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Ion conducting behaviour and morphology of solid polymer electrolytes based on a regioselectively substituted cellulose ether with PEO side chains

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The $LiCF_3SO_3$ complexes of a thermotropic cellulose ether having PEO side chains (TPEOCELL) were prepared and the effects of salt concentration on the conductivity and morphology were investigated. A linear dependence of log (conductivity) on reciprocal temperature occurs in these systems, with activation energies for ion transport in the range 53–73 kJ mol^{-1}. TPEOCELL shows a periodic lamellar-like internal structure which is ascribed to the presence of cholesteric ordering. By contrast, its complexes exhibit an array structure composed of granular-like entities which coalesce irregularly to form a rough morphology. This morphological feature is taken to represent a liquid crystalline polymer–salt network in which a form of anisotropic microphase separation occurs.

Introduction

The remarkable complexing ability of poly(ethylene oxide) (PEO) has long been recognised[1,2] and intensively utilised in the construction of solid polymer electrolytes. Over the past twenty years or so, the structures receiving most attention have been amorphous copolymers or networks, with grafts or blocks of PEO, in which ambient conductivities of the order of 10^{-4} S cm^{-1} have been achieved.[3–6] However, this is insufficient for practical applications (*ca.* 10^{-3} S cm^{-1}). The preparation of a solvent-free polymer electrolyte with a high ambient conductivity and desirable mechanical properties is still a challenge to material scientists.

Recently the self-assembly properties of liquid crystals have been utilised in this field, and a number of liquid crystalline complexes capable of forming ionically conductive layers or channels of PEO have been reported.[7–12] Examples include side chain liquid crystalline systems reported by Imrie *et al.*,[7,8] main chain liquid crystalline systems reported by Ward *et al.*,[9,10] and amphiphilic low-dimensional systems reported by Wright *et al.*[11,12] The advantages of these systems are (a) good mechanical properties can be achieved without a significant loss of ion mobility (most of the ions are confined to PEO layers or channels and ion mobility is independent of large scale segmental relaxation[13]), and (b) the liquid crystalline structures result in an anisotropy which provides the possibility for enhancement of conductivity along a preferred direction.[10]

Cellulose is an abundant naturally-occurring polymer used commercially; it is both renewable and biodegradable. It is also a rich source of liquid crystalline polymers as many of its derivatives have been found to form liquid crystalline phases in concentrated solutions or in the melt which is attributable to the inherent semirigid nature of the cellulose backbone. Efforts to combine the liquid crystalline properties of selected cellulose derivatives with the ion conducting properties of PEO are currently being pursued in this laboratory, primarily by the incorporation of oligo(ethylene oxide) side chains onto the cellulose backbone.[14] A regioselectively substituted cellulose ether, 6-*O*-trityl-2,3-*O*-diPEOcellulose (TPEOCELL), has been synthesized recently which forms a right-handed chiral nematic mesophase at room temperature with a selective reflection band in the visible region.[15] The PEO side chains are about seven units long and specifically situated at the C-2 and C-3 positions of the anhydroglucose units comprising the cellulose backbone, as is shown in Fig. 1. In this paper we report on the studies of its ion conducting behaviour and the morphology of its $LiCF_3SO_3$ complexes.

Experimental

The preparation of TPEOCELL will be fully described elsewhere;[15] briefly, 6-*O*-tritylcellulose (prepared from a cellulose of $M_n \approx 30\,000$ g mol^{-1}) was treated with the monoidide of PEO ($M_n \approx 350$ g mol^{-1}) in DMSO. The product was precipitated into diethyl ether, its chloroform solution treated with silica gel prior to three further reprecipitations into diethyl ether. The product was characterised by ^1H NMR and had degrees of substitution of ~1.1 for the trityl group and ~1.9 for the PEO group.

