Synthesis of Crown Ether Polymers Incorporating 12- and 13-Membered Tetraoxa Rings Linked to Poly(propylene Oxide) and Poly(phosphazene) Backbones and Behaviour of the Lithium-doped Materials

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The synthesis of a set of 12- and 13-membered crown ether polymers is reported. An oxyethylene chain separates the macrocyclic ring from either a poly(propylene oxide) or a poly(phosphazene) backbone. Addition of Li^+ ions to these amorphous polymers and the related poly(methacrylate) polymers results in increases in T_g and the 12-O_4 polymers show the largest increases. This behaviour is correlated with changes in the ^{13}C NMR spectra of the polymers as Li^+ is added, and the relative sensitivity of the 12-O_4 polymers is related to their enhanced tendency to form 2:1 complexes (ring:Li^+). Parallel observations were found on examination of the ionic conductivities of the lithium-doped materials, with the 13-O_4 polymers showing lower conductivities and in the polypropylene oxide-based polymers the backbone did not contribute significantly to the overall charge transport.

Lithium-doped amorphous polymeric materials that possess high ionic conductivity at ambient temperatures continue to be investigated in detail because of the variety of applications that may result from the development of an all solid-state, rechargeable 'lithium-based' battery.[1] The archetypal polymer for this application is poly(ethylene oxide) (PEO) which when doped with $LiClO_4$ or $LiCF_3–SO_3$ possesses high ionic conductivity above its glass-transition temperature (T_g). The high levels of conductivity only occur at elevated temperatures and it is believed that the dopant lithium ions cross-link different PEO chains reducing polymer segmental motion leading to an elevated T_g and a reduced ionic mobility. Various strategies have evolved in order to enhance ionic conductivity at lower temperatures, including the addition of low molecular weight plasticising agents or functionalisation of the polymer backbone with suitable cation-solvating side-chains. Although overall charge transport involves the mobility of both the anion and the cation (thus 'non-co-ordinating' anions such as triflate or perchlorate are preferred to inhibit ion-pairing), most work has focussed on the nature of cation solvation in the amorphous polymer. Given that in PEO conductivity was found to be highest at an oxygen to lithium ratio of 8:1, it was originally postulated[1] that this may correspond to a situation where four oxygens are involved in Li^+ complexation with a similar four-oxygen site vacant, on average. With this in mind and with reference to the well-defined tendency of 12-, 13- and 14-membered tetra-oxa crown ethers to form complexes with the Li^+ ion, we and others have been studying the effect of introducing such crown-ether moieties into polymeric systems.[2–5]

A series of 12-, 13- and 14-membered 'crown-ether' polymers was prepared in which a poly(methacrylate) backbone was functionalised with the various tetraoxa rings, spaced out by a simple alkyl or oxyethylene chain.[2,3] For a given glass-transition temperature, the 12-ring materials showed higher ionic conductivities than the corresponding 14-ring systems and this was rationalised in terms of a faster rate of Li^+ exchange in the 12-ring series perhaps coupled with an enhanced tendency of the 12-ring systems to form 2:1 (L:M) complexes, thereby promoting more effective counterion separation.

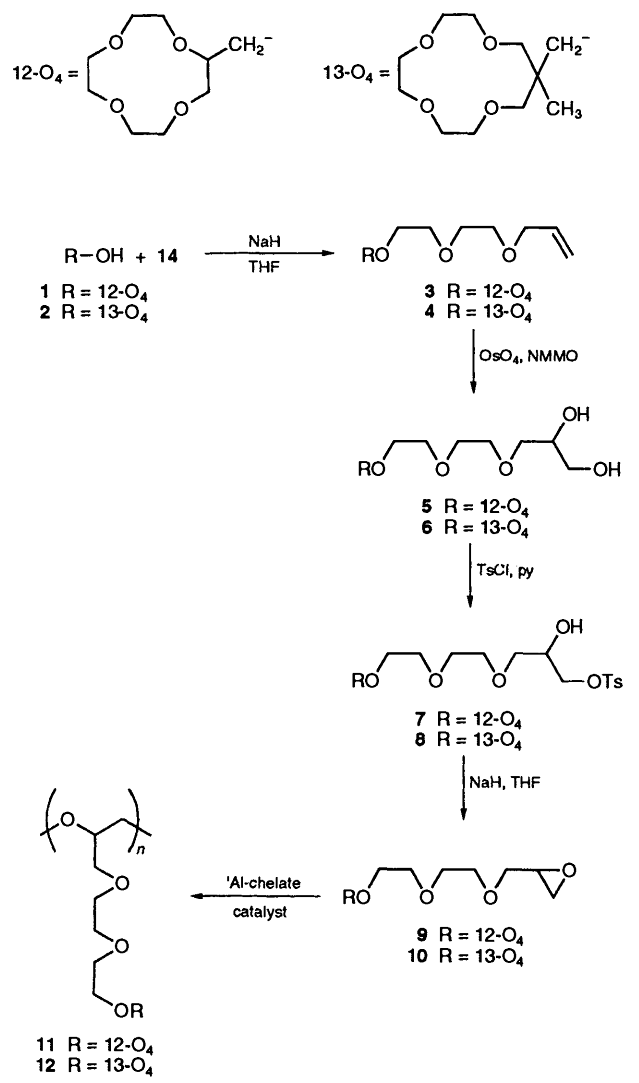
Ionic conductivity is an activated process and is a sensitive function of temperature and of the glass-transition temperature of the material. In the standard Vogel–Tammann–Fulcher equation [eqn. (1)], which is an empirical relationship based upon free-volume theory, the measured conductivity is dependent upon the concentration of charge carriers (anions and cations) and on the temperature (T_o is an ideal glass transition temperature).

$$\sigma = AT^{-\frac{1}{2}}\exp\{-E_a/K(T - T_o)\} \qquad (1)$$

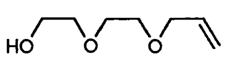
Transport is also an activated process and this is reflected in the dependence on E_a which is an activation energy term related to the energy barrier for ion migration. Accordingly, what is required for high ionic conductivity is a material that possesses a low glass-transition temperature, and wherein T_g does not increase markedly as the dopant lithium concentration increases. With this in mind we have synthesised a series of polymers with either poly(propylene oxide) or poly(phosphazene) backbones incorporating 12-and 13-O_4 crown ether rings, and investigated the variation of T_g with dopant lithium concentration in parallel with some ^{13}C NMR studies of the complexation process and with reference to the ionic conductivities of the doped materials.

Results and Discussion

Syntheses.—The macrocyclic starting materials for the monomer synthesis were the alcohols **1** and **2**.[2,6] Introduction of the spacing oxyethylene chain was achieved by reaction of **1** or **2** with the toluene-*p*-sulfonate **14** (itself prepared from the monoallyl ether **13**) in THF in the presence of NaH to give the allylic ethers **3** and **4** (Scheme 1). Oxidation to the corresponding 1,2-diols **5** and **6** was achieved using *N*-methylmorpholine oxide catalysed by the presence of OsO_4 and conversion into the corresponding epoxide monomers **9** and **10** involved the intermediacy of the rather labile monotoluene-*p*-sulfonates **8** and **9**. As has been noted by other workers,[7] although this route is not the most direct for synthesising the desired epoxides, it is the most practicable. For example when **3** and **4** were reacted directly with either *m*-chloroperbenzoic and/or magnesium monoperoxyphthalate although **9** and **10** were formed (in *ca.* 55 and 60% yield, respectively) they were contaminated with significant amounts of the related methyl ketone, formed by a formal hydride shift. These impurities



Scheme 1



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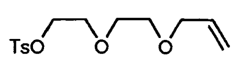

