



A new polymer electrolyte based on a discotic liquid crystal triblock copolymer

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ARTICLE INFO

Article history:

Received 30 August 2012

Received in revised form 9 January 2013

Accepted 12 January 2013

Available online 21 January 2013

Keywords:

Solid polymer electrolytes

Poly(ethylene oxide)

Discotic liquid crystal

Block copolymer

Lithium perchlorate

Ionic conductivity

Activation volume

ABSTRACT

A discotic liquid crystal triblock copolymer consisting of a central main chain triphenylene-based liquid crystal block capped at both ends by blocks of poly(ethylene oxide) (PEO) ($M_w = 2000 \text{ g mol}^{-1}$) has been doped with lithium perchlorate in an EO:Li 6:1 ratio. The polymer electrolyte exhibits a phase separated morphology consisting of a columnar hexagonal liquid crystal phase and PEO-rich regions. The polymer electrolyte forms self-supporting, solid-like films. The ionic conductivity on initial heating of the sample is very low below *ca.* 60 °C but increases rapidly above this temperature. This is attributed to the melting of crystalline PEO-rich regions. Crystallisation is suppressed on cooling, and subsequent heating cycles exhibit higher conductivities but still less than those measured for the corresponding lithium perchlorate complex in poly(ethylene glycol) ($M_w = 2000 \text{ g mol}^{-1}$). Instead the triblock copolymer mimics the behaviour of high molecular weight poly(ethylene oxide) ($M_w = 300,000 \text{ g mol}^{-1}$). This is attributed, in part, to the anchoring of the short PEG chains to the liquid crystal block which prevents their diffusion through the sample. Temperature and pressure variations in ion mobility indicate that the ion transport mechanism in the new material is closely related to that in the conventional PEO-based electrolyte, opening up the possibility of engineering enhanced conductivities in future.

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1. Introduction

The demand for all solid-state electrochemical devices, and most notably solid-state lithium rechargeable batteries, continues to stimulate interest in solid polymer electrolytes (SPE) [1,2]. An SPE is an ionically conducting solid comprising salt dissolved in a polymeric solvent [3], whose advantages include improved processability, flexibility, increased safety considerations arising from the absence of organic solvents and favourable dimensional stability [1]. This potential has yet to be realised, however, because it is difficult to combine all these qualities within a given material. To highlight these problems, and to identify possible solutions to them, we may consider a typical SPE consisting of a solution of a lithium salt in a polyether such as poly(ethylene oxide). In such a system, the backbone forms helical arrangements within which the cations are solvated, and the motion of both cations and anions is intrinsically linked to the motions of the polymer segments [4]. This coupling of ion mobility to the local viscosity of the polymer means that ionic conductivity decreases dramatically as the glass transition is approached, although the formation of ion pairs must also be taken into account [5]. Much research has focussed on reducing the

glass transition temperature so as to speed up the motions of the polymer segments but this is deleterious to mechanical stability. This is especially important to battery applications where a high shear modulus is required to inhibit dendrite growth which often results in internal short circuits and device failure [6]. Although the overwhelming majority of polymer electrolytes fit this general pattern of behaviour [5], we note, however, that crystalline polymer electrolytes are also being investigated [7,8].

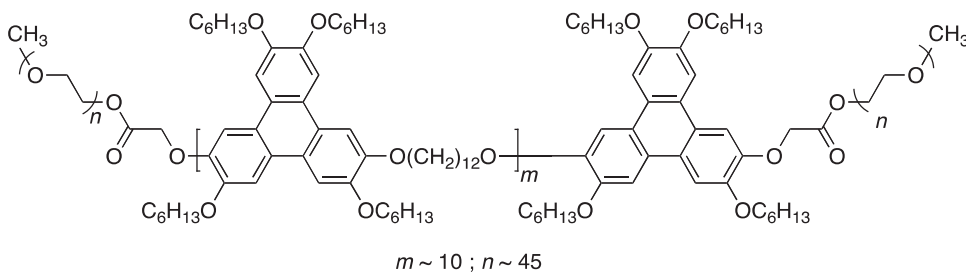
A promising design approach in the development solid polymer electrolytes has recently been adopted to simultaneously address these apparently conflicting demands of decreasing the local viscosity while maintaining mechanical integrity, involves the use of block copolymers. Here, one block provides the ionically conducting medium while the second confers mechanical integrity (see, for recent examples, [9–13]). The microphase separation of the two differing blocks yields a system which displays the properties of the individual blocks locally, but exhibits composite behaviour macroscopically. Recently, Osuji et al. have reported the properties of a block copolymer consisting of a poly(ethylene oxide) block linked to a side chain liquid crystal polymer (SCLCP) block [14,15]. This system showed microphase separation consisting of hexagonally packed cylinders of PEO dispersed in a smectic A matrix consisting of the SCLCP blocks.

