 493 (1981).

17. Blonsky, P.M., Clancy, S., Hardy, L.C., Harris, C.S. Spindler, R., Shriver, D.F., Poly. Mat. Sci. Eng. 53 , 736 (1985).

18. Blonsky, P.M., Shriver, D.F., Austin, P., and Allcock, H.R., Solid State Ionics 18 & 19, 258 (1986).

19. Blonsky, P.M., Shriver, D.F., Austin, P., Allcock, H.R., J. Am. Chem. Soc. 106. 6854 (1984).

20. Berthier, C., Gorecki, W., Minier, M., Armand, M.B., Chabagno J.M. and Rigaud, P., Solid State Ionics 11, 91, 1983.

21. Armand, M.B., Chabagno, J.M., Duclot, M.J., 'Fast Ion Transport in Solids.' Eds. Vashishta, P., Mundy, J.N., Shenoy, G.K., Elsevier North Holland Inc., p131 (1979).

22. Watanabe, M., Nagaoka, K., Kanba, M., Shinohara, I., Polymer J. 14, 877 (1982).

23. Cowie, J.M.G., Martin, A.C.S., Polymer Bull. 17, 113 (1987).

24. Tadokoro, H., Chatani, Y., Yoshihara, T., Tahara, S., Murahashi, S., Makromol. Chem. 73, 109 (1964).

25. Davidson, W.H.T., J. Chem. Soc. 3270 (1955).

26. Yoshihara, T., Tadokoro, H., Murahashi, S., J. Chem. Phys. 41, 2902 (1964).

27. Matsuura, H., Miyazawa, T., J. Polym. Sci. A-2 7, 1735 (1969).

28. Takahashi, Y., Tadokoro, H., Macromolecules 6, 672 (1973).

29. Maxfield, J., Shepherd, I.W., Polymer 16, 505 (1975).

30. Dechter, J.J., J. Polym. Sci., Polym. Lett. 23, 261 (1985).

31. Tadokoro, H., Macromol. Rev. 1, 119 (1966).

32. Watanabe, M., Nagano, S., Sanui, K., Ogata, N., Solid State Ionics 18 & 19, 338 (1986).

33. Acierno, D., Bianchi, E., Ciferri, A., De Cindio, B., Migliaresi, C., Nicholais, L., J. Polym. Sci. Part C. 54, 259 (1976).

34. Clancy, S., Shriver, D.F., Ochrymowycz, L.A., Macromolecules 19, 606 (1986).

35. Takagishi, T., Okuda, S., Kuroki, N., Kozuka, H., J. Polym. Sci. Polym. Chem. 23, 2109 (1985).

36. Wintersgill, M.C., Fontanella, J.J., Calame, J.P., Smith, M.K., Jones, T.B., Greenbaum, S.G., Adamić, K.J., Shetty, A.N., and Andeen, C.G., Solid State Ionics 18 & 19, 326 (1986).

37. Weston, J.E., Steele, B.C.H., Solid State Ionics 7, 81 (1982).

38. Minier, M., Berthier, C., Gorecki, W., Solid State Ionics 9 & 10, 1125 (1983).

39. Papke, B.L., Ratner, M.A., Shriver, D.F., J. Electrochem. Soc. 129, 1694 (1982).

40. Papke, B.L., Ratner, M.A., Shriver, D.F., J. Electrochem. Soc. 129, 1434 (1982).

41. Catlow, C.R.A., Chadwick, A.V., Greaves, G.N., Moroney, L.M. and Worboys, M.R., Solid State Ionics 9 & 10, 1107 (1983).