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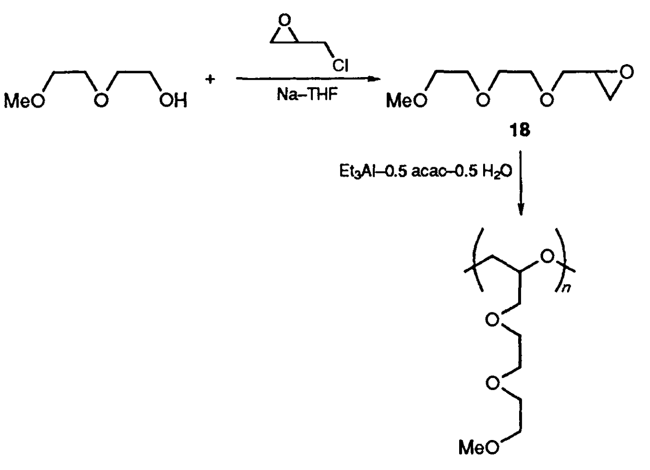
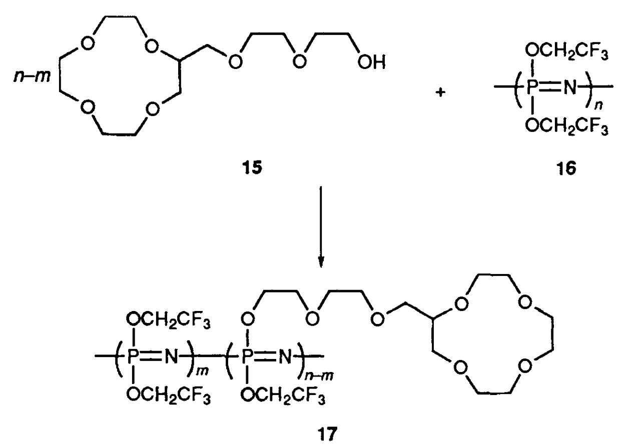
proved difficult to separate. Polymerisation of the epoxides **9** and **10** was undertaken according to a literature procedure using an ill-defined Lewis-acidic aluminium chelate catalyst,[8] prepared by reaction of Et_3Al with 0.5 equiv. of water and acetylacetone. The resultant polymers **10** and **11** (obtained in 67 and 58% yield, respectively, after purification), were purified by successive precipitation into hexane. The polymers obtained contained no traces of aluminium and the 12-O_4 polymer **11**, had a relatively low T_g (−43 °C) with a molecular weight (M_n) of 77 200, as measured by GPC in aqueous sodium nitrate against PEO standards. The 13-O_4 polymer, **12**, possessed a lower molecular weight (M_n = 29 500), and a similar glass transition temperature (T_g = −36 °C). For purposes of comparison, the acyclic epoxide 1,2-epoxy-4,7,10-trioxaundecane **18** was prepared by reaction of the sodium salt of the monomethyl ether of diethyleneglycol with epichlorohydrin, followed by polymerisation as described above (Scheme 2), to yield poly(**18**) as a soft gel (T_g = −69 °C, M_n = 29 300).

In order to prepare a poly(phosphazene) analogue, the extended-chain 12-O_4 alcohol, **15**,[2] was converted into the sodium alkoxide (NaH, THF) and was reacted in THF with poly[bis(1,1,1-trifluoroethoxy)phosphazene], **16**, prepared according to the method of Allcock.[9] The resultant polymer, **17**, Scheme 3, was a viscous oil (T_g = −34 °C, M_n = 49 000) and



Scheme 2



Scheme 3

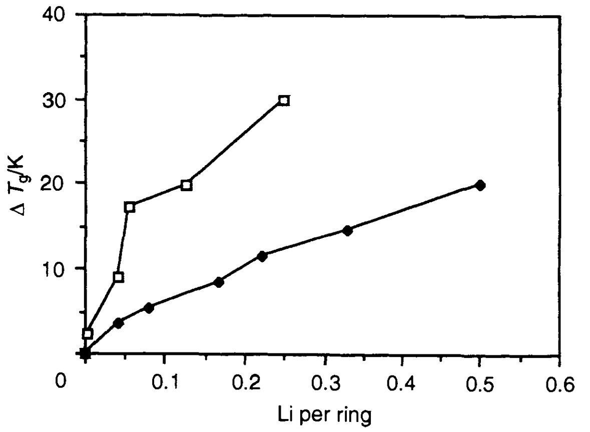


Fig. 1 Variation of T_g with added $LiCF_3SO_3$ for the 12-O_4 based polymer, **11** (□) and for the 13-O_4 polymer, **12** (◆)

combustion analysis revealed that it was 69 ± 5% functionalised with the desired macrocyclic moieties.

Li^+ *Complexation Studies.*—Addition of anhydrous lithium trifluoromethanesulfonate (lithium triflate) to the polymers **11** and **12** results in an increase in the glass-transition temperature (Fig. 1). For the 12-O_4 ring system there was a sharp increase in T_g at very low added Li^+ levels (0.01–0.04 Li^+ per ring) and the increase in T_g is clearly more sensitive to the amount of added lithium than with the 13-O_4 polymer. Similar behaviour (Fig. 2) is observed with the 12-, 13- and 14-O_4 methacrylate-based polymers, **19**, **21** and **20** (prepared as described in ref. 2). These are consistent with the formation of a number of 2:1 (12-

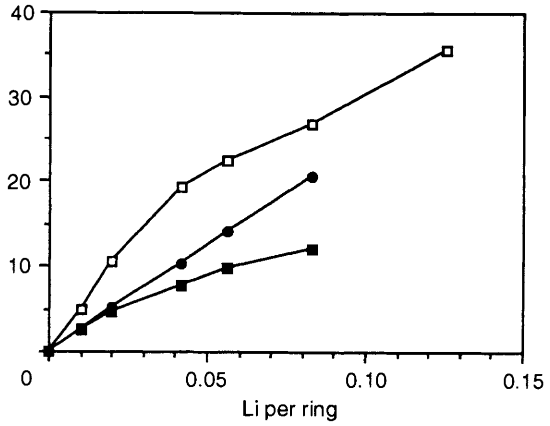
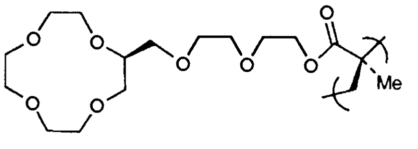


Fig. 2 Variation of T_g with added $LiCF_3SO_3$ for the poly(methacrylate) crown materials incorporating 12-O_4 (□) **19**; 13-O_4 (●) **21**; 14-O_4 rings (■) **20**



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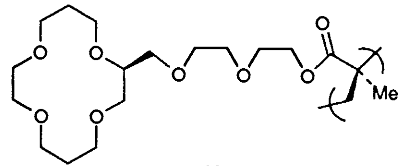

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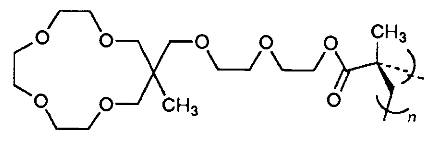

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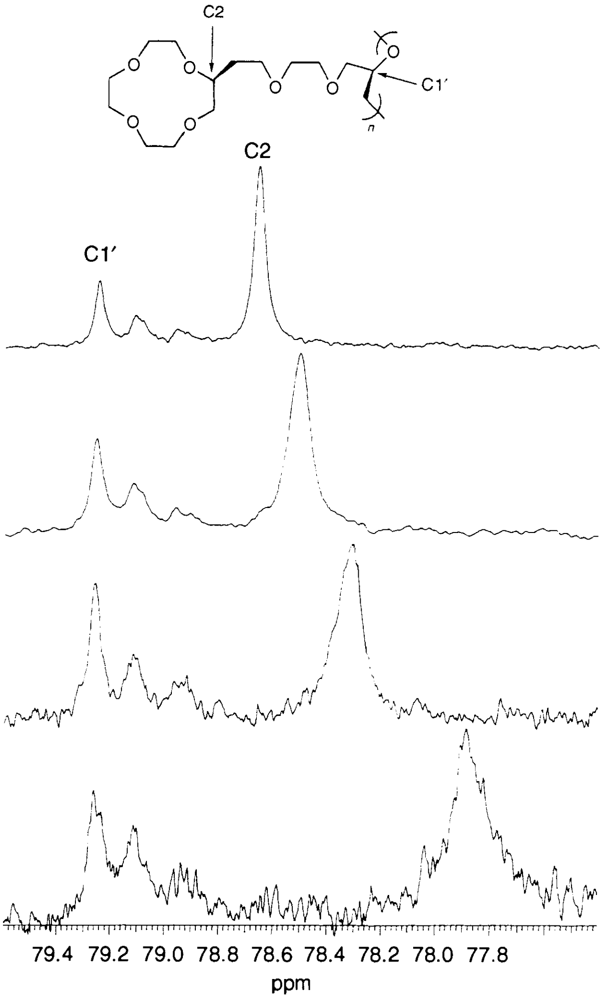


