Ionic conduction of lithium and magnesium salts within laminar arrays in a smectic liquid-crystal polymer electrolyte

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Three polymers having the structure shown below where $R = -C_{16}H_{33}$ or $-C_{12}H_{25}$ and n = 5 or 6 (coded C16O5, C16O6 and C12O6), have been synthesised and their complexes with LiClO₄, LiBF₄, LiCF₃SO₃, LiBr and Mg(ClO₄)₂ have been prepared.



In a previous publication¹ the preparations of one of a series of polyethers having the general formula shown above and of its complex with LiBF₄ were reported. In that system, coded C16O5 : LiBF₄ (1 : 1), the side substituent was $-C_{16}H_{33}$ and there were five skeletal oxygens, n, per repeating unit. The repeating unit was therefore 18 skeletal bonds in length and so imitated the repeating unit of the 2_1 helix of the sodium^{2,3} or lithium⁴ salt complexes of poly(ethylene oxide) (PEO). It was shown that each mol of repeating unit of the polymer incorporates a maximum of 1 mol of the lithium salt in the complex. It was also demonstrated¹ that, at temperatures between sidechain melting (ca. 40°C) and the isotropic temperature (ca. 90 °C), a liquid-crystal phase was formed in the complex. A smectic structure, having layers of extended helical polyethercation adducts separated by layers of interdigitating alkyl chains and layers of anions, was proposed. These series of nalkyl-substituted polymers are identified by the codes CmOn, where *m* denotes the number of carbons in the alkyl side chain and *n* the number of oxygen atoms per repeating unit in the polyether backbone. The complexes are identified CmOn : MX (p:q), where MX is the complexing salt and p and q are the molar proportions of polymer repeating unit and salt, respectively.

Here, we report structural studies and measurements of the ionic conductivities of complexes of LiBF_4 , LiCIO_4 , LiCF_3SO_3 , LiBr and $\text{Mg}(\text{ClO}_4)_2$ with the substituted polyethers C12O6, C16O5 and C16O6.

Experimental

5-Hexadecyloxybenzene-1,3-dimethanol was prepared from 37 g of 5-hydroxyisophthalic acid (Aldrich), 150 ml of ethanol and 2 ml of concentrated sulfuric acid which were refluxed for several hours to give the diester. After ethanol was removed under vacuum the white crystals were washed with water and then dissolved in ethyl acetate (200 ml). The solution was washed sequentially with aqueous sodium hydrogen carbonate solution and water and dried over magnesium sulfate. After concentration under vacuum, white needles separated from the solution (yield 92%; melting point 106 °C). The diester, hexadecylbromide and acetone were refluxed in the presence of potassium carbonate for 24 h. Water was added and the 5-hexadecyloxybenzene-1,3-dicarboxylic acid diethyl ester was extracted into pentane. The alkoxy-diester was reduced using lithium aluminium hydride in diethyl ether. the alkoxybenzenedimethanol was recrystallised from dichloromethane (yield 80%; melting point 91 °C). Microanalysis: required: (%) C (76.14), H (11.18), O (12.68); found: (%) C (76.07), H (11.40), O (12.53).

5-dodecyloxybenzene-1,3-dimethanol was prepared by a similar procedure using dodecyl bromide (yield 89%; melting point 81 °C) molecular mass from mass spectrometry; found 322.25, expected 322.49 ($C_{20}H_{34}O_{3}$).

Tetraethylene glycol dichloride was prepared by refluxing equimolar proportions of tetraethyleneglycol and thionyl chloride in dimethylformamide. The mixture was distilled and the product collected at 130 °C under ca. 1 mm pressure. Poly[tetraoxyethyleneoxymethylene (5-hexadecyloxy-1,3phenylene) methylene], (C16O5) was prepared by heating equimolar proportions of 5-hexadecycloxybenzene-1,3-dimethanol and tetraethylene glycol dichloride with 8 molar equivalents of potassium hydroxide at 90 °C in dimethylsulfoxide for several days (adaptation of the etherification procedure advocated by Johnstone and Rose⁵). The polymer was isolated by precipitation in water and extraction in chloroform. Unreacted monomer and lower oligomers were removed by extraction with hot methanol. C12O6 and C16O6 were prepared by solid-state polymerisations. The appropriate 5alkyloxybenzene-1,3-dimethanol and potassium hydroxide (2.5 mol) were dissolved in methanol. The solvent and water were

removed under vacuum and the solid residue was ground to a finely divided form with pentaethylene glycol di-*p*-tosylate under nitrogen. The mixed powders were heated to 90 °C under vacuum. The polymer product was precipitated in water and unreacted monomer was extracted with hot methanol.

