Synthesis of Functionalised 12-,13- and 14-Membered Crown Ethers Bearing Exocyclic Polymerisable Groups and the Binding Properties and Conductivities of their Lithium Doped Polymers

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The synthesis of a series of [12], [13] and [14]-membered crown ethers bearing an exocyclic polymerisable methacrylate is reported. The spacing group between the ring and the methacrylate is either a simple alkyl chain, $[CH_2]$ or $[CH_2]_6$, or an oxydiethylene chain. The relative binding ability of the 'mono and di-substituted' macrocyclic rings towards Li^+ is compared by ^{13}C NMR analysis. Radical polymerisation gives the amorphous polymers in which the glass transition temperature is primarily controlled by the nature of the spacer group. In the lithium doped polymers, for a given glass transition temperature, T_g, the [12]-ring materials show enhanced ionic conductivities over the [14]-ring analogues which may be related to the lower rate of lithium exchange (in the former series) or to an enhanced tendency of the [12]-ring systems to form 2:1 complexes with more effective counterion separation.

Ionically conducting materials continue to be studied intensively because of the variety of technological applications that may result, such as low-weight, all solid-state, lithium batteries. Following the pioneering work on the dissolution of lithium salts in poly(ethylene oxide),[1] it is now appreciated that in such materials charge transport occurs in the amorphous phase and not in the ordered crystalline phase and that formation of ion pairs, triplets and other aggregates is also important in determining the conductivity. In addition, charge transport involves both the lithium cation and the associated anion. Various strategies have been promulgated in efforts to enhance ionic conductivity with the aim of achieving high ionic conductivity (say 10^{-4} to 10^{-3} S cm^{-1}) at room temperature in a lithium doped polymeric electrolyte.[2] Conductivity is an activated process and is a sensitive function of the glass-transition temperature.† Accordingly it is preferable to work with a native polymer that possesses a low T_g which is not particularly sensitive to the addition of anhydrous lithium salts. In the archetypal system, [poly(ethylene oxide)—'PEO'], the addition of lithium salts (usually as the triflate or perchlorate to inhibit ion-pairing) causes a considerable structural reorganisation. In essence, the lithium ions cross-link different PEO chains and the increased degree of order is associated with an elevated glass-transition temperature which reduces polymer segmental motion. As a result, ionic mobility is impaired and reduced levels of ionic conductivity ensue. In PEO, a maximum in conductivity is observed at an O/Li ratio of 8:1. This could be considered to correspond to a system in which each Li^+ ion is solvated by four oxygens, with a proximate 4-oxygen binding site vacant.

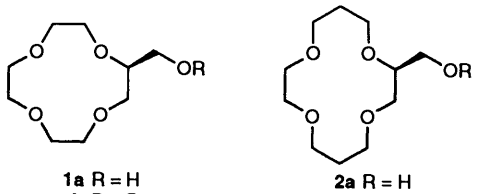
Alternative lithium binding sites have been considered, including all oxygen crown ethers[3] and polyazaoxa crowns.[4] For example a 16-crown-5 ring has been linked to a flexible polyphosphazene backbone.[3] More well-defined complexes with lithium are formed with [14] and [12]-O_4 rings. The 14-membered tetraoxa-ligand is known to form relatively strong complexes with lithium in which the ion sits in the plane of the ring.[5] In contrast in the [12]-O_4 system, the lithium ion sits above the ring plane[6,7] and may therefore be expected to show some tendency to form 2:1 complexes. Thus in the 1:1 complexes, the [14]-O_4 ring should form complexes in which both cation solvation and anion separation are more effective. On the other hand, the mobility of the lithium ion (either in solution or in an amorphous solid-phase) may be higher in systems with proximate [12]-O_4 rings than with [14]-O_4 rings. The higher stability of lithium complexes in a [14]-O_4 series may be expected to be associated with slower rates of ion decomplexation and a higher free-energy of activation for lithium dissociation.

In an effort to probe the relative importance of the degree of lithium solvation (using systems in which lithium binding is associated locally with a small change in ligand conformation) and the mobility of both the solvated cation and the associated anion, a study has been undertaken of the lithium binding and transport properties of a series of [12], [13] and [14]-O_4 functionalised polymers based on a conventional poly(methacrylate) backbone, *i.e.* a 'comb-branch' polymer. The distance between the putative lithium binding site and the polymer main chain has been varied using either a simple alkyl chain or an oxyethylene chain. Increasing the separation between the backbone and the crown ether groups in this way was expected to lower the T_g of the doped and undoped polymer. With the oxyethylene spacer, the exocyclic β-oxygen was also considered to play an active role in lithium solvation. Ligation of lithium by such a β-oxygen (forming a 5-ring chelate) has been observed in various monomeric [14]-O_4 derivatives.[8] A preliminary account of some of this work has appeared.[9]

Results and Discussion

Syntheses. The starting materials for the synthesis of the monomers were the 2-benzyloxymethyl derivatives, *e.g.* **1b**, **2b**, **25** of the [12], [13] and [14]-O_4 crown ethers.[10] These were prepared by condensation of the appropriate linear ditoluene-*p*-sulfonate with racemic 5-phenyl-4-oxapentan-1,2-diol.[8,10] Debenzylation was effected by catalytic hydrogenolysis[8] [$Pd(OH)_2$/C/H_2/EtOH, TsOH] to give the corresponding alcohols **1a** and **2a**. Esterification with methacryloyl chloride (Et_2O, Et_3N) gave the 'short-chain' monomers **3** and **4**. For the formation of the oxyethylene-extended monomers **11** and **12**, mono-benzylated diethylene glycol, **5a**,[11] was converted into the iodide **6c** *via* the toluene-*p*-sulfonate **6b** in 71% overall yield.