Fig. 3 ^{13}C NMR spectrum of **11** (CD_2Cl_2; 293 K) showing changes in the ring (*ca.* 78 ppm) CHO and 'backbone' CHO resonances as $LiCF_3SO_3$ is added (0, 0.01, 0.02, 0.043 Li^+ per ring)

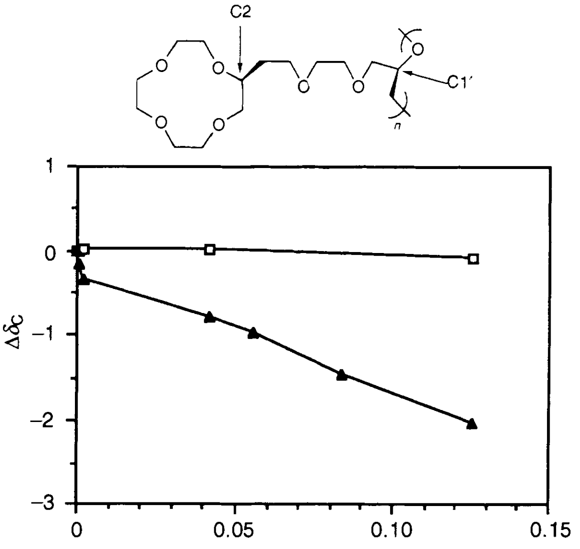
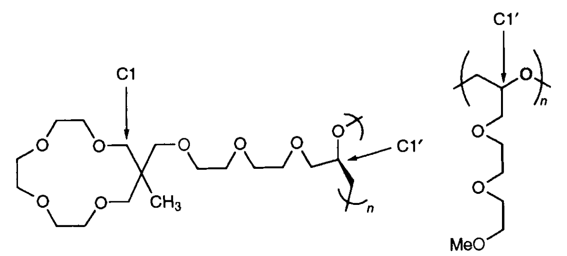


Fig. 4 Variation of the ^{13}C NMR chemical shift of the ring (▲) and 'backbone' (□) CHO resonances in **11** as $LiCF_3SO_3$ is added

O_4 ring:Li^+) complexes in the polymer matrix which serve to increase the degree of order in the polymeric chains, either through cross-links between chains or within individual chains. For the 14-O_4 system in particular (Fig. 2), lithium complexation occurs preferentially in a 1:1 manner, and there is relatively little change in the ring or polymer conformation accompanying Li^+ binding. Indeed, it is well established that in monomeric systems, Li^+ binds in the plane of a 14-O_4 ring,[10] whereas it tends to form 2:1 complexes with a 12-O_4 macrocycle.[11]

The changes in the ^{13}C NMR spectrum of **11** and **12** that occur upon sequential addition of lithium triflate were monitored (CD_2Cl_2 solution 293 K). Addition of Li^+ ions to **11** (in the range 0.01–0.125 Li^+ per ring) caused an immediate shift and broadening in the ring C2 'CHO' resonance (Figs. 3 and 4). Thus at 0.125 Li^+ per 12-O_4 ring, the C2 ring resonance had shifted to lower frequency by 2 ppm and its line width had broadened from 4 Hz to 27 Hz. At the same time, the polymer backbone CHO resonance, C1, remained unchanged (both in δ_C and in $\omega_{\frac{1}{2}}$) indicating that the Li^+ ions were being preferentially complexed by the macrocyclic binding site. This effect is illustrated in Fig. 4 for a dopant Li^+ level of 0.01 to 0.42 cations per macrocycle. Similar effects were seen with **12**: addition of Li^+ ions up to a dopant level of 0.5 (Li^+ per ring) caused no significant change in the chemical shift of the backbone CHO resonance. Beyond this level, which represents a 50% occupancy of the available macrocyclic binding sites, the chemical shift of the backbone methine, CHO, did change and at a Li^+ dopant level of one ion per ring, $\Delta\delta_{C1}$ was 0.38 ppm, associated with a significant increase in its linewidth (Fig. 5). These observations again may be interpreted in terms of



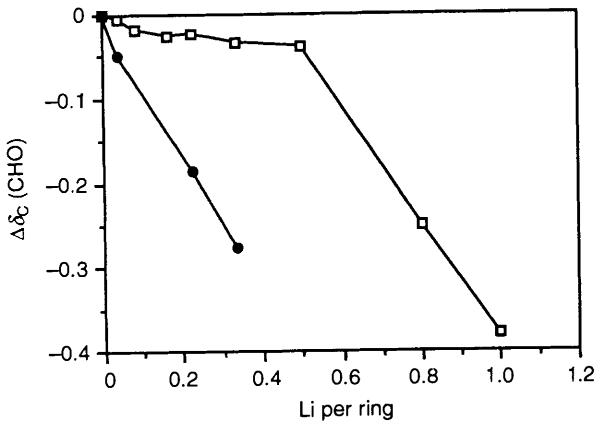


Fig. 5 Variation of the ^{13}C NMR chemical shift for the 'backbone' CHO resonances (C1′) in **12** (□) and poly(**18**) (●) with added lithium concentration (Li$^+$ per ring is equivalent to Li$^+$ per four oxygens)

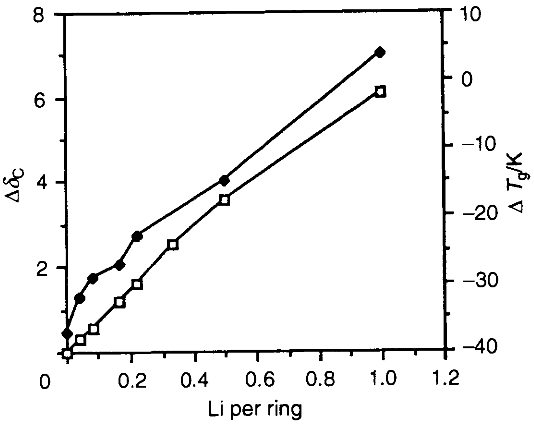


Fig. 6 Correlation of the change in T_g (◆) and the shift in the ^{13}C NMR resonance (□) of the C1 ring carbon (CH_2O) with added lithium concentration for the polymer **12**

preferential solvation of Li$^+$ by the ring oxygens, and suggest that with this 13-O_4 ring system also, some degree of 2:1 complexation may be occurring given that the onset of binding to the oxygens of the PEO chain is only apparent at Li$^+$: ring ratios of greater than 0.5.

As a control experiment, lithium triflate was added to the acyclic polymer, poly(**18**), and as soon as the Li$^+$ ions were added, the backbone CHO resonance shifted to a significantly lower frequency (Fig. 5).

When the variation of T_g with lithium dopant level for **12** is compared with the change in the ^{13}C NMR chemical shift of a ring carbon, it is evident that the two phenomena follow a similar trend (Fig. 6). Whilst this correlation may be interpreted in different ways, it is tempting to speculate that the increase in T_g observed with the 13-O_4 polymer (and also the 12-O_4 polymer, **11**) may be directly related to the degree of chain 'cross-links' associated with the formation of 2:1 complexes. Of course the spacing oxyethylene chain may also offer lower affinity sites for Li binding, thereby creating another mechanism for intrachain cross-linking leading to enhanced T_g values. Other possible causes of an elevation in T_g with added salt include 'anion'-based cross-links, where the anion bridges two two-cation binding sites. Furthermore, a general rigidification of the polymer chains is likely to be associated with a reduction in the flexibility of the cycles and the spacing groups following ion binding.