We now seek to extend their approach by reporting the properties of a new polymer electrolyte prepared by dissolving LiClO_4 in

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a discotic liquid crystalline triblock polymer, **1** [16],



Here, triblock copolymer **1** consists of a main chain polymeric discotic liquid crystal capped at both ends with blocks of poly(ethylene oxide), PEO ($M_W = 2000 \text{ g mol}^{-1}$). The volume fraction of PEO in the triblock copolymer is approximately 27% [16]. Furthermore, **1** undergoes microphase separation to give both lamellar and columnar structures which will be discussed further in Section 3, and shows solid-like mechanical properties up to 120°C , together with excellent thermal stability [16]. We now report the thermal, structural and electrochemical characterisation of a triblock copolymer **1**: LiClO_4 complex having the composition 6:1 (AO:Li ratio). AO refers to active oxygens defined in terms of their ability to coordinate the lithium ions, which in turn is influenced both by steric factors and the donicities of individual oxygens. In making this calculation, we have counted only the ether oxygens in the poly(ethylene oxide) blocks, although we cannot rule out the possibility that some salt will reside in the liquid crystal-rich phase and we discuss this possibility later. For comparative purposes, we have also characterised the corresponding 6:1 (AO:Li) polyethylene glycol (PEG) ($M_W = 2.000 \text{ g mol}^{-1}$): LiClO_4 complex.

2. Experimental

The synthesis of the triblock copolymer **1** has been described in detail elsewhere [16]. Triblock copolymer **1** has a weight average molecular weight (M_W) of $18,600 \text{ g mol}^{-1}$ and an associated polydispersity of 1.65 relative to polystyrene standards. The polymer electrolyte samples were prepared by the solvent casting method. LiClO_4 (Aldrich, 98%) was dried under vacuum at 140°C for several days prior to use. Stoichiometric amounts of triblock copolymer **1** and LiClO_4 were dissolved in chloroform and anhydrous acetonitrile, respectively. The solutions were combined and stirred overnight to give a clear pale brown solution. This was cast on Teflon rings and the solvents allowed to evaporate slowly at room temperature. The as-cast polymer electrolytes were free-standing and additionally dried at room temperature under dynamic vacuum for 24 h to remove any residual traces of solvent. All manipulations prior to the variable-temperature or variable-pressure conductivity measurements were performed in an argon-filled glove-box. The PEG: LiClO_4 complex was prepared using the same procedure.

The thermal behaviour of the polymer electrolytes was investigated by differential scanning calorimetry (DSC) using a Mettler Toledo DSC822^e differential scanning calorimeter equipped with a TSO 801RO sample robot and calibrated using indium and zinc standards. The heating profile in all cases was heat, cool and reheat at $10^\circ\text{C min}^{-1}$. Phase behaviour was studied using polarising light microscopy using an Olympus BH2 polarising light microscope equipped with a Linkam TMS 92 hot stage. X-ray diffraction studies were performed at room temperature using $\text{Cu K}\alpha$ radiation from a Philips XPERT diffractometer.

For variable-temperature (VT) conductivity measurements, the polymer electrolytes were sandwiched between two stainless steel electrodes in a Teflon conductivity cell. The cell was placed in a thermostatic bath to control the temperature during the

measurements. For variable-temperature variable-pressure (VPVT) measurements, the polymer electrolyte disks were sandwiched between gold electrodes with attached silver wires. The assembly was sealed by silicone encapsulation to protect the electrolyte from the oil in the high-pressure autoclave while at the same time transmitting the hydrostatic pressure to the sample. Details of the high-pressure autoclave (Stansted Fluid Power Ltd., England) have been given elsewhere [17]. All dc conductivities were determined by conventional impedance spectroscopy using a Solartron 1260 Impedance Analyser.

3. Results and discussion

3.1. Phase behaviour and structure

Fig. 1 shows the second heating DSC trace obtained for an essentially amorphous PEG: LiClO_4 6:1 (AO:Li) complex which contains a glass transition with a mid-point value of -40°C and a very weak endotherm at 74°C assigned to the melting of crystalline regions. The DSC trace for the second heat cycle of salt-free triblock copolymer **1** is shown as the lower trace in Fig. 1. It consists of two endothermic transitions and a weak second order transition. The broad endothermic transition with a peak temperature of 32°C ($\Delta H = 17.9 \text{ J g}^{-1}$) corresponds to the melting of crystalline regions of the PEO blocks. This is somewhat lower than the melting point of salt-free poly(ethylene glycol) dimethyl ether ($M_W \sim 2000$), ca. 53°C , probably because the attachment of the PEO chains to the discotic liquid crystal block inhibits their ability to pack efficiently within the crystalline phase. The new and weaker endotherm with a peak temperature of 111°C ($\Delta H = 6.38 \text{ J g}^{-1}$) corresponds to the clearing temperature of the liquid crystal component containing the discotic blocks. A weak second order transition with a mid-point which is just visible at about -41°C is assigned to the glass transition of amorphous regions of the, again salt-free PEO blocks.

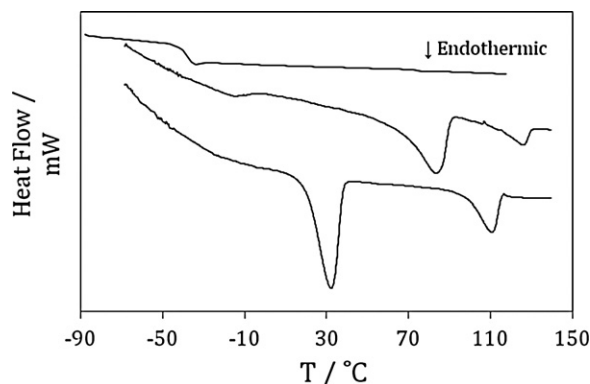


Fig. 1. DSC second heating scans for the PEG: LiClO_4 6:1 (AO:Li) complex (upper trace), the triblock copolymer, **1**, (lower trace) and the 6:1 (AO:Li) 1: LiClO_4 complex (middle trace).

