

Polymer Electrolytes Based on Poly (oxyethylene)

Key Words:

polymer electrolytes, poly (oxyethylene),
conductivity, impedance spectroscopy

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ABSTRACT

The chemistry of the published works on polymer electrolytes is briefly reviewed. The preparation of poly(oxyethylene) prepared from PEG400 and uniform EG with $m=3$ to 6 is represented. The structural (NMR & GPC), thermal (DSC) and conductivity properties of the polymers are discussed. It is shown that the T_g of the electrolytes increases linearly with increasing salt concentration. However the melting behaviour of electrolytes from PEG400 is different from those with uniform EG, s. The conductivity of all the samples is compared and it is elucidated that the electrolyte of PEG400 is the best ion conductor in the series studied with conductivity of $< 10 \text{ Scm}$ at room temperature.

INTRODUCTION

A polymer electrolyte is a polymer with a salt mixture which can support ionic conductivity. Poly(oxyethylene) was the first polymer to be investigated as a solvent for ionic salts [1], and its potential for use as a polymer electrolyte in solid-state batteries was recognised by Armand in 1978 [2]. Since that time it has been established that polymers containing sequences of oxyethylene units are uniquely suited to this application.

Poly(oxyethylene) $-(\text{OCH}_2\text{CH}_2)-$

Solubility

One important factor determining the choice of poly(oxyethylene) is the ready solubility of many salts in this polymer. A polyether is a good electron donor, and so is a good solvent for cations. Small cations are most readily dissolved since crown-ether-like complexes can be formed

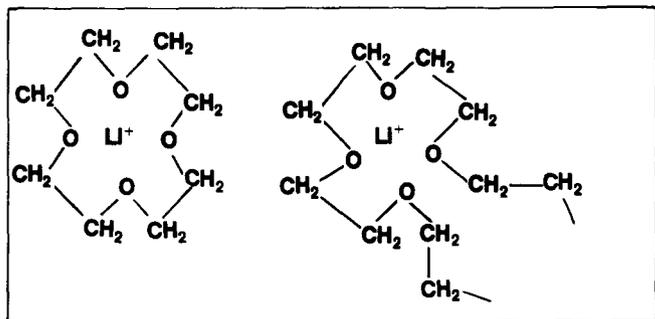


Figure 1: Solvation of Li^+ by crown ether or poly(oxyethylene)

Conversely a polyether is a poor electron acceptor, and so is a poor solvent for anions. Large, polarisable anions are most easily dissolved. The various factors combine well in salts such as lithium perchlorate (LiClO_4) and lithium triflate (LiCF_3SO_3) (Table 1)

Table 1: Solubility of salts in poly(oxyethylene)

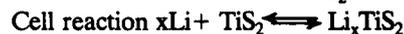
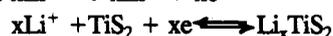
| | Li^+ | Na^+ | K^+ | Mg^{++} | Ca^{++} |
|----------------------------|---------------|---------------|--------------|------------------|------------------|
| F^- | - | - | - | - | - |
| Cl^- | + | - | - | + | - |
| Br^- | + | + | - | + | + |
| I^- | + | + | + | + | + |
| SCN^- | + | + | + | + | + |
| ClO_4^- | + | + | + | + | + |
| CF_3SO_3^- | + | + | + | + | + |

Lithium Battery

A possible application of a poly(oxyethylene) electrolyte is in a solid-state battery. One typical cell is shown below. The electrodes are reversible to Li^+ , one being a lithium metal electrode (positive) and the other being a lithium ion insertion electrode (negative).

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Poly(oxyethylene) electrolyte: cell reactions



Such a battery can be made as a thin film (figure 2). The total thickness of the battery (two electrodes, electrolyte and current collector) can be less than 0.2 mm, and the thickness of the electrolyte film itself can be less than 50 μm .

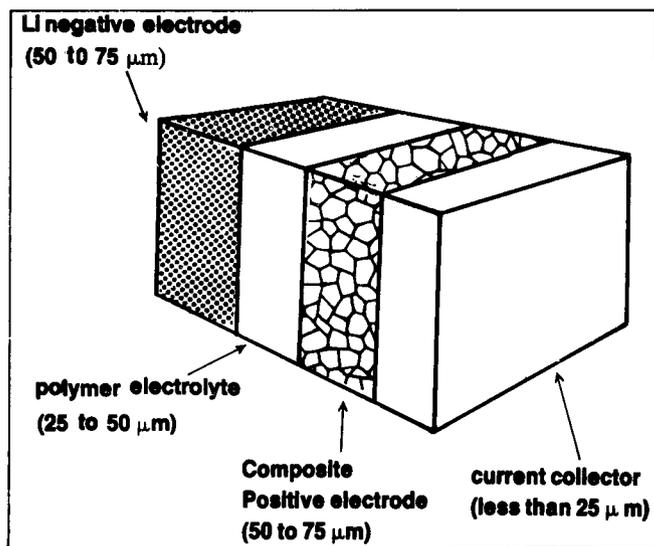


Figure 2: Thin-film solid-state battery

An advantage of the thin-film construction, made possible by use of flexible polymers, is ease of fabrication to give large electrode areas with consequent high performance (Figure 3).