† In the Vogel–Tammann–Fulcher approximation, based on the free-volume theory, $\sigma = AT^{-\frac{1}{2}}\exp[-E_a/K(T^1 - T_0)]$ where E_a is a 'pseudo-activation' energy, T_0 is the ideal glass-transition temperature, and A is a constant proportional to the charge carrier concentration.



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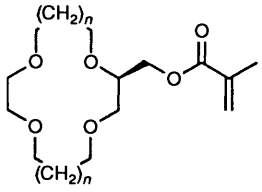
b R = Bz

2a R = H
b R = Bz



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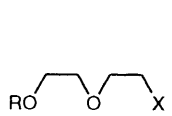
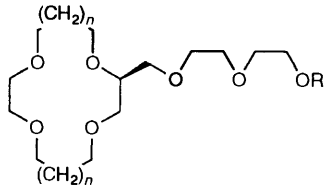
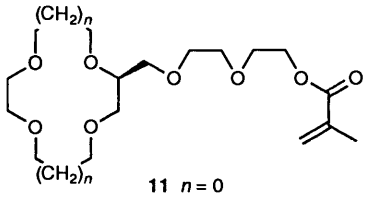
4 $n = 1$



5a X = OH, R = Bz
b X = OH, R = Me
6a X = OTs, R = Bz
b X = OTs, R = Me
c X = I, R = Bz



7 $n = 0$, R = Bz
8 $n = 1$, R = Bz
9 $n = 0$, R = H
10 $n = 1$, R = H



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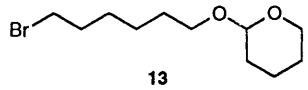
12 $n = 1$



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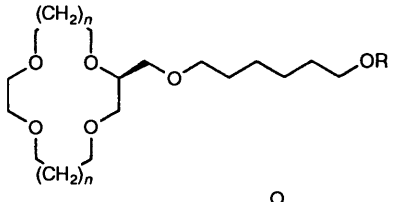
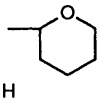
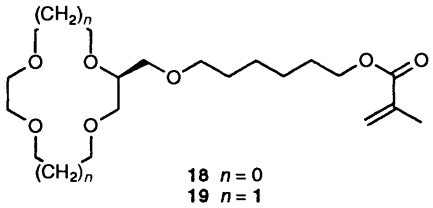


14 $n = 0$, R =

15 $n = 1$, R =



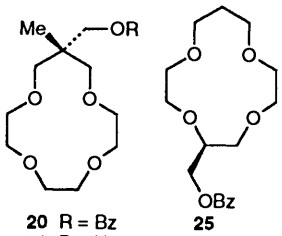
16 $n = 0$, R = H
17 $n = 1$, R = H



18 $n = 0$
19 $n = 1$

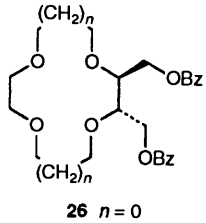
This iodide **6c** was coupled with the thallous alkoxide of **1a** or **2a** to give the benzyl ethers **7** and **8** (71 and 62% respectively). Hydrogenolysis of the benzyl group and formation of the methacrylates **11** and **12** from the alcohols **9** and **10** proceeded in good yield.

The introduction of a C_6 spacer between the ring and the methacrylate moiety was achieved *via* the intermediacy of the tetrahydropyranyl 'ethers' **14** and **15**, prepared (62% and 65% respectively) from the protected alkyl halide **13** and the thallous alkoxides of **1a** and **2a**. Deprotection (MeOH, HCl) offered the alcohols **16** and **17** in quantitative yield and conversion into the methacrylate esters **18** and **19** proceeded cleanly. The methacrylates were purified by chromatography on neutral alumina immediately prior to polymerisation. Reactions in this sequence are summarised in Scheme 1.



