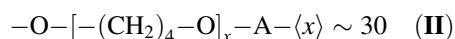


Fig. 1. Structural models of **I:II:LiClO₄**. (a) Schematic diagram. Solid lines: polymer **I**, dashed lines: polymer **II**; (b) molecular dynamics model of the end view of the helices. Red spheres: oxygens, green spheres: lithium ions, purple spheres: anions, small grey spheres are carbons and hydrogens. The experimental d spacing (40.4 Å) was applied as a constraint to the molecular dynamics model.

In this paper we report enhanced ambient conduction from solvent-free LiClO_4 complexes of **I** blended with a second, high molar mass copolymer of poly(tetramethylene oxide) (**II**).



In (**II**) the units $-\text{A}-$ are either $-\text{CH}_2-$ (**II**C1) or $-\text{CH}_2\text{C}(\text{=CH}_2)\text{CH}_2-$ (**II**D4). Both **I** and **II** are prepared to high molar mass ($\langle M_w \rangle = 8 \times 10^4$ and 4×10^4 , respectively) giving thin films with good mechanical properties.

2. Experimental

Polymer **I** was prepared as described previously [7,8]. Polymers **II** were prepared by standard Williamson condensation of hydroxy-terminated polytetrahydrofuran ($\langle M_n \rangle = 1688 \text{ g mol}^{-1}$ either with CH_2Cl_2 (50% solution) and excess powdered KOH (8 mol ratio) at room temperature (**II**C1) or with $\text{ClCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{Cl}$ (equimolar mixture) and excess KOH at 60°C (**II**D4). Polymers **II** were purified by washing with dilute aqueous acetic acid. Complexes were prepared by mixing polymer **I** (1 mol repeating unit), polymer **II** (7 mol of $[-(\text{CH}_2)_4-\text{O}-]$ units) and Li salt (1.5 mol) in a mixed solvent of dichloromethane/acetone. After removal of solvent with mechanical agitation complexes were dried under vacuum and stored in a desiccator. Cells for dc measurements were assembled with lithium metal electrodes and polyethylene separators under argon. The Li electrodes were prepared from freshly-pressed Li pellets (ca. 2 mm) in paraffin oil. The cell for ac measurements was assembled using indium tin oxide (ITO) coated glass electrodes with a cellulose acetate film separator. The dc current versus time plots were obtained with the cell under vacuum using a Solartron 1287A Electrochemical Interface in potentiostatic mode. The ac impedance measurements (ITO electrodes) were obtained over the range 1–64 kHz using a 1287A in conjunction with a Solartron 1250 Frequency Response Analyser.

3. Results and discussion

Wide to small angle X-ray analysis in conjunction with differential scanning calorimetry indicate that strands of polymer **II** disrupt the alkyl side chains of polymer **I** reducing the side chain melting temperature from a peak of ca. 45°C in complexes such as **I:LiClO₄** (1:1) or the equimolar blended complexes such as **I:C₁₈H₃₈:LiClO₄** (1:1:1) to ca. 34°C in **I:II:LiClO₄** blends. X-rays reveal a long spacing (ca. 41 Å) and, at 4.1 Å, hexagonal packing of crystalline alkyl side chains below melting but no indication of crystallinity involving the EO segments or their adducts with Li salts. These observations suggest a model for the **I:II:Li** salt complexes as shown in the schematic diagram of Fig. 1(a) and supported by the molecular dynamics model of Fig. 1(b). The latter indicates that the stoichiometric equivalent of polymer **II** for each repeat unit is a *heptamer segment* extending over the unit cell. The pure polymers **II** are semi-crystalline melting at ca. 20°C but dissolve Li salts to form an *amorphous* phase to a maximum concentration [ether oxygen]/ $[\text{Li}^+] \cong 10$. Compositions with [salt]/[repeat unit of **I**] \geq ca.1 are required to form the helical adduct [7–11] and in this work the blended complexes are therefore, denoted **I:II:Li** salt (2:2:3). The second digit denotes an equimolar molar proportion of heptamer **II** segment and the third suggests adequate salt to fill the helices with some vacancies available in **II**.

In Fig. 2i are presented dc measurements on complexes **I:II:Li** salt (2:2:3) in cells with Li electrodes (Li | **I/II**-Li salt | Li). In Fig. 2i(a) the salt is LiClO_4 and the cell was polarised with 10 mV at 30°C . Remarkably, the current increases stepwise over ca. 24 h corresponding to isothermal Li^+ conductivity increasing from ca. 10^{-6} to $2 \times 10^{-3} \text{ S cm}^{-1}$ in an apparent ‘self-tracking’ process. In Fig. 2i(c) the same phenomenon is observed with a LiClO_4 complex at 25°C and 100 mV polarisation although, a lower conductivity is achieved (ca. $3 \times 10^{-4} \text{ S cm}^{-1}$) within the period of the experiment. However, with mixed salts $\text{LiClO}_4\text{:LiBF}_4$ (0.75:0.75) at 25°C a conductivity of

