Ionic conductivity in oligo(ethylene oxide) esters of poly(itaconic acid)–salt mixtures: effect of side-chain length

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A series of poly(itaconic acid) esters with oligo(ethylene oxide) side chains have been prepared in which the side chains contain from one to seven ethylene oxide units. These materials can form amorphous solid solutions with $LiClO_4$ and $NaClO_4$. The glass transition temperatures and a.c. ionic conductivities of these polymer–salt mixtures have been examined as a function of side-chain length, salt concentration and temperature. It has been found that the polymer with seven ethylene oxide units per side chain produces a polymer electrolyte with the highest conductivities between 10^{-3} and 10^{-6} S cm^{-1} for the temperature range 400 K to ambient. In these systems the flexibility of the polymer chain seems to be a controlling feature as reflected in the polymer–salt T_g values.

(Keywords: poly(itaconic acid); conductivity; glass transition temperature; side-chain length; chain flexibility)

INTRODUCTION

Poly(ethylene oxide) (PEO) has a structure that is particularly suitable for dissolving a wide range of inorganic salts to form homogeneous solid solutions. This leads to partial ionization of the salt and the production of ionic charge carriers capable of sustaining conductivity levels in the range 10^{-3}–10^{-6} S cm^{-1}. The PEO–salt systems suffer from one major drawback in that PEO is partially crystalline at room temperature, and as ionic conduction takes place in the amorphous regions of the polymer, acceptable conductivities are only achieved after the temperature of the system exceeds the melting point of PEO, which is about 338 K.

While there are several ways by which the crystallinity can be reduced[1] and totally amorphous systems obtained, the method selected by ourselves and others is to prepare comb–branch structures by attaching short ethylene oxide (EO) unit sequences to an existing polymer backbone. Thus substitution of poly(methacrylic acid)[2], poly(itaconic acid)[3], polysiloxane[4] and polyphosphazene[5] has produced comb–branch polymers with oligo(ethylene oxide) as the side chains of varying lengths. Other similar structures have been synthesized from oligo(ethylene oxide) macromonomers[6,7] or the copolymerization of ethylene oxide with glycidyl ethers[8].

The dissolution of the salt in the polymer is assisted by complexation of the cation by the ether oxygens in PEO whose structure is particularly conducive to providing a suitable, 'oxygen lined', environment for this purpose. Other polyethers are not so effective because of either steric restrictions or a less favourable spatial distribution of the oxygens in the chains. The length of the side chains can also be of some importance and we have demonstrated[9] that, in polymers prepared from oligo(ethylene oxide) macromonomers, a side-chain length of approximately five EO units is the optimum to give the highest conductivity levels.

The ionic conductivity in poly(itaconate ester)s with three EO units in each side chain has been reported previously[10] and this study is expanded here to examine changes induced in the ionic conductivity when the side chains vary in length from one to seven EO units.

EXPERIMENTAL PROCEDURES

Monomer preparation

Diesters of itaconic acid were prepared by acid-catalysed esterification in toluene solution using a 3–4 molar excess of the appropriate predried alcohol[11]. The latter were monomethoxy-terminated ethylene glycols, which were purified either by distillation or by ether and chloroform extraction. Glycols with one, two, three and five EO units were single-chain-length materials, but the higher esters were prepared from glycols with nominal molecular weights of 350 and 550 and so these samples have a small distribution of side-chain length centred on an average of seven and 12 EO units respectively.

Polymerization

Polymers were prepared in bulk using a free-radical initiator, α,α′-azobisisobutyronitrile, at reaction temperatures of 328–333 K. Samples were isolated by precipitation into diethyl ether and ether/cyclohexane mixtures from chloroform solutions.

Characterization

Both monomers and polymers were characterized using i.r. and n.m.r. analysis. Number-average molecular weights were obtained for the polymer samples using a Knauer membrane osmometer with methyl ethyl ketone

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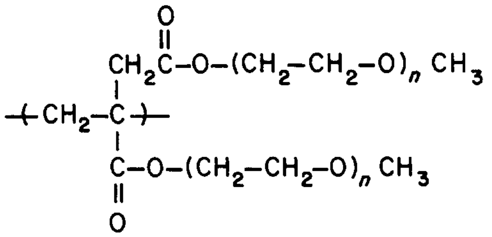
Table 1 Molecular weights and glass transition temperatures for poly(itaconate oligo(ethylene oxide) ester)s

Starting alcohol	EO units in side chain	Polymer code	$M_n \times 10^{-3}$	DP_n	T_g (K)
2-Methoxyethanol	1	PDMEO(1)I	86	360	303
2-(2-Methoxyethoxy)ethanol	2	PDMEO(2)I	131	392	252
3,6,9-Trioxadecanol	3	PDMEO(3)I	44	104	218
3,6,9,12,15-Pentaoxahexadecanol	5	PDMEO(5)I	90	150	216
Poly(ethylene glycol)methyl ether, $MW = 350$	⟨7⟩	PDMEO(7)I	37	47	213
Poly(ethylene glycol)methyl ether, $MW = 550$	⟨12⟩	PDMEO(12)I	28	23	220[a]

[a] Melting point at 298 K

as solvent, at a measuring temperature of 306 K. Details of the monomers and polymer samples are listed in *Table 1*.

