Polymer electrolytes based on polyesters of thiodipropionic acid: 1. Synthesis, characterization and ionic conductivity measurements

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A series of aliphatic polyesters of 3,3'-thiodipropionic acid and linear glycols containing a different number of ethylene oxide groups has been prepared and characterized. These polymers show low values of glass transition temperature and appear, at room temperature, as highly viscous liquids, in which $LiClO_4$ can be dissolved easily. The resulting transparent semi-solid solutions behave as polymer electrolytes with high ionic conductivity, which has been investigated as a function of $LiClO_4$ concentration, temperature and chemical structure, i.e. the number of thioether sulfur and ether oxygen atoms in the backbone. The main factors that affect conductivity are the glass transition temperature and the solvating capacity for the lithium ions. It was found that both the oxygen and sulfur atoms contribute to solvating lithium ions.

(Keywords: polymer electrolytes; thiodipropionic acid polyesters; ionic conductivity; glass transition temperature; $LiClO_4$ salt complexes)

INTRODUCTION

Polymer solid electrolytes, based on lithium salts ($LiClO_4$, $LiSO_3CF_3$, etc.) dissolved in a polymeric matrix, have received much attention in recent years for their potential applications in solid state lithium rechargeable batteries and in lithium insertion electrochromic devices[1,2].

It is well known that ether groups in the host polymer have a particular ability to solvate salts to form polymer electrolytes having conductivity values useful for electrochemical applications[3]; the majority of systems described nowadays are based on polymers carrying ethylene oxide groups in the main or side chain. The chemical structure of the polymer matrix is often modified in order to reduce the crystallinity, while maintaining a low value of the glass transition temperature; in this way it is possible to achieve quite high conductivity values at room temperature[4–6].

In this work we have prepared polymer electrolytes based on aliphatic polyesters of 3,3'-thiodipropionic acid (TDPA) and linear glycols containing from zero to four ethylene oxide (EO) groups, with the aim of studying the effect of the simultaneous presence of ether and thioether groups. In order to elucidate the contribution to conductivity due to thioether groups, about which very little has been reported in the literature[7], we have also examined the behaviour of polyelectrolytes based on polyesters of pimelic acid (PA), where a thioether group has been replaced by a methylene group.

EXPERIMENTAL

Synthesis of polymers

Polyesters were synthesized from dimethyl 3,3'-thiodipropionate and various glycols (in a molar ratio 1:1.1), namely ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TEEG) and pentaethylene glycol (PEG), using $Ti(OBu)_4$ (0.34 wt% with respect to the reagents) as the catalyst. All the reagents were supplied by Aldrich and were used without any purification.

The syntheses were carried out in bulk, at temperatures of 170–180°C, according to the usual two-stage polycondensation procedure. In the first stage, under nitrogen atmosphere, methanol was distilled off; in the second stage the pressure was reduced to about 10^{-3} mmHg in order to complete the polycondensation. A similar procedure was used for the synthesis of polyesters based on PA and EG, DEG and TEG.

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Polymer samples were washed in diethyl ether and dried in vacuum at 90°C overnight. All the polymers synthesized are transparent and highly viscous liquids at room temperature.

Polymer characterization

The polymers were characterized by *FT*i.r. (Bruker IFS 48) and ^{1}H n.m.r. (Varian XL-200) spectroscopy.

Differential scanning calorimetry (Perkin Elmer DSC-7) was used to measure the glass transition temperature (T_g), with a heating rate of 20°C min^{-1}, in the temperature range from −90 to 100°C. Annealing at −10°C for 1 h was performed in some cases.

Terminal-group content was determined in order to evaluate the molecular weight of polymers. Hydroxyl-group content was determined by titration after a quantitative esterification with acetic anhydride[8]. Carboxyl terminal groups were measured on samples dissolved in $CHCl_3$ by titration with a 0.05 N solution of KOH in CH_3OH.