Ionic conductivities of the lithium-doped materials over a range of salt concentrations varying O:Li from 250:1 to 12:1 (for the crown-polymers, ring oxygen to Li$^+$ only) have been measured over the temperature range 10–140 °C and from −20 to +120 °C for poly(**18**), using standard ac impedance spectroscopic methods in the frequency range 1–100 kHz. Maximum conductivities at ambient temperatures were obtained at a dopant level of 18:1 with modest conductivities for the crown ether polymers, but much higher values for the acyclic polymer poly(**18**) (Fig. 7). This is simply a consequence of the much lower T_g values found with lithium doped poly(**18**). In a 'reduced conductivity' plot the strong dependence of σ on T_g may be accounted for adequately. In such a plot of $\log(\sigma T^{\frac{1}{2}})$ *vs.* $1/(T - T_o)$ where $T_o = T_g - 60$ K (Fig. 8), the 12- and 13-O_4 polypropylene oxide polymers are compared with the 12-, 13- and 14-O_4 methacrylate polymers studied previously by us.[2,3] For the 12-O_4 methacrylate and propylene oxide polymers virtually indistinguishable behaviour was observed reflecting the absence of any involvement in charge transport for the respective backbone moieties. This strongly indicates that the backbone oxygens in the epoxy-polymers play no part in lithium solvation as was suggested by the ^{13}C NMR results.

The conductivity of the lithium-doped [13]-poly(propylene oxide) was significantly lower than that of the 12-O_4 analogue (approximately by an order of magnitude), and this was a greater difference than was found in the methacrylate series. The lower conductivity in the 13-ring series of polymers compared to the 12-analogues may reflect the reduced tendency of the 13-rings to form 2:1 complexes. This tendency for 2:1 complex formation leads to better anion–cation separation than is the case for a 1:1 complex where the counterion may still bind strongly (*e.g.*, in an 'axial site' when the four ring oxygens occupy coplanar positions) and hence higher conductivities are expected associated with improved ionic mobilities. The lower conductivities of both of the 13-O_4 polymers may additionally be related to the absence of a binding interaction with the oxygen that is β to the ring (in contrast with the favourable interaction which may occur with the 12- and 14-O_4 polymers **19** and **20**).[2,3] The exocyclic β-oxygen in the 13-ring polymers is attached to a quaternary carbon centre on the C-3 fragment of the ring, and ligation to lithium, if occurring at the same time as binding to the four-ring oxygens, creates a rather strained bicyclic chelate.

For all of the crown polymers the slope of the reduced conductivity plots are similar reinforcing the conclusion that, at these salt concentrations, the oxygens in the backbones play no significant part in lithium solvation. The acyclic polymer poly(**18**) gave a lower slope (Fig. 8), and this difference was found to be more pronounced at lower salt concentrations. Such behaviour supports the notion of stronger binding of lithium by the rings than is the case with the acyclic model polymer, and also indicates that there is a greater 'effective' activation energy for the migration of ions between crown binding sites which impedes ionic mobility.

Further comparative studies, detailing the ionic conductivity of these materials as a function of dopant lithium concentration (and its variation with polymer T_g) will be reported subsequently.

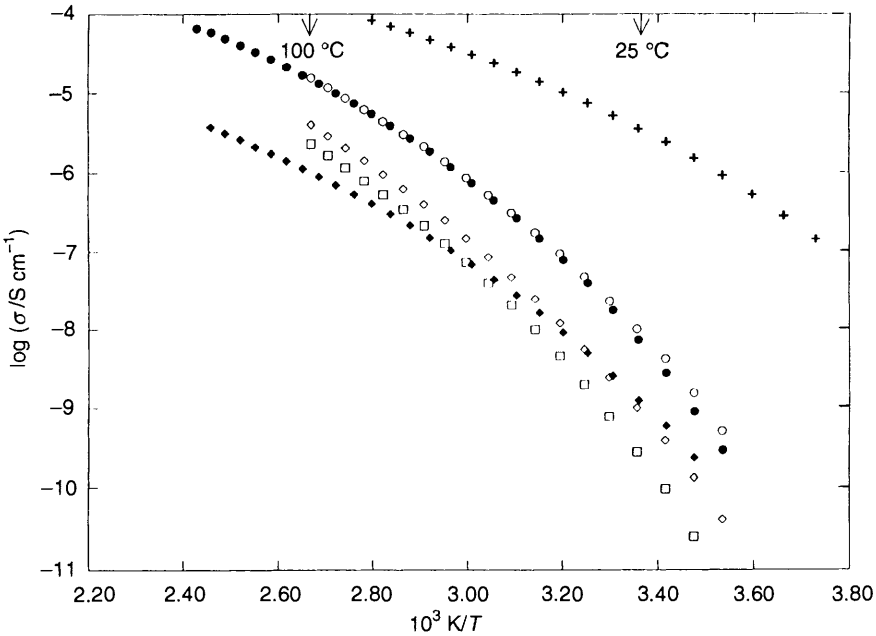


Fig. 7 Variation of the logarithm of ionic conductivity with $1/T$ for polymer: $LiCF_3SO_3$ mixtures at 18:1 (ring O:Li) ratio; (◇) **21**, (□) **20**, (○) **19**, (●) **11**, (◆) **12**, (+) **(18)**$_n$

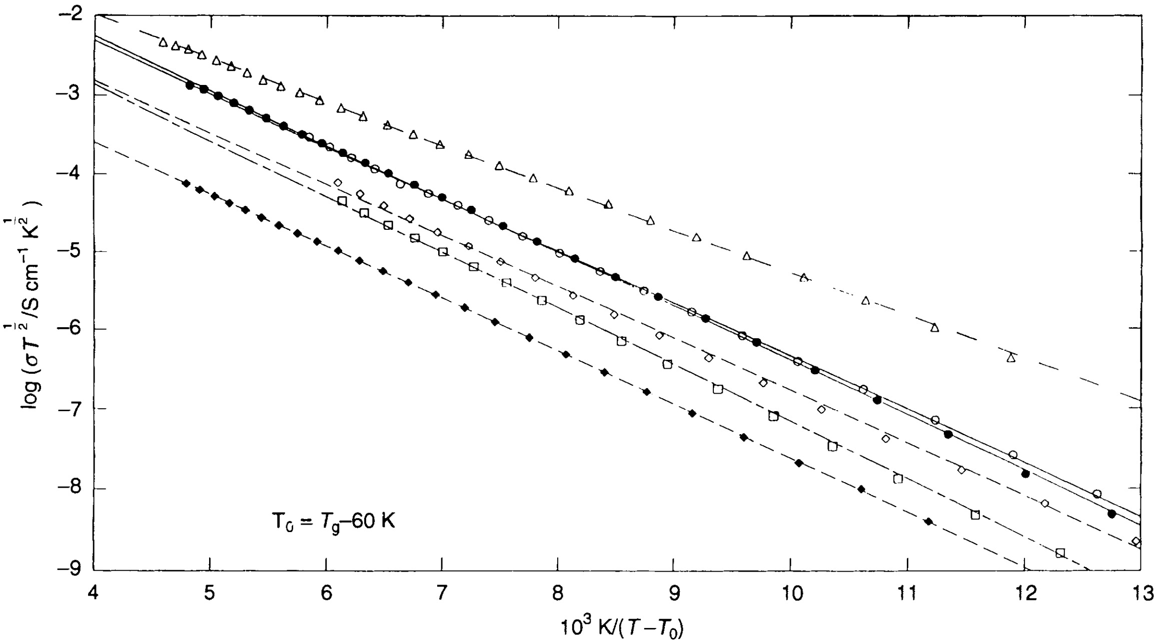


Fig. 8 Variation of conductivity with $T^{-\frac{1}{2}}$ in lithium-doped polymer–salt mixtures (18:1 ring O:Li), allowing for the effect of T_g; (○) **19**, (◇) **21**, (□) **20**, (●) **11**, (◆) **12**, (△) **(18)**$_n$

Experimental

General procedures and instrumentation are as reported in ref. 2, and compounds **1** and **2** were prepared as described in refs. 2 and 3.