The repeat unit of the polymers prepared is:



$$\left[CH_2 - \overset{\substack{CH_2\overset{O}{\overset{\|}{C}}-O-(CH_2-CH_2-O)_n\,CH_3\\ |}}{\underset{\substack{|\\ \underset{\underset{O}{\|}}{C}-O-(CH_2-CH_2-O)_n\,CH_3}}{C}} \right]$$

where $n = 1, 2, 3, 5, \langle 7\rangle, \langle 12\rangle$ and the angular brackets indicate that this is an average value.

Preparation of polymer–salt mixtures

Rigorously dried methanol was used as the solvent for co-dissolution of the polymer and the salt, and films of the mixture were prepared by casting, followed by evaporation of the solvent in a dry glove-box. The samples were dried further in vacuum at 330–340 K for 2–3 days prior to use. Determination of the moisture content of the polymer–salt complex formed, using a Karl-Fischer titration method, showed this to be less than 0.01%.

A.c. conductivity measurements

Measurements were carried out as described elsewhere[3], using an a.c. conductivity meter (1.59 kHz) and under anhydrous conditions in a glove-box. Each sample was allowed to equilibrate for 1 h at each temperature before a measurement was made and the range covered was ambient to 400 K.

Glass transition temperatures

A Perkin–Elmer DSC-2 differential scanning calorimeter was used to measure the glass transition temperature, T_g, for samples with (*Table 2*) and without (*Table 1*) salt. The T_g was taken as the midpoint of the baseline shift that occurs during the glass-to-rubber transition.

RESULTS AND DISCUSSION

Ionic conductivity occurs in the amorphous regions of a polymer matrix and is assisted by the flexibility of the chain. Consequently at any particular temperature the conductivity level achieved will in general be higher for a polymer whose initial T_g is low than for one whose initial T_g is relatively higher. This effect is complicated by the fact that complexation of a salt by the polymer usually raises the T_g and the rate of increase of T_g with added salt can vary for different systems.

Glass transition temperatures

For the poly(itaconate ester)s used here it has been shown[12] that the T_g of the polymer decreases with increasing side-chain length but eventually passes through a shallow minimum when $n \approx 4$, after which there is a slight rise in T_g for larger values of n. Recorded in *Table 1* are the T_g values for the samples prepared here, which suggests that this minimum is extended to $n = \langle 7\rangle$. However, this sample will have a small polydispersity of chain lengths, which may distort this observation. The increase in T_g observed is normally caused by an increasing tendency for the longer side chains to crystallize. Thus the oligo(ethylene oxide) comb–branch structures prepared using polysiloxane backbones[13] exhibit crystallinity for samples with $n \geq 8$. When the polymer backbone is derived from poly(methacrylic acid) the onset of crystallinity again occurs when $n > 8$ and a sample with $n = 7$ was amorphous[14]. This can be contrasted with the observations by Andrei *et al.*[15] for a comb–branch sample, poly(3,6,9,12,15,18,21,24-octaoxapentacos-1-ene), i.e. $n = 7$, which exhibited pronounced side-chain crystallinity ($T_m = 265$ K). Similarly Tonge *et al.*[16] found that the polyphosphazenes with pendant oligo(ethylene oxide) units were amorphous for $n < 7$ but that a sample with $n = 7$ had a semicrystalline nature with $T_m = 261$ K. In the poly(itaconate)s there is no evidence of crystallinity up to $n = \langle 7\rangle$ but a crystalline melting point was detected at 298 K for the sample with $n = \langle 12\rangle$. This latter sample was not investigated further.

The effect of added salt on T_g is reflected in the data listed in *Table 2* for the various samples mixed with two salts, $LiClO_4$ and $NaClO_4$. In both cases the relative increase $\Delta T_g = [T_g(\text{salt}) - T_g(\text{no salt})]$ is very small for the PDMEO(1)I sample and greatest for PDMEO(3)I. Cation binding thus appears to be poor when $n = 1$, if ΔT_g is taken as an indication of the solvating capacity of the polymer for the salt, and this is also reflected in the conductivity levels. This might imply that sample PDMEO(3)I should then exhibit the best conductivity levels because ΔT_g is largest for this sample, but this is not the case, and so other factors must also contribute.

