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Discussion

Replies to comments contained in “Conductivity hysteresis in polymer electrolytes incorporating poly(tetrahydrofuran)” by O. Akbulut, et al., Electrochim. Acta 52 (2007) 1983

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Abstract

DSC indicates that first-heating endotherms at 95 and 100–115 °C in poly(tetramethylene oxide)-based polymers with $LiClO_4$ and $LiBF_4$, respectively, arise from the decomposition of phase-separated $LiClO_4 \cdot 3H_2O$ and a pre-melting transition in phase-separated $LiBF_4$ and not from organized adducts with poly(tetramethylene oxide) as asserted by Akbulut et al. and other literature. Water in the $LiClO_4$ system, at least (absent in freeze-dried samples), could account for higher conductivities reported by Akbulut et al. than observed by the present authors. Irreversibility of $\log \sigma$ versus$1/T$ in these weakly ionophilic systems apparently arises from slow dissolution of lithium salts together with morphological changes in mixtures of the self-organising systems C*m*O*n* (**I**) with the ‘grain boundary bridging’ copolymer $–[–(CH_2)_4–O–]_x–(CH_2)_{12}–$ (**II**). A three-component system **I**:**II**:$LiBF_4$ to which 9 wt% of tetrahydrofuran had been purposefully added showed *deterioration* in conductivity compared with the system without THF addition. This suggests that solvent-inhibition of self-organization is contrary to the suggestion by Akbulut et al. that irreversible transformation to a high ambient conductivity ($\sigma = 10^{-4}$ to 10^{-3} S cm^{-1}) regime arises from plasticization by the 3 wt% of volatiles, generated by thermal decomposition of **II** in a three-component mixture, that they report. The irreversible transformation to higher conductivities is also observed in systems heated to maximum temperatures between 50 and 80 °C for which degradation was shown to be negligible.
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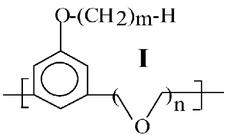
Keywords: Poly(tetramethylene oxide); Lithium salts; Self-organising polymer electrolytes; Thermal degradation; Grain boundaries

1. Introduction

In recent years we have sought to develop low-dimensional polymer and copolymer electrolytes C*m*O*n*, **I**, wherein alkyl side-chains $m = 12$–18 and skeletal ether oxygens $n = 1$–5, in which lithium salts migrate as aggregates within channels and cavities in the crystalline (c) and liquid crystalline (lc) superstructure [1–11]. The ionophobic C*m*O1:Li salt mixtures have very low conductivities but solid-state ^{7}Li and ^{19}F NMR linewidths are narrow and temperature-independent down to −20 °C indicating high mobilities of neutral (uncharged) aggregates LiA, $(LiA)_2$ within the cavities and channels, uncoupled to the side-chain melting temperatures at 40–50 °C which mark the transition between c and lc states [12]. The ionophilic C*m*O5:Li salt (1:1) (and C*m*O4:Li salt (1:1)) complexes are the most conductive homopolymer systems and NMR indicates a complex picture in which high ^{7}Li mobility persists into the c phase down to −25 °C in well-organized samples.



I

The most conductive systems studied by the present authors have been based upon the block copolymers C*m*O1O5 (*p*%). The minor proportion ($p = 20$–30 mol%) of the ionophilic C*m*O5 (or C*m*O4) give rise to conductive materials presumably incorporating both charged $(Li_2A)^+$, $(Li_3A_2)^+$ and uncharged salt aggregates. The narrowest NMR linewidths [12] indicate high temperature-independent uncoupled mobilities from 60 °C

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down to −70 °C. This holds the promise of high sub-ambient conductivities presumably by a ‘carrier-hopping’ mechanism

$$\mathrm{LiA} + \mathrm{Li}^+ \rightarrow \mathrm{Li_2A}^+;$$

$$\mathrm{LiA} + \mathrm{Li_2A}^+ + \mathrm{LiA} \rightarrow \mathrm{LiA} + \mathrm{LiA} + \mathrm{Li_2A}^+$$

However, the lamellar structure of the crystals and liquid crystals of copolymers, **I** give rise to ‘grain boundaries’ which impede the transfer of ions across a film of **I**:Li salt in the course of electrical impedance measurements. The well-defined minima in the Z' versus Z'' plane at intermediate frequencies thus correspond to ‘grain boundary resistances’, $R_{\mathrm{gb},}$ rather than ‘internal crystal resistance’ $R_{\mathrm{int},}$ which should be observed at the minima bounding the grain boundary arcs at higher frequency (see Fig. 1). The latter should reflect the mobilities observed by NMR since they depend on the greater bulk of the material.