Preparation of polymer–salt mixtures (polymer electrolytes)

$LiClO_4$ (Aldrich) was dried in vacuum for 3 h at 140°C. The polymer electrolytes, at different molar ratios of polyester/$LiClO_4$, were prepared by mixing the two components in an argon-filled glove box. The mixtures were heated under magnetic stirring for 2 h at 120°C to facilitate the dissolution of the salt in the polymeric matrix, always under an argon atmosphere. The electrolytes obtained are in all cases transparent semi-solid solutions with viscosity higher than that of the base polymers.

Table 1 Glass transition temperature, terminal-group content and molecular weight of polyesters of thiodipropionic acid and pimelic acid

Polymer	T_g (°C)	Terminal-group content (meq g^{-1})		M_n[a]
		COOH	OH	
PTDPA-EO(0)	−47	6×10^{-3}	$<1\times10^{-3}$	970[b]
PTDPA-EO(1)	−40	4×10^{-3}	0.614	3230
PTDPA-EO(2)	−42	6×10^{-3}	0.652	3040
PTDPA-EO(3)	−46	3×10^{-3}	0.806	2470
PTDPA-EO(4)	−47	3×10^{-3}	0.880	2260
PPA-EO(0)[c]	−54	1.64	$<1\times10^{-3}$	1210
PPA-EO(1)[c]	−50	0.461	$<1\times10^{-3}$	4340
PPA-EO(2)[c]	−54	0.472	0.771	1610

[a] Calculated from the overall terminal-groups content, neglecting the presence of cyclic molecules

[b] 970 meq g^{-1} of –(OOCCH$_3$) terminal groups were estimated from ^{1}H n.m.r. analysis

[c] In these cases the syntheses were carried out starting from the acid instead of methyl ester

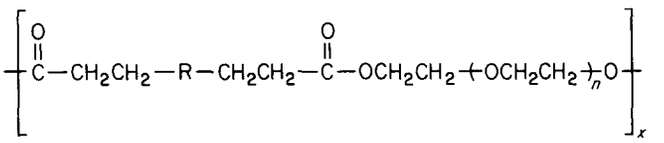
Characterization of polymer electrolytes

Differential scanning calorimetry (Perkin Elmer DSC-7) was used to evaluate the glass transition temperature: the heating rate was 20°C min^{-1}, in the temperature range from −80 to 100°C.

The conductivity was evaluated by complex impedance technique, with blocking electrode cells sealed in an argon-filled glove box, using a frequency response analyser (Solartron 1255) coupled to a potentiostat/galvanostat (PAR 273) in the frequency range from 0.1 Hz to 100 kHz. The impedance results were analysed by Boukamp's fitting program[9]. Each sample was allowed to equilibrate for 1 h at any temperature before measurement; the temperature range covered was from 25°C to 80°C.

RESULTS AND DISCUSSION

Polyesters having the general formula (**1**) were synthesized as described in the Experimental section.



(**1**)

where R and n in the different cases are:

Polymer	R	n
PTDPA-EO(0)	S	0
PTDPA-EO(1)	S	1
PTDPA-EO(2)	S	2
PTDPA-EO(3)	S	3
PTDPA-EO(4)	S	4
PPA-EO(0)	CH_2	0
PPA-EO(1)	CH_2	1
PPA-EO(2)	CH_2	2

*FT*i.r. and ^{1}H n.m.r. spectra are consistent with the expected formula.

Despite their regular chemical structure, all the samples were shown to be completely amorphous from d.s.c. measurements, even after annealing at −10°C for 1 h. The T_g values, as shown in *Table 1*, are low in every case and lie in a narrow range (from −40 to −55°C).

The T_g values for polyester–$LiClO_4$ mixtures are reported in *Table 2* on the basis of (S+O)/Li molar ratio (O/Li in the case of PPA polyesters). In the calculation of this ratio all the atoms of sulfur and oxygen in the backbone, excluding the terminal groups and carbonylic oxygen, have been considered.