At temperatures above 111 °C, the triblock copolymer **1** is not birefringent when viewed through the polarised light microscope. On cooling below 111 °C, a poorly defined sandy or threaded birefringent texture is observed. This texture remained unchanged after annealing for prolonged periods because of the high viscosity of the phase.

These observations are consistent with previous X-ray diffraction studies which have shown the liquid crystal phase to be a hexagonal columnar phase, Col_h, and that above the melting point of the PEO blocks, the copolymer exhibits microphase separation in which PEO rods forming a hexagonal array are dispersed within a matrix of Col_h phase comprising the discotic blocks [16]. Below the melting point of the PEO blocks, their crystallisation leads to the formation of a lamellar microphase separated structure again with an underlying Col_h phase. Above the clearing temperature of the discotic blocks a disordered (isotropic) structure is obtained [16].

Fig. 1 also shows (middle trace) the DSC second heating trace for the 6:1 (AO:Li) **1**:LiClO₄ complex. This contains the same two endotherms, and the second order transition which we can again assign to the glass transition of the PEO-rich phase. The position of the glass transition is marked more clearly in the complex than in the undoped system by the appearance of the relaxation overshoot, and has a mid-point value of –25 °C. This is 16 °C higher than that seen for the undoped polymer **1**, implying that the salt has preferentially dissolved in the PEO phase. Almost certainly, the increase in *T_g* reflects the stiffening of the chains as instigated by strong Li–O interactions, which may be reinforced by interaction with the more rigid discotic blocks. The latter view is reinforced by the observation that the triblock copolymer complex has a *T_g* some 15 °C higher than that seen for the corresponding PEG complex. The stronger of the two endotherms has a peak temperature of 83 °C ($\Delta H = 18.6 \text{ J g}^{-1}$) (Fig. 1, middle trace), and we assign this to the melting of the crystalline PEO:LiClO₄ phase. The melting temperature is in good agreement with the published phase diagram [18] showing a crystalline phase of around or slightly less than the complex with a 6:1 stoichiometry. The higher temperature endotherm with a peak temperature of 126 °C ($\Delta H = 2.91 \text{ J g}^{-1}$) again corresponds to the clearing transition associated with the discotic blocks, and is associated with loss of birefringence when viewed through the polarising microscope. Specifically, a sandy birefringent texture is formed on cooling the sample below 126 °C which remains unchanged on annealing for prolonged periods. The increase in the Col_h-isotropic transition temperature on doping with lithium perchlorate shown in Fig. 1 suggests enhanced phase separation between the microphases arising from the ionic character of the doped phase. Similar increases in the clearing temperature were seen on the addition of lithium perchlorate to side chain liquid crystal polymers based on a poly(ethylene oxide) backbone and containing either rod-like [19–21] or disc-like [22] mesogenic side chains.

Fig. 2 shows the intensity profile of the X-ray diffraction pattern of the triblock copolymer **1**:salt complex at room temperature. A sharp, first order reflection is evident in the low angle region with an associated *d*-spacing of 17.5 Å ($2\theta = 5.0^\circ$) and this corresponds to the intercolumnar distance within the Col_h phase. The shoulder to the wide-angle peak with an associated periodicity of 3.5 Å ($2\theta = 25.4^\circ$) corresponds to the disc–disc separation in the columns comprising the Col_h phase.

It is also clear from Fig. 2 that extensive crystallisation has not occurred in this sample of the doped polymer. Based on the work of Robitaille and Fauteux, the weak peaks at 7.2 Å ($2\theta = 12.3^\circ$) and 4.4 Å ($2\theta = 20.2^\circ$) are characteristic of the formation of a 5:1 (AO:Li) PEO-LiClO₄ crystalline phase [18]. The broad and rather diffuse wide-angle band reflects the absence of extensive three-dimensional ordering in the system.

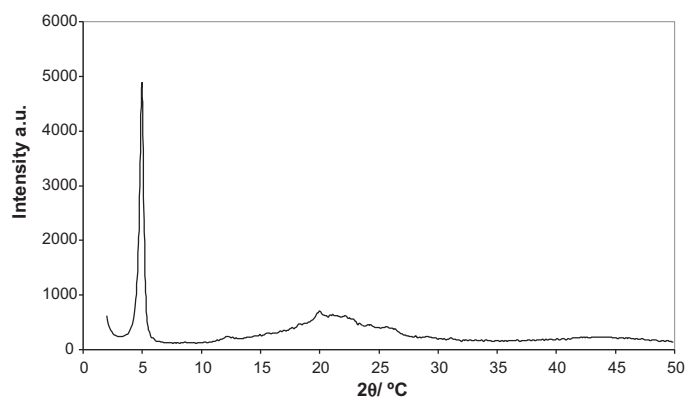


Fig. 2. The intensity profile of the X-ray diffraction of the 6:1 (AO:Li) **1**:LiClO₄ complex at room temperature.