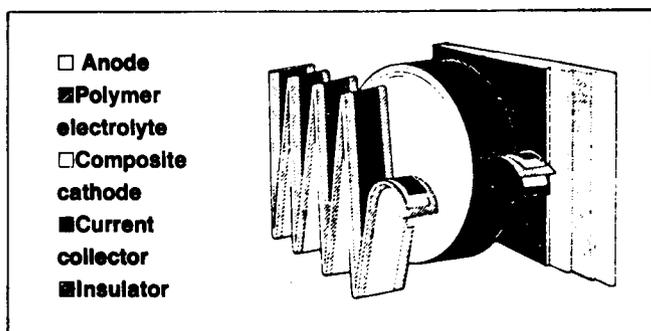


Figure 3: Large-area thin-film solid-state battery

This battery will work well at moderately-high temperatures. A summary of working conditions of such a battery are:

Poly(oxyethylene) electrolyte battery

80°C

current-density > 10 A m⁻² at 20 V

energy density > 100 W kg⁻¹

stable through 1000 charge / discharge cycles

Other Devices

Solid-state batteries are but one of the possible uses for polymer electrolytes. Other devices using polymer electrolytes are:

- (i) Electrochromic displays - devices which change their appearance in response to an electrical signal
- (ii) Chemical sensors: e.g. H⁺ sensor based on
H₂, Pt / electrolyte / H_xWO₃
- (iii) Fuel cell: e.g. H₂, Pt / electrolyte / O₂, Pt
Proton conductor (PEO + H₃PO₄)

Crystallinity

There are no problems with the mechanical stability and shelf life of a poly(oxyethylene) electrolyte devices, and the outlook for development seems good. The problem is that poly(oxyethylene) electrolytes are not directly useful at room temperature, due to crystallisation of the polymer. Ionic conductivity is through the non-crystalline elastomeric phase. Poly(oxyethylene) has a melting point of about 70°C and is highly crystalline at room temperature, particularly if it has been annealed at that temperature for a period of time. Poly(oxyethylene) electrolytes batteries must be heated above 70°C in order to achieve high efficiency.

Room-temperature Battery

For efficient operation of a device at room temperature, the polymer electrolyte must be non-crystalline. The requirements are:

- (i) good solvent for salts
- (ii) non-crystalline at room temperature
- (iii) high chain mobility (low T_g)
- (iv) good mechanical properties (high molecular weight)
- (v) chemical stability (e.g. in contact with lithium)

High-molecular-weight poly(oxyethylene) is satisfactory on all counts except (ii). As a working criterion for the polymer + salt mixture, its conductivity at room temperature should be at least 10⁻⁴ S cm⁻¹.

Review of Published Work

The polymers of interest can be subdivided into three types: comb, linked and statistical copolymers (Figure 4). In each case the polymer is designed to have the required mechanical strength.

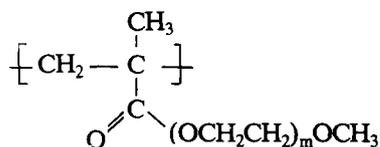
Comb Copolymers

The followings are the examples of non-crystalline comb copolymers synthesised and tested as polymer electrolytes.

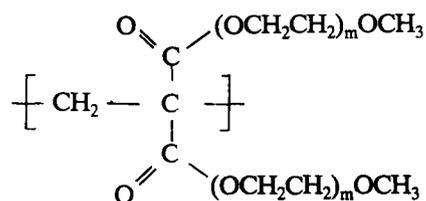
Polymethacrylate Smid, Xia (1984) [3]

Ward, McIntyre (1984) [4]

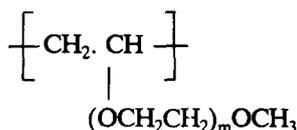
Narrow distribution: m = 8,22 (side-chain crystallisation)



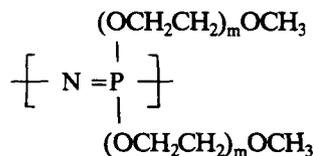
Polyitaconate Cowie, Martin (1987) [5]
Uniform: $m = 1$ to 7



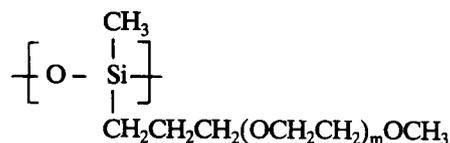
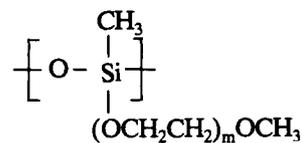
Polyvinylether Cowie (1987) [6]
Uniform: $m > 3$



Polyphosphazene Shriver, Allcock (1984) [7]
Uniform: $m = 1$ to 4
Narrow distribution: $m = 7$ to 42 (side-chain crystallisation)



Polysiloxane
Ward et al (1986) [10]
Narrow distribution: $m = 8, 12$



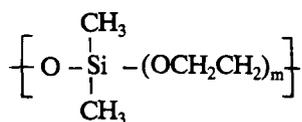
Linked polymers

These are polymers with oxyethylene blocks linked by another unit. Many linking units are possible. Examples are

Dimethylsiloxane link

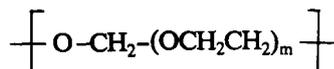
Watanabe et al (1984) [12]

Uniform: $m = 1$ to 4 , narrow distribution: $m = 9$



Oxymethylene link Booth et al (1986) [13]

Uniform $m = 3$ to 6 , narrow distribution: $m = 4$ to 14



Generally high molecular weights are difficult to achieve, since linking is a condensation procedure. However this is not the case for the oxymethylene-linked polymer, for which molecular weights $M > 10^5$ are routinely obtained.