If the data are plotted as ΔT_g against $[M^+]/[EO]$, as shown in *Figures 1a* and *1b*, then it can be seen that a saturation level is approached above $[M^+]/[EO] = 0.15$.

Table 2 Glass transition temperatures for oligo(ethylene oxide)-substituted poly(itaconic acid) polymers as a function of side-chain length and added salt

	$NaClO_4$					$LiClO_4$			
$[M^+]/[EO]$	PDMEO(1)I	PDMEO(2)I	PDMEO(3)I	PDMEO(5)I	PDMEO(7)I	PDMEO(1)I	PDMEO(2)I	PDMEO(3)I	PDMEO(7)I
0.0125	303.5	261.0	229.0	224.5	220.5	303.5	255.0	230.0	217.5
0.0170	–	–	244.0	–	–	–	261.0	240.0	–
0.020	–	–	248.0	229.0	–	–	–	243.5	–
0.025	305.5	266.5	252.0	231.0	220.5	–	267.0	246.0	221.5
0.033	–	–	254.0	–	–	307.0	–	–	–
0.050	308.0	275.0	255.5	243.0	236.5	–	275.0	253.0	232.5
0.067	–	–	265.0	253.0	244.0	–	–	256.0	241.5
0.100	–	–	273.0	–	264.0	–	–	269.5	–
0.125	310.0	306.0	287.0	282.5	279.0	309.5	296.0	288.0	281.5
0.167	–	–	–	–	285.0	313.0	–	–	–
0.200	–	–	305.5	–	292.5	–	–	312.5	–
0.250	318.0	334.0	306.5	303.5	293.5	315.5	323.0	309.0	281.0
ΔT_g (K)	15.0	82.0	88.0	87.5	81.0	12.5	71.0	80.5	68.5

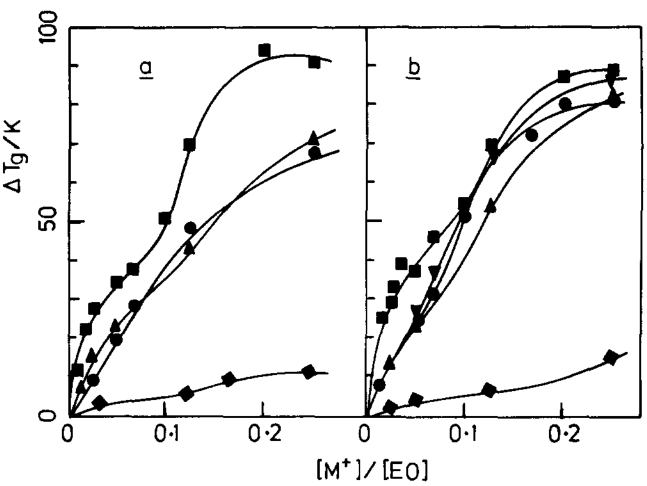


Figure 1 Increase in the glass transition temperature ΔT_g with added salt, for (a) $LiClO_4$ and (b) $NaClO_4$: PDMEO(1)I (◆), PDMEO(2)I (▲), PDMEO(3)I (■), PDMEO(5)I (▼), PDMEO(7)I (●)

In most cases ΔT_g is larger when $NaClO_4$ is used but the differences are not great.

Conductivity measurements

The temperature dependence of the log(conductivity) for each polymer host mixed with $NaClO_4$ in varying amounts is shown in *Figure 2*. The conductivities increase with increasing temperature as expected but the behaviour is essentially non-Arrhenius. Similar behaviour was observed when $LiClO_4$ was used as the salt. The conductivity is also a function of both the salt concentration and the side-chain length. The latter effect can be seen more clearly by comparing log σ values at a fixed composition ratio $[M^+]/[EO]=0.125$, as shown in *Figure 3*, and this salt level is close to that at which the maximum conductivities have been achieved for both salts. The differences are highlighted further in *Figure 4*, where the conductivity is seen to become progressively larger as the side-chain length is changed from one EO unit to approximately seven EO units. For example, at a temperature of 370 K, the conductivity for sample PDMEO(7)I is approximately two orders of magnitude higher than that for PDMEO(1)I, when $NaClO_4$ is the added salt. The results indicate that the dissociation of the salt to produce charge carriers appears to be enhanced with lengthening side chain up to $n=\langle 7\rangle$ at salt concentrations less than $[M^+]/[EO]=0.10$. Kobayashi *et al.*[17] have also observed that salt dissociation is more extensive in methacrylate polymers with the longer oligo(ethylene oxide) side chains.