20 R = Bz
21 R = H

25



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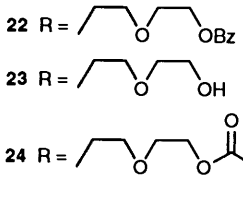
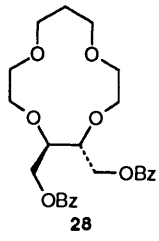


22 R =
23 R =
24 R =



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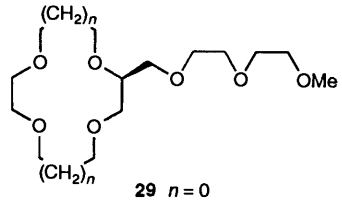
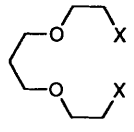
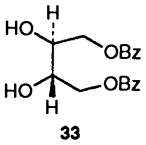


29 $n = 0$
30 $n = 1$



31 X = Cl
32 X = OTs



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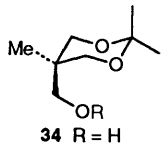
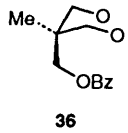


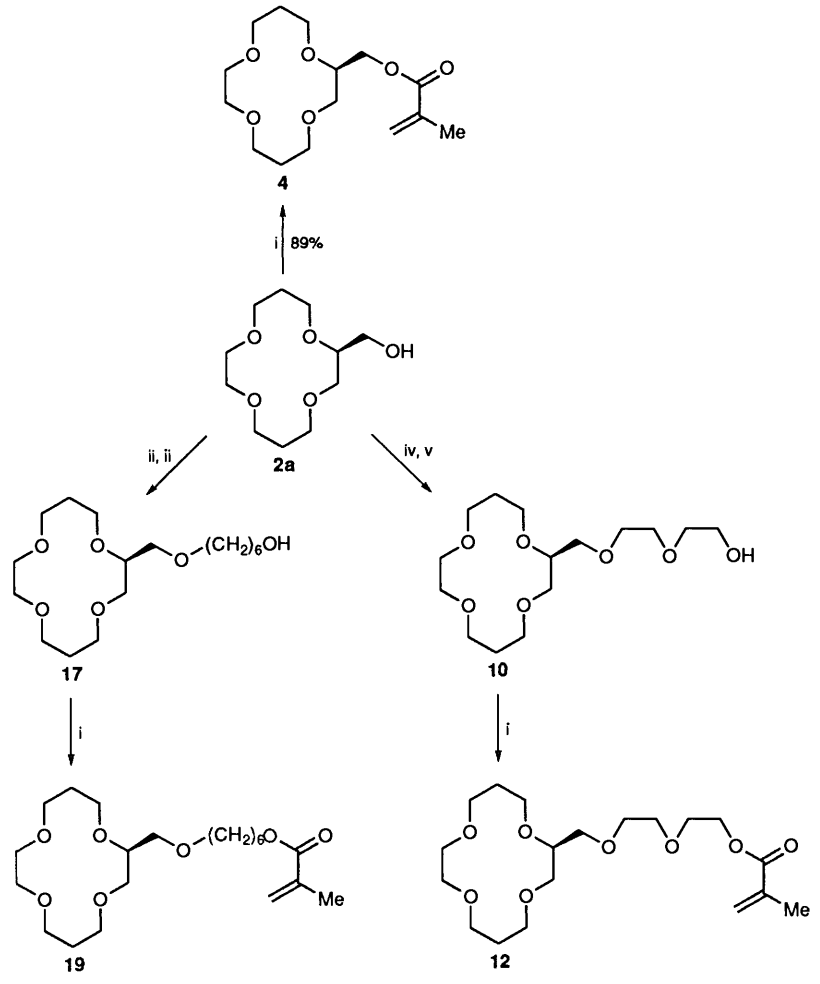
34 R = H
35 R = Bz



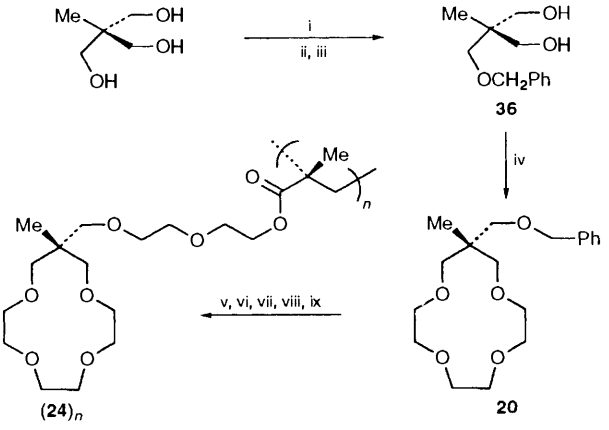
36

As a result of the relatively low yield of the [13]-ring benzyl ether **25**, an alternative synthesis of a [13]-O_4 monomer was sought (Scheme 2). Conversion of 1,1,1-tris(hydroxymethyl)-ethane to the mono-benzyl diol **36** was achieved *via* the isopropylidene derivatives **34** and **35** in 35% overall yield. Co-condensation of the diol **36** with the toluene-*p*-sulfonate of triethyleneglycol—in a lithium templated cyclisation—afforded the cyclic benzyl ether **20** in 44% yield after chromatography on neutral alumina. Conversion into the oxyethylene extended methacrylate **24** proceeded as described earlier, *via* the alcohols **21** and **23** and the benzyl ether **22** (Scheme 2).