The NMR experiments involving sequential additions of a lithium salt were carried out as follows. Approximately 0.1 g of polymer was accurately weighed into a preweighed 10 cm^3 flask equipped with a stirrer bar. CD_2Cl_2 was then added and after being stirred to dissolve the polymer, the solution was transferred to a 5 mm NMR tube and the ^{13}C NMR spectrum (100 MHz) acquired. The solution was then washed back into the flask with more dichloromethane and the solvent was allowed to evaporate off under a stream of dry nitrogen to leave the polymer which was dried at 40 °C, < 0.01 mmHg to constant mass. The flask was re-weighed, and the amount of lithium trifluoromethanesulfonate required to give the desired O:Li ratio (counting only the O atoms in the ring, *i.e.*, 4 per repeat unit) was added *via* pipette, as a 0.1% solution in acetone. The acetone was evaporated off under a stream of nitrogen and the flask again dried under vacuum to constant mass. A small sample (*ca.* ~3 mg) was removed for differential scanning calorimetric analysis and the rest dissolved again in CD_2Cl_2 for NMR measurement. This was repeated for each different O:Li ratio, taking account each time of the contribution of the salt to the mass of the repeat unit.

At the higher salt concentrations (above 8:1) the polymer did not dissolve completely in CD_2Cl_2 so a vortex plug was used to maintain an even distribution of the gel in the NMR tube.

For the acyclic polymer the salt level used was calculated by assuming that it had the same mass as the 12-O_4 polymer.

Aqueous GPC was done using 1.0 mol dm^{-3} sodium nitrate solution, buffered to pH 7.0, as the eluent through a PL aquagel-OH 50 column using methanol as a flow marker. The detector was a Knaur differential refractometer and calibration was against poly(ethylene oxide) standards. The chloroform system used a Waters 590 pump and R401 differential refractometer with three columns in series–PL gel 5μ 100 A, 1000 A and 1 × 10^5 A. The flow marker was toluene and calibration was against polystyrene standards.

Ionic conductivities were measured by alternating current impedance spectroscopy as described in refs. 2 and 3.

3,6-*Dioxanon*-8-*en*-1-*ol* **13**.—A 1 dm^3 flask fitted with condenser, dropping funnel and nitrogen inlet was flushed with nitrogen and then charged with diethylene glycol (50 g, 0.47 mol), sodium hydroxide (24 g, 0.6 mol), tetrabutylammonium hydrogensulfate (1.45 g, 4.3 mmol) and dry THF (300 cm^3).

Allyl bromide (40 cm^3, 55.9 g, 0.46 mol) in THF (160 cm^3) was added slowly and the mixture heated to reflux for 3 h. It was then cooled, filtered and the volatiles removed to leave a brown oil. This was dissolved in water (600 cm^3) which was washed with toluene (2 × 150 cm^3) and the organic fraction concentrated to give a residue which was distilled under vacuum through a 20 cm Vigreux column to give a colourless oil (b.p. 59–60.5 °C, 0.35 mmHg, 35.1 g, 51%) (Found: C, 57.5; H, 9.65. $C_7H_{14}O_3$ requires: C, 57.5 and H, 9.83%); δ_H(CDCl$_3$) 6.02–5.63 (1 H, m, CH), 5.34–5.15 (2 H, m, =CH$_2$), 4.04–4.01 (2 H, m, OCH_2CH=), 3.80 (1 H, br s, OH) and 3.73–3.56 (8 H, m, CH$_2$O); δ_C(CDCl$_3$) 134.9, 117.5, 73.0, 72.4, 70.6, 69.7 and 61.7.

3,6-*Dioxanon*-8-*en*-1-*yl Toluene*-p-*sulfonate* **14**.—The alcohol **13** (20 g, 0.137 mol) was placed in a 500 cm^3 conical flask with pyridine (200 cm^3) and cooled to −20 °C in dry ice–acetone. Tosyl chloride (28.77 g, 0.151 mol) was added slowly with stirring, keeping the temperature at −20 °C. When all the solids had dissolved, the flask was sealed and kept at −20 °C for 3 days, after which the contents were poured onto ice (1 dm^3) which was then acidified with conc. HCl (300 cm^3). This was extracted with dichloromethane (2 × 150 cm^3) and these extracts were combined and washed with 2 mol dm^{-3} HCl (3 × 50 cm^3), sat. NaHCO$_3$ (2 × 50 cm^3) and water (2 × 50 cm^3) before being concentrated to a yellow oil (40.12 g, 97.6%); δ_H(CDCl$_3$) 7.79 (2 H, d, *J* 8.3, ArH), 7.34 (2 H, d, *J* 8.3, ArH), 6.00–5.78 (1 H, m, =CH–), 5.33–5.13 (2 H, m, =CH$_2$), 4.20–4.15 (2 H, m, –CH$_2$OSO$_2$–), 4.05–3.95 (2 H, m, CH_2CH=) and 3.71–3.50 (6 H, m, CH$_2$O); δ_C(CDCl$_3$) 145.3 (C–S), 135.1 (C=), 133.4 (*C*–CH$_3$), 130.3 (ArC), 128.4 (ArC), 117.5 (C=), 72.6, 71.2, 69.8, 69.1 (CH$_2$O) and 22.0 (CH$_3$); *m*/*z* (dci) 401 (M$^+$ + 1, 100%) (Found: C, 41.6; H, 5.3. $C_{14}H_{20}SO_5$ requires: C, 42.0; H, 5.00%).

2-(2,5,8-*Trioxaundec*-10-*enyl*)-1,4,7,10-*tetraoxacyclododecane* **3**.—A two-necked 100 cm^3 flask was charged with the 12-O$_4$ alcohol **1** (5.00 g, 24.3 mmol), and the sulfonate, **14** (8.00 g, 26.7 mmol), fitted with a septum and a condenser and the system was dried at 50 °C, > 0.1 mmHg. The system was filled with argon and then THF (30 cm^3) and sodium hydride (0.96 g, 40 mmol) were added. The mixture was refluxed under argon for 3.5 h, cooled and then 2 mol dm^{-3} HCl (20 cm^3) was added slowly down the condenser to give a brown solution. The volatiles were then removed on a rotary evaporator and the residue taken up in dichloromethane (60 cm^3)–water (15 cm^3). Aqueous sodium hydroxide was added until the pH was > 10, the organics were separated and the aqueous phase was extracted with more dichloromethane (2 × 60 cm^3). The combined organic extracts were then washed with water (25 cm^3) and concentrated to a brown oil (8.98 g). This was purified by column chromatography (alumina; 1:1 hexane–dichloromethane changing to 2% methanol in dichloromethane) to yield a pale brown oil (6.54 g, 81%) (Found: C, 57.4; H, 9.19. Calc. for $C_{16}H_{30}O_7$: C, 57.5; H, 9.04%); δ_H(CDCl$_3$) 6.02–5.82 (1 H, m, CH=), 5.83–5.64 (2 H, m, =CH$_2$), 4.05–4.00 (2 H, m, CH_2CH=) and 3.92–3.45 (25 H, m, CH$_2$O and CHO); δ_C(CDCl$_3$) 134.5 (C=), 116.8 (C=), 78.3 (CHO), 72.0, 71.4, 71.1, 70.63, 70.60, 70.40, 70.39, 70.36, 70.33, 70.1, 69.9 and 69.1 (CH$_2$O); *m*/*z* (ammonia CI) 352 (M$^+$ + 18, 98%), 335 (M$^+$ + 1, 48), 56 (43) and 44 (100).