To summarise, the *T_g* for the doped triblock copolymer is at a higher temperature than that seen for the PEG complex, suggesting that the liquid crystal block anchors, at least to some extent, the PEO block and stiffens the chains. The effect of this on ion mobility will be discussed later. The melting of the crystalline regions in the PEG complex appears to occur at a slightly lower temperature than seen for those in the doped triblock copolymer. This may reflect the fact that the effective concentration of Li ions in the crystal phase in the latter is higher, as is indeed suggested by the X-ray diffraction pattern.

3.2. Temperature dependence of ion transport

The various dc conductance behaviours of the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex are summarised in the form of Arrhenius plots in Fig. 3. These values are not normalised according to the PEO-content, but refer instead to the actual material under investigation. The as-cast polymer electrolyte exhibited very low conductivities, *i.e.*, below $10^{-9} \text{ S cm}^{-1}$, at low temperatures. Significant ionic conductivity was found only after heating the sample above *ca.* 70 °C, corresponding to the melting of the PEO-rich phase, and the formation of the microphase separated structure where conducting pathways exist throughout the PEO-rich phase. The ionic conductivity increased sharply with increasing temperature, reaching a value of *ca.* $10^{-4} \text{ S cm}^{-1}$ at 93 °C. On cooling, the conductivity decreased in a continuous fashion to reach a value of *ca.* $10^{-7} \text{ S cm}^{-1}$ at 5 °C, indicating that the crystallisation of the PEO-rich phase had been suppressed. On reheating, a very small hysteresis in the conductivity was observed and a maximum value of $1.5 \times 10^{-4} \text{ S cm}^{-1}$ was reached at 105 °C.

The difference in the conducting behaviour between the first heating of the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex and its subsequent reheating can be clearly seen in the complex plane plots of $-Z''$ against Z' . Fig. 4 compares these impedance plots measured on first heating at 73 °C and on subsequent reheating at 41 °C. These particular temperatures were selected for comparison because the complex exhibited nearly equal conductivities in both instances. The impedance plots contain one or more flattened arcs corresponding to complex electrolyte behaviour indicating that the sample contains differently conducting regions associated with the complex structure. The spikes, seen at low frequencies, are indicative of complex electrode behaviour. The dc resistance of the sample is taken as the value of Z' where the electrode spikes touch down on the Z' axis and this procedure was adopted in all the conductivity measurements reported here.

Fig. 4 reveals that the impedance plot for the first-heat sample obtained at 73 °C is much flatter than that obtained on reheating

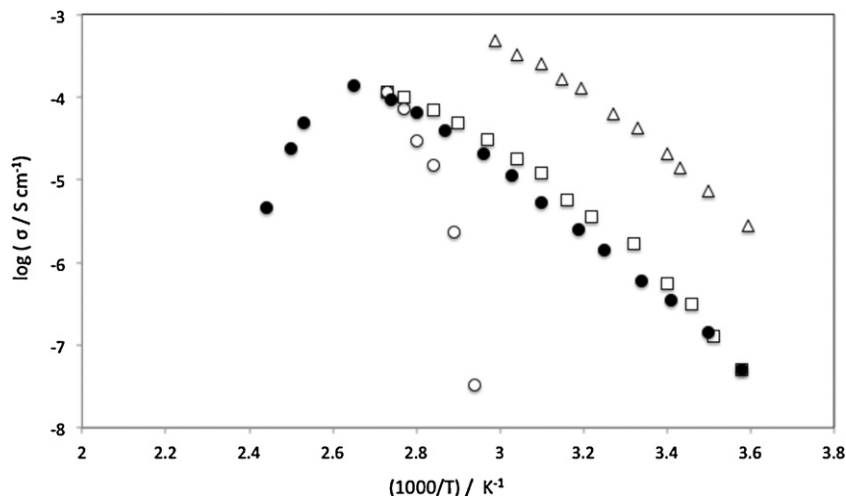


Fig. 3. Arrhenius plots of $\log(\sigma/S\text{ cm}^{-1})$ against reciprocal temperature for the discotic triblock copolymer **1**:LiClO₄ (AO:Li=6:1) complex. Open circles indicate the first heating, open squares the subsequent cooling and filled circles the second heating of the sample. Also shown are the data for the corresponding PEG 2000:LiClO₄ complex denoted by triangles.

the sample to 41 °C, and consists of at least two arcs corresponding to the migration of ions through poorly and well conducting phases. We attribute these two conducting regions to the presence of crystalline and amorphous PEO-rich phases, respectively. By contrast, the impedance plot measured on subsequent reheating to 41 °C contains a single, well-defined arc of a semi-circle, which reinforces the view that crystallisation had not occurred during the cooling and subsequent reheating processes. This behaviour shows that the same conductivity may be arrived at *via* different pathway morphologies depending on the presence or absence of crystalline material.

On further increasing temperature during the reheating cycle, the conductivity fell abruptly at temperatures above *ca.* 105 °C, see Fig. 3. This temperature is lower than the Col_h-isotropic transition temperature of the complex estimated as the maximum of the endothermic peak observed in the DSC trace, see Fig. 1, but we note that this transition is rather broad, and the decrease in conductivity does correspond with the onset of the clearing transition. Accordingly, we attribute the decrease in conductivity to the disordering of the microphase structure and to the resulting disruption in the percolation pathways located in the PEO-rich microphase.