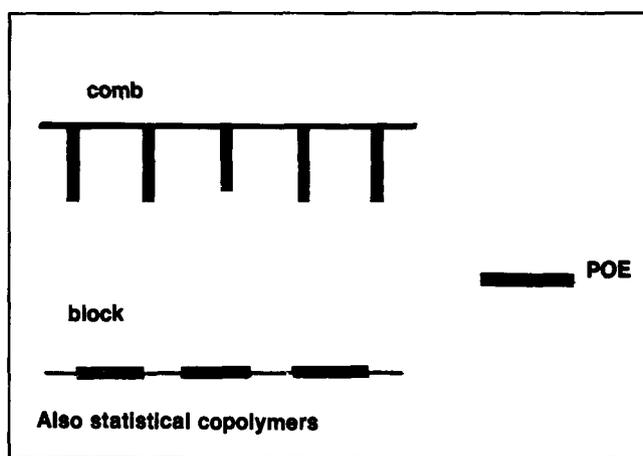


Figure 4: Copolymers for use as polymer electrolytes

Statistical Copolymers

Examples of statistical copolymers prepared for use in polymer electrolytes are shown in Figure 5. Copolymers of high molecular weight ($M \sim 10^6$) can be readily prepared by use of a coordination catalyst (e.g. Vandenberg catalyst) [14].

A high proportion of the second monomer must be

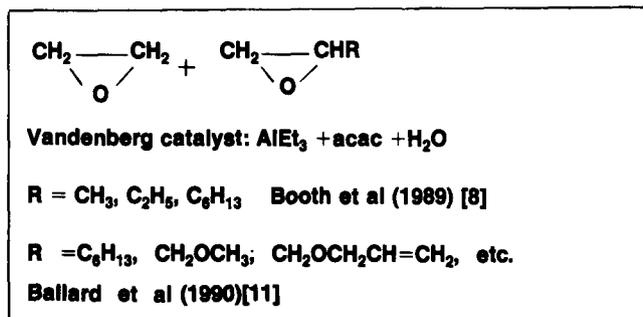


Figure 5: Statistical copolymers

incorporated into a statistical Copolymer in order to reduce the

melting point to room temperature. This is because the melting point depends largely on the longest oxyethylene sequences in the statistical distribution of chain lengths. There are no very long sequences in the linked copolymer. The point is compared in Figure 6 where the melting points of statistical and linked copolymers are compared (X_{oe} = mole fraction of oxyethylene units).

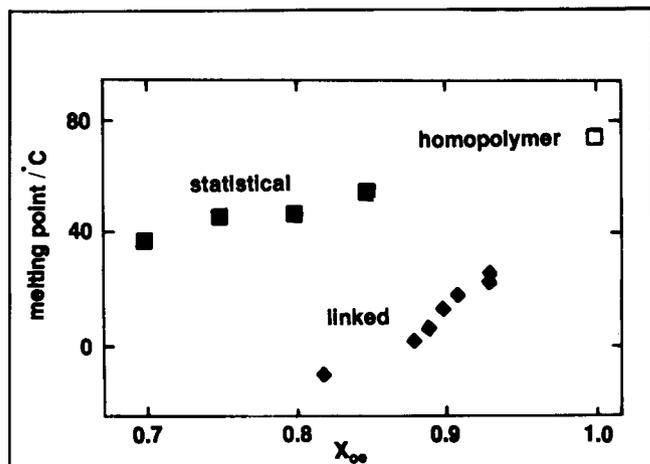


Figure 6: Comparison of melting points of statistical and linked copolymers

Comparison of Copolymers

A problem in comparing the properties of one copolymer with another is that the conductivity of the polymer electrolyte (i. e. the mixture of polymer and salt) varies with the salt used, the salt concentration and the temperature of measurement as well: A comparison of polymers as polymer electrolytes should quantify the following requirements:

- (i) same salt
- (ii) optimum concentration (for highest conductivity)
- (iii) same temperature (what is room temperature)
- (iv) high molecular weight (liquid copolymers have high conductivity)

The salt concentration is most troublesome, since the conductivity goes through a maximum as salt concentration is increased from a low value (see later), and optimum (maximum) conductivities should be compared. The ideal conditions are not usually met but, bearing in mind the problems, it is possible to pick out the best candidates for room temperature application.

Among the comb copolymers (Table 2) those with a polysiloxane backbone have the best room temperature conductivity, but the molecular weight is low. Taking MW > 50,000 as a minimum (for mechanical strength), only the polymethacrylate [3] meets this requirement, but its conductivity is low. Note the very low conductivity of the poly(oxyethylene) electrolyte at 20 °C.

Table 2: Comb copolymers: optimum conductivities

| Copolymer | MW | Salt | T/°C | σ/Scm^{-1} | reference |
|-------------------|-----------------|-------------|------|--------------------------|-----------|
| Polymethacrylate | | triflate | 20 | 2×10^{-5} | [4] |
| Polymethacrylate | $> 10^5$ | perchlorate | 20 | 1×10^{-5} | [3] |
| polyitaconate | 4×10^4 | perchlorate | 20 | 2×10^{-6} | [5] |
| polyvinylether | 3×10^4 | perchlorate | 50 | 4×10^{-5} | [6] |
| polyphosphazene | | triflate | 20 | 3×10^{-5} | [7] |
| polysiloxane | 2×10^4 | perchlorate | 20 | 6×10^{-5} | |
| poly(oxyethylene) | 10^6 | triflate | 20 | $< 10^{-7}$ | [13] |

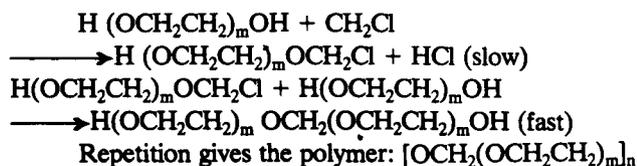
Of the linked and statistical copolymers (Table 3) the oxymethylene - linked poly(oxyethylene) best meets the twin requirements. Note that the siloxane - linked polymer is a liquid.