2-(10,11-*Dihydroxy*-2,5,8-*trioxaundecyl*)-1,4,7,10-*tetraoxacyclododecane* **5**.—This preparation was carried out according to the procedure of Gokel.[7]

A 25 cm^3 conical flask was charged with the alkene **3** (5.50 g, 19.5 mmol), acetone (6.3 cm^3), water (4.0 cm^3), *N*-methylmorpholine *N*-oxide (2.52 g, 21.5 mmol) and a 2.5% w/v solution of osmium tetraoxide in *tert*-butyl alcohol (0.6 cm^3). The flask was stoppered and the contents stirred for 18 h. Sodium sulfite (2.0 g) was added and after a further 1 h, acetone (50 cm^3) was added. The mixture was filtered through Celite and concentrated to a brown oil. Water (10 cm^3) was added to the residue and the pH adjusted to < 2 with 2 mol dm^{-3} HCl. It was found that the diol could not be extracted into dichloromethane so all the volatiles were removed under vacuum to give a brown oil (8.49 g) which was purified by column chromatography (alumina; 0–15% methanol in dichloromethane) to yield a colourless oil (5.63 g, 78%) (Found: C, 52.7; H, 8.65. Calc. for $C_{16}H_{32}O_9$: C, 52.2; H, 8.75%); δ_H(CDCl$_3$) 3.92–3.30 (32 H, m); δ_C(CDCl$_3$) 78.3 (CH), 72.6 (CHOH), 71.4, 71.1, 70.67, 70.59, 70.52, 70.42 (3 C), 70.38, 70.28 (2 C), 70.1, 69.8 (CH$_2$O) and 63.7 (CH$_2$OH); *m*/*z* (CI) 386 (M$^+$ + 18, 56%), 369 (M$^+$ + 1, 100), 295 (96) and 133 (42).

2-(10-*Hydroxy*-11-*toluenesulfonyloxy*-2,5,8-*trioxaundecyl*)-1,4,7,10-*tetraoxacyclododecane* **7**.—A Schlenk tube was charged with the diol **5** (92.52 g, 6.84 mmol), which was then dried at 60 °C, < 0.1 mmHg for 2 h. The tube was then filled with argon, and pyridine (anhydrous 6 cm^3) was added *via* steel cannula. The solution was then cooled to −30 °C in a dry ice–diethylene glycol bath. A solution of tosyl chloride (1.31 g, 6.90 mmol) in pyridine (anhydrous, 6 cm^3) was made up under argon in another Schlenk tube and also cooled to −30 °C before being transferred *via* a cannula, to the other tube, which was then kept at −20 °C for 5 days. The pyridine was then removed at room temperature under vacuum to leave a dark, viscous residue which was extracted with diethyl ether (3 × 40 cm^3). The tarry residue was dissolved in dichloromethane (100 cm^3) and washed with 6 mol dm^{-3} HCl (2 × 7 cm^3) to leave a pale yellow solution. This was then combined with the ether extracts and the solvents were removed on a rotary evaporator to leave a dark oil. This was redissolved in dichloromethane (100 cm^3) and washed with more 6 mol dm^{-3} HCl (10 cm^3) and reconcentrated to a brown oil (3.11 g, 87%) TLC analysis (alumina; 2% methanol in dichloromethane) indicated that the sulfonate product (R_f = 0.3) converted slowly into the desired epoxide (R_f = 0.55) so it was quickly used in the next step without full characterisation and further purification; δ_H(CDCl$_3$) 7.80 (2 H, d, *J* 8.2, ArH), 7.34 (2 H, d, *J* 8.2, ArH), 4.15–3.45 (30 H, m, CH$_2$O, CHO and OH) and 2.45 (3 H, s, CH$_3$); *m*/*z* (dci) 522 (M$^+$ + 1, 35%).

2-(10,11-*Epoxy*-2,5,8-*trioxaundecyl*)-1,4,7,10-*tetraoxacyclododecane* **9**.—A two-necked 100 cm^3 flask was charged with the sulfonate, **7** (3.10 g, 5.95 mmol). This was dried by being stirred at room temperature for 4 h under vacuum. The flask was then filled with argon, and THF (80 cm^3) and sodium hydride (0.6 g, 25 mmol) were added. The cloudy grey mixture was stirred under argon for 20 h and then filtered through a glass sinter to give a yellow filtrate which was concentrated on a rotary evaporator to a yellow oil (1.82 g). This was taken up in 3% dichloromethane in hexane and filtered through Celite to give a colourless solution which was re-concentrated to a pale yellow oil (1.80 g, 86%); δ_H($CDCl_3$) 3.95–3.41 (27 H, m, CH_2O and CHO), 3.19–3.15 (1 H, m, CHO), 2.81–2.78 (1 H, m, C*H*H) and 2.61 (1 H, m, CH*H*); δ_C($CDCl_3$) 78.5 (CHO), 72.0, 71.7, 71.4, 70.95, 70.91, 70.80, 70.67 (4 C), 70.64, 70.3 and 70.2 (CH_2O), 50.8 (C-10 epoxy) and 44.2 (C-11 epoxy); *m*/*z* (dci) 351 (M^+ + 1).

As the epoxide group had been found to be sensitive to acid, base and metal cations, it was stored at −20 °C and used in the polymerisation as quickly as possible.

Polymerisation of the Epoxide **9** *to the Polymer* **11**.—(*i*) *Initiator* Et_3Al–$0.5H_2O$–0.5*acac*. This was prepared according to the method of Vandenberg[8] as follows.

A Schlenk tube was fitted with a septum and dried under vacuum. It was then filled with argon and charged with 1.0 mol dm^{-3} Et_3Al in hexane (Aldrich, 15 cm^3) and distilled diethyl ether (15 cm^3) and then cooled in an ice–water bath. Distilled water (135 mm^3, 7.5 mmol) was then syringed in over 30 min. The mixture was then allowed to warm to room temperature and stirred for 2 h, before being replaced in the ice bath. Acetylacetone (768 mm^3, 0.75 g, 7.5 mmol) was then syringed in over a period of 1 h and the yellow solution was allowed to stir under argon overnight prior to use.

(*ii*) *Polymerisation*. A Schlenk tube fitted with a stirrer flea and rubber septum was weighed and then charged with the epoxide **9**. The system was then dried at 40 °C under vacuum for 2 h and re-weighed to give the mass of epoxide (0.80 g, 2.28 mmol). The tube was placed under a positive pressure of argon, and freshly distilled toluene (3 cm^3) and initiator (0.5 cm^3) were added by syringe. The septum was replaced by a water-cooled cold finger condenser and the tube was placed in an oil bath at 110 °C. Three further portions of initiator (0.5 cm^3) were added at hourly intervals. Before each addition the tube was cooled and, taking care to maintain the blanket of argon, a small sample was withdrawn, diluted with dichloromethane. TLC analysis (alumina; 2% methanol in dichloromethane) showed conversion of the epoxide (R_f = 0.6) into the desired polymer (R_f = 0.0–0.05). After the final addition of initiator the temperature was lowered to 60 °C for 14 h, after which the yellow mixture was very viscous and TLC confirmed the loss of almost all the epoxide.

The tube was cooled in an ice bath and then distilled water (10 cm^3), 2 mol dm^{-3} HCl (2 cm^3) and dichloromethane (20 cm^3) were added. After 20 min of stirring at reflux the remaining polymer gel was broken up with a glass rod. The upper aqueous layer was pipetted off and 2 mol dm^{-3} HCl (10 cm^3) was added and the tube was shaken to give a white emulsion. Dichloromethane (20 cm^3) was added and the mixture was centrifuged (1900 rpm, 15 min). The upper aqueous layer was pipetted off again and the cloudy white organic phase was concentrated on a rotary evaporator to yield a sticky, yellow, rubbery polymer (1.04 g). This was dissolved in chloroform (950 cm^3) and the cloudy solution left to stand for 3 days at −20 °C. Suspended solid was then removed by further centrifugation and the supernatant was carefully pipetted off into stirred hexane (400 cm^3). The hexane was decanted and the precipitated polymer was re-dissolved in dichloromethane (200 cm^3) which was then washed with water (20 cm^3). TLC (alumina; 2% methanol in dichloromethane) showed only baseline material. The volatiles were removed and the polymer dried under vacuum overnight at 40 °C (0.54 g, 67%).

Analysis for aluminium at this stage gave (Al) = 0.06%, equivalent to an O:Al^{3+} ratio of 1000:1. Further solution and precipitation (hexane) gave material with < 0.01% Al.

GPC in aqueous 1.0 mol dm^{-3} sodium nitrate solution against poly(ethylene oxide) standards gave M_n = 77 200.

DSC gave T_g = −43 °C.