Also shown in Fig. 3 is the corresponding Arrhenius plot for the PEG 2000:LiClO₄ complex. It clearly parallels the second heating trace for the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex measured over the same temperature range. We note, however, that the absolute conductivity values for the PEG 2000:LiClO₄ complex are some 1.5 orders of magnitude higher than those measured for the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex at the same temperatures. This observation raises the question as to whether PEG 2000 is the appropriate material to use in assessing the conductivity behaviour seen for the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex. Accordingly, in Fig. 5, we compare the ionic conductivities of the 6:1 (AO:Li) complexes of the triblock copolymer **1**, PEG 2000 and PEO ($M_w = 300,000\text{ g mol}^{-1}$) [23]. It is clear that below 105 °C the ionic conductivities of the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex are very similar to those of the high molecular weight PEO:LiClO₄ 6:1 (AO:Li) complex despite the considerable differences in structure and chemical composition.

The molecular weight dependence of ionic conductivity for PEO-based complexes has before now [24,25] been attributed to changes in the mechanism of ion transport. In the molecular weight independent regime, corresponding to molecular weights above the

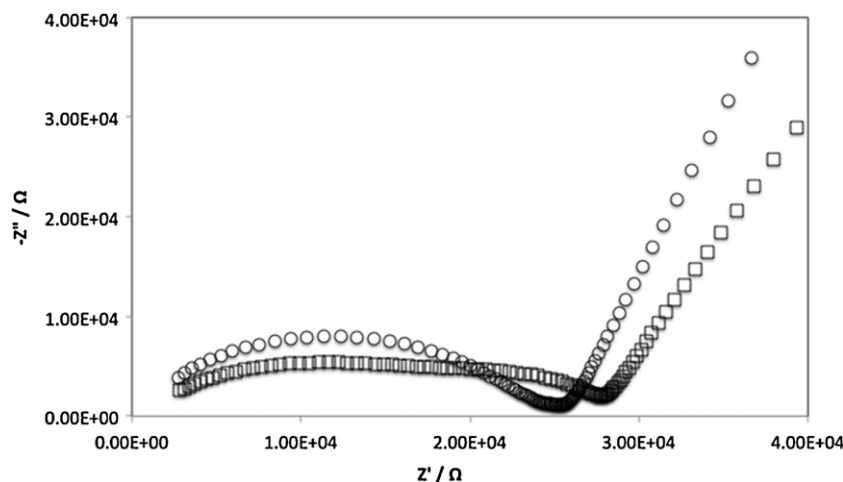


Fig. 4. Complex Z^* plots for the discotic triblock copolymer **1**:LiClO₄ (AO:Li=6:1) complex measured during the first heating of the sample at 73 °C (□) and on the second heating at 41 °C (○).

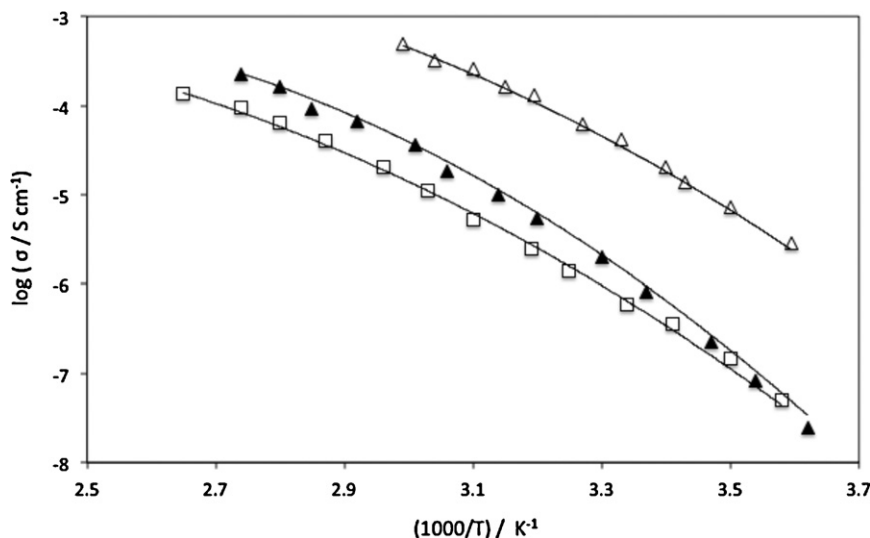


Fig. 5. Arrhenius plots of $\log(\sigma / \text{S cm}^{-1})$ against reciprocal temperature for the discotic triblock copolymer **1**:LiClO₄ (AO:Li = 6:1) complex (open squares), the PEG 2000:LiClO₄ complex (open triangles) and the PEO (300,000):LiClO₄ complex (filled triangles) [23]. The ionic conductivities have been measured on heating. The lines show the fitting of the data according to the relevant VTF equations (see text and Table 1).

critical polymer entanglement limit, ion transport is thought to involve only segmental motions of the polymer chains, while for molecular weights lying below the entanglement limit, and in the molecular weight dependent regime, an additional transport mechanism operates in which ions diffuse together with their host polymer chains. The molecular weight dependent regime for PEO-based electrolytes is generally thought to extend up to molecular weights in the range of several thousand g mol^{-1} , although this depends on the chemical nature of the dissolved salt as well as the polydispersity of the polymer [25].