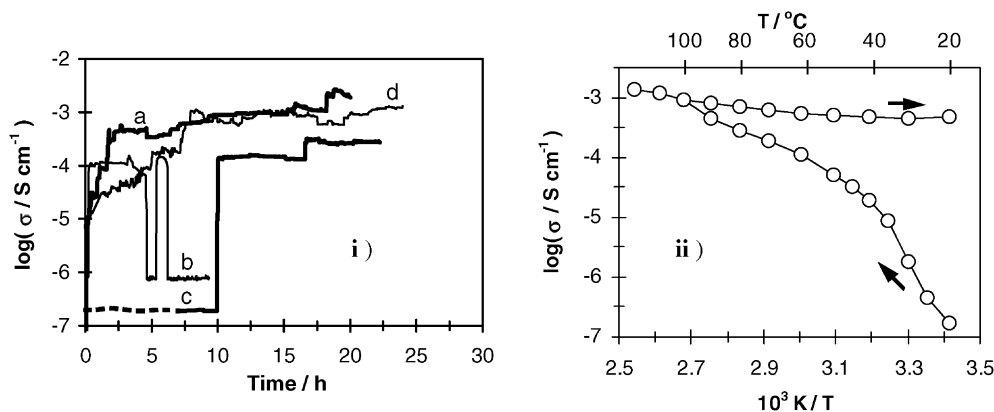


Fig. 2. (i) The dc polarisation with lithium electrodes (under vacuum). (a) **I:II**D4:LiClO₄ (2:2:3), 10 mV at 30°C; (b) **I:II**D4:LiClO₄ (2:2:3), 10 mV at 20°C; (c) **I:II**C1:LiClO₄ (2:2:3), 100 mV at 25°C; (d) **I:II**C1:LiClO₄:LiBF₄ (2:2:1.5:1.5), 100 mV at 25°C. (ii) Temperature dependence of ac conductivity of **I:II**C1:LiClO₄ (2:2:3) between ITO electrodes (under vacuum). Arrows indicate the direction of heating.

$10^{-3} \text{ S cm}^{-1}$ is again observed. This suggests that the ‘fluidity’ in the interhelical anion spaces (see Fig. 1) at 30°C, Fig. 2i(a), was restored by the disorder of the anion mixture, Fig. 2i(c). In Fig. 2i(b) the same cell as in Fig. 2i(a), using LiClO₄ alone, was cooled to 20°C and the run restarted. The enhanced conductivity level of $10^{-4} \text{ S cm}^{-1}$ is re-established very quickly in this case suggesting a ‘memory’ of the structural reorganisation achieved at 30°C. This level is maintained for ca. 5 h before ‘breaking down’, possibly due to crystallisation shrinkage at the electrode–electrolyte interface or phase separation of **I** and **II**.

The enhanced dc conductivities are supported by ac impedance measurements on the blended complexes using ITO-coated glass electrodes. The $\log \sigma$ versus $1/T$ plot of Fig. 2ii shows an ambient conductivity similar to that of the dc measurement before heating and rising to ca. $10^{-3} \text{ S cm}^{-1}$ at 100°C. However, on cooling this high level of conductivity is maintained down to ambient. This suggests that structural reorganisation from a rapid high temperature ‘tracking’ process in the ac field may have been ‘frozen in’ on cooling to ambient. More extensive ac experiments have demonstrated very low temperature dependence of conductivity from 20°C down to -5°C ($\sigma = 8 \times 10^{-5} \text{ S cm}^{-1}$).

The unsaturation in $-\text{CH}_2\text{C}(\text{=CH}_2)\text{CH}_2-$ clearly allows the possibility of cross-linking for the purpose of stabilising the morphology in a post-organisational reaction. However, this facility has yet to be systematically exploited and will be discussed in a future publication.

In seeking mechanisms for ‘tracking’ we note that the blend is subjected to cursory mechanical shear in the plane of the film (parallel to the electrodes) when the film is prepared during which it is anticipated that polymer **II** (with the more extensive skeletal domain) will promote orientation of conducting planes *bc* (see Fig. 1) in the direction

normal to the electrodes. Furthermore, imposition of the field is expected to bring about a new steady-state redistribution of ions between the channels of polymers **I** and **II** environment promoting vacancies in **I** in which ions are presumed the more mobile ($\sigma = 7 \times 10^{-7} \text{ S cm}^{-1}$ for complexes of pure **II** with LiClO₄ at 25°C [ether oxygen]/[salt] = 10). The distributions of ions between **I** and **II**, their relative mobilities and the identification of premelting (order–disorder) transitions which could account for the low temperature dependence of conductivity are subjects of further work.

Acknowledgements

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