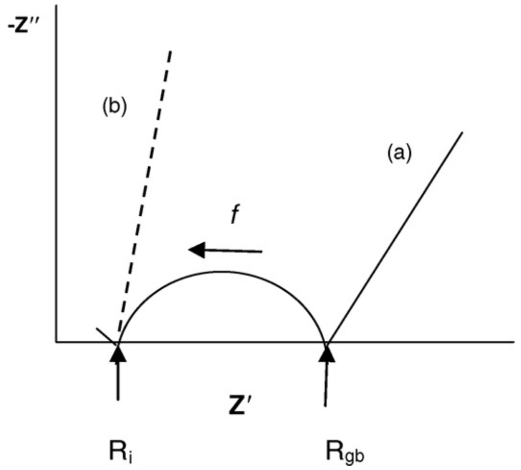

Fig. 1. Schematic diagram of impedance spectrum of a crystalline polymer electrolyte (a) showing both ‘grain boundary’ resistance, R_{gb}, and ‘internal’ resistance, R_{i}; (b) with a ‘salt bridge’ which eliminates the grain boundary resistance.

In order to facilitate the transfer of ions and aggregates between crystallites of **I** and to effectively eliminate the grain boundary impedances we have blended **I** with a second flexible ‘ion-bridge’ linear copolymer, **II**. When enclosed between crystallites of **I** polymer **II** is intended to match the weakly ion-coordinating environment of **I**. As illustrated in Fig. 2 aggregates of Li salt would be destabilized in an ionophilic ‘ion trap’ environment, such as poly(ethylene oxide). On the other hand, a hydrocarbon such as polyethylene would present an impermeable barrier. Copolymers of poly(tetramethylene oxide) (or ‘polytetrahydrofuran’ denoted PTHF) represent a compromise between these extremes. The polymer **II** system we have mostly investigated [3–12] has been synthesized by copolymerization of poly(tetramethylene oxide) with dodecamethylene segments, –$(\mathrm{CH_2})_{12}$– (denoted PTHFC12) not only to promote cohesion at the interface between **II** and the alkyl side-chains of **I** but also to increase the thermal stability of the polymer (see below). After blending by dissolution of the **I**:**II**:Li salt mixtures in organic solvents, freeze-drying and compacting, the blend was heated to the lc—*isotropic* region (80–110 °C). With the sample confined within the conductivity cell there is an initial rise in conductivity from 10^{-8} to $10^{-7}\,\mathrm{S\,cm^{-1}}$ at ambient to between 10^{-4} and $10^{-3}\,\mathrm{S\,cm^{-1}}$ at the higher temperature whereupon a demonstrable [8,11] morphological transformation (Fig. 3) gives rise to an irreversible change to a

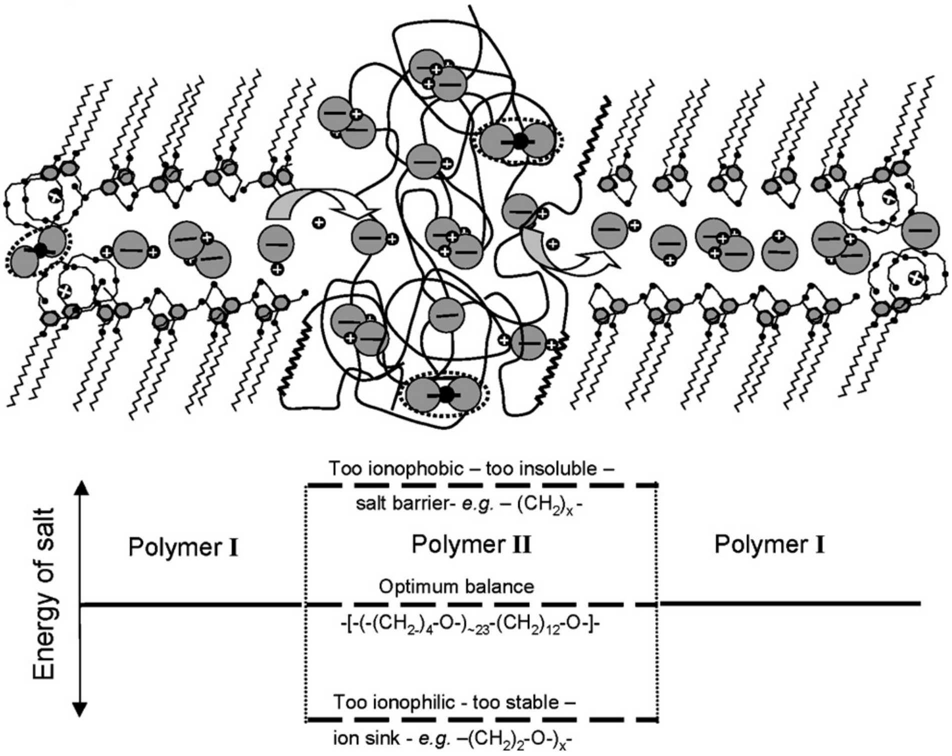

Fig. 2. Schematic representation of **I**:**II**:**I** interfacial structure.

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