A range of the TPEOCELL complexes was prepared by dissolving appropriate proportions of $LiCF_3SO_3$ and polymer in anhydrous acetonitrile and slowly evaporating the solvent under a dry nitrogen atmosphere. The complexes were dried under vacuum to constant weight and allowed to homogenise

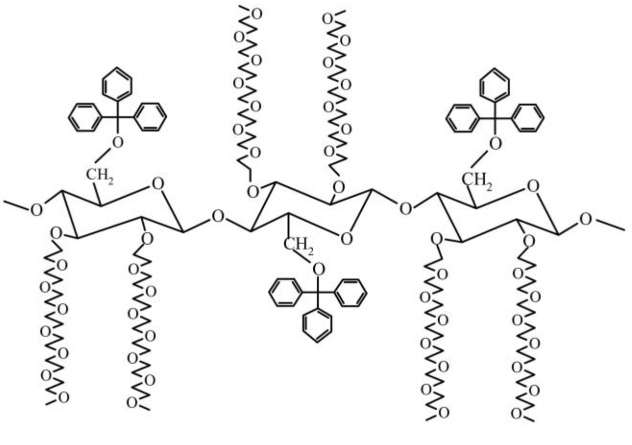

Fig. 1 Schematic representation of TPEOCELL.

for two days in a desiccator before measuring the conductivities. The concentration of salt is recorded as the molar ratio of lithium ions to oxygens in the polymer chain, [Li]/[O]. Although oxygens in the PEO side chains and those of the cellulose backbone are counted the latter probably play a minor role in ion coordination since they lack the conformational freedom to adopt the coordination geometry of the ethylene oxide units.[16]

The glass transition temperatures (T_g) of the complexes were measured using a DSC 2010 TA instrument at a heating rate of 10 K min^{-1} in a nitrogen atmosphere. Optical textures were identified with an Olympus BH-2 polarised light microscope equipped with a Linkam PR600 hot stage; the clearing temperatures (T_{cl}) were determined as the temperatures at which all birefringence completely disappeared at a heating rate of 10 K min^{-1}.

The ionic conductivities were ascertained by a.c. impedance spectroscopy using a Solartron 1255 frequency response analyser connected to a Solartron 1286 electrochemical interface. The frequency range used was 1 to 10^5 Hz. The complexes were handled in a glove bag flushed with dry nitrogen; the sample was placed between stainless-steel blocking electrodes, using a PTFE spacer to ensure constant sample thickness, and was then loaded into a sealed measuring cell under a nitrogen atmosphere. The temperatures used covered the range of 293–373 K and were controlled by a Haake thermostat bath. Each sample was allowed to equilibrate for 1 h at each measuring temperature before the a.c. impedance spectrum was recorded. The bulk resistance (R_Ω) was obtained by fitting the impedance spectrum to the equivalent circuit shown in Fig. 2 using the complex plane non-linear least square-fitting method.[17]

The internal fracture surface morphologies of TPEOCELL and its complexes were examined in a Philips XL30 Environmental Scanning Electron Microscope (ESEM) using a Cryo-Stage in high vacuum mode. An accelerating voltage of 20 kV was used. The dried samples were placed on PTFE plates and allowed to equilibrate overnight in a desiccator prior to measurement; the PTFE plates with samples on them were then dipped into liquid nitrogen so that the samples were easily removed without being deformed. The samples were then immediately frozen at 83 K before being transferred under vacuum to the cryogenic preparation chamber where they were fractured in a direction perpendicular to the surface. The fractured surfaces were gold sputter coated and examined at 93–103 K.