Fig. 5 shows that the ionic conductivity of the PEG 2000:LiClO₄ complex is around an order of magnitude higher than that seen for the PEO (300,000):LiClO₄ complex and hence, lies in the molecular dependent regime. By comparison, the ionic conductivities of the triblock copolymer **1**:LiClO₄ complex are similar to those of the PEO (300,000):LiClO₄ complex and lie therefore in the molecular weight independent regime established for PEO-based salt complexes [25] even though the PEO block in the copolymer has the same molecular weight as the PEG sample. We attribute this to the anchoring of the PEO chains to the liquid crystal blocks in the triblock copolymer, which in turn prevents the diffusion of the shorter chains through the sample, so reducing the ionic conductivity. We will return to this observation later.

Temperature dependences of ionic conductivities have been further compared using the Vogel–Tamann–Fulcher (VTF) equation (see, for example, [26] and references cited therein), where:

$$\sigma = A \exp\left(\frac{-B}{T - T_0}\right) \quad (1)$$

Here A expressed in S cm^{-1} is a pre-exponential term and is related to the number of charge carriers, B is an ‘activation parameter’ and T_0 is the ideal glass or zero mobility temperature, both expressed in Kelvins. We note that the VTF equation represents a relatively over simplified treatment of the data and indeed, several authors have

shown its failure in identifying liquid–liquid transitions [26–28]. Notwithstanding these comments, however, fitting of the data shown in Fig. 5 for each polymer:LiClO₄ 6:1 (AO:Li) complex leads us to the parameters listed in Table 1. For comparative purposes these data refer to non-crystalline materials. It is immediately apparent that the main difference between the complexes is the much larger pre-exponential term observed for the PEG complex. It is striking, however, that the values of T_0 for all three complexes are so similar. This strongly suggests that ion mobility is confined to the PEO-rich phase.

3.3. Pressure dependence of ion transport

As part of our continuing investigations into the effects of pressure on ion transport [23,26,29,30], we have measured the conductivities of the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex at temperatures above and below 60 °C as a function of pressure. We present here only data obtained above 60 °C to avoid problems associated with partial crystallinity. Thus, Fig. 6 shows the complex impedance plots for the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex collected at 75 °C, and at pressures varying from 50 to 186 MPa. The touchdown points seen in Fig. 6 are not as well-defined as those in Fig. 4, but we can obtain them reliably enough from the back-extrapolation of the electrode spikes to where they meet the Z' axis. Fig. 7 shows the resulting linear plot of $\ln Z'$ versus P , from which we can obtain a value of $(\partial \ln Z' / \partial P)_T = 1.05 \times 10^{-8} \text{ Pa}^{-1}$.

We define the activation volume V_A for ion transport [23,29,30] as

$$V_A = -RT \left(\frac{\partial \ln \sigma}{\partial P} \right)_T \quad (2)$$

and so if we neglect any changes in cell constant, we can obtain this quantity for ion transport directly from $V_A = RT(\partial \ln Z' / \partial P)_T$. This

Table 1

The parameters obtained from the VTF analysis (see text) of the data shown in Fig. 5. Also listed are the glass transition temperatures, T_g , for each polymer:LiClO₄ 6:1 (AO:Li) complex measured using DSC. The values for PEO (300,000) have been taken from [23].

Host polymer	$\ln(A/\text{S cm}^{-1})$	B (K)	T_0 (K)	T_g (K)	$T_g - T_0$ (K)
Triblock copolymer 1	−0.51	1650	179	248	69
PEG 2000	1.83	1480	178	233	55
PEO (300,000)	−0.31	1342	197	248	51

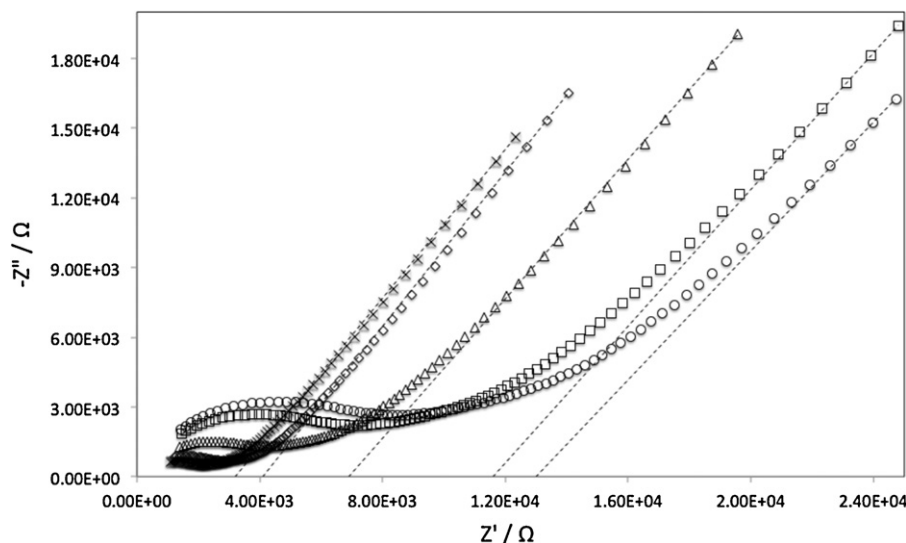


Fig. 6. Complex impedance plots for the discotic triblock copolymer **1**:LiClO₄ (AO:Li = 6:1) complex measured at various pressures at 75 °C: 186 (○), 170 (□), 116 (△), 75 (◇) and 50 (×) MPa, showing how the touchdown points are obtained by extrapolation (see text).

gives a value of $V_A = 29 \text{ cm}^3 \text{ mol}^{-1}$, which, as we will see, is very similar to that reported for the PEO (300,000):LiClO₄ 6:1 (AO:Li) complex [23].