Table 2 Glass transition temperatures of polymer electrolytes based on thiodipropionic acid and pimelic acid as a function of (S+O)/Li and O/Li molar ratio, respectively

	T_g (°C)						T_g (°C)		
(S+O)/Li	PTDPA-EO(0)	PTDPA-EO(1)	PTDPA-EO(2)	PTDPA-EO(3)	PTDPA-EO(4)	O/Li	PPA-EO(0)	PPA-EO(1)	PPA-EO(2)
11	−37	−25	−22	−21	−23	11	−35	−31	−33
13	−36	−25	−24	−27	−26	13	−38	−33	−35
18	−39	−26	−28	−30	−31	18	−43	−38	−39
22	−39	−28	−30	−33	−34	22	−43	−41	−40

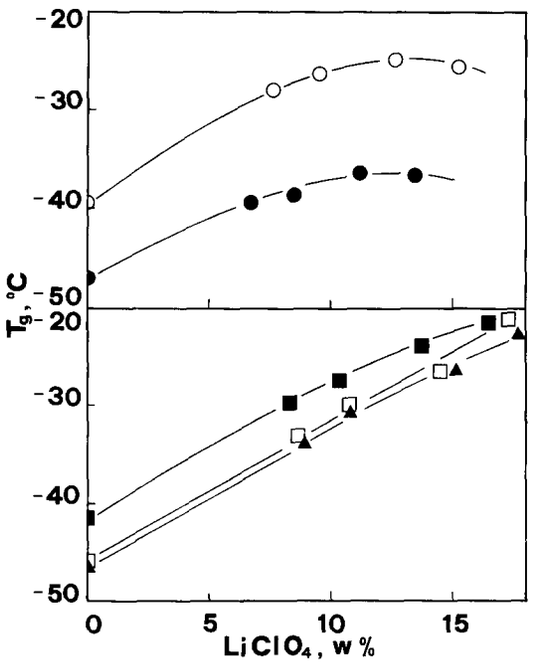


Figure 1 Glass transition temperatures of polymer electrolytes *versus* $LiClO_4$ concentration. ●, PTDPA-EO(0); ○, PTDPA-EO(1); ■, PTDPA-EO(2); □, PTDPA-EO(3); ▲, PTDPA-EO(4)

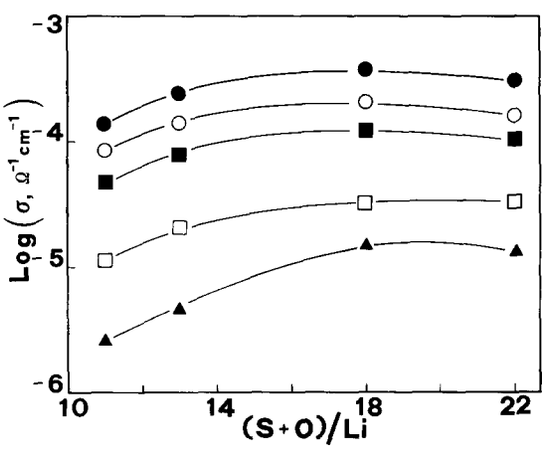


Figure 2 Dependence of conductivity on (S+O)/Li molar ratio for PTDPA-EO(4) at different temperatures: ▲, 25°C; □, 40°C; ■, 60°C; ○, 70°C; ●, 80°C

In *Figure 1*, T_g values for polymer electrolytes containing polyesters based on TDPA are plotted against the weight per cent of $LiClO_4$. For each sample, it is evident that an increase of T_g occurs with increasing content of $LiClO_4$ in the polymer, as expected by a stiffening of the chains due to the complex formation. Similar effects have been reported in the literature for different polyesters[10,11].

In *Figures 2* and *3* the conductivities of the polymer electrolytes PTDPA-EO(4) and PPA-EO(2) are reported as a function of the molar ratio of (S+O)/Li and O/Li, respectively. In the first case, ionic conductivity shows the presence of a maximum with a decrease of conductivity when the lithium salt concentration increases, as previously reported for other polymers[12,13]. On the contrary, in the case of polymer electrolytes based on PA, the conductivity is almost constant with $LiClO_4$ content in the range of concentrations considered; in this latter case there may be a strong contribution to the protonic conductivity due to the high concentration of carboxyl terminal groups.