Results and discussion

Thermal properties

The salt-free polymer is a viscous fluid at room temperature with a glass transition temperature of 221 K. The variation of T_g values of the $LiCF_3SO_3$ complexes, with the [Li]/[O] ratios ranging from 0.038 to 0.125, is illustrated in Fig. 3 as a function of the [Li]/[O] ratio. These increase progressively with increasing salt concentration, indicating a reduction in the polymer chain mobility which can be attributed to the formation of intra- and intermolecular transient crosslinks *via* coordination between the cations and the ether oxygens. These complexes are anisotropic fluids at room temperature, typically displaying marbled or sanded textures under crossed polars. The liquid crystalline phases formed by the complexes are nematic, and this is supported by earlier work where it was found that the undoped polymer forms a thermotropic chiral nematic mesophase at room temperature, and that progressive addition of $LiCF_3SO_3$ interferes with the formation of a cholesteric structure and causes a phase transition from a chiral nematic to a nematic phase.[15]

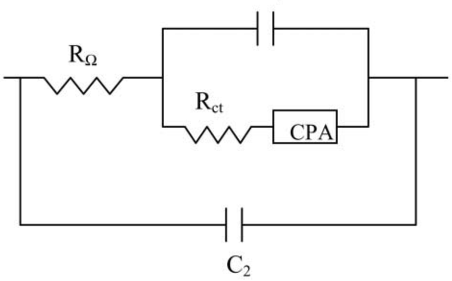

Fig. 2 Equivalent circuit used in the data fitting of the a.c. impedance spectrum. R_Ω represents the bulk sample resistance and R_{ct} is the charge transfer resistance; C_1 and C_2 are the geometric and double layer capacitances respectively; CPA is the empirical phase constant element.[17]

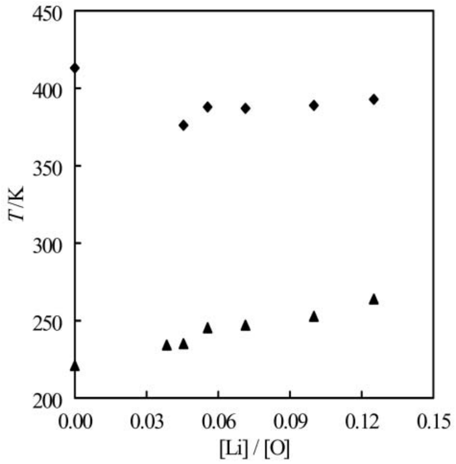

Fig. 3 Variation of the glass transition temperatures (T_g = ▲) and the clearing temperatures (T_{cl} = ◆) as a function of the [Li]/[O] ratio.

Fig. 3 also illustrates the variation of the clearing temperature (T_{cl}) as a function of the [Li]/[O] ratio. The T_{cl} values of the complexes are noticeably lower than that of the undoped polymer, and increase only slightly with increasing salt concentration, thereby producing a narrowing liquid crystalline range with increasing salt concentration. This T_{cl} behaviour for the TPEOCELL complexes is different from that observed in two related cellulosic systems,[14] in which the trityl function is absent, where the addition of $LiCF_3SO_3$ results in T_{cl} values which are always greater than that of the undoped parent polymer and the conductivities are approximately one order of magnitude higher. The reason for this difference in T_{cl} behaviour is unclear, but is most likely to be associated with the corresponding structural differences. It can be reasonably assumed that thermal stability of the ordered phase is enhanced by oxygen coordination based on the evidence of the increases in T_{cl}. The hydrophobic and bulky trityl group at the C-6 position of the anhydroglucose units of the backbone must then make accommodation of the salt in the PEO side chains less favourable and thereby exerts a destabilising effect on the liquid crystalline phase.

Ion conductivity

The ionic conductivities of the complexes were measured from room temperature to 373 K, so that all the complexes remained in the liquid crystalline state during these measurements. The bulk conductivities of the complexes range from $\sim 10^{-7}$ S cm^{-1} at room temperature to $\sim 10^{-4}$ S cm^{-1} at 373 K. In this respect these cellulose-based systems, although comparable with other PEO-based systems,[18] have gained no obvious enhancement in ion conduction from the presence of the liquid crystalline phase. This might variously be ascribed to the presence of the semirigid cellulose backbone and/or to the bulky hydrophobic trityl groups impeding the ion movements.