The molar masses of the polymers were estimated by gel permeation chromatography using chloroform as solvent and sharp fractions of polystyrene (Polymer Laboratories) as calibration standards; the GPC peak maxima corresponded to *ca*. 10^5 g mol⁻¹ for C16O5, 5000 g mol⁻¹ for C16O6 and 10 200 for C12O6.

The complexes were prepared by dissolving the appropriate proportions of the salt and polymer repeating unit in acetone. After removal of the solvent the mixture was heated at $50 \,^{\circ}$ C for 2 h in dry-nitrogen atmosphere to ensure uniform dissolution of the anhydrous salt in the polymer.

SAXS-WAXS was carried out with an MAR Research Image Plate area detector using graphite-monochromatised Cu-K α radiation ($\lambda = 1$, 54 Å). Thermal analysis was preformed over the range -10 to 110 °C using a Stanton-Redcroft model 671 DTA with sub-ambient facility and a Perkin Elmer DSC7 series Thermal Analysis System. Hotstage polarised light microscopy was carried out using a Lincam PR600 heated stage. Molecular modelling was performed with the MACROMODEL 3D software package using MM2 force field. The microscope was a Reichert-Jung POLYVAR.

Complex impedance measurements on the complexes were performed using a Solartron 1286 electrochemical interface and 1250 frequency response analyser operating over the frequency range 5 Hz-64 kHz. All electrical measurements were performed under vacuum using sputtered gold electrodes on predried samples. Prior to measurement over a range of temperatures the samples were held at a temperature of approximately T_i (see Table 1) under vacuum for several hours in the conducting measuring cell. The conductivity was monitored throughout this period and when it became sensibly constant the sample was slowly cooled in order to develop the texture and the conductivity data were recorded during a heating cycle.

Results and Discussion

Molecular structures of the uncomplexed polymers C16O5, C16O6, C12O6

The uncomplexed polymer C16O5 has been shown¹ to have a laminar (crystal smectic) structure below the side-chain melting temperature of 37.2 °C (see the thermal analysis trace of C16O5 in Fig. 1(a). SAXS and WAXS analysis combined with energy-minimisation molecular modelling indicated that the $-C_{16}H_{33}$ side chains are organised in a hexagonal lattice and the polyether backbone has a helical conformation in the crystalline state [see Fig. 2(a) and (b)]. The laminar structure has an interlayer spacing of 37.7 Å. Above 37.2 °C, the uncomplexed polymer is isotropic in the polarising microscope but a broad small-angle X-ray peak suggests some local retention of the laminar molecular structure.

Structural analysis of the uncomplexed C16O6 confirms a similar structure to C16O5 with an interlayer spacing of 39.7 Å but the slightly larger helical turn between side chains renders the structure somewhat less stable and the side-chain melting temperature is reduced to $34.5 \,^{\circ}$ C [Fig. 1(c)].

The uncomplexed polymer C12O6 is the least thermally stable of the three polymers. The thermal analysis trace in Fig. 1(e) shows that side-chain melting occurs at -8.2 °C. A glass transition, which cannot be clearly identified in the C16On polymers, is also apparent at -32 °C in C12O6. Although sub-ambient X-ray facilities were not available to us to study



Fig. 1 Differential scanning calorimetry traces, heating rate = 10° C min⁻¹: (a) C16O5, (b) C16O5 · LiClO₄ (1:1), (c) C16O6, (d) C16O6 · LiClO₄ (1:1), (e) C12O6 (f) C12O6 · LiClO₄ (1:1), (g) C16O5 · Mg(ClO₄)₂ (1:0.5), (h) C16O6 · Mg(ClO₄)₂ (1:0.5)

the C12O6 system below side-chain melting, broad peaks are observed at both small and wide angles in the liquid state of this system at 20 °C. These correspond to distances of 26.1 and 4.4 Å, respectively. Energy-minimised modelling of C12O6 confirms that the system is disordered at 20 °C and that the comparatively small d spacing may arise from extensive overlap of irregular extended molecular conformations [see Fig. 2(c)].