Table 3: Linked and statistical copolymers: optimum conductivities

| Copolymer | MW | Salt | T/°C | σ/Scm^{-1} | reference |
|-------------------|-------------------|-------------|------|--------------------------|-----------|
| link | | | | | |
| dimethylsiloxane | 3×10^3 | perchlorate | 25 | 1×10^{-4} | [12] |
| oxymethylene | $> 10^5$ | triflate | 20 | 4×10^{-5} | [13] |
| comonomer | | | | | |
| propylene oxide | $> 5 \times 10^5$ | perchlorate | 20 | $\sim 10^{-5}$ | [8] |
| glycidyl ethers | $\sim 10^6$ | triflate | 20 | $\sim 2 \times 10^{-5}$ | [11] |
| poly(oxyethylene) | $\sim 10^6$ | triflate | 20 | $> 10^{-7}$ | [13] |

Oxymethylene - linked Poly(oxyethylene) Prepared from PEG 400 preparation

The Polymer is easily prepared from readily available starting materials, e. g. polyethylene glycol 400, dichloromethane, KOH. The reaction is based on the williamson reaction. It is not a conventional condensation reaction: exact matching of molar ratios of reactants is not required. Indeed one of the reagents, dichloromethane, is used as solvent. This is because of the very-high reactivity of the chloroether intermediate.



The reaction was carried out in a 250 cm³ round bottom 3 neck flask equipped with a mechanical stirrer, a water condenser and a pressure equalizing dropping funnel.

All the equipment was oven-dried and purged with nitrogen before use.

Finely ground KOH (20 g) CH_2Cl_2 (10 cm^3) were mixed at room temperature under dry nitrogen. Ethylene glycol (10 cm^3) was added quickly from the dropping funnel.

After 10 min. CH_2Cl_2 (2 cm^3) was added. This addition of CH_2Cl_2 was continued 3 times at 10 min. intervals.

The resulting mixture was stirred in the dark at room temperature for 16 h. Then the mixture was diluted with CH_2Cl_2 (50 cm^3) and filtered of solid inorganics.

At this time the solvent was rotary evaporated the product was a colourless rubber.

Rings and chains

The reaction can lead to rings and chains. A GPC curve typical of the reaction product is shown (Figure 7). There are two peaks, corresponding to long chains ($\text{MW} > 10^5$) and small cyclic molecules ($\text{MW} < 2000$). The proportion of rings varies with reaction conditions, particularly the dilution: high dilution favours ring formation.

The cyclics can be separated from the chains by precipitating the polymer from dilute solution in toluene by adding heptane [13] (Figure 7). The cyclics are interesting molecules in themselves, and have been discussed elsewhere [9]

Chain Structure by NMR

The chain structure was verified by ^{13}C NMR (Figure 8).

Thermal Properties by DSC

Oxymethylene - linked poly(oxyethylene) prepared from PEG 400 crystallises well below room temperature and melts at about 13°C . The quenched copolymer shows (Figure 9) a glass transition at $T_g \sim -65^\circ\text{C}$ and rather complicated melting behaviour, attributed to the formation of two crystalline forms. The less - stable crystals melt at about 0°C , the more - stable at about 13°C . Annealed samples give an uncomplicated DSC curve with a single melting peak at 13°C (Figure 9). The heat of fusion is only about 30 J g^{-1} , corresponding to a crystallinity of $X \sim 15\%$ of ideal (210 J g^{-1}). [compare poly (oxyethylene): $X \sim 70\%$ of ideal]. The low melting point (below room temperature) and the low degree of crystallinity below T_m are, of course, the thermal properties needed for a good low - temperature polymer electrolyte.

Conductivity

When mixed with salt, within the concentration range of interest, oxymethylene-linked poly (oxyethylene) does not crystallise down to very low temperatures. This is illustrated in Figure 10 for the copolymer prepared from PEG400, which in the pure state gives a melting peak in DSC at 13°C .

As a consequence, and in contrast to poly (oxyethylene) itself, the linked copolymer can be used in studies of conductivity without complication from crystallisation. Note that the glass transition temperature of the copolymer with a salt mixture