42. Hibma, T., Solid State Ionics 9 & 10, 1101 (1983).

43. Yang, L.L., McGhie, A.R., Farrington, G.C., J. Electrochem. Soc. 133, 1380 (1986).

44. Yang, L.L., Huq, R., Farrington, G.C., Chiodelli, G., Solid State Ionics 18 & 19, 291 (1986).

45. Fontanella, J.J., Wintersgill, M.C., Calame, J.P., Andeen, C.G., J. Polym. Sci. Polym. Phys. 23, 113 (1985).

46. Partick, A., Glasse, M., Latham, R., Linford, R., Solid State Ionics 18 & 19, 1063 (1986).

47. Abrantes, T.M.A., Alcacer, L.J., Sequeira, C.A.C., Solid State Ionics 18 & 19, 315 (1986).

48. Blumberg, A.A., Pollack, S.S., Hoeve, C.A.J., J. Polym. Sci. A 2, 2499 (1964).

49. Moacanin, J., Cuddihy, E.F., J. Polym. Sci. Part C, 14, 313 (1966).

50. Wetton, R.E., James, D.B., Whiting, W., J. Polym. Sci., Polym. Lett. 14, 577 (1976).

51. James, D.B., Wetton, R.E., Brown, D.S., Polymer, 20, 187 (1979).

52. James, D.B., Wetton, R.E., Brown, D.S., Am. Chem. Soc. Div. Polym. Chem. 19, 347 (1978).

53. Lundberg, R.D., Bailey, F.E., Callard, R.W., J. Polym. Sci. A-1 4, 1563 (1966).

54. Watanabe, M., Ikeda, J., Shinohara, I., Polymer J. 15, 175 (1983).

55. Cameron, G.G., Ingram, M.D., Sorrie, G.A., J. Electroanal. Chem. 198, 205 (1986).

56. Hannon, M.J., Wissbrun, K.F., J. Polym. Sci., Polym. Phys. 13, 113 (1975).

57. Wissbrun, K.F., Hannon, M.J., J. Polym. Sci., Polym. Phys. 13, 223 (1975).

58. Xia, D.W., Soltz, D., Smid, J., Solid State Ionics, 14, 221 (1984).

59. Nagaoka, K., Naruse, H., Shinohara, I., J Polym. Sci., Polym. Lett. 22, 659 (1984).

60. Cowie, J.M.G., 'Polymers: Chemistry and Physics of Modern Materials', Intertext, Aylesbury (1973).

61. Watanabe, M., Oohashi, S., Sanui, K., Ogata, N., Kobayashi, T. and Ohtaki, Z., Macromolecules 18, 1945 (1985).

62. Watanabe, M., Sanui, K., Ogata, N., Macromolecules 19, 815 (1986).

63. Wong, T., Brodwin, M., Papke, B.L., Shriver, D.F., Solid State Ionics 5, 689 (1981).

64. Fontanella, J.J., Wintersgill, M.C., Calame, J.P., Andeen, C.G., Solid State Ionics 8, 333 (1983).

65. Wintersgill, M.C., Fontanella, J.J., Calame, J.P., Figueroa, D.R. and Andeen, C.G., Solid State Ionics 11, 151 (1983).

66. Ansari, S.M., Brodwin, M., Stainer, M., Druger, S.D.,
Ratner, M.A. and Shriver, D.F.,
Solid State Ionics 17, 101 (1985).