Examination of the isothermal conductivities of the various polymer–salt mixtures at a temperature of 403 K reveals the increase in σ with increasing side-chain length but also the presence of a maximum in log σ as a function of $[M^+]/[EO]$ ratios as the side chain becomes longer in the order $n=1 \geqslant n=2 > n=5, \langle 7\rangle > n=3$. This behaviour agrees reasonably well with the prediction by Angell[18] that the maximum in conductivity moves to lower salt concentrations as the rate of change of T_g with added salt increases. Comparison of these changes with the data in *Figure 1* tends to confirm this trend. Similar behaviour can be seen at most temperatures, and in systems with both salts, as shown in *Figures 5a* and *5b* where the maxima are more pronounced at lower

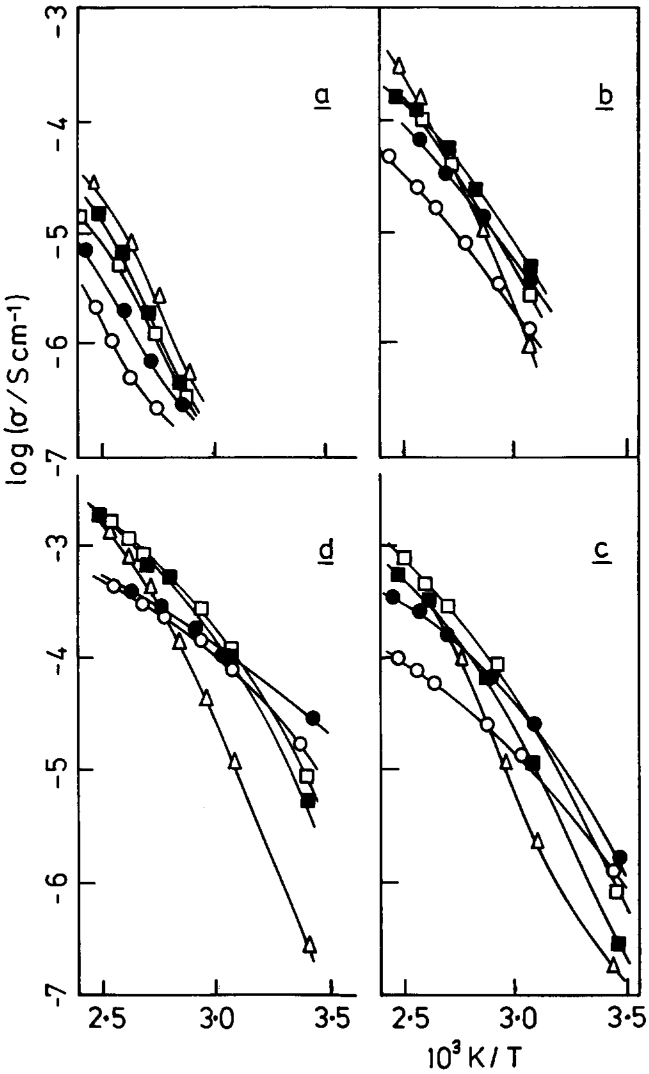


Figure 2 Reciprocal temperature dependence of log(conductivity) for (a) PDMEO(1)I, (b) PDMEO(2)I, (c) PDMEO(3)I and (d) PDMEO(7)I, using $NaClO_4$ in the ratios $[Na^+]/[EO]$ of 0.0125 (○), 0.025 (●), 0.05 (□), 0.067 (■) and 0.125 (△)

temperatures. Angell has also suggested that the maxima in log σ are a consequence of the balancing of opposing effects. At low salt concentrations there is a build-up of charge carriers resulting in an increase in the conductivity, but as more salt is added the progressive increase in T_g leads to a drop in chain flexibility and eventually to a drop in the conductivity owing to restricted mobility of the charge carriers in the more rigid matrix. The flexibility effect can be minimized if the data are normalized by plotting log σ at a constant temperature above the T_g of the system at a particular salt concentration. The outcome is shown in *Figure 6* for PDMEO(3)I at (T_g+60) K, (T_g+100) K and (T_g+130) K for both $LiClO_4$ and $NaClO_4$ as added salts. In all cases the maxima are no longer obvious and a plateau in log σ is reached at high salt concentrations when chain flexibility should be essentially a constant contribution. The retardation of the increase in log σ at higher salt concentrations is then more likely to be caused by the changing number or character of the effective charge carriers, i.e. there will be increasing participation of ion triplets or higher aggregates, which will be less efficient charge carriers. It also highlights the fact that there will be an optimum concentration of salt at which a particular system will produce the highest conductivity levels.

Effect of sample T_g *on the conductivity*

If chain flexibility is believed to be an important contributing factor in determining the conductivity in polymer–salt systems, then it is of interest to make comparisons between conductivity data collected for different polymer structures but at a fixed temperature above the T_g recorded for each system. In this way conductivity levels at constant chain flexibility can be compared irrespective of side-chain length or polymer backbone structure.