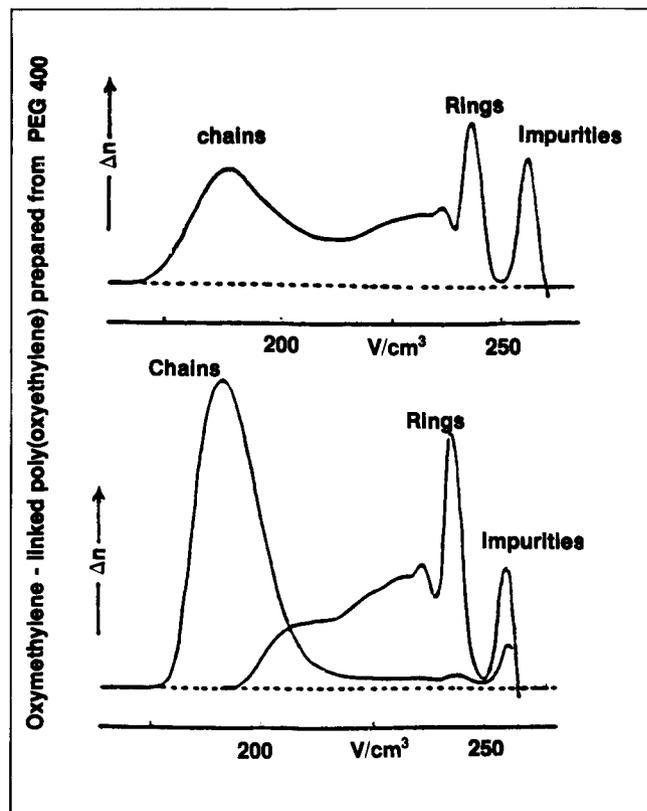


Figure 7: GPC curves

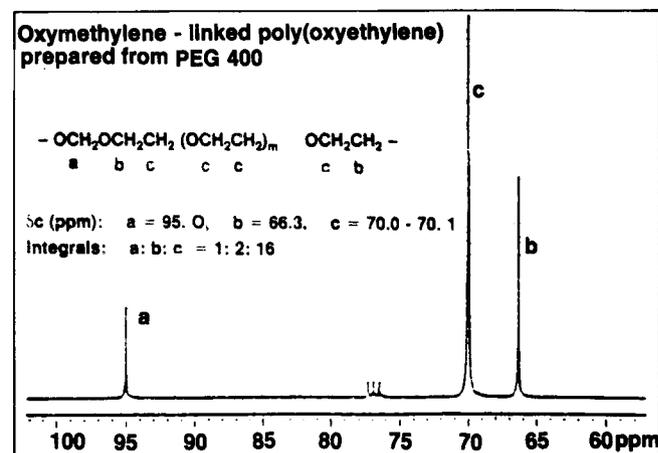


Figure 8: NMR spectrum and assignments

($T_g \sim -50^\circ\text{C}$) is higher than that of the pure copolymer ($T_g = -65^\circ\text{C}$).

Effect of Salt Concentration on T_g

The value of T_g is found to vary linearly with salt concentration (Figure 11). A linear increase of T_g with Li/O has been found for other polymers.

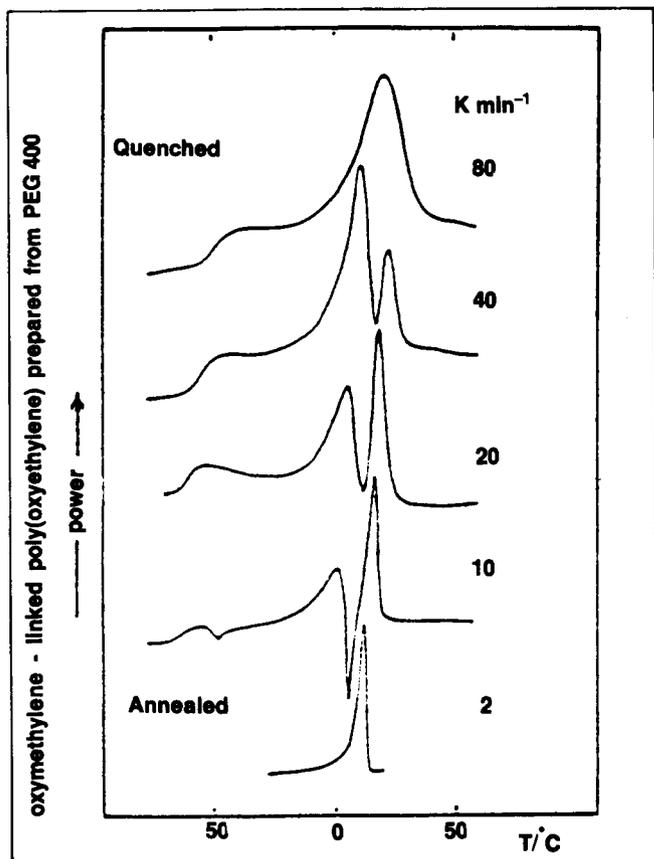


Figure 9: DSC

Effect of Salt Concentration on Conductivity

Generally LiClO_4 or LiCF_3SO_3 are used. The salt concentration is usually expressed as the mole ratio of salt to oxyethylene oxygen (Li/O) or its inverse (O/Li). Typically a plot of conductivity against O/Li at a given temperature show a maximum (Figure 12). Since a variation of several orders of magnitude is observed, a plot of \log_{10} against salt concentration Li/O is used.

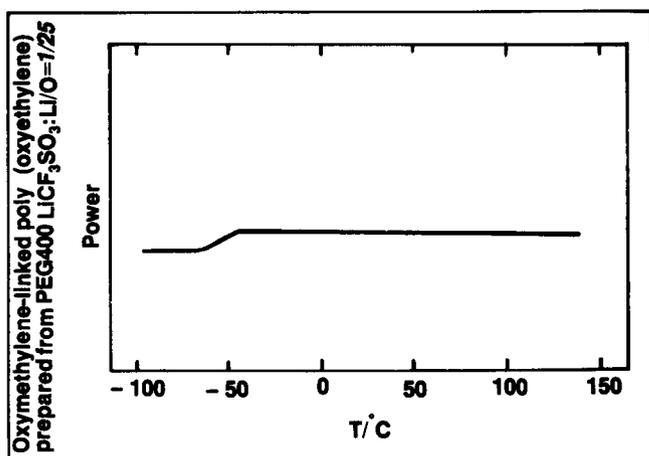


Figure 10: DSC: oxymethylene-linked poly (oxyethylene)

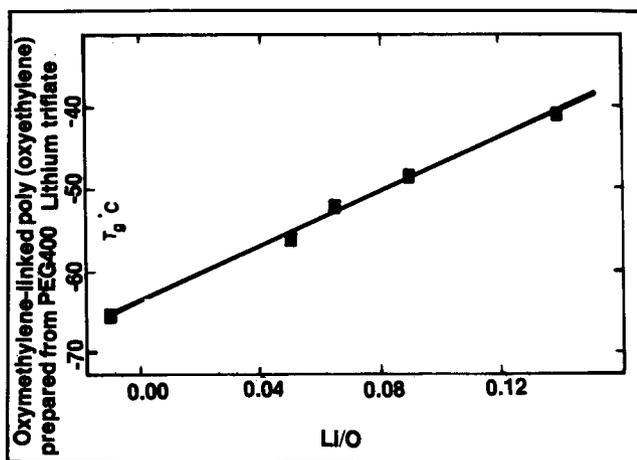


Figure 11: Glass transition temperature vs salt concentration

The plot shown is typical: starting at a low value of $10^{-7} \text{ S cm}^{-1}$ characteristic of the copolymer, the conductivity increases rapidly with the Li/O ratio over the low concentration range, but reaches a maximum at or about $\text{Li/O} = 0.03$ to 0.4 ($\text{O/Li} = 30$ to 25) before decreasing again. The initial rise in conductivity is due to the increase in the number of charge carriers. The final decrease is attributed to the formation of ion pairs (and larger clusters) and to the increase in the viscosity of the polymer electrolyte.