67. Se, K., Adachi, K., Kotaka, T.,
Polymer J. 13, 1009 (1981).

68. Wetton, R.E., James, D.B., Warner, F.P.,
Am. Chem. Soc. Div. Polym. Chem. 19, 353 (1978).

69. Wetton, R.E., James, D.B., Warner, F.P.,
Adv. Chem. Ser. 187, 253 (1980).

70. Wright, P.V., Br. Polym. J. 7, 319 (1975).

71. Harris, C.S., Shriver, D.F., Ratner, M.A.,
Macromolecules 19, 987 (1986).

72. Chiang, C.K., Davis, G.T., Harding, C.A., Takahashi, T.
Solid State Ionics 18 & 19, 300 (1986).

73. Takahashi, T., Davis, G.T., Chiang, C.K., Harding, C.A.
Solid State Ionics 18 & 19, 321 (1986).

74. Tsuchida, E., Ohno, H., Tsunemi, K.,
Electrochimica Acta. 28, 591 (1983).

75. Tsunemi, K., Ohno, H., Tsuchida, E.,
Electrochimica Acta. 28, 833 (1983).

76. Reich, S., Michaeli, I.,
J. Polym. Sci., Polym. Phys. 13, 9 (1975).

77. Watanabe, M., Kanba, M., Nagaoka, K., Shinohara, I.,
J. Polym. Sci., Polym. Phys. 21, 939 (1983).

78. Spindler, R., Shriver, D.F.,
Macromolecules 19, 347 (1986).

79. Watanabe, M., Togo, M., Sanui, K., Ogata, N.,
Kobayashi, T., Ohtaki, Z.,
Macromolecules 17, 2908 (1984).

80. Watanabe, M., Rikukawa, M., Sanui, K., Ogata, N., Kato, H., Kobayashi, T., Ohtaki, Z., Macromolecules 17, 2902 (1984).

81. Dupon, R., Papke, B.L., Ratner, M.A., Shriver, D.F., J. Electrochem. Soc. 131, 586 (1984).

82. Armstrong, R.D., Clarke, M.D., Electrochimica Acta. 29, 1443 (1984).

83. Stainer, M., Hardy, L.C., Whitmore, D.H. and Shriver, D.F., J. Electrochem. Soc. 131, 784 (1984).

84. Chiang, C.K., Davis, G.T., Harding, C.A., Aarons, J., Solid State Ionics 9 & 10, 1121 (1983).

85. Armand, M., Solid State Ionics 9 & 10, 745 (1983).

86. Watanabe, M., Ikeda, J., Shinohara, I., Polymer J. 15, 65 (1983).

87. Angell, C.A., Solid State Ionics 9 & 10, 3 (1983).

88. Vogel, H., Physik Z. 22, 645 (1921).

89. Tammann, V.G., Hesse, W., Z. Anorg. Allg. Chem. 156, 245 (1926).

90. Fulcher, G.S., J. Amer. Ceram. Soc. 8, 339 (1925).

91. Angell, C.A., J. Phys. Chem. 68, 1917 (1964).

92. Angell, C.A., J. Phys. Chem. 70, 3988 (1966).

93. Angell, C.A., J. Phys. Chem. 70, 2793 (1966).

94. Angell, C.A., Bressel, R.D., J. Phys. Chem, 76, 3244 (1972).

95. Killis, A., Le Nest, J.F., Cheradame, H., Makromol. Chem., Rapid Commun. 1, 595 (1980).

96. Cowie, J.M.G., Martin, A.C.S., Polymer, 28, 627 (1987).

97. Ratner, M.A.,'Polymer Electrolyte Reviews 1', Ed. MacCallum, J.R., Vincent, C.A., Elsevier Applied Science Publishers, Essex, P173 (1987).