This has been done for three samples, two poly(itaconates), PDMEO(3)I ($T_g=218$ K) and PDMEO(7)I ($T_g=213$ K), and a comb–branch polymer prepared from an oligo(ethylene oxide) macromonomer with three EO units per side chain, $PVMEO_3$ ($T_g=206$ K), results for which have been reported elsewhere[9]. There are small differences in the T_g values for each polymer and the rate of change of T_g with added $LiClO_4$ is also not a constant factor, so a comparison was made first of the

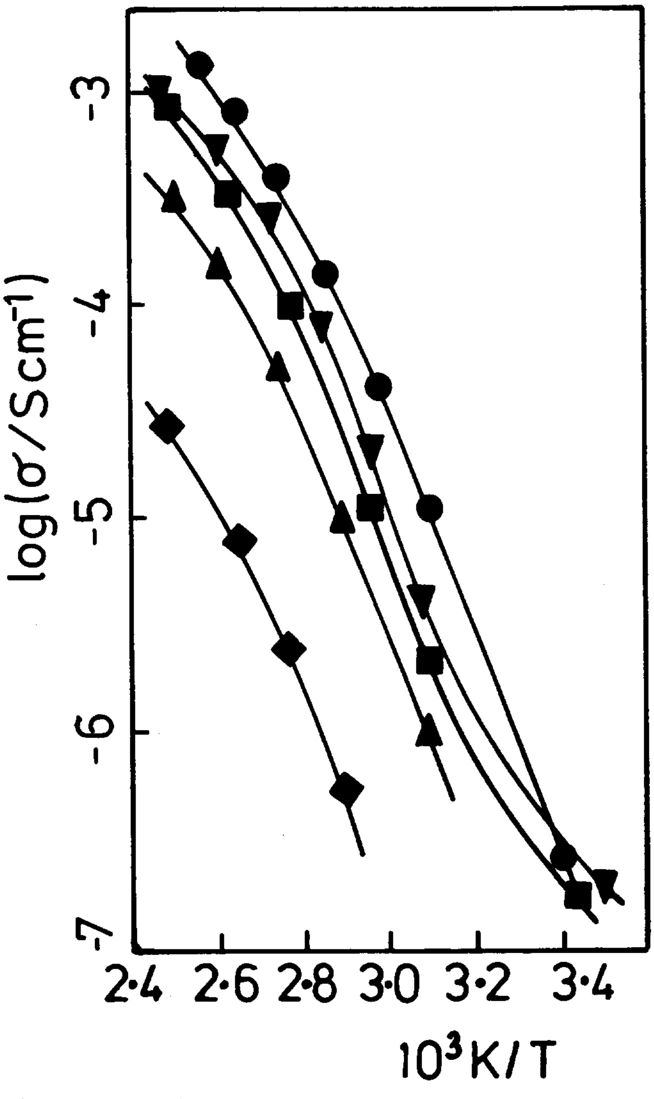


Figure 3 Comparison of the temperature dependence of conductivity as a function of the side-chain length for $NaClO_4$–polymer mixtures at a fixed $[Na^+]/[EO]=0.125$: PDMEO(1)I (◆), PDMEO(2)I (▲), PDMEO(3)I (■), PDMEO(5)I (▼), PDMEO(7)I (●)

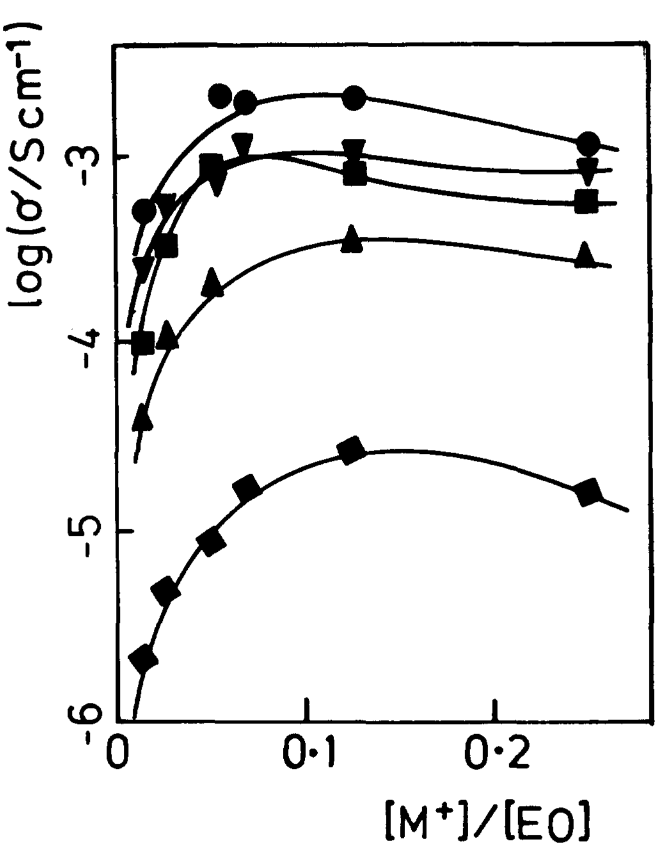


Figure 4 Isothermal plot of log(conductivity) against salt concentration for $NaClO_4$ – polymer mixtures at 403 K. Sample notation as for *Figure 3*