Solution viscosity measurements in acetone (concentration = 1–0.2%, Ubbeholde viscometer, 25 °C) gave the intrinsic viscosity as 32.09 cm^3 g^{-1} extrapolating from the inherent viscosity and 32.37 cm^3 g^{-1} extrapolating from the reduced viscosity. Both lines showed pronounced curvature at low dilutions (the 0.2% point was ignored in the calculation of intrinsic viscosity), a feature of polyelectrolytes which may indicate the binding of residual Al^{3+} giving rise to distortion of molecular shape or intramolecular attractions; δ_H($CDCl_3$) 3.87–3.44 (30 H, m); δ_C($CDCl_3$) 78.84, 78.67 (the in-chain CHO resonance for *rr*, *mr* and *mm* triads), 78.46 (macrocyclic CHO), 71.61, 71.3, 70.81 (2 C), 70.70, 70.60 (3 C), 70.46 (2 C), 70.27, 70.12 and 69.89 (CH_2O).

12-*Methyl*-12-(2,5,8-*trioxaundec*-10-*enyl*)-1,4,7,10-*tetraoxacyclotridecane* **4**.—The alcohol **2** (4.75 g, 20.3 mmol), the sulfonate **14** (6.75 g, 20.3 mmol) and sodium hydride (1.00 g, 41 mmol) in THF (50 cm^3) were reacted as described for the 12-O_4-analogue, **3**. The product was a brown oil (6.63 g) which was purified by column chromatography (alumina; 1:1 hexane–dichloromethane changing to 2% methanol in dichloromethane) to yield the product as a pale yellow oil (6.10 g, 82%) (Found: C, 59.8; H, 9.53. Calc. for $C_{18}H_{34}O_7$: C, 59.6; H, 9.46%); δ_H($CDCl_3$) 5.92 (1 H, m, =CH–), 5.24 (1 H, m, =CH_2), 4.03 (2 H, m, OC*H*$_2$CH=), 3.71–3.58 and 3.37 (26 H, m, CH_2O) and 0.95 (3 H, s, CH_3); δ_C($CDCl_3$) 134.7 (=CH), 116.9 (=CH_2), 74.8, 72.1, 71.6 (2 C), 71.1, 70.6, 70.3, 70.1 (2 C), 69.79 (2 C), 69.75 (2 C), and 69.4 (CH_2O), 40.5 (> C <) and 17.5 (CH_3); *m*/*z* (EI) 363 (M^+ + 1, 100%), 133 (42), 129 (36) and 217 (28); *m*/*z* (CI) 380 (M^+ + 18, 93%), 363 (M^+ + 1, 100) and 292 (24).

12-(10,11-*Dihydroxy*-2,5,8-*trioxaundecyl*)-12-*methyl*-1,4,7,10-*tetraoxacyclotridecane* **6**.—The alkene **4** (5.90 g, 16.3 mmol), *N*-methylmorpholine *N*-oxide (2.14 g, 18.2 mmol), osmium tetraoxide (0.5 cm^3; 2.5% w/v solution) were reacted in acetone (5.3 cm^3) and water (3.4 cm^3) as described for the 12-O_4-analogue, **5**. The reaction was stirred overnight after which ^{1}H NMR analysis of a sample indicated the presence of *ca.* 10% remaining alkene, so further *N*-methylmorpholine *N*-oxide (0.6 g) and osmium tetraoxide solution (0.2 cm^3) were added and the mixture stirred for 3 days.

The product was isolated as described for **5** to yield a brown oil which was purified by column chromatography (alumina; 0–15% methanol in dichloromethane) to give a colourless oil (4.25 g, 66%) (Found: C, 54.6; H, 9.4. Calc. for $C_{18}H_{36}O_9$: C, 54.5; H, 9.15%); δ_H($CDCl_3$) 3.90–3.85, 3.71–3.54 and 3.42–3.31 (31 H, m, CHO and CH_2O), 3.05 (2 H, v br s, OH) and 0.95 (3 H, s, CH_3); δ_C($CDCl_3$) 74.9 (CHOH), 72.9, 71.6 (2 C), 71.1, 70.8, 70.5 (2 C), 70.4, 70.13 (2 C), 69.84 (2 C) and 69.75 (2 C) (CH_2O), 63.9 (CH_2OH), 40.6 (> C <) and 17.6 (CH_3); *m*/*z* (CI) 414 (M^+ + 18, 100%), 397 (M^+ + 1, 50) and 102 (21).

12-(10-*Hydroxy*-11-*toluene*-p-*sulfonyloxy*-2,5,8-*trioxaundecyl*)-12-*methyl*-1,4,7,10-*tetraoxacyclotridecane* **8**.—The diol **6** (2.02 g, 5.1 mmol) and tosyl chloride (0.97 g, 5.1 mmol) were reacted in pyridine as described for the 12-O_4-analogue **7**. After the pyridine had been removed, the residue was dissolved in dichloromethane (60 cm^3) and washed with 2 mol dm^{-3} HCl (2 × 10 cm^3) and water (20 cm^3). The volatiles were removed under vacuum to leave a brown oil (2.56 g, 91%) which was used directly in the next step without further purification.

TLC analysis (alumina; 1% methanol in dichloromethane) showed four components: R_f = 0 (polar impurities, small), R_f = 0.23 (monosulfonate, major), R_f = 0.65 (small) and R_f = 0.82 (disulfonate, small); δ_H($CDCl_3$) 7.79 (2 H, d, *J* 8.1, ArH), 7.35 (2 H, d, *J* 7.9, ArH), 4.15–3.92 and 3.75–3.30 (31 H, m, CHO and CH_2O), 2.45 (3 H, s, $ArCH_3$) 1.3 (1 H, br s, OH) and 0.94 (3 H, s, CH_3); *m*/*z* (EI) 551 (monosulfonate M^+ + 1, 38%), 705 (disulfonate $M^+ + 1$, 3); m/z (CI) 568 (monosulfonate $M^+ + 18$, 37%), 551 ($M^+ + 1$, 9) and 772 disulfonate $M^+ + 18$, 8).

12-(10,11-*Epoxy*-2,5,8-*trioxaundecyl*)-12-*methyl*-1,4,7,10-*tetraoxacyclotridecane* **10**.—The brown oily sulfonate **8** (2.56 g, 4.66 mmol), was reacted with sodium hydride (0.5 g, 20 mmol) in THF (120 cm^3) as described for the 12-O_4-analogue **9**. After evaporation of the THF, the brown oil was taken up in hexane (100 cm^3) and filtered through Celite to give a colourless filtrate which was concentrated on a rotary evaporator to give a colourless oil (1.56 g). To remove any residual sodium ions, the oil was dissolved in water (25 cm^3) which was then extracted with dichloromethane (2 × 50 cm^3). The solvent was removed under reduced pressure to yield a colourless oil which was dried overnight under vacuum (1.55 g, 88%); δ_H($CDCl_3$) 3.81 (1 H, dd, J 12.0, 3.1, OCHH–$C_{epoxide}$), 3.71–3.56 and 3.46–3.32 (27 H, m, CH_2O), 3.17 (1 H, m, CH), 2.80 (1 H, dd, J 4.8, 4.4, $C_{epoxy}$$H$H), 2.61 (1 H, dd, J 4.8, 2.8, C_{epoxy}HH) and 0.95 (3 H, s, CH_3); m/z (dci) 379 ($M^+ + 1$, 100%); δ_C($CDCl_3$) 74.82 (CH_2O–C_{11} ring), 71.87, 71.59, 71.12, 70.71, 70.56, 70.34, 70.14, 69.70 and 69.35 (CH_2O), 50.74 (C-10 epoxy), 44.16 (C-11 epoxy), 40.55 (ring C-12) and 17.55 (Me) (Found: C. 57.4; H, 9.31. $C_{18}H_{34}O_8$ requires C, 57.1; H, 9.02%).