98. Armand. M., Chabagno, J.M., Duclot, M., 2nd Int. Conf. on Solid Electrolytes, St Andrews, Scotland (1978).

99. Watanabe. M., Rikukawa, M., Sanui, K., Ogata, N., J. Appl. Phys. 58, 736 (1985).

100. Archer, W.I., Armstrong, R.D., Electrochimica Acta. 26, 167 (1981).

101. Ferloni, P., Chiodelli, G., Magistris, A., Sanesi, M., Solid State Ionics 18 & 19, 265 (1986).

102. Bhattacharja, S., Smoot, S.W., Whitmore, D.H., Solid State Ionics 18 & 19, 306 (1986).

103. Bouridah, A., Dalard, F., Deroo, D., Armand, M.B., Solid State Ionics 18 & 19, 287 (1986).

104. Bannister, D.J., Davies, G.R., Ward, I.M., McIntyre, J.E., Polymer 25, 1291 (1984).

105. Rietman, E.A., Kaplan, M.L., Cava, R.J., Solid State Ionics 17, 67 (1985).

106. Kobayashi, N., Uchiyama, M.,.Tsuchida, E., Solid State Ionics 17, 307 (1985).

107. Watanabe, M., Sanui, K., Ogata, N., Inoue, F., Kobayashi, T., Ohtaki, Z., Polymer J. 16, 711 (1984).

108. Leveque, M., Le Nest, J.F., Gandini, A., Cheradame, H., J. Power Sources 14, 27 (1985).

109. Sequeira, C.A.C., North, J.M., Hooper. A., Solid State Ionics 13, 175 (1984).

110. Gorecki, W., Andreani, R., Berthier, C., Armand, M., Mali, M., Roos J. and Brinkmann, D., Solid State Ionics 18 & 19, 295 (1986).

111. Leveque, M., Le Nest, J.F., Gandini, A., Cheradame, H., Makromol Chem, Rapid Commun. 4, 497 (1983).

112. Cheradame, H., I.U.P.A.C. Macromolecular Div., 27th Int. Symp. Macromolecules, Strasbourg, Ed. Benoit, H., Rempp, P., p251 (1981).

113. Sorensen, P.R., Jacobsen, T., Electrochimica Acta. 27, 1671 (1982).

114. Sorensen, P.R., Jacobsen, T., Solid State Ionics, 9 & 10, 1147 (1983).

115. Dupon, R., Whitmore, D.H., Shriver, D.F., J. Electrochem. Soc. 128, 715 (1981).

116. Chadwick, A.V., Strange, J.H., Worboys, M.R., Solid State Ionics, 9 & 10, 1155 (1983).

117. Newman, D.S., Hazlett, D., Mucker, K.F., Solid State Ionics 3/4, 389 (1981).

118. Billmeyer, F.W., 'Textbook of Polymer Science', Ed 2., Wiley-Interscience, New York (1972).

119. MacCallum, J.R., Smith, M.J., Vincent, C.A., Solid State Ionics 11, 307 (1984).

120. Guyot, A., Hamaide, T., Le Mehaute, A., Crepy, G., and Marcellin, G., Polym. Prep., Am. Chem. Soc., Div. Polym. Chem. 26, 112 (1985).

121. Killis, A., Le Nest, J.F., Gandini, A., Cheradame, H., J. Polym. Sci., Polym. Phys. 19, 1073 (1981).

122. Killis, A., Le Nest, J.F., Gandini, A., Cheradame, H., Makromol. Chem. 183, 1037 (1982).

123. Killis, A., Le Nest, J.F., Gandini, A., Cheradame, H., and Cohen-Addad, J.P., Polym. Bull. 6, 351 (1982).

124. Killis A., Le Nest, J.F., Gandini, A., Cheradame, H., Macromolecules 17, 63 (1984).

125. Killis, A., Le Nest, J.F., Gandini, A., Cheradame, H., Cohen-Addad, J.P., Solid State Ionics 14, 231 (1984).

126. Watanabe, M., Suzuki, A., Santo, T., Sanui, K., Ogata, N., Macromolecules 19, 1921 (1986).

127. Giles, J.R.M., Greenhall, M.P., Polym. Comm. 27, 360 (1986).

128. Fish, D., Xia, D.W., Smid, J., Macromol. Chem. Rapid. Commun. 6, 761 (1985).

129. Adamić, K.J., Greenbaum, S.G., Wintersgill, M.C., Fontanella, J.J., J. Appl. Phys. 60, 1342 (1986).

130. Allcock, H.R., Austin, P.E., Neenan, T.X., Sisko, J.T., Blonsky, P.M., and Shriver, D.F., Macromolecules 19, 1508 (1986).