Interestingly, a linear Arrhenius dependence of log (conductivity) on reciprocal temperature was observed for these complexes. The majority of the solid polymer electrolytes that have been investigated are essentially amorphous systems, in which a nonlinear dependence is generally observed and fitted well to the semi-empirical Vogel–Tamman–Fulcher (VTF) equation.[19] Such a response is argued to arise from the conducting process characteristic of solid polymer electrolytes wherein ion motion is strongly coupled to local relaxation of the polymer chains and so reflected in a more pronounced temperature dependence. Arrhenius behaviour is more commonly found in liquid electrolyte systems[20] and in gelled polymer electrolyte systems[16,21] in which segmental motion plays a less important role in the ion conduction process. However Arrhenius behaviour is also reported in some semi-crystalline systems at temperatures above their melting points.[22] The significance of the Arrhenius temperature dependence in the TPEOCELL complexes is, as yet, not clear.

The apparent activation energies (E_a) for ion transport in TPEOCELL complexes, calculated from the Arrhenius slopes, range from 53 to 73 kJ mol^{-1}, being of the same order of magnitude as other amorphous systems[23] which follow the VTF equation and the calculation of the activation energy involves the use of the Adam–Gibbs configurational entropy model.[24] The dependence of E_a on salt concentration is well described by $E_a = (245.2 \pm 11.1) \times ([\mathrm{Li}]/[\mathrm{O}]) + (43.6 \pm 0.9)$ over the range $0.03 \leqslant [\mathrm{Li}]/[\mathrm{O}] \leqslant 0.13$. The increase of E_a with increasing salt concentration indicates a reduction in ion mobility, which is mainly caused by two effects. Firstly, as ion–ion interactions in solid polymer electrolytes are extensive,[19] increasing the salt concentration leads to aggregation of ion species and a consequent reduction in the overall ion mobility. Ion mobility is also reduced as a consequence of the restriction in chain flexibility imposed by the increasing concentration of coordination crosslinks between cations and ether oxygens and is reflected by the rise in T_g.

Fig. 4(a) presents isothermal plots of log σ as a function of salt concentration for the TPEOCELL complexes which show distinct maxima which move to higher salt concentration as the temperature is raised. The occurrence of a maximum conductivity at a certain salt concentration is generally explained as a result of two opposing effects caused by rising salt concentration, the increasing number of charge carriers and the reducing mobility of the charge carriers as noted above. In these systems, the shift of the maxima towards higher salt concentration with increasing temperature indicates that the contribution of the number of charge carriers towards the conductivity becomes more dominant at higher temperatures. By replotting the data at a reduced temperature (T–T_g), the temperature effect of segmental mobility on the conductivity can be formally discounted and the complexes compared at constant chain flexibility. As shown in Fig. 4(b), over the temperature range studied, conductivities continuously increase within the [Li]/[O] range used. Similar analysis of other systems[3,23] showed that maxima still persist and move to higher but constant salt concentrations. Maxima may exist at higher concentrations, but polymer–salt phase separation in the present system precluded this investigation.

Environmental scanning electron microscopy

One advantage of environmental scanning electron microscopy (ESEM) is that measurements can be made at very low temperatures and this enables examination of the internal structure of a liquid crystalline polymer with a low T_g by quenching the liquid crystalline order into a glassy state. Fig. 5(a) shows that the fracture surface of the undoped polymer, which exhibits a chiral nematic phase at room temperature,[15] consists of layer-type features. These lamellar bands align approximately parallel to the fracture surface with the layer edges protruding