It is noteworthy that most of these polymer electrolytes are potentially useful for practical applications, because of the high values of conductivity at 80°C ($10^{-3}\ \Omega^{-1}\ cm^{-1}$) and at room temperature ($10^{-5}\ \Omega^{-1}\ cm^{-1}$). This important feature can be explained by the low T_g values and by the absence of crystallinity at any temperature (even below room temperature).

In the case of polymer electrolytes based on TDPA, the conductivity becomes progressively higher as the number of EO groups in the repeating units (r.u.) increases from one to four: this behaviour is shown in *Figure 4* for the molar ratio (S+O)/Li = 18, as a typical example. The samples based on PTDPA-EO(0) show a surprisingly high conductivity considering the absence of EO moieties, probably because of the very low values of molecular weight and T_g.

The conductivities of polymer electrolytes based on PA (*Figure 5*) are also generally high, probably because of the low T_g values of the samples and a protonic contribution due to carboxyl terminal groups. Also in this case, the conductivity increases progressively with increasing number of EO groups in the r.u.

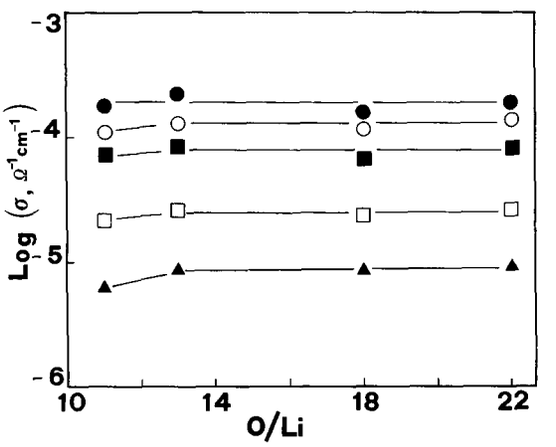


Figure 3 Dependence of conductivity on O/Li molar ratio for PPA-EO(2) at different temperatures: ▲, 25°C; □, 40°C; ■, 60°C; ○, 70°C; ●, 80°C

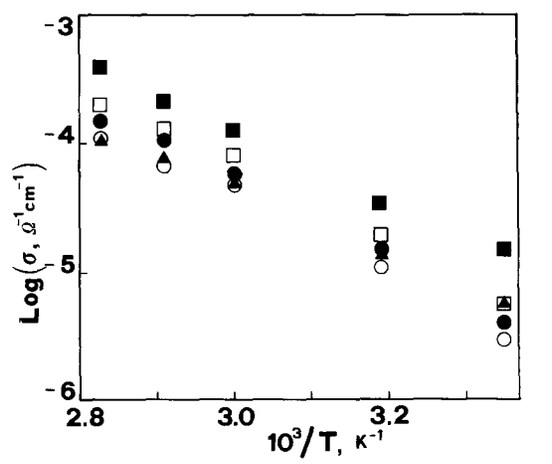


Figure 4 Arrhenius plot of conductivity for the polyesters based on thiodipropionic acid, at the constant ratio (S+O)/Li = 18. ■, PTDPA-EO(4); □, PTDPA-EO(3); ●, PTDPA-EO(2); ○, PTDPA-EO(1); ▲, PTDPA-EO(0)

In all cases conductivity is rather well correlated to temperature by an Arrhenius-type equation (*Figures 4* and *5*). The activation energy was calculated to range between 50 and 60 kJ mol^{-1} — higher values than those reported in the literature for electrolytes based on other polymers[4].