Effect of Temperature on Conductivity

The effect of temperature on the conductivity of a polymer electrolyte with a given salt concentration is often represented by an Arrhenius plot of $\log_{10} \sigma$ against $1/T$ (Figure 13)

From 100°C to 25°C the conductivity decreases by about 1 decade, from about 5×10^{-4} to about $5 \times 10^{-5} \text{ S cm}^{-1}$. Note that the Arrhenius plot is not linear: we will return to this point in a moment.

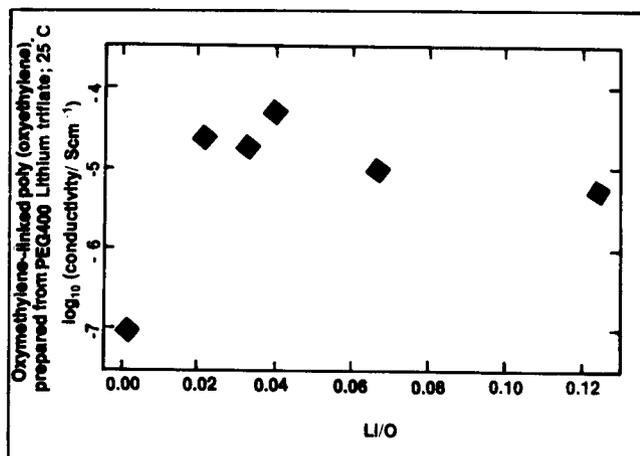


Figure 12: Log10 vs salt concentration

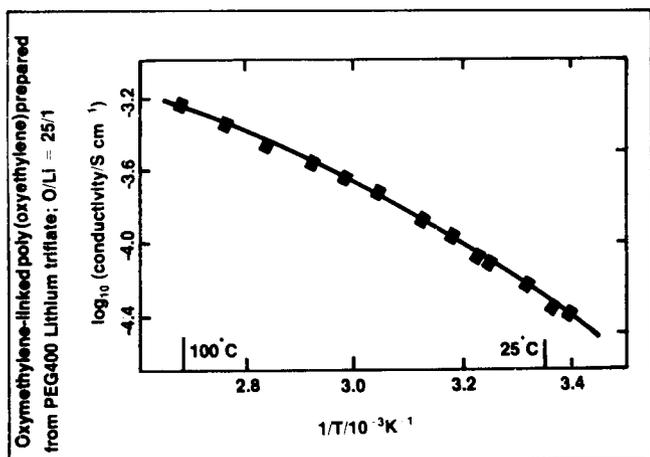


Figure 13: $\text{Log}_{10} \sigma$ vs Inverse temperature: Arrhenius plot

This behaviour, which is typical of a non-crystalline-polymer electrolyte, can be compared with the behaviour of poly(oxyethylene) itself (Figure 14). Crystallisation reduces the conductivity from $>10^{-3} \text{ S cm}^{-1}$ at 100°C to $<10^{-7} \text{ S cm}^{-1}$ at room temperature.

VTF Plot

It has just been noted that the Arrhenius plot is not linear even for the non-crystalline system (see Figure 13). A better representation of the temperature dependence is given by Vogel-Tamman-Fulcher equation

Arrhenius equation $\sigma = A \exp(-B/T)$

VTF equation $\sigma = A \exp(-B/(T - T_0))$

or $\log \sigma = \log A - B/(T - T_0)$

Where A is a constant related to the number of charge carriers
 $B = E/R$ is a molar activation energy of conduction divided by gas constant

T_0 is a temperature related to T_g

The characteristic temperature T_0 can be thought of as the equilibrium (ideal) glass transition temperature, i. e. the

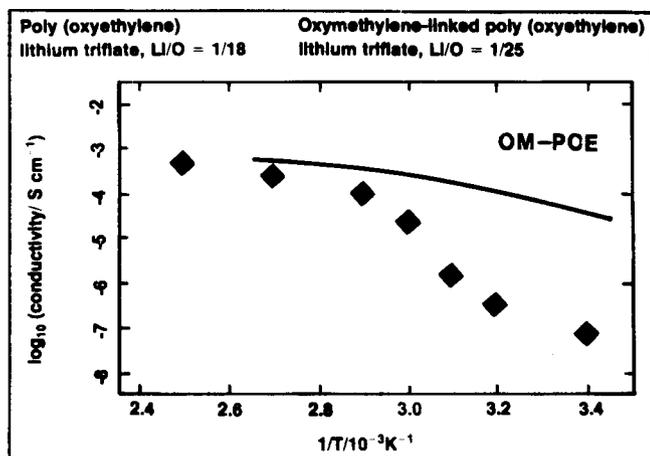


Figure 14: $\text{Log}_{10} \sigma$ vs inverse temperature: Arrhenius plot

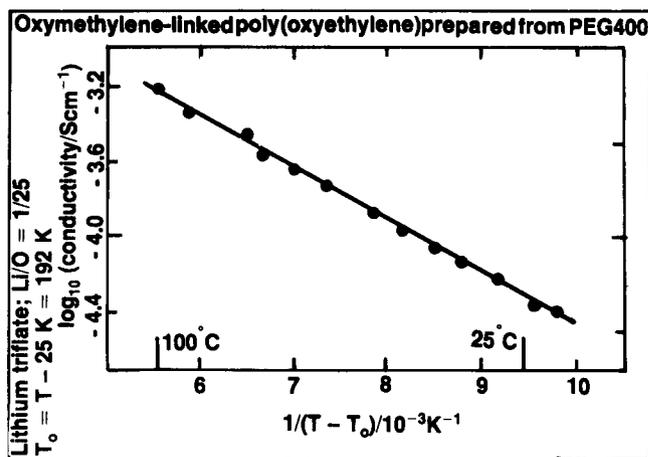


Figure 15: VTF Plot

temperature at which free volume vanishes. Various values of T_0 have been advocated: e. g. T_g (polymer), T_g (electrolyte) - 50K. The form of the plot is not sensitive to the choice of T_0 though, the values of the parameters do vary.