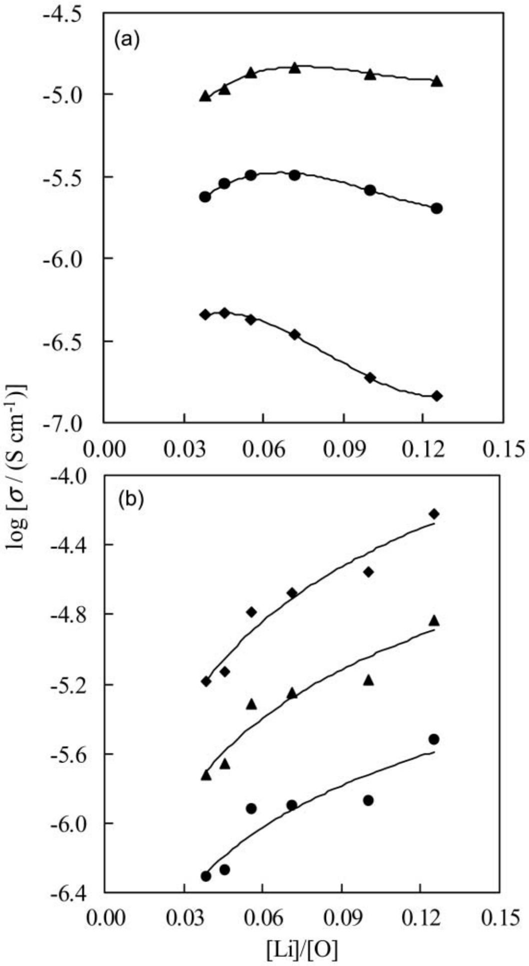

Fig. 4 Isothermal plots of log conductivity against the [Li]/[O] ratio for the TPEOCELL–$LiCF_3SO_3$ complexes, (a): (◆) $T = 293$ K; (●) $T = 320$ K; (▲) $T = 340$ K, and (b): (●) T–$T_g = 60$ K; (▲) T–$T_g = 80$ K; (◆) T–$T_g = 100$ K.

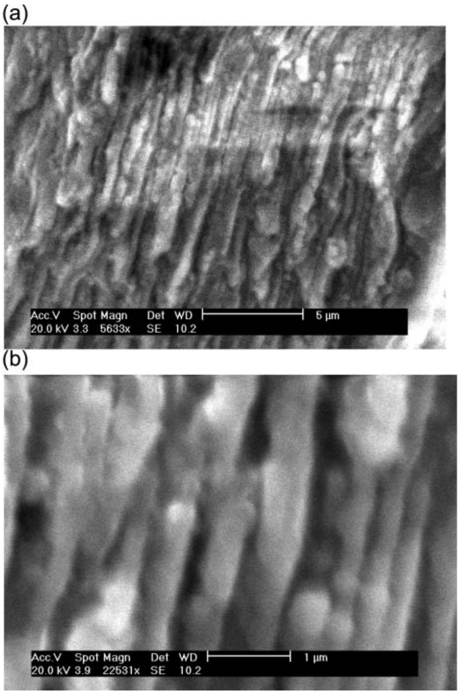

Fig. 5 ESEM micrographs of TPEOCELL fracture surface morphology (scale bars are shown on the figure).

perpendicular to the fracture surface. Under higher magnification (Fig. 5(b)), these layer features exhibit an apparent width of *ca.* 330–480 nm. Periodic lamellar structures have been reported in the morphologies of several cellulosic composites,[25–27] which were prepared by polymerising cholesteric liquid crystalline solutions of cellulose derivatives in common monomers. Similar morphologies were observed in films of cellulose derivatives cast from cholesteric liquid crystalline solutions.[28] It has thus been argued[25–28] that such lamellar arrangments are associated with the cholesteric ordering of a parent lyotropic system which is trapped by polymerisation, or alternatively by solvent evaporation. The ESEM results presented here are the first observation of this morphology in a thermotropic chiral nematic cellulose derivative.