3.4. Mechanisms of ion transport

As already indicated, the results presented in Sections 3.2 and 3.3 point very strongly to the close links between the mechanisms of conduction in the triblock copolymer **1**:LiClO₄ 6:1 (AO:Li) complex and in neat PEO electrolytes. The main difference, as revealed by the VTF analysis, is the major shift in the pre-exponential factor between the PEG 2000-based complex and those containing either the triblock copolymer **1** or PEO (300,000).

The higher B value seen for the triblock copolymer **1**:LiClO₄ complex must also be mentioned, since it may point to either some trapping of mobile ions in the LC-rich phase at lower temperatures and/or to some loss of flexibility of the EO chains which has already been signalled by the changes in the DSC trace, see Fig. 1. In terms of Angell's concept of strength and fragility, this latter effect would correspond to an increase in strength and a loss of fragility in the system, which usually has adverse implications for ion mobility see, for example, [5].

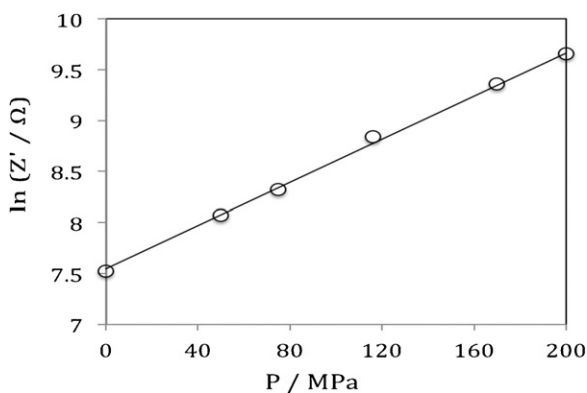


Fig. 7. Dependence of dc resistance (see discussion of Fig. 6) on pressure for the discotic triblock copolymer **1**:LiClO₄ (AO:Li = 6:1) complex. Note the value of Z' obtained at atmospheric pressure (0.1 MPa) used in the calculation of the corresponding conductivity shown in Fig. 5 falls on same line as the high-pressure data.

The virtual identity of the T_0 values suggests that the underlying mechanisms for the conduction process in the triblock copolymer **1**:LiClO₄ and PEG 2000:LiClO₄ complexes are, however, identical. The higher value of T_0 seen for the PEO (300,000):LiClO₄ complex may be simply an artefact of the VTF analysis [26–28]. This prompts the question as to whether T_0 or T_g is the more useful parameter for assessing the conductivity mechanism. It is noteworthy that the triblock copolymer **1** and PEO (300,000)-based complexes have the same value of T_g (Table 1). Furthermore, the triblock copolymer **1** complex has the largest ($T_g - T_0$) value implying an increase in strength in terms of strength-fragility concepts [5]. We will consider later the structural implications of these observations and how conductivity may be further optimised.

We can further characterise the behaviour of the triblock copolymer by comparing the activation volume of $29 \text{ cm}^3 \text{ mol}^{-1}$ with that for ion transport in a PEO ($M_W = 300,000 \text{ g mol}^{-1}$):LiClO₄ 6:1 complex for which we previously reported a value of $26 \text{ cm}^3 \text{ mol}^{-1}$ at 70 °C [23]. The broad similarity of these two values is strongly indicative of a common transport mechanism involving segmental motions of the PEO chains. This reinforces the view stated earlier that ion mobility is essentially restricted to the PEO-rich phase.

Recently, we have presented a fresh analysis of variable pressure-variable temperature (VP-VT) data in which we introduced *process moduli* [26,29,30] relevant to both ion transport and structural relaxations in amorphous materials. The relevant modulus for ion transport M_σ is given by the ratio E_A/V_A . E_A is defined here as the *instantaneous* activation energy, given from the VTF equation simply as,

$$E_A = -R \frac{\delta \ln \sigma}{\delta(1/T)} = \frac{BRT^2}{(T - T_0)^2} \quad (3)$$

and V_A is the corresponding activation volume given by Eq. (2). Substituting in numerical values, we obtain for the triblock copolymer complex at 75 °C, $M_\sigma = 58.2 \text{ kJ mol}^{-1}/30 \text{ cm}^3 \text{ mol}^{-1} = 1.95 \text{ GPa}$. We may then compare this with a value determined directly from data found in [23] for the PEO ($M_W = 300,000 \text{ g mol}^{-1}$):LiClO₄ 6:1 complex, for which at 70 °C, $M_\sigma = 61.8 \text{ kJ mol}^{-1}/26.4 \text{ cm}^3 \text{ mol}^{-1} = 2.3 \text{ GPa}$. Once again the similarity of these two values points to a common conduction mechanism that is operating in PEO-based electrolytes.