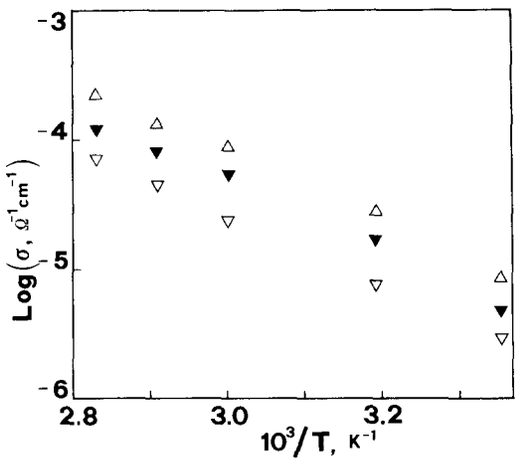


Figure 5 Arrhenius plot of conductivity for polyesters based on pimelic acid, at the constant ratio O/Li = 13. △, PPA-EO(2); ▼, PPA-EO(1); ▽, PPA-EO(0)

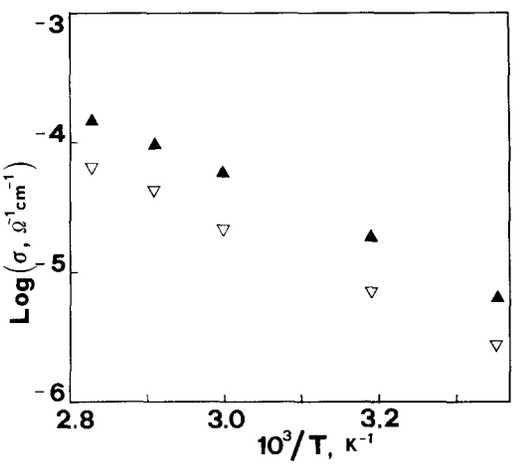


Figure 6 Arrhenius plot of conductivity for polyesters without ethylene oxide units, at the constant ratio (S+O)/Li = 13. ▲, PTDPA-EO(0); ▽, PPA-EO(0)

The comparison of the conductivity of the two electrolytes based on polymers not containing ether groups, that is PTDPA-EO(0) and PPA-EO(0), gives insight on the contribution from thioether groups (–S–). In fact it appears that the conductivity of PTDPA-EO(0) is higher than that of PPA-EO(0) at all temperatures (*Figure 6*). On the other hand the conductivity of PPA-EO(0) samples is consistent with some data reported in the literature for polyesters without EO groups in the r.u.[11,14,15]. Since the molecular weights of the two samples are similar and a contribution to the conductivity of sample PPA-EO(0) may derive from the relatively high content of carboxyl groups, we can reasonably conclude that sulfur ether moieties contribute significantly to increasing the conductivity.

The solvation effect of cations by both thioether sulfur and ether oxygen atoms becomes still more evident if data are compared at constant chain flexibility[10], that is by plotting conductivity against a reduced temperature ($T - T_g$). This comparison has been made in *Figure 7* for electrolytes based on polyesters of TDPA; in this case there is a regular trend in conductivity as a result of increasing number of EO moieties in the r.u. This is seen even for the sample PTDPA-EO(0) which in *Figure 4* shows, in some cases, a conductivity higher than that of polyesters containing EO groups.

The specific solvation effect of thioether sulfur is clearly shown in *Figures 8* and *9*, in which plots of conductivity against the reduced temperature are reported for pairs of electrolytes based on polymers of TDPA and PA having the same number of EO groups in the r.u. It is evident that in all cases, electrolytes based on TDPA have conductivities higher than those of electrolytes based on PA. This solvation effect for cations by sulfur atoms has also been emphasized by Clancy *et al.*[7] for poly(alkylenesulfides) and silver salts, even if in that case conductivity values were low.

CONCLUSIONS

Polymer electrolytes based on $LiClO_4$ doped polyesters of glycols containing ethylene oxide groups and aliphatic