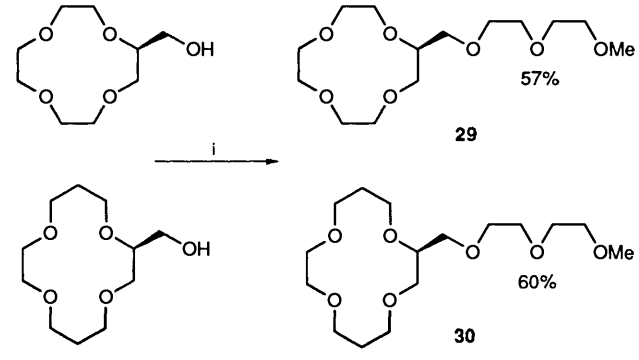
The 2,3-bis(benzyloxymethyl) ethers **26**, **27** and **28** were also prepared in lithium templated cyclisations in order to compare the relative binding efficiencies of mono- and di-substituted crowns. Moreover, such disubstituted crowns—when further converted into 'the related' bis-methacrylates—could serve as



Scheme 1 *Reagents and conditions:* (i) $CH_2C(CH_3)COCl$, Et_3N, Et_2O; (ii) $Br[CH_3]_6O\overline{CHO[CH_2]_3CH_2}$ TlOEt, MeCN; (iii) H_2O^+, MeOH; (iv) 6a, THF, NaH; (v) H, Pd–C, EtOH



Scheme 2 *Reagents and conditions:* (i) $C(CH_3)_2OMe_2$, H^+; (ii) $PhCH_2Cl$, OH^-, THF Bu_4NHSO_4 (cat.); iii, AcOH; (iv) $[TsO-(CH_2)_2-O-CH_2]_2$, $LiOBu^t$, Bu^t OH; (v) Pd–C, H_2, EtOH; (vi) **6a**, NaH, THF; (vii) Pd–C, H_2, EtOH); (viii) $CH_2(CH_3)COCl$, Et_3N, Et_2O; (ix) AIBN, EtCOMe



Scheme 3 *Reagents:* (i) **6b**, NaH, THF

cross-linking agents (*e.g.* when added as $\leqslant 1$ mol%) in the polymerisation of the corresponding mono-substituted systems, in order to control molecular weight and gel content. The simple mono-methyl ethers **29** and **30** were also prepared from the diols **1a** and **2a** by reaction with the toluene-*p*-sulfonate **6b** (NaH/THF) (Scheme 3). These simple ethers serve as model-compounds to assess the intrinsic differences in ionic conductivity (12 *vs.* 14 ring) when doped directly with lithium triflate.

The polymers of each methacrylate monomer were prepared by standard free radical polymerisation using azabis(isobutyronitrile) as the initiator in a solution of boiling butan-2-one. The resultant polymers were purified by repeated precipitation in hexane and were dried thoroughly. Molecular weights were typically in the range 20–30 000 and polymer tacticities were very similar to those found with simple poly(methacrylates) as revealed by ^{13}C NMR.[12] With poly(**18**), for example (Fig.1), there is a well-spaced triad for the quaternary carbon, and the mr and rr diads are distinct in the carbonyl and α-methyl region. There is relatively little change in the position of the CH_2O resonances following polymerisation and the single CHO resonance at *ca.* 78 ppm is similar and quite distinct in both the [14]-O_4 extended monomethyl ether, methacrylate and in the polymer (Fig. 2).