The uncomplexed polyethers therefore have crystalline phases with stabilities decreasing in the sequence: C16O5 > C16O6 > C12O6. This sequence presumably reflects both the decreasing stability of the side-chain hexagonal crystalline material with decrease in the length of the alkyl



Fig. 2 Energy minimisation molecular modelling of (a) and (b) C16O5, and (c) C12O6 $\,$

Table 1	X-Ray and	thermal	data for	complexes	with lithium	and magnesium	salts
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	$d/{ m \AA}$			7	T	A 77	
polymer	20 °C	55 °C	D/A (20 °C)	/°C	/°C	ΔH /kJ mol ⁻¹	
C16O5	37.7	broad	4.15	+ 37.2	34	30.8	
$C16O5 \cdot LiBF_4 (1:1)$	42.9	45.0	4.17	+ 43.6	89	24.4	
$C16O5 \cdot LiBF_4$ (1 : 0.8)	44.6	47.2	4.17	+43.7	85	22.4	
C16O5 · LiBF ₄ (1 : 0.5)	40.9	41.6	4.16	+ 42.6	77	25.8	
$C16O5 \cdot LiBF_4$ (1 : 0.2)	41.1	broad	4.18	+ 40.3	42	34.5	
C16O5 LiClO ₄ (1 : 1)	44.6	46.8	4.17	+43.5	143	21.3	
$C16O5 \cdot LiClO_4 (1:0.5)$	42.9	46.8	4.16	+ 42.5	83	24.4	
C16O5 · LiBr (1 : 1)	44.6	46.8	4.17	+ 42.8	98	26.7	
$C16O5 \cdot LiCF_{3}SO_{3}(1:1)$	44.6	47.0	4.17	+43.1	64	24.4	
C16O5 LiCF $_{3}SO_{3}$ (1 : 0.5)	45	46.3	4.16	+ 43.4	55	26.6	
$C16O5 \cdot Mg(ClO_4)_2 (1:0.5)$	44.0	45.1	4.15	+43.0	131	33.9	
C16O6	39.7	broad	4.15	+ 34.5	32	28.6	
C16O6-LiBF ₄ (1 : 1)	45.7	48.3	4.18	+40.2	82	31.2	
$C16O6-LiBF_{4}$ (1:0.5)	43.6	46.9	4.16	+44.8	72	39.4	
$C16O6-LiClO_4$ (1:1)	46.1	48.2	4.17	+40.0	135	28.0	
$C16O6-Mg(ClO_4)_2$ (1:0.5)	46.2	47.9	4.18	+44.1	114	29.1	
C12O6	broad	broad	broad	-8.2	-8	8.8	
C12O6-LiBF ₄ (1 : 1)	47.2	49.2	4.3	+ 2.3	50-70	3.9	
C12O6-LiClO ₄ (1 : 1)	43.0	43.0	4.5	+ 1.6	50-70	16.1	

d = small-angle spacing, D = wide-angle spacing, $T_m =$ melting temperatures from DSC runs, $T_i =$ isotropic temperatures as observed by hot-stage polarised light microscopy, $\Delta H =$ heat of crystal side-chain melting per repeating unit.

substituent and the reduced probability of coalescence of adjacent side groups with increase in length of the intervening oligoether skeletal segment.

Thermal and X-ray data for polyethers and their complexes are summarised in Table 1.