TPEOCELL has a reflection band in the visible region (605 nm) as a consequence of adopting a right-handed chiral nematic phase at room temperature;[15] from the de Vries equation[29] this corresponds to a pitch length of $\sim$400 nm. Comparison with the thickness of the layers measured by ESEM implies that each layer, shown in Fig. 5, represents one helical turn of the chiral nematic phase in TPEOCELL. Other authors[30,31] report a closer correlation between layer thickness and half the pitch length in cellulosic derivatives. This however may reflect other structural differences or methods of film preparation. Here it seems that the primary cholesteric order spacing of TPEOCELL molecules at room temperature is preserved by rapid quenching into the vitreous state. There is an arguable structural parallel between TPEOCELL and lyotropic cellulose solutions in general. The mesogenic units in both systems stem from the rigidity of the cellulose backbone; whereas in the latter the solvent is a conventional small molecule, for TPEOCELL effective solvation is provided by the attached flexible oligo(ethylene oxide) units.

In contrast to the undoped material, $LiCF_3SO_3$ complexes of TPEOCELL present an altogether rougher ESEM texture, shown in Fig. 6(a) for [Li]/[O] = 0.071, but one which still displays a sense of order in the form of approximately parallel array-like arrangements. These arrays are composed of granular-like entities, and are aligned parallel to the fracture surface. On a closer view (Fig. 6(b)), each array is not well defined but is "roughened" by the irregular aggregations of the neighbouring granular-like entities. Similar morphological features have also been observed in the $LiCF_3SO_3$ complexes of related cellulose derivatives[14] and could prove to be representative of this type of liquid crystalline polymer–salt network. Although the surface morphology contains elements of order, these occur on a scale (*ca.* 1–2 μm) far above that of simple nematic alignments. Various ion aggregates are likely at the salt levels used[19] and so there is the possibility of microphase separation wherein the complexed ions and ionic aggregates are distinguishable, yet are still influenced by some underlying residual anisotropy. However, since conduction in these complexes remains at a modest level, a truly continuous "ionic" phase must be discounted.

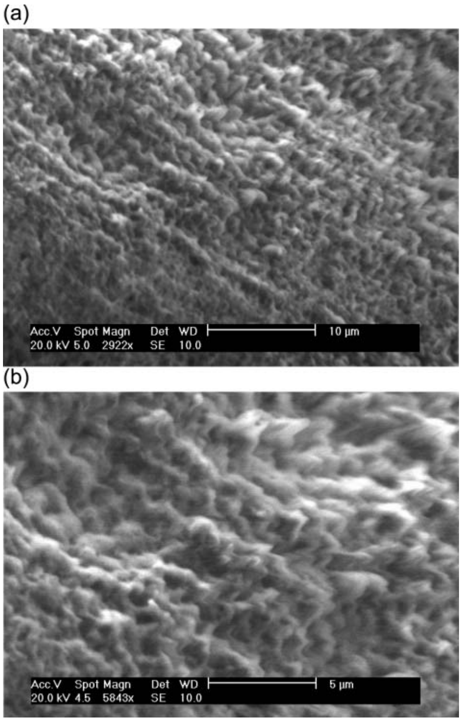

Fig. 6 ESEM micrographs of the TPEOCELL–$LiCF_3SO_3$ complex fracture surface morphology with [Li]/[O] = 0.071 (scale bars are shown on the figure).

Conclusions

The ion conducting behaviour of the liquid crystalline systems comprising of TPEOCELL and $LiCF_3SO_3$ complexes has been examined. These complexes exhibit a linear dependence of log σ on $1/T$, with activation energies for ion transport in the range $53 \sim 73$ kJ mol^{-1}, and the maximum conductivities move to higher salt concentrations as the temperature is raised. Two kinds of morphological features were identified. Undoped TPEOCELL shows a periodic lamellar-like texture on its fractured surface, and this is correlated with a chiral nematic order, while its $LiCF_3SO_3$ complex displays a roughened, array-like arrangement. This is speculatively associated with microphase-separated regions.

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