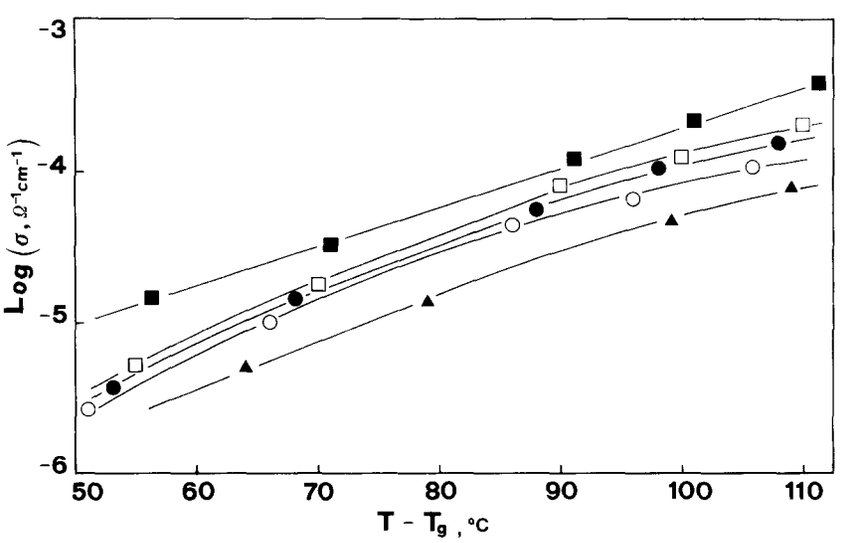


Figure 7 Conductivity *versus* reduced temperature ($T - T_g$) at a fixed ratio (S+O)/Li = 18 for polyesters based on thiodipropionic acid. ■, PTDPA-EO(4); □, PTDPA-EO(3); ●, PTDPA-EO(2); ○, PTDPA-EO(1); ▲, PTDPA-EO(0)

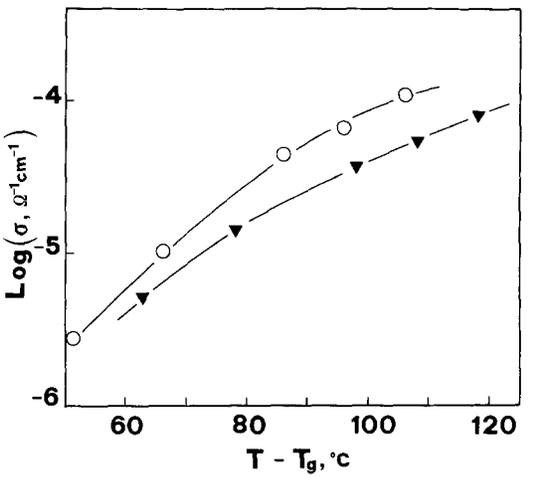


Figure 8 Conductivity *versus* reduced temperature ($T-T_g$) at a fixed ratio (S+O)/Li=18. ○, PTDPA-EO(1); ▼, PPA-EO(1)

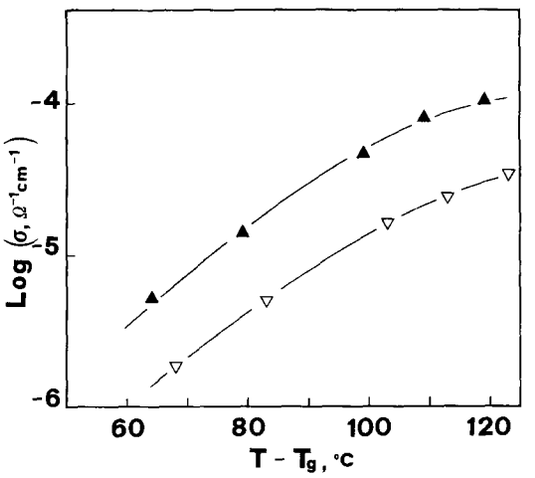


Figure 9 Conductivity *versus* reduced temperature ($T-T_g$) at a fixed ratio (S+O)/Li=18. ▲, PTDPA-EO(0); ▽, PPA-EO(0)

(thiodipropionic and pimelic) acids, show conductivity values of the order of $10^{-5}\,\Omega^{-1}\,cm^{-1}$ at room temperature. A comparison of the different aliphatic polyesters investigated proves that the controlling factors of conductivity are the glass transition temperature of the polymer–salt mixture (rather low in these systems) and the solvating capacity for the cations of both the oxygen and sulfur atoms in the backbone. The high ionic conductivity of these polymer electrolytes gives potential for practical applications in light batteries and ultra-thin electrochromic devices; investigations of the electrochemical performances of these electrolytes are in progress.

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