We may now return to Fig. 3 in which we see three different patterns of conductivity behaviour. Firstly, during the initial heating of the sample, a rapid increase in conductivity is observed, which we have already attributed to the melting of the PEO-rich phase. Secondly, on subsequent cooling from a temperature below the clearing temperature, we see a much weaker temperature dependence in the conductivity which persists once the sample is reheated. We have attributed this pattern of behaviour to the suppression of the crystallisation in the PEO-rich phase.

On approaching the clearing temperature of the discotic phase, we see a dramatic decrease in conductivity which is coincident with the ODT of the polymer [16]. We may ask to what extent this latter behaviour may be considered a general observation. There are two comparable systems reported in the literature and these are both block copolymers containing an ethylene-oxide block and a side-chain liquid crystal block, although both contain rod-like rather than disc-like liquid crystal groups [15,31]. Both copolymers exhibit microphase separation in which cylindrical PEO rods forming an hexagonal array are dispersed within a matrix of smectic A phase comprising the liquid crystal blocks. In one of these examples [31], the ionic conductivity perpendicular to the electrodes decreases close to the smectic A-isotropic transition temperature, while that parallel to the electrodes simply increases on increasing temperature. In the other example [15], the conductivity perpendicular to the electrodes falls on approaching the smectic A-isotropic transition, but Arrhenius behaviour is recovered after the transition; while the conductivity parallel to the electrodes, and that of a randomly aligned sample, shows an inflection rather than a decrease at the transition temperature. For this latter polymer, the order disorder transition is coincident with the smectic A-isotropic transition. The authors suggested that the reduction in the anisotropic conductivity may be attributed to the diffusion involving ions moving outside the PEO cylinders, leading to a reduction in charge carriers and this remains an open question. However, they considered it more likely that morphological changes were lying at the root of the decreasing conductivity. Specifically, they suggested that the onset of conformational changes resulting in enhanced layer fluctuations in the smectic A phase on increasing temperature could account for the decrease in conductivity [15].

Based on these previous reports, the third pattern of behaviour seen in Fig. 3 suggests that the sample has, at least to some extent, spontaneously aligned during the initial melting process. This alignment would be largely lost on passing through the clearing temperature and would have the effect of disrupting percolation pathways through the PEO-rich phase. This could account for the reduced conductivity. Further speculation must now await further studies on this class of materials.

4. Conclusions

This study has highlighted both the opportunities and the problems to be overcome in adapting this design approach to the development of new polymer electrolytes. On one hand, we have succeeded in incorporating an amorphous PEO-rich phase into a self-supporting solid matrix, but on the other hand the conductivity does not match that of the incorporated phase. Moreover, it could be further compromised if extensive crystallisation is allowed to occur. On the positive side, the conductivities reported here for a discotic liquid crystal material are seen to be some two orders of magnitude higher than for aligned samples of analogous rod-like liquid crystal materials [15,31].

We have shown that the triblock copolymer **1**:LiClO₄ complex quite remarkably mimics the behaviour of a high molecular weight PEO (300,000):LiClO₄ complex, not only in terms of conductivities but also in the values of their activation energies and volumes, and

in the derived process modulus for ion transport [30]. However, we must stress that we are not suggesting that the behaviour of the block copolymer complex is molecular weight independent. Rather by looking at our data and the simple VTF treatment, we attribute the lower conductivity of the triblock copolymer compared with the low molecular weight PEG complex to the additional tortuosity associated with long range ion transport in the PEO phase. This is distinct from the behaviour seen in neat PEO complexes. Thus for the 300,000 molecular weight PEO-based sample, the ion mobility is restricted by chain entanglements, while for the triblock copolymer **1**, the effect is associated with a reduction in percolation efficiency arising from the anchoring of the PEO chains to the liquid crystal blocks.

To gain improved electrolyte performance our study points to three complementary strategies. First, we should increase the volume fraction of the PEO in the block copolymer. This would have the effect of enhancing percolation efficiency, *i.e.*, increase the pre-exponential factor in Eq. (1) and furthermore, by increasing chain flexibility, reduce the value of the *B* parameter also seen in Eq. (1). Then, by varying the AO:Li ratio we could minimise the tendency to crystallisation seen in Fig. 3, which in unfavourable circumstances may strongly affect conductivities below 60 °C. Finally we could utilise the strategy described recently by Osuji et al. [15], in which they applied an external magnetic field to align the underlying liquid crystal phase in order to optimise the orientation of the conducting pathways. Their procedure brought about an order of magnitude increase in conductivity which, for our system, would effectively counteract the decrease in conductivity shown in Fig. 3, yielding a value of conductivity of around 10⁻³ S cm⁻¹ at 60 °C within a mechanically robust matrix. In such an aligned sample, the ionic conductivity of PEO would be considered to have been fully optimised. This is a promising prospect for various electrochemical applications and we consider warrants further study.

Acknowledgements

We acknowledge the financial support for this work from the EPSRC. The support of the SHEFC for a Research Development Grant to purchase the autoclave system is also gratefully acknowledged.

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