Complexes of C16O5 and C16O6 with LiClO₄, and LiBF₄ and Mg(ClO₄)

Fig. 3 shows a polarised light optical micrograph of C16O6 \cdot LiClO₄ (1:1) in the liquid-crystal state at 55 °C. The texture shown is observed from ambient temperature until *ca*. 135 °C. The side-chain melting temperature is increased in the complex to 43.5 °C [see Fig. 1(b)], which is now identified as a crystal to liquid-crystal transition. The 'broken-fan' texture,



Fig. 3 Optical micrograph of C16O6 \cdot LiClO₄ (1 : 1) viewed between crossed polars at 55 °C (liquid state), scale bar = 20 μ m

which is typical of a smectic A system,⁶ is common to both crystalline and liquid-crystalline phases, but there is a loss in colour of the birefringence in the liquid-crystalline phase. The birefringence finally disappears at *ca.* 143 °C. The broadened wide-angle X-ray traces at temperatures above 43.5 °C [Fig. 4(a)] show that the endotherm marks the melting of the $-C_{16}H_{33}$ hexagonal lattice but the small-angle peak remains very sharp and intense throughout this transition. The textures of the C16O5 systems and the textures of the complexes of Mg(ClO₄)₂ with both C16O5 and C16O6 appear essentially identical to Fig. 3.

Following the discussions of the previous publication¹ concerned with $C16O5 \cdot LiBF_4$ (1:1), the structure of the $C16O5 \cdot LiClO_4$ (1:1) complex in the crystalline state at ambient temperature is illustrated schematically in Fig. 5. In the equimolar complexes, each Li⁺ ion is encapsulated within a single turn of the polyether helical backbone in which the five oxygen atoms are turned towards the helix axis. The model also features interdigitation of ranks of side chains from mutually inverted molecules of adjacent layers. The alkyl side chains become more disordered in the liquid-crystalline state. As Table 1 shows, the increase in the interlayer spacing, d, on passing from pure polymer to its complex, is accounted for by the space required to accommodate a layer of perchlorate ions (diameter = 4.72 Å).

The X-ray data show no evidence for regular spacing between helices (ca. 9 Å) within the same layer. In the schematic representation of Fig. 5, therefore, the 'end view' of the helices shows them not to be precisely collinear but randomly placed at slightly different levels within each molecular layer. This aspect of the structure of the layers is receiving closer investigation from electron density distribution studies.

This molecular model for the crystalline and liquidcrystalline states is seemingly appropriate for all the complexes of C16O5 and C16O6 with the Li⁺ salts studied so far. However, as Table 1 shows, the liquid crystal-isotropic temperatures for C16O5 \cdot LiClO₄ (1 : 1) and C16O6 \cdot LiClO₄ (1 : 1) determined by hot-stage polarised light microscopy, are considerably higher than in the other C16On-Li⁺ systems which all become isotropic over the range 70–100 °C. The ClO₄⁻ anion may perhaps be the most effective interlayer space-filler at higher temperatures. It is of interest that similar well organised smectic systems are also formed when LiBr is complexed with the C16On polymers in contrast with PEO LiBr which is a fully amorphous complex.



Fig. 4 X-Ray diffraction scans, small-angle to wide angle, $q = 4\pi(\sin \theta)/\lambda$: (a) C16O5 · LiClO₄ (1:1), 20 °C (----), 55 °C, (---), 143 °C (·····); (b) C16O5 · Mg(ClO₄)₂ (1:0.5), 20 °C (----), 55 °C (---), 135 °C (·····)

Fig. 6(a)-(d) shows higher resolution small-angle peaks at constant exposure time for LiClO₄ complexes with C16O5, C16O6 and C12O6 at 55 °C. The increasing peak width at half height clearly demonstrate that the C16O5 \cdot LiClO₄ (1:1) complex has the most extensive organised laminar texture and the C12O6 complex is the least organised.