The Polymerisation of **10** (*to Give the Polymer* **12**).—The epoxide **10** (1.85 g, 4.88 mmol), was polymerised in toluene (7 cm^3) with the same initiator (4 × 1 cm^3 of the standard initiator solution described above) and by the same method as that used for the 12-O_4-analogue **9**. At the end of the reaction the mixture was a yellow gel. The tube was cooled and toluene (20 cm^3) was added but the gel would not dissolve so it was transferred to a beaker and left to stir for 3 days with water (10 cm^3), 2 mol dm^{-3} HCl (5 cm^3) and dichloromethane (100 cm^3). After this time, most of the solvents had evaporated to leave a cloudy, white, organic gel with a colourless aqueous phase. The aqueous phase was decanted off and the gel was dissolved in dichloromethane (200 cm^3). This was stirred with 2 mol dm^{-3} HCl (20 cm^3) and then separated and concentrated to a volume of *ca.* 50 cm^3. This solution was dripped into hexane (400 cm^3) and the polymer separated as a rubbery lump. The hexane was decanted off and the polymer was stirred overnight in methanol (100 cm^3) to give a colourless solution which was filtered through a coarse sinter and then reduced in volume to *ca.* 50 cm^3 before being re-precipitated in hexane (400 cm^3). The polymer was dissolved in dichloromethane (30 cm^3) and filtered and the solvent evaporated off to yield a residue that was dried under vacuum overnight to give a sticky, rubbery, clear, colourless material (1.08 g, 58%). Analysis for aluminium (atomic absorption) found no detectable level of residual aluminium. $T_g = -36$ °C. GPC in aqueous 1 mol dm^{-3} sodium nitrate solution gave M_n = 29 500; δ_H($CDCl_3$) 3.71–3.28 (31 H, m, CH_2O and CHO) and 0.95 (3 H, s, CH_3); δ_C($CDCl_3$) 78.86 and 78.68 (CHO), 74.9, 71.7 (2 C), 71.4, 71.1, 70.76, 70.5, 70.3, 70.2 (2 C), and 69.8 (5 C) (CH_2O), 40.6 (>C<) and 17.7 (CH_3).

Poly{[P,P-*Bis*(2,2,2-*trifluoroethoxy*)*phosphazene*]-co-[P-(1,4,7,10-*tetraoxaundecan*-2-*yl*-3,6-*dioxaheptyloxy*)-P-(2,2,2-*trifluoroethoxy*)*phosphazene*]} **17**.—Poly P,P-[bis(2,2,2-trifluoroethoxy)phosphazene], **16**, was prepared according to the procedure of Allcock[9] and then reacted with the macrocyclic alkoxide using the procedure of Andrei.[5]

A 500 cm^3, three-necked flask was fitted with an argon inlet, a pressure equalising dropping funnel and a condenser, flushed with argon and then charged with the alcohol **15** (2.65 g, 9.0 mmol), dry THF (100 cm^3) and sodium hydride (0.5 g, 20 mmol). The flask was lowered into an oil bath at 60 °C and a solution of **16** (0.99 g, 4.07 mmol), in dry THF (100 cm^3) was added over a period of 3 h. The grey suspension immediately turned brown and was left to stir at 60 °C for 1 week.

The cloudy, brown mixture was allowed to cool and then filtered through a coarse sinter. The filtrate was reduced in volume to *ca.* 30 cm^3 and then dripped into cyclohexane (400 cm^3) to give a brown, fibrous lump of polymer. The cyclohexane was decanted off and the polymer was dissolved in dichloromethane (300 cm^3). This was shaken with 2 mol dm^{-3} HCl (30 cm^3) and then with distilled water (30 cm^3) to give a yellow emulsion which was left to settle out overnight. The yellow organic layer was separated and the solvent removed under reduced pressure to yield a dark, viscous oil which was taken up in THF (30 cm^3) and reprecipitated into cyclohexane (300 cm^3). The cyclohexane was decanted and the polymer dissolved in THF (30 cm^3) and reprecipitated in hexane (400 cm^3) before being dried under vacuum to give a dark, very viscous oil (1.41 g). DSC gave the T_g of the polymer as -34 °C, and GPC in aqueous solution (1.0 mol dm^{-3} sodium nitrate) gave M_n = 49 000 (Found: C, 45.3; H, 7.87; N, 2.50; F, 8.24. Calc. for $C_4H_4NF_6O_2P$: C, 19.7; H, 1.64; N, 5.76; F, 46.9 and for $C_{26}H_{50}NO_{14}P$: C, 49.4; H, 7.92; N, 2.22%). The C analysis is consistent with a degree of substitution of 74% and the F analysis with a degree of substitution of 64%; δ_H($CDCl_3$) 4.40–3.40 (br m); δ_C($CDCl_3$) 78.5 (CHO), 71.5, 71.3, 70.7, 70.2 (all br) and 65.3 (v br); δ_P(CD_3COCD_3) -3.67 (br s) and -5.17 (br s); δ_F($CDCl_3$) -74.04 (small t, J 8.6), -74.10 (small t, J 8.7) and -74.41 (v large s, v br).

10,11-*Epoxy*-2,5,8-*trioxaundecane* **18**.—A 1 dm^3 flask was filled with argon and then charged with 2-(2-methoxyethoxy)-ethanol (40 g, 0.33 mol) and dry THF (200 cm^3). The flask was cooled with a water bath while freshly cut sodium (8.8 g, 0.38 mol) was added. The mixture was stirred overnight to allow the sodium to dissolve.

The flask was cooled in a dry ice–acetone bath and epichlorohydrin (42.3 g, 0.46 mol) in THF (100 cm^3) was added over 15 min. The mixture was stirred for 2 h and then the flask was lifted from the dry ice–acetone bath and allowed to warm to room temperature and was then stirred for a further 21 h.

Ether was then added to make up the volume to *ca.* 800 cm^3 and the mixture was filtered and acidified with glacial acetic acid (25 cm^3) and the solvent was removed under reduced pressure to yield a brown oil. This was distilled under vacuum through a 50 cm vigreux column to give a colourless oil (18.8 g, b.p. 55–57 °C, 0.01 mmHg) which was further purified by column chromatography (alumina; ethyl acetate–hexane 1:4) to give a colourless oil (11.7 g, 20%); δ_H($CDCl_3$) 3.81–3.37 (10 H, m, CH_2O), 3.37 (3 H, s, CH_3O), 3.15 (1 H, m, CH), 2.79 (1 H, m, OCHH) and 2.60 (1 H, m, OCHH); δ_C($CDCl_3$) 72.34, 72.27, 71.07, 70.95, 70.89 (CH_2O), 59.32 (CH_3O), 51.12 and 44.51 (C_{epoxy}); m/z (dci, ammonia) 194 ($M^+ + 18$, 56%) and 177 ($M^+ + 1$, 23%) (Found: C, 54.3; H, 9.15. $C_8H_{16}O_4$ requires: C, 54.5; H, 9.10%).

Polymerisation of **18**.—A 50 cm^3 flask was fitted with a septum and a condenser and connected to a vacuum line. It was filled with argon and then charged with **18** (4.00 g, 22.6 mmol), toluene (4 cm^3) and a sample of the initiator solution (4 cm^3). The mixture was stirred for 40 min and then heated under reflux for 90 min during which time the viscosity increased noticeably. The mixture was then stirred at room temperature for 17 h and heated under reflux again for 1 h, transferred to a larger flask, and toluene (50 cm^3) and 2 mol dm^{-3} HCl (40 cm^3) were added. After 1 h at reflux the volatiles were removed on a rotary evaporator to give a yellow gel.

To remove any remaining aluminium, the gel was dissolved in toluene (250 cm^3) and refluxed in a Soxhlet extractor filled with 4 Å sieves for 4 h. It was then cooled and filtered through HiFlo and concentrated on a rotary evaporator and traces of remaining monomer were removed by distillation at 70 °C under vacuum onto a cold finger. The polymer was a soft, yellow gel (1.32 g, 33%). GPC gave $M_n = 29\,300$, $T_g = -69$ °C; $\delta_H(CDCl_3)$ 3.72–3.45 (13 H, m, CH_2O and CHO) and 3.37 (3 H, s, OCH_3); $\delta_C(CD_2Cl_2)$ 79.22, 79.11 and 78.99 (CHO resonance for *rr*, *mr* and *mm* triads), 72.21, 71.45 (br), 71.10, 70.75, 70.70 and 70.08 (br) (CH_2O) and 58.94 (CH_3O).

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