



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

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## 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].

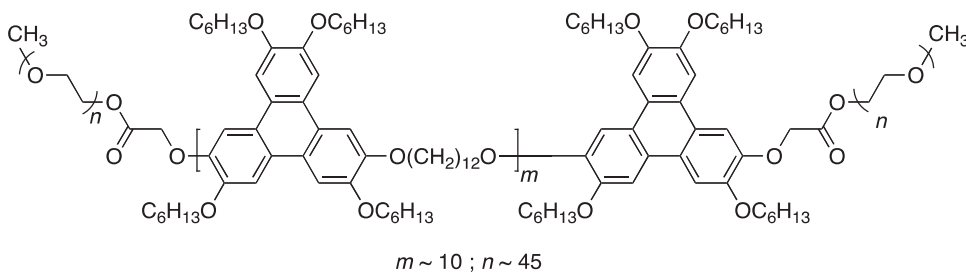
A promising design approach in the development solid polymer electrolytes has recently been adopted to simultaneously address these apparently conflicting demands of decreasing the local viscosity while maintaining mechanical integrity, involves the use of block copolymers. Here, one block provides the 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<sub>4</sub> 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  $120^\circ\text{C}$ , together with excellent thermal stability [16]. We now report the thermal, structural and electrochemical characterisation of a triblock copolymer **1**: $\text{LiClO}_4$  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) ( $M_W = 2.000 \text{ g mol}^{-1}$ ): $\text{LiClO}_4$  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.  $\text{LiClO}_4$  (Aldrich, 98%) was dried under vacuum at  $140^\circ\text{C}$  for several days prior to use. Stoichiometric amounts of triblock copolymer **1** and  $\text{LiClO}_4$  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: $\text{LiClO}_4$  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<sup>e</sup> 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: $\text{LiClO}_4$  6:1 (AO:Li) complex which contains a glass transition with a mid-point value of  $-40^\circ\text{C}$  and a very weak endotherm at  $74^\circ\text{C}$  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  $32^\circ\text{C}$  ( $\Delta H = 17.9 \text{ J g}^{-1}$ ) 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.  $53^\circ\text{C}$ , 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  $111^\circ\text{C}$  ( $\Delta H = 6.38 \text{ J g}^{-1}$ ) 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  $-41^\circ\text{C}$  is assigned to the glass transition of amorphous regions of the, again salt-free PEO blocks.

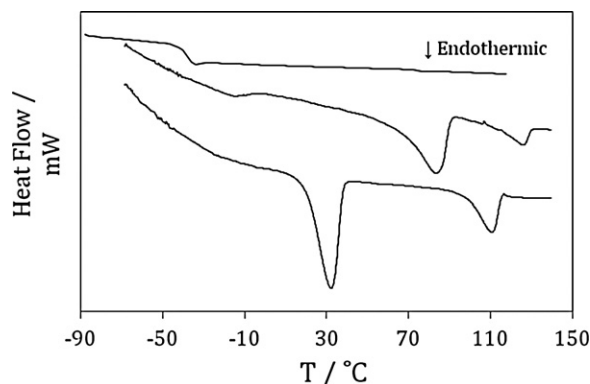


Fig. 1. DSC second heating scans for the PEG: $\text{LiClO}_4$  6:1 (AO:Li) complex (upper trace), the triblock copolymer, **1**, (lower trace) and the 6:1 (AO:Li)  $\text{LiClO}_4$  complex (middle trace).

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