In the (1:0.5) complexes with Li⁺ [(Fig. 6(b)] liquid-crystal phases are also formed above side-chain melting but slightly lower transition temperatures than for the corresponding (1:1) complexes are apparent in these cases (see Table 1). The organisation in these structures arises mainly from the sidechain interactions in forming the helical 'tube' rather than the templating effect of the cations which predominates in organised PEO complexes. In Fig. 7(a)-(d) the effect of LiBF₄



Fig. 5 Schematic diagram of the structure of C16O5 lithium salt (1:1) complexes at ambient temperature (below side-chain melting temperature), (+) Li^+ , (-) ClO_4^- , BF_4^- etc. d = spacing of smectic layers (see Table 1) (a) side view, (b) end view

content on the degree of organisation of C16O5 complexes at 55 °C is demonstrated. Liquid-crystal phases are present for complexes which are at least 'half-filled' with salt but C16O5 \cdot LiBF₄ (1:0.5) is less well organised than the complexes with more salt and C16O5 \cdot LiBF₄ (1:0.2) is clearly isotropic.



Fig. 6 X-Ray diffraction scans at constant time exposures, smallangle resolved, LiClO₄ complexes with (a) C16O5, (b) C16O5 (1:0.5), (c) C16O6, (d) C12O6



Fig. 7 X-Ray diffraction scans at constant time exposures, small-angle resolved. C16O5 \cdot LiBF₄ complexes (a) 1 : 0.8, (b) 1 : 1, (c) 1 : 0.5, (d) 1 : 0.2

The C16On \cdot Mg(ClO₄)₂ (1:0.5) complexes are isomorphous with the C16On \cdot LiX(1:1) complexes and although only half of the helical turns are accommodated by cations there are equal concentrations of anions in the interhelical spaces. The interlayer spacing is in excellent agreement with that of $C16O5 \cdot LiClO_4$ (1:1) (Table 1) and the broken-fan texture is as well defined as that of Fig. 3. The side-chain melting temperatures of the $Mg(ClO_4)_2$ complexes [see Table 1 and Fig. 1(g) and (h)] are also the same as those of the monovalent cations and the T_i is also high as in the other complexes with ClO₄⁻ anions. The X-ray tracings [Fig. 4(b)] indicate that the laminar helical structures in both $C16O5 \cdot Mg(ClO_4)_2$ (1:0.5) and the analogous C16O6 complex are extensive although close inspection of the halfheight widths of the small-angle peaks (not shown) suggest that the peak of $C16O5 \cdot Mg(ClO_4)_2$ (1:0.5) may be the narrower.

C12O6 · LiClO₄ (1 : 1) and C12O6 · LiBF₄ (1 : 1) complexes

A thermal analysis trace for the $C12O6 \cdot LiClO_4$ (1:1) complex is also shown in Fig. 1(f). The side-chain melting temperature increases to 1.6 °C in the complex. This temperature apparently also represents a crystal-liquid crystal transition. A glass transition at -5 °C is also apparent in Fig. 1(f). The textures of C12O6 \cdot LiClO₄ (1 : 1) in the liquid state, as viewed in the polarising microscope, have much poorer definition than that shown in Fig. 3 appearing as a bright, granular morphology. X-Ray investigation of the C12O6 LiClO₄ (1:1) complex at 20 °C indicates an interlayer spacing d = 42.7 Å. As may be seen in Fig. 5(d) the small-angle X-ray peak is significantly broader than in the liquid-crystal state of $C16O5 \cdot LiClO_4$ (1:1) and $C16O6 \cdot LiClO_4$ (1:1). We conclude from these observations that, while crystal and liquidcrystal states occur in the complexes of C12O6, these systems incorporate a significantly greater proportion of disorganised material than is present in the analogous C16O5 and C16O6 complexes. The disorder is presumed to arise from polymer chains having essentially random-coil backbone conformations as shown schematically in Fig. 8. Although the C_{12} alkyl side chains may coalesce together, the tendency towards intramolecular coalescence of adjacent substituents along the chain



Fig. 8 Schematic diagram illustrating the structure of C12O6 lithium salt complexes

and helical conformations is significantly less than in C16On systems.