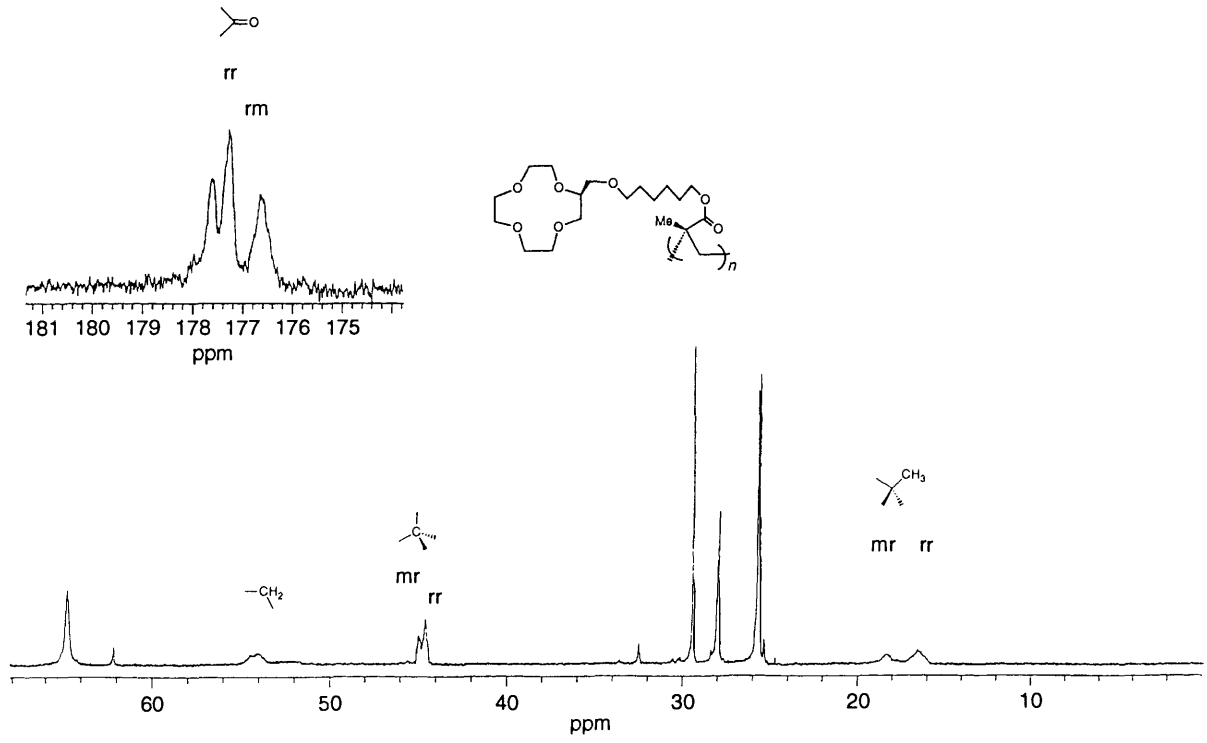


Fig. 1 Partial proton decoupled ^{13}C NMR spectrum of poly(**18**) ($CDCl_3$, 293 K), showing elements of polymer tacticity

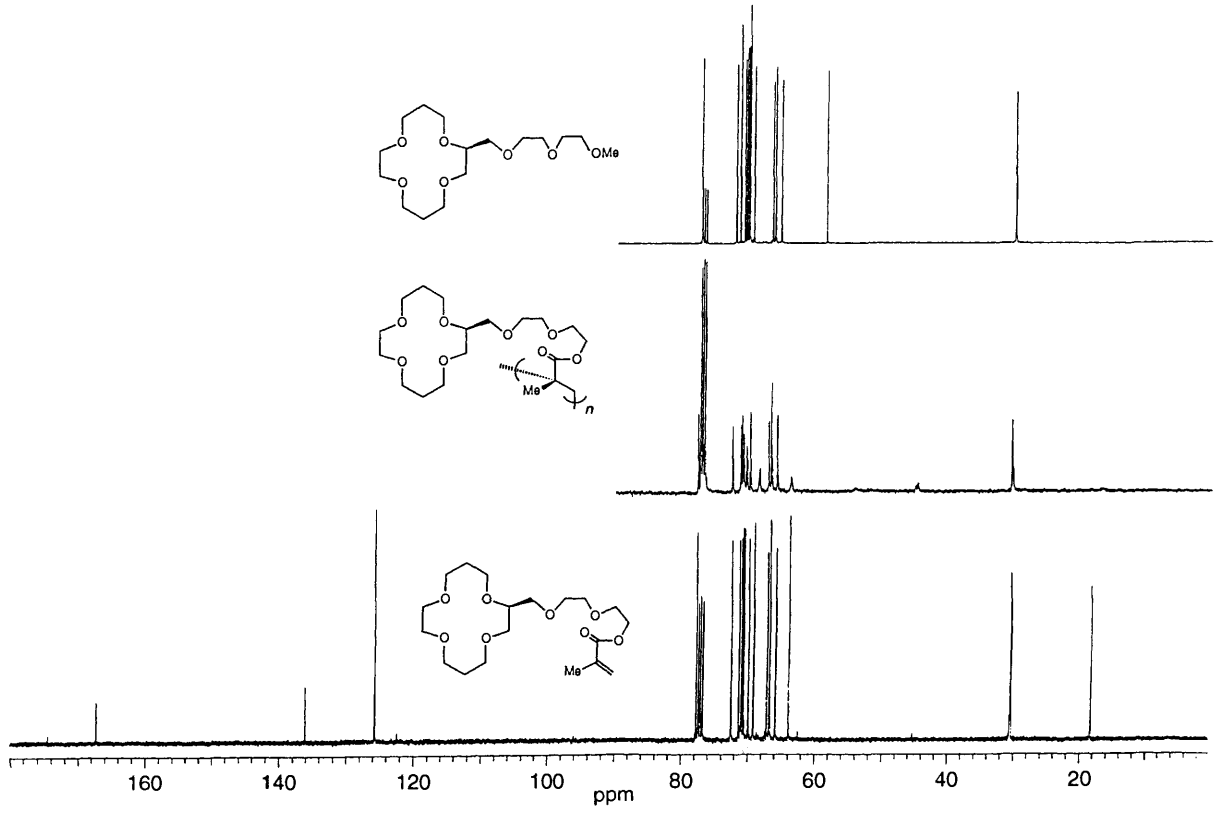


Fig. 2 Proton-decoupled ^{13}C NMR spectrum of [14]-O_4 compounds ($CDCl_3$, 293 K, 100 MHz)