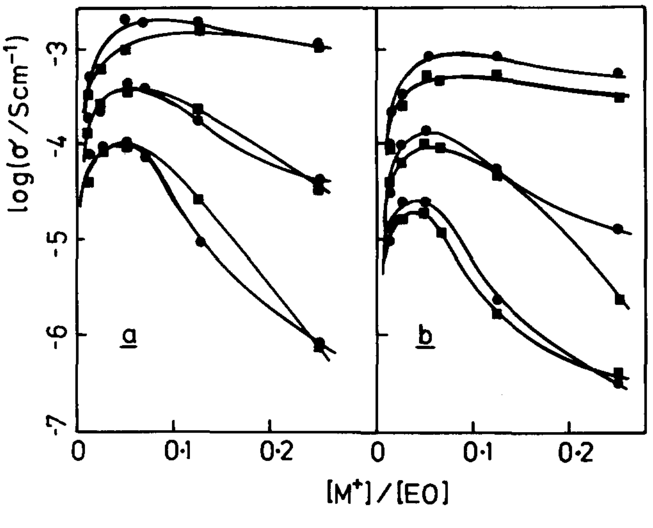


Figure 5 Dependence of conductivity on salt concentrations at fixed temperatures of 323, 353 and 403 K for $LiClO_4$ (■) and $NaClO_4$ (●): (a) PDMEO(7)I and (b) PDMEO(3)I

conductivities as a function of salt concentration at a constant temperature of $(T - T_g) = 100$ K. The data are plotted in *Figure 7* and little significant difference in the conductivities can be observed. This concordance was also found to hold over a wider temperature range, as shown in *Figure 8* for a fixed $[Li^+]/[EO]$ ratio of 0.125, where the T_g values for the polymer–$LiClO_4$ mixtures are now $T_g = 287$ K for PDMEO(3)I, $T_g = 279$ K for PDMEO(7)I and $T_g = 260$ K for $PVMEO_3$. The results seem to imply that when the oligo(ethylene oxide) side chain is long enough to coordinate the cation efficiently then the T_g of the polymer–salt mixture will control the level of conductivity achieved at a particular temperature. Thus concordance occurs in these data at a constant $(T - T_g)$, or constant chain flexibility, for each polymer, but the actual conductivities at any given working temperature are in the order $PVMEO_3 >$ PDMEO(7)I > PDMEO(3)I. While the analysis of the data is limited, one can conclude for the poly(itaconate) polymers that the T_g is then the major factor controlling conductivity levels, rather than the requirement of a critical side-chain

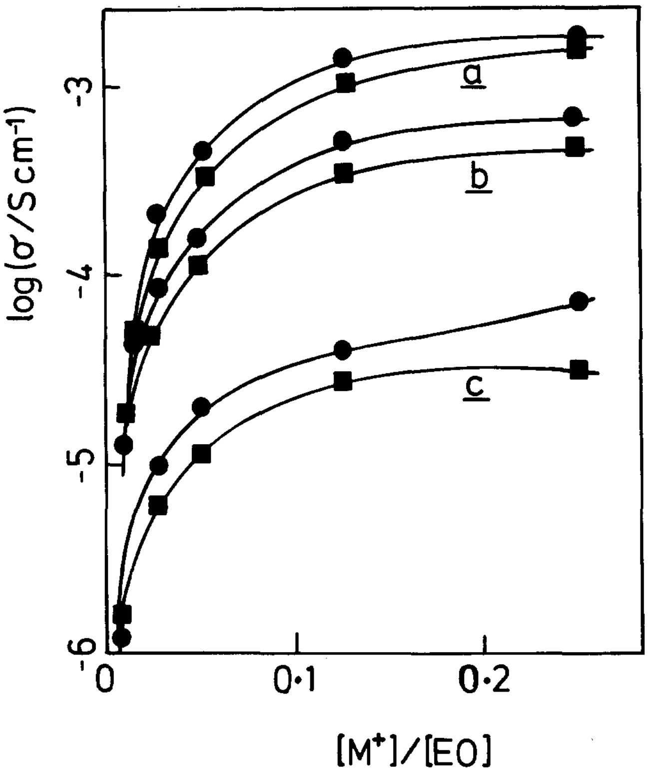


Figure 6 Effect of changing salt concentration on the conductivity at various reduced temperatures of (a) $T_g + 130$ K, (b) $T_g + 100$ K and (c) $T_g + 60$ K