The usefulness of the VTF equation is illustrated in (Figure 15): the plot is an excellent straight line.

Other Oxymethylene - linked Poly (oxyethylene)s

High - molecular - weight copolymers have been prepared from a number of precursors. Both polyethylene glycols with narrow molecular weight distributions and uniform oligomers have been used. A summary, which includes their thermal properties, is given Table 4

Note that $T_g \sim -65^\circ\text{C}$ for all the copolymers, but that the melting point and heat of fusion vary with the oxyethylene block length and block - length distribution.

Melting Points

The variation of melting point with chain length is shown in (Figure 16).

The copolymers prepared from the polydisperse glycols have generally lower melting points. These copolymers have no definite repeat unit, since the oxyethylene blocks have a

Table 4: Oxymethylene - linked copolymers

| Precursor | block length m | $T_m/^\circ\text{C}$ | $\Delta H_{fus}/\text{Jg}^{-1}$ | $T_g/^\circ\text{C}$ |
|------------|----------------|----------------------|---------------------------------|----------------------|
| PEG200 | 4.5 | -15 | 20 | -65 |
| PEG400 | 9.1 | +13 | 30 | -65 |
| PEG600 | 13.6 | +26 | 50 | -65 |
| tri - EG | 3 | -5 | 20 | -62 |
| tetra - EG | 4 | +34 | 62 | -63 |
| Penta - EG | 5 | +7 | 39 | -67 |
| hexa - EG | 6 | +31 | 57 | -64 |

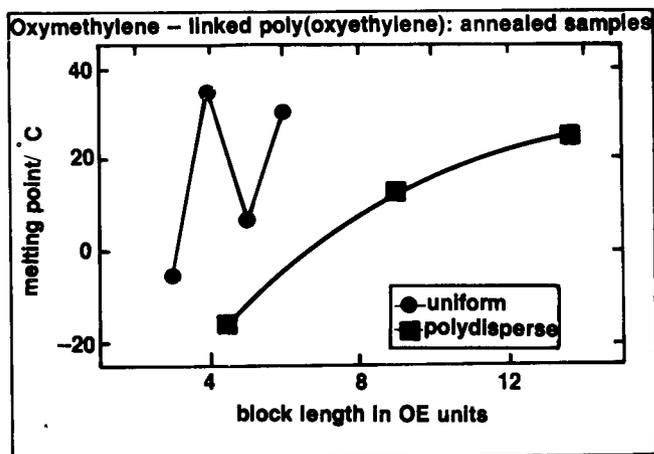


Figure 16: Melting temperature vs block length

range of lengths, and they crystallise in a defective poly (oxyethylene) structure. In fact their melting temperatures are very similar to those of their precursors.

The copolymers prepared from uniform glycols have definite repeat units, e.g. the copolymer prepared from triethylene glycol has exactly 3 oxyethylene units and one oxymethylene per repeat unit. Accordingly, they crystallise into different structures. The pronounced even - odd effect is evidence of this.

Heat of Fusion

The same odd - even effect can be seen in the heats of fusion (Figure 17)

The explanation of the even - odd effect in the thermal properties of the copolymers prepared from the uniform oligomers must lie in different crystal packings of the even and odd copolymers: however we have no X - ray data to confirm this.

Effect of Oxyethylene Block Length on Conductivity

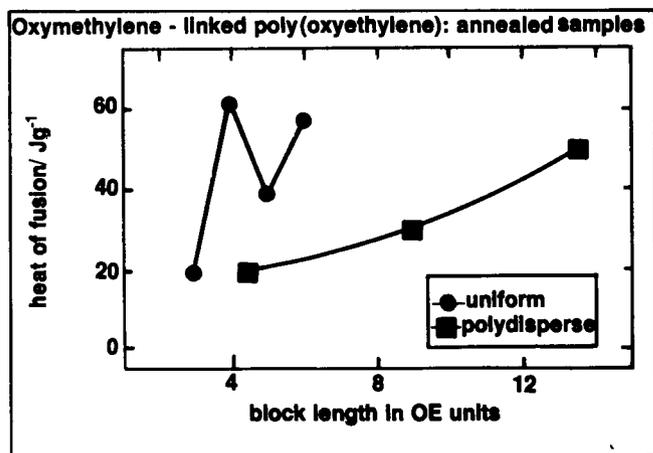


Figure 17: Heat of fusion vs block length

The copolymers prepared from the uniform oligomers are ideal for examining the effect, if any, of the oxyethylene block length on conductivity.