131. Blonsky, P.M., Shriver, D.F., Austin, P. and Allcock, H.R., Poly. Mat. Sci. Eng. 53, 118 (1985).

132. Bannister, D.J., Doyle, M., Macfarlane, D.R., J.Polym. Sci., Polym. Lett. 23, 465 (1985).

133. Fish, D., Khan, I.M., Smid, J., Makromol. Chem. Rapid Commun. 7, 115 (1986).

134. Hall, P.G., Davies, G.R., McIntyre, J.E., Ward, I.M., Bannister, D.J. and Le Brocq, K.M.F., Polym. Comm. 27, 98 (1986).

135. Bouridah, A., Dalard, F., Deroo, D., Cheradame, H., Le Nest, J.F., Solid State Ionics 15, 233 (1985).

136. Xia, D.F. and Smid, J., J. Polym. Sci., Polym. Lett. 22, 617 (1984).

137. Bannister, D.J., Davies, G.R., Ward, I.M. and McIntyre, J.E., Polymer 25, 1601 (1984).

138. Kobayashi, N., Uchiyama, M., Shigehara, K., and Tsuchida, E., J. Phys. Chem. 89, 987 (1985).

139. Kobayashi, N., Takashi, H., Ohno, H., Tsuchida, E., Polymer J. 18, 661 (1986).

140. Tsuchida, E., Ohno, H., Tsunemi, K., Kobayashi, N., Solid State Ionics 11, 227 (1983).

141. Xia, D.W., Silberman, R., Cabasso, I., Smid, J., Polym. Preprints. Div. Polym. Chem., Am. Chem. Soc. 26, 72 (1985).

142. Ferguson R., PhD Thesis, University of Stirling (1983).

143. Glover, C.A.,'Polymer Molecular Weights, Part 1', Ed. Slade, P.E., Marcel Dekker Inc, New York, p142 (1975).

144. Watson, E.S., O'Neill, M.J., Justin, J., Brenner, N., Anal. Chem. 36, 1233 (1964).

145. O'Neill, M.J., Anal. Chem. 36, 1238 (1964).

146. Ginnings, D.C. and Furukawa, F.T., J. Am. Chem. Soc. 75, 522 (1953).

147. Gillham, J.K., Review Paper, AIChE Journal 6, 1066 (1974).

148. Mathias, L.J., Canterbury, J.B., South, M., J.Polym. Sci., Polym. Lett. 20, 473 (1982).

149. Baker, B.R., Schaub, R.E., Williams, J.H., J. Org. Chem. 17, 116 (1952).

150. Angell, C.A., Solid State Ionics, 18 & 19, 72 (1986).

151. MacCallum, J.R., Vincent, C.A., 'Polymer Electrolyte Reviews 1', Ed. MacCallum, J.R., Vincent, C.A., Elsevier Applied Science Publishers, Essex p23 (1987).

152. Cotton, F.A., Wilkinson, G., 'Advanced Inorganic Chemistry', Ed 3, Wiley Interscience, New York.

153. Bailer, J.C., Emeleus, H.J., Nyholm, R., Trotman-Dickenson, A.F., 'Comprehensive Inorganic Chemistry - 1', Pergamon Press, Oxford, p660 (1973).

154. Weast, R.C., Astle, M.J., Beyer, W.H., 'C.R.C. Handbook of Chemistry and Physics', 67th Ed, C.R.C. Press, Florida, 1986. Tables D100-D112.