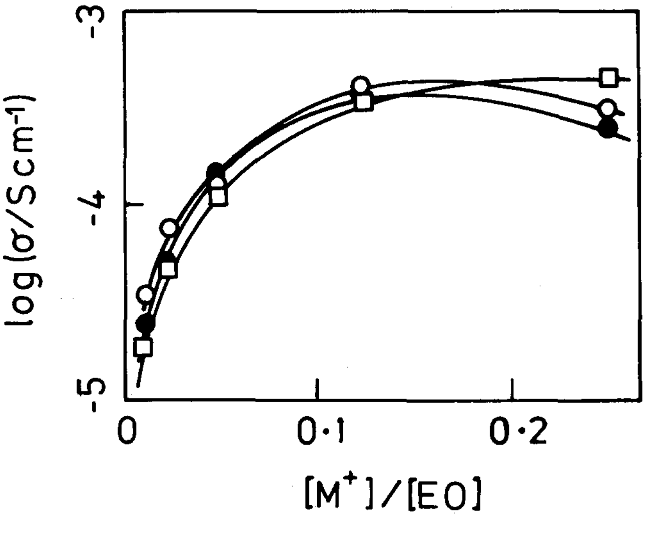


Figure 7 Reduced temperature plot at $T - T_g = 100$ K for PDMEO(3)I (□), PDMEO(7)I (○) and the poly(oligo(ethylene oxide)) sample (●)

length for most effective ionization of the salt. The polymer with side chains $n=\langle 7\rangle$ is internally plasticized to a greater extent than that with the shorter $n=3$ side chains and the overall T_g for PDMEO(7)I is lower, hence higher conductivities are achieved when salt is added, for any particular temperature of measurement.

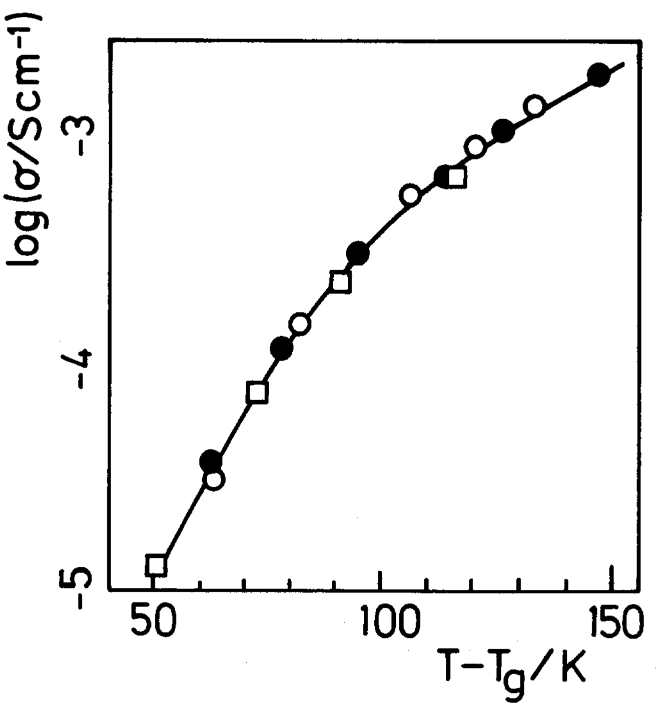


Figure 8 Variation of conductivity with reduced temperature ($T-T_g$) at a fixed $[Li^+]/[EO]=0.125$. Samples and notation as in *Figure 7*

This is not the case in the previously reported PVMEO$_n$ series[9], where the respective T_g values were 206 K ($n=3$), 208 K ($n=5$) and 211.5 K ($n=6$). In this case the maximum conductivities were obtained for sample $n=5$ and the side-chain length appeared to be the controlling factor. Perhaps a reason for this difference may lie in the higher density of side chains per monomer unit in the poly(itaconate)s, which could allow effective cation coordination at shorter chain lengths, thereby maximizing the salt ionization sooner.

Data analysis

The temperature dependence of the conductivity in the poly(itaconate oligo(ethylene oxide) ester)s is predominantly non-Arrhenius and can be analysed more effectively using the Vogel–Tammann–Fulcher equation:

$$\sigma=\sigma_0 \exp[-B/(T-T_0)] \qquad (1)$$

where σ_0, B and T_0 are constants that are a function of the model used to interpret the data. Application of the Adam–Gibbs configurational entropy model[19,20] has been used in a reasonably satisfying manner to describe the ionic conductivity in poly(itaconate)s with poly (propylene glycol) side chains[3] and polymers prepared from oligo(ethylene oxide) macromonomers[6]. The model defines T_0 as the temperature at which the configurational entropy of the system is zero and predicts this to be about 50 K lower than T_g. The constant B is then a complex accumulation of terms:

$$B=T_0 S_c^* \Delta\mu / kT\Delta C_p \qquad (2)$$

where k is the Boltzmann constant, $\Delta\mu$ is the potential energy barrier hindering the cooperative movement of a