The low proportion of organised material in C12O6 complexes is also reflected in the low heats of fusion for the side chains given in Table 1. C16O5 complexes have, generally, slightly lower ΔH values than those of C16O6 and either of the respective pure polymers [except in the case of C16O5 \cdot Mg(ClO₄)₂ (1:0.5)]. It seems that in the C16On systems the organisation of the side chains is influenced to a small extent by the cationic association with the helical substructure and that the relative heats of fusion do not necessarily reflect the extent of organisation of the two-dimensional laminar texture. The latter should be strongly dependent, for example, on the rigidity of the polyether salt adduct. However, the heats for C12O6 systems would seem to be too low to be accounted for alone by the 25% less of hydrocarbon material in the complexes.

Thus, it is concluded that for the three polymers under consideration the degrees of organisation of the complexes with lithium salts: laminar, helical material and random coil material, follow the sequence C16O5 > C16O6 > C12O6. As mentioned above, the laminar textures of both the C1605 and C1606 complexes with Mg(ClO₄)₂ are well organised with the former being perhaps the most extensive.

Ionic conductivity

Fig. 9 shows complex impedance plots Z' vs. Z'' for C16O5 · LiClO₄ (1:1) over a range of temperatures. In the crystalline state (36.3 °C) the semicircle is complete. Throughout the liquid-crystal state the semicircle is still apparent although becoming less complete with increasing temperature. The capacitive component of the complex impedance is thus evidence of the heterogeneity of the laminar texture. Since salt rapidly separates in the isotropic state of this system the corresponding complex impedance becomes highly scattered and is not shown here. However, for the C16O5 · LiBF₄ (1:1) complex reported previously⁷ the isotropic state (T > 89 °C) is evidenced by the virtual disappearance of the semicircle over a similar frequency range.

Fig. 10(a) shows log σ vs. 1/T for the three polymers C12O6, C16O6 and C16O5 complexed with LiBF₄ and Fig. 11 shows similar plots for LiClO₄ and Mg(ClO₄)₂ complexes. Conductivity plots for complexes of C16O5 with LiCF₃SO₃ and LiBr are shown in Fig. 12. Notwithstanding the high proportion of hydrocarbon material within the complexes, the highest conductivities approach those of the corresponding



Fig. 9 Complex impedance spectra of $C16O5 \cdot LiClO_4$ (1:1) at different temperatures in the frequency range 5 Hz-64 kHz

 $P(EO)_6$ LiX systems which are shown for comparison. An increase in conductivity at an inflection in the plots is apparent in the region of the crystal to liquid-crystal transition temperatures. Increases in gradient are apparent for C16On systems in the region 60-70 °C in LiClO₄, LiBr and LiCF₃SO₃ complexes and in the region 80-110 °C for LiClO₄ and LiBF₄ complexes, which temperature range includes the optically observed *T* for the latter.

In Fig. 10(b) conductivity plots for C16O5: LiBF₄ (1:1) having polymer molar masses 115000 and 5000 g mol⁻¹ are compared. It is clear that the polymer molecular weight has little influence on the conductivities (X-ray analysis also shows very little difference in the organisation of these materials). This shows that the conductivities depend on the organisation of the materials and that the translation of low molecular complexes is playing an insignificant part in the conductivity behaviour.

With LiBF₄ and LiClO₄ [Fig. 10(a) and (11)] the conductivities of the $CmOn \cdot LiX(1:1)$ complexes in the liquid-crystal and liquid-isotropic phases follow the sequence: C16O5 > C16O6 > C12O6. This might be considered contrary to expectation on the basis of a simple structural model in which conduction is impeded by the ionophobic hydrocarbon material and promoted by longer ethoxy sequences as in the amorphous PEO systems. In such a model the complexes



Fig. 10 (a) $\log \sigma vs. 1/T$: C16O5 · LiBF₄ (1 : 1) (■), C16O5 · LiBF₄ (1 : 0.8) (★), C16O5 · LiBF₄ (1 : 0.5) (●) LiBF₄ · C16O5 (1 : 0.2) (+), C16O6 · LiBF₄ (1 : 1) (□), C16O6 · LiBF₄ (1 : 0.5) (○), C12O6 · LiBF₄ (1 : 1) (□), P(EO)₆ · LiBF₄ (---). (b) $\log \sigma vs. 1/T$: C16O5 · LiBF₄ (1 : 1) molar mass 115 000 g mol⁻¹ (●), C16O5 · LiBF₄ (1 : 1) 115 000 g mol⁻¹ (■).

with C12O6 should give rise to the higher conductivities. However, the observed sequence clearly shows that the most organised of the liquid systems, the C16O5 complexes, provides the most conductive pathways and the most disorganised, the C12O6 systems, is the least conductive.