Binding Studies.—In order to assess the relative ability of the [12], [13] and [14]-O_4 derivatives to bind lithium ions, ^{13}C and ^{7}Li NMR studies were carried out. Incremental addition of lithium triflate (or $LiClO_4$) to methanol (CD_3OD) solutions of the ligands **1b**, **2b**, **25**, **26**, **27**, **28** and **20** resulted in shifts of the ligand ^{13}C resonances. Stronger 1:1 binding was observed for the [14]-O_4 ligands **2b** and **27** with a sharper titration curve evident than the corresponding [13]-O_4 or [12]-O_4 ligands. The disubstituted crown **27** also seemed to bind more strongly than the analogous monosubstituted derivative **2b** (Figs. 3–6). There is a noticeable inflection in the titration curves of the [12]-O_4 and [13]-O_4 derivatives **1b**, **25** and **20** at low salt:ligand ratios. This is most likely to be associated with intermediate formation of a 2:1 (ligand:Li^+) sandwich struc-

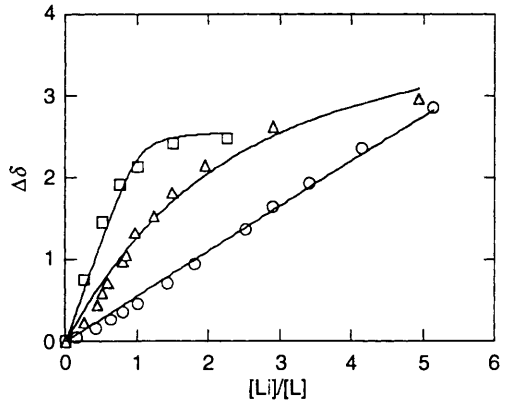


Fig. 3 Variation of $\Delta\delta_C(CD_3OD, 293\ K)$ with lithium:ligand (Li/L) ratio for the dibenzyl ethers, **26** (○), **27** (□) and **28** (△) (ring *C*HO resonance shown)

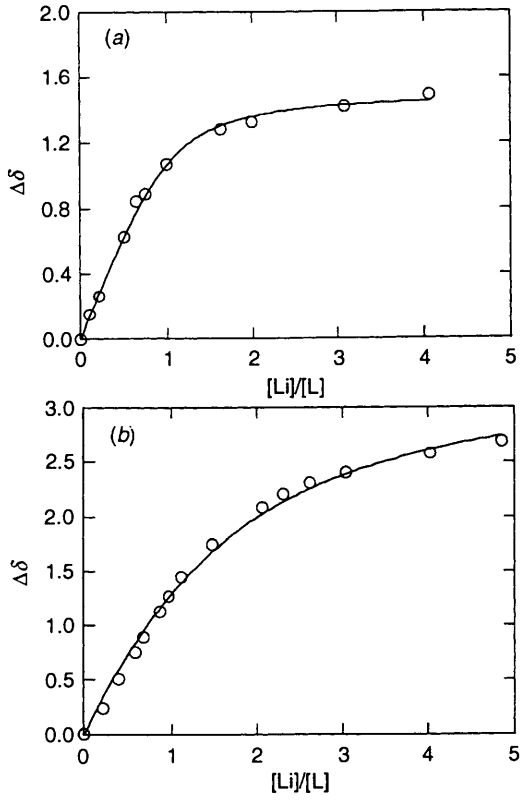


Fig. 4 Variation of $\Delta\delta_C$(ring *C*HO, CD_3OD, 293 K) with Li/L ratio for the [14]-O_4, **2b** (upper) and [13]-O_4, **25**, monobenzyl ethers, (lower)

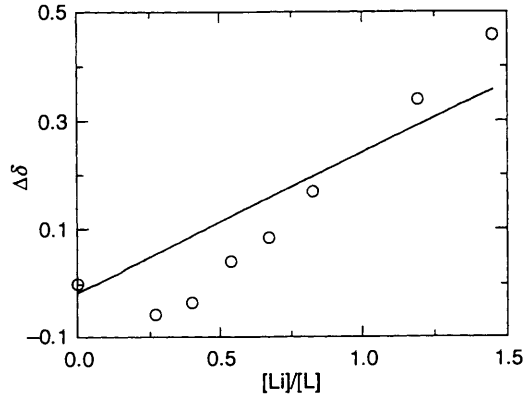


Fig. 5 Variation of $\Delta\delta_C$(ring *C*HO, CD_3OD, 293 K) with Li/L ratio for the [12]-O_4 benzyl ether **1b**

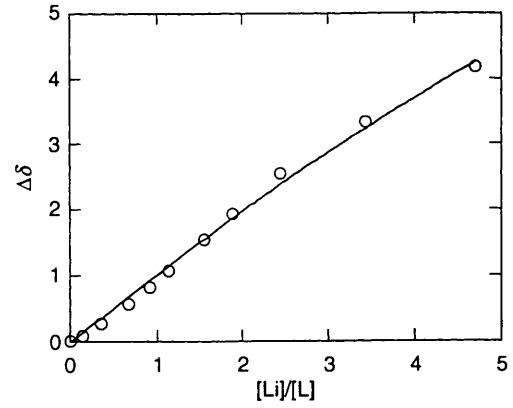


Fig. 6 Variation of $\Delta\delta_C$(ring *C*HO, CD_3OD, 293 K) with Li/L ratio for the [13]-O_4 benzyl ether, **20**

Table 1 Estimated binding constants for lithium complex formation (293 K, CD_3OD)