155. Atkins, P.W., 'Physical Chemistry', Oxford University Press, Oxford, p826 (1978).

156. Cowie, J.M.G., Ferguson, R., Martin, A.C.S., Polym. Comm. 28, 130 (1987).

157. Binks, A.E., and Sharples, A., J. Polym. Sci. A-2 6, 407 (1968).

158. Gibbs, J.H. and DiMarzio, E.A., J. Chem. Phys. 28, 373 (1958).

159. Sorensen, P.R., and Jacobsen, T., Polym. Bull. 9, 47 (1983).

160. Lee, Y.L., Crist, B., J. Appl. Phys. 60, 2683 (1986).

161. Robitaille, C.D., Fauteux, D., J. Electrochem. Soc. 133, 315 (1986).

162. Dupon, R., Papke, B.L., Ratner, M.A., Whitmore, D.H., Shriver, D.F., J. Am. Chem. Soc. 104, 6247 (1982).

163. Papke, B.L., Dupon, R., Ratner, M.A., Shriver, D.F., Solid State Ionics 5, 685 (1981).

164. Cohen, M.H. and Turnbull, D., J. Chem. Phys. 31, 1164 (1959).

165. Turnbull, D. and Cohen, M.H., J. Chem. Phys., 34, 120 (1961).

166. Turnbull, D. and Cohen, M.H., J. Chem. Phys. 52, 3038, (1970).

167. Adam, G., Gibbs, J.H., J. Chem. Phys. 43, 139 (1965).

168. Tanzella, F.L., Bailey, W., Frydrych, D., Farrington, G.C., Story, H.S., Solid State Ionics 5, 681 (1981).

169. Barker, R.E., Pure & Appl. Chem. 46, 157 (1976).

170. Armstrong, R.D. and Clarke, M.D., Solid State Ionics 11, 305 (1984).

171. Nicholson, M.M. and Weismuller, T.P., J. Electrochem. Soc. 132, 89 (1985).

172. Hoover, M.F. and Butler, G.B., J. Polym. Sci., Part C 45, 1 (1974).

173. Eisenberg, A., J. Polym. Sci., Part C 45, 99 (1974).

174. Williams, M.W., J. Polym. Sci., Part C 45, 129 (1974).

175. Hardy, L.C. and Shriver, D.F., J. Am. Chem. Soc. 107, 3823 (1985).

APPENDIX A

Calculation to Determine the Molar Mass of the "Equivalent Monomeric Unit" for Various Polymers.

Using the configurational entropy model of Adam and Gibbs, values obtained on linearization of conductivity-temperature data using the Vogel-Tammann-Fulcher equation could be interpreted in a meaningful manner, as described in Chapter Seven. To use the configurational entropy model in this study, however, the molar heat capacity for a "monomeric segment" of a comb-shaped polymer had to be calculated. As explained in Section 7.1.3., it is unrealistic to assume that the complete monomer unit in a comb-shaped polymer would behave in a similar manner to the monomeric segment in a linear polymer. A much smaller "equivalent monomeric unit" was therefore established.

An ethylene oxide (EO) or propylene oxide (PO) unit (depending on the character of the solvating unit in the sidechain of the polymeric host) was assumed to be a suitable fragment of the extremely large monomer unit which could be considered comparable to the monomeric segment in a linear polymer. The "equivalent monomeric unit" which was finally used to define molar quantities when applying the configurational entropy model to comb-shaped polymers included a contribution representative of the non-ethereal sections of the monomer unit (such as the itaconate backbone and sidechain terminal groups) in addition to the main contribution introduced from the previously discussed ether unit.

The molar mass (M(eq)) of the "equivalent monomeric unit" or monomeric segment for each polymeric host was calculated as shown below.

$$M(eq) = \frac{\text{Molar Mass of a Monomeric Unit}}{\text{Number of Solvating Units per Monomeric Unit}} \qquad A$$

The relevant data required to calculate M(eq) for each polymer of interest are displayed in Table A.

Table A

Details required for Calculation of M(eq) for Various Polymers

Polymeric Host	PDMEO3I	PDPPGI	PVEMEO3
Molar Mass of Monomeric Unit/gmol^{-1}	422	2080	190
Solvating Units in the Monomer	EO	PO	EO
Solvating Units per Monomeric Unit	6	34	4(a)
M(eq)/gmol^{-1}	70.3	61.2	47.5

a)

The sidechain in VEMEO3 contains 3 EO units, however, the backbone $-CH_2-CH_2-O-$ group was considered comparable to an additional EO unit. VEMEO3 was therefore assumed to contain 4 solvating units.