The experiments suggest that the higher conductivities of

the C16O5 systems arise from ions or ion aggregates moving in the relatively unimpeded two-dimensional spaces between the helices in the laminar texture as shown in Fig. 5. The lower conductivities of the C12O6 complexes suggest that ion 'tunnelling' through the hydrocarbon material is not an important process.



Fig. 12 Log σ vs. 1/T: C16O5 · LiCF₃SO₃ (1:1) (●), C16O5 · LiCF₃SO₃ (1:0.5) (□), C16O5 · LiBr (1:1) (■), P(EO)₆ · LiCF₃SO₃ (---) (data from ref. 8)

The steep increases in conductivity which are apparent in log σ vs. 1/T plots for the lithium salt complexes coincide with side-chain melting and the crystal to liquid-crystal transition. However, in the magnesium salt complexes the crystal to liquid-crystal transition occurs at the same temperature (42-44 °C, see Table 1) as in the lithium salt complexes but the steep conductivity increase occurs at a significantly higher temperature (ca. 55 °C). Thus the steep increases in conductivities shown in Fig. 10(a) and (b), 11 and 12 may signify 'ionloosening' within the two-dimensional spaces rather than the creation of new conducting pathways, such as tunnelling through the alkyl layers in the material. (There is no indication of an exotherm at ca. 55 °C in the Mg(ClO₄)₂ complexes; this may perhaps arise from compensating exothermic processes such as cation-anion associations). Presumably, anion mobility predominates, as in PEO, but one may speculate that the Li⁺ ... ethoxy bonds have a similar degree of lability in the helical environment of these CmOn polymers as in the random coil environment of the corresponding PEO systems. The C16O5 \cdot Mg(ClO₄)₂(1:0.5) system has a conductivity which is between one and two orders of magnitude below that of the corresponding LiClO₄ system. Assuming that, as for $PEO \cdot Mg(ClO_4)_2$ systems,⁹ this is essentially a pure anion conductor, then a degree of lability in the $Li^+ \cdots C1605$ association is implied, notwithstanding the helical organisation. However, the C16On \cdot Mg(ClO₄)₂ systems differ from the lithium salt complexes in that the system with C16O6 is more conductive than for the one with C16O5 in the liquid phases. Since the X-ray data reveal little difference in the laminar organisation of these systems the greater conductivity may signify a weaker association of ions with the larger C16O6 polyether helix.

Fig. 10(a) shows conductivity data for C16O5 · LiBF₄ complexes with composition (1 : 0.2), (1 : 0.5) and (1 : 0.8). The first mentioned does not form a liquid-crystal phase above sidechain melting (40.3 °C) whereas the last forms a stable liquid crystal phase with $T_i = 85$ °C. In accord with the above discussion for lithium salt complexes the more organised system is the more conductive being close to the plot for the (1 : 1) complex. The system (1 : 0.5) is apparently liquid crystalline above side-chain melting but its conductivity is similar to the (1 : 0.2) system so that presumably the degree of order is not great.

The organised polymer complexes discussed in the present work would seem to demonstrate a novel architecture for ion migration, at least as far as organic polymer matrices are concerned. Since the conducting pathways are confined to two dimensions, comparison of the ionic mobilities with those within the three-dimensional random coil networks of more conventional polymer electrolytes is not straightforward. However, these materials may also be deposited as monomolecular or multimolecular layers by the Langmuir–Blodgett technique¹⁰ which should enable determination of the anisotropy of conduction along and between the laminar structures. Further work on the structure and electrical properties of both bulk and LB-deposited complexes is in progress.

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 $P(EO)_6 \cdot LiClO_4 (---)$

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