Ligand	log *K*	Limiting $\Delta\delta^a$
2b	1.86	2.59
27	2.50	1.51
1b	n.d.	n.d.
26	n.d.	n.d.
20	< 0	n.d.
25	0.19	3.42
28	0.08	4.30

[a] For the CHO resonance, unless otherwise stated, to higher frequency, n.d. = not determined.

ture. The titration curves were fitted to a model involving simply 1:1 complex formation using an iterative least-squares analysis (details in the Appendix). The curves shown in Figs. 3 and 6 are calculated values fitted to the experimental points. The higher formation constants for 1:1 complex formation with the [14]-O_4 compounds [for **2b** and for **27**] (Table 1), contrast with low values found with the [12]-O_4 compounds. Attempted fitting in the [12]-O_4 series gave a *K* value of $\leqslant 1$. In the region of low lithium to ligand ratios where 2:1 binding is most favoured, negative deviations from the 1:1 binding curve are expected if the 2:1 'sandwich' complex is characterised by a smaller (or indeed, negative *e.g.* **1b**) chemical shift difference. This effect is observed for all ligands except the [14]-O_4 ligands where 1:1 binding is strongest. That the data is relatively well fitted to a 1:1 model is suggestive that the degree of 2:1 binding (in this solvent) is modest, and is most pronounced with the [12]-O_4 monobenzyl ligand, **1b**. Of course, it must be borne in mind that methanol is a strongly competitive ligand for the Li^+ ion, and in less polar solvents (and in the amorphous polymer) stronger binding is likely.

Addition of lithium triflate to a CD_2Cl_2 solution of the polymers, [poly(**3**)] and [poly(**4**)] was monitored by ^{13}C NMR, particularly observing the 'sharp' CHO resonance at *ca.* 76 ppm, [$\omega_{\frac{1}{2}}$(293 K) = 25 Hz]. Addition of lithium to poly(**3**) led to immediate line-broadening of many ligand resonances: at a stoichiometry of 20:1 ring oxygens to Li^+, the peak width at half-height of the ring CHO resonance was 70 Hz and did not change up to a stoichiometry of *ca.* 12:1 (ring O:Li). Cooling the sample down to −30 °C led to a broadening of all the resonances while heating to 100 °C (in $C_2D_2Cl_4$) caused a slight sharpening of resonances, but without any marked resolution of resonances. In contrast, addition of $LiCF_3SO_3$ to [poly(**4**)] resulted in significantly less line-broadening. In the absence of Li^+, two distinct CHO resonances were observed at 76.64 and

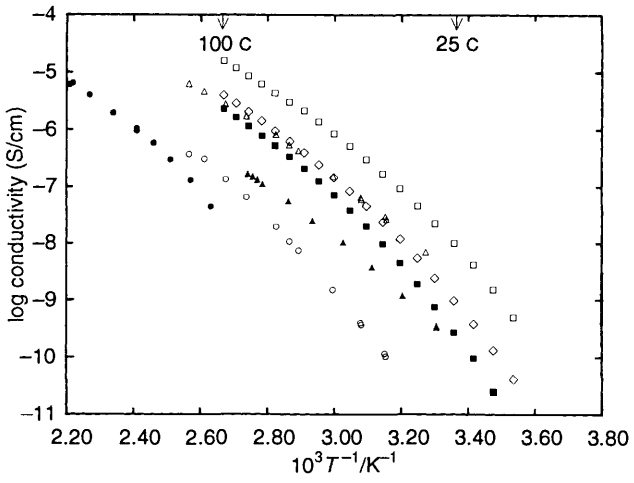


Fig. 7 Variation of the logarithm of ionic conductivity with $1/T$ for polymer: $LiCF_3SO_3$ mixtures at 18:1 (ring O:Li) ratio: [14]-O_4 short-chain methacrylate, poly(**4**), (●); [12]-O_4 short-chain methacrylate, poly(**3**), (○); [12]-O_4 $[CH_2]_6$ methacrylate, poly(**18**), (△); [14]-O_4 $[CH_2]_6$ methacrylate, poly(**19**), (▲); [13]-O_4 (EO)methacrylate, poly(**24**), (◇); [14]-O_4 (EO)methacrylate, poly(**12**), (■); [12]-O_4 (EO)methacrylate, poly(**11**), (□)

Table 2 Glass transition temperatures for methacrylate polymers and polymer–salt mixtures

		T_g/°C	
Polymer (poly-*n*)	T_g/°C	18:1	12:1
3	0	+17	+23
4	+31	+44	+44
11[c]	−25	−10	0
12[b]	−10.5	−1.5	±1.2
18	−26	−7	−5
19	−20	−24	−20
(24)	−18	−3	+1

[a] T_g of $LiCf_3SO_3$ doped polymer at [O:Li] given. The oxygen to lithium ratio refers to the ring oxygens only. [b] Another sample of this polymer, which had a higher gel content and was therefore more likely to retain solvent gave values of −55, −55 and −50 °C for the T_g values at the shown doping levels. The retained solvent must have plasticised the material in this case. [c] Another sample of this polymer, also with a higher gel content gave values of −30, −24 and −22 °C for the undoped and doped polymer. Again some degree of solvent retention may have been occurring despite prolonged drying (80 °C/0.3 mmHg).