Oxymethylene - linked poly (oxyethylene) from uniform oligomers

- $[\text{OCH}_2(\text{OCH}_2\text{CH}_2)_m] - m = 3, 4, 5 \text{ and } 6$

Non - crystalline when mixed with salt (LiClO_4)

T_g increases Linearly with Li/O

One might suppose (see Figure 1) that minimum of four contiguous oxyethylene units would be required in order to maximise solubility and thereby, optimise conductivity. When mixed with salt, within the concentration range of interest ($1/8 < \text{Li/O} < 1/40$), the copolymers generally do not crystallise at room temperature: an exception is the copolymer prepared from hexaethylene glycol, which crystallises below 30°C in mixtures dilute in salt. Consequently, as noted earlier for the copolymer prepared from polydisperse PEG400, there are no complications from crystallisation in the temperature ranges studied.

The effect of salt on T_g was found to be similar to that found for the less-ordered copolymer (Figure 18).

A plot of conductivity against salt concentration can be used to compare the behaviours of the polymer electrolytes formed from the four copolymers (Figure 19).

As expected, the effect of salt concentration parallels that found for the "PEG400" copolymer (Figure 12). It is apparent that the conductivities of the linked copolymer prepared from triethylene glycol are generally lower than those of the other three copolymers.

An alternative way of presenting the data, taking into account the temperature dependence of conductivity, is by a VTF plot (Figure 20)

Again there is a clear distinction between the behaviour of the linked copolymer prepared from triethylene glycol and the others. The lines drawn through the points in (Figure 20) correspond to the values of A and E listed below.

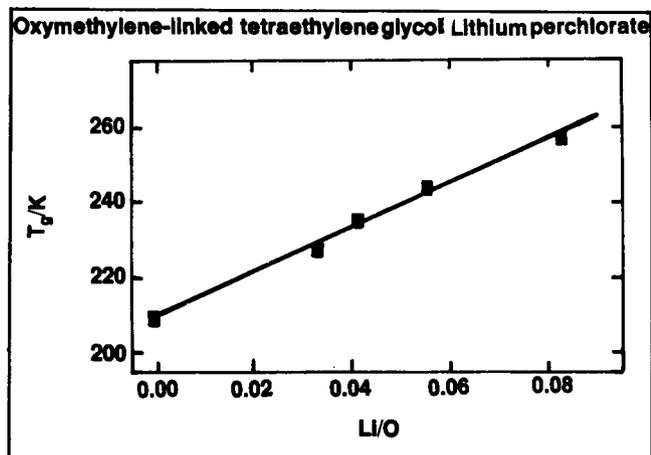


Figure 18: Glass transition temperature vs salt concentration

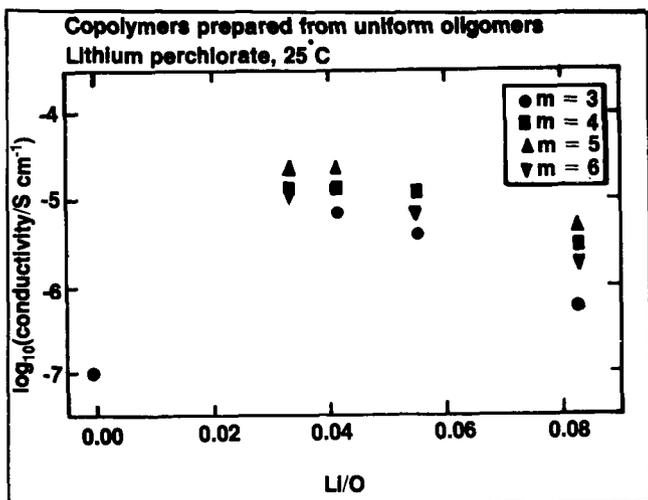


Figure 19: $\log_{10}\sigma$ vs salt concentration

VTF parameters for oxymethylene - linked poly (oxyethylene)s
Lithium triflate. Li/O = 1/24

| | triethylene glycol | tetra-, penta - and hexaethylene glycol |
|------------------------|--------------------|-----------------------------------------|
| A / S cm ⁻¹ | 0.22 | 0.32 |
| E/kJ mol ⁻¹ | 9.0 | 7.3 |

The absolute values of these parameters depends very much on the assumptions made in drawing the plots (value of T_0 , etc). The relative values are significant. It is clear that

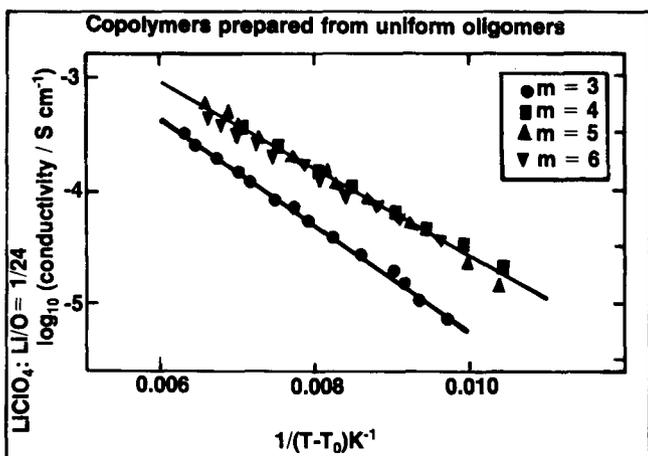


Figure 20: VTF plot: $T_0 = T_g - 25^\circ\text{K}$

there are fewer charge carriers in the 'triethylene glycol' system (lower value of A) and that motion of the charge carriers in the 'triethylene glycol' system is energetically more difficult (higher value of E).

Conclusions

Oxymethylene - linked poly (oxyethylene) is a useful solvent for salts and so a useful component of polymer electrolytes. It can be conveniently prepared to high molecular weight from a variety of glycol precursors. The optimum conductivity measured at room temperature is higher than those reported for other useful polymer/salt systems.

Oxymethylene-linked poly (oxyethylene)s can be used model compounds in studies of conductivity. Our own work has concentrated on the details of chain structure. We have proved that there is a distinct advantage in having at least four contiguous oxyethylene units in the chain.

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