Table 3 Best-fit parameters from non-linear least-squares analysis of conductivity data

Polymer	Salt	$[M^+]/[EO]$	B (K)	T_0 (K)	T_g-T_0 (K)
PDMEO(1)I	$NaClO_4$	0.05	1092	237.3	70.5
	$NaClO_4$	0.125	935	251.5	58.5
	$NaClO_4$	0.25	1595	221.0	97.5
	$LiClO_4$	0.05	2390	187.6	120.5
	$LiClO_4$	0.25	2975	184.8	130.5
PDMEO(2)I	$NaClO_4$	0.0125	1330	186.4	74.5
	$NaClO_4$	0.05	1166	209.3	65.5
	$NaClO_4$	0.125	1386	221.4	85.0
	$NaClO_4$	0.25	581	261.4	72.5
PDMEO(3)I	$NaClO_4$	0.0125	794	195.7	33.5
	$NaClO_4$	0.05	1090	201.7	54.0
	$NaClO_4$	0.125	1127	233.3	55.0
	$NaClO_4$	0.25	1278	241.0	65.5
	$LiClO_4$	0.0125	590	212.5	17.5
	$LiClO_4$	0.05	1423	180.9	72.0
	$LiClO_4$	0.125	1061	236.3	51.5
	$LiClO_4$	0.25	1646	239.7	69.5
PDMEO(5)I	$NaClO_4$	0.0125	613	207.1	17.5
	$NaClO_4$	0.05	735	217.4	25.5
	$NaClO_4$	0.25	1115	255.5	48.0
PDMEO(7)I	$NaClO_4$	0.125	563	209.0	11.5
	$NaClO_4$	0.05	748	213.7	23.0
	$NaClO_4$	0.125	1039	233.4	44.5
	$NaClO_4$	0.25	1287	239.0	54.5
	$LiClO_4$	0.0125	591	212.6	5.0
	$LiClO_4$	0.05	607	217.4	15.0
	$LiClO_4$	0.125	1140	210.0	51.5
	$LiClO_4$	0.25	1255	238.4	42.0

Table 4 Activation energies for sample PDMEO(3)I/NaClO$_4$ mixtures

$[Na^+]/[EO]$	$\Delta\mu$ (kJ mol^{-1})	E_a (kJ mol^{-1})	Temp. range (K)
0.0125	56.6	26	333–400
0.050	84.1	46	333–400
0.125	97.5	100	322–357
0.250	128.5	122	322–370

chain segment whose size is the minimum capable of undergoing a spatial rearrangement independent of its environment, S_c^* is the configurational entropy associated with such a rearrangement (which can be approximated by $k \ln 2$) and ΔC_p is the heat capacity change experienced on moving from the glass to the rubber-like state.

A non-linear least-squares minimization procedure was used to evaluate the constants in equation (1) and these are shown in *Table 3*. Using the values of $(T_g - T_0)$ K as a guide to how well the model appears to describe the data, it can be seen that for PDMEO(1)I and PDMEO(2)I the values are consistently higher than the predicted 50 K. For samples with longer side chains the agreement is somewhat better, with PDMEO(3)I the most satisfactory, where agreement is good for PDMEO(5)I and PDMEO(7)I only when $[M^+]/[EO]$ is greater than 0.05. A further analysis was made using the data for PDMEO(3)I. Experimental measurement of ΔC_p for that sample mixed with NaClO$_4$ gave an average value of 47.1 J K^{-1} mol^{-1}, which was used in equation (2) to allow estimation of $\Delta\mu$. The latter values are shown in *Table 4*, where they are compared with the apparent activation energy E_a calculated by assuming that Arrhenius behaviour prevailed over restricted temperature ranges. There is reasonable concordance at high salt concentrations but divergence at the lower concentrations. Both sets of values increase with added salt, which is consistent with the idea that there is a loss of chain flexibility with increasing coordination of polymer chain and cation.

Analyses of this nature should be treated with some caution, however, and the model tested here is not entirely convincing; neither does it necessarily provide much information on the actual mechanism of conduction.

CONCLUSIONS

The maximum conductivity levels in these poly(itaconate) structures are achieved when samples with $n = \langle 7 \rangle$ are used. By comparison with data from other systems, it would appear that the glass transition temperature of the polymer–salt mixture is the controlling factor rather than side-chain length. Thus the sample with $n = \langle 7 \rangle$ has the lowest T_g and so yields the highest conductivity at any particular temperature, thereby emphasizing that a high chain flexibility is also a critical factor in these polymer electrolyte systems.

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