76.54 ppm. At a dopant level of 20:1 (ring O:Li^+) the resolution of the two peaks (presumably due to two diastereoisomers) was lost but $\omega_{\frac{1}{2}}$(293 K, 100 MHz) was only 30 Hz, and only increased to 50 Hz at a stoichiometry of *ca.* 12:1 (ring O:Li). These results may be interpreted in terms of the differing effect of added lithium on polymer chain mobility. In the [12]-O_4 series, addition of Li^+ ions may promote chain 'cross-links' *via* formation of 2:1 complexes although cross linking through the anions between the chains is also possible. This would have the effect of reducing chain mobility and hence would broaden all observed resonances. In the [14]-O_4 polymer this effect is much less pronounced and the observed broadening may be related simply to an increase in the variety of environments caused by partial doping with Li^+ ions and/or slow lithium exchange between adjacent rings. Cooling of the solution simply slowed down chain motion leading to line-broadening before any other coalescence phenomenon could be observed.

The relative ease of lithium exchange (*i.e.* between free and bound states) with the [12] and [14]-O_4 benzyl ethers **1b** and **2b**, was studied by ^7Li NMR in the relatively weakly co-ordinating solvent CD_3NO_2. With **2b**, signals due to free and bound Li^+ were discerned at low temperature (≤ −10 °C, $\Delta\delta_{Li} = 0.5$ ppm) and a coalescence phenomenon was observed (T_c = 283 K) for which a free energy of activation, ΔG_c, of 65 (±2) kJ mol^{-1} was calculated. With **1b**, no coalescence was observed down to −40 °C, suggesting that the activation energy for Li^+ exchange in the [12]-O_4 series is ≤50 kJ mol^{-1}. These observations are in accord with the ^{13}C NMR results and with previous results.[8] In summary, the [14]-O_4 systems form stronger 1:1 complexes than the corresponding [12]-O_4 ligands which may result in enhanced cation/anion-separation but will also be associated with a higher energy barrier for lithium migration from one binding site to another. In the [12] and [13]-O_4 series, binding of Li^+ in 1:1 complexes is weaker but there is a tendency to form 2:1 complexes (both with the 'monomer' in solution and possibly with the swollen polymer) which could enhance cation/anion separation. In addition, the [12]-ring systems offer more rapid kinetics of Li^+ exchange than the [14]-O_4 analogues.

Lithium Transport in Polymers.—The lithium-doped polymers were obtained by mixing anhydrous solutions of the polymer and of lithium triflate in acetone followed by solvent evaporation and drying under reduced pressure (80 °C/0.3 mmHg). Addition of lithium caused only slight increases in the polymer T_g with the [14]-O_4 polymers **4**, **12** and **19**, while with poly(**3**) (a [12]-O_4 short-chain methacrylate), and the extended chain homologues [poly(**11**), poly(**18**) and poly(**24**)], the first addition of lithium caused a more marked increase in T_g (+17 °C, on average). Similar increases in T_g with added salt have been noted in [12]-O_4 comb-branch polyphosphazenes[13] even though the backbone is of different flexibility. It is tempting to speculate that this difference in behaviour may be related to the different lithium-binding behaviour of the [14] *versus* the [12] and [13] rings. With the [14]-ring polymers, lithium complexation is associated with only a small change in ring conformation and similar quadrangular [3434] conformations should be adopted by the ring in the free and bound state. On the other hand, as noted in the ^{13}C NMR studies, addition of Li^+ to the [12]-O_4 systems may result in a number of 2:1 (L:Li) complexes increasing the ordering of the polymeric chains and leading to increased T_g values.

The ionic conductivity of the lithium-doped materials was measured over the temperature range 0 to +180 °C using route a.c. impedance spectroscopy methods in the frequency range 0–63 KHz. At a doping level of 18:1 (ring O:$LiCF_3SO_3$), modest conductivities were measured for the polymers with relatively high glass transition temperatures, *i.e.* the 'short-chain' [12] and [14]-O_4 methacrylates. The polymers with a spacer group ($[CH_2]_6$ or $CH_2CH_2OCH_2CH_2O$) between the ring and the backbone possess lower T_g values and higher conductivities. A comparison of the conductivities of the doped [12]-polymers with the [14]-analogues, (Fig. 7), reveals that the [12]-ring polymers have the higher conductivity values. This difference is highlighted for the [12] and [14]-O_4 extended polymers in a plot of log ($\sigma T_{\frac{1}{2}}$) *versus* $1/T - T_0$, assuming that $T - T_0$ is 60 K (Fig. 8). It is still a moot point whether this difference is caused either by the relative ease of Li^+ migration from one [12]-O_4 binding site to another or to the tendency of the [12]-O_4 ring systems to promote 2:1 complexation thereby enhancing anion–cation separation (thereby reducing ion pairing and aggregation which is a factor known to reduce conductivity).

Experimental

^1H, ^{13}C and ^7Li NMR spectra were recorded on a Varian VXR 400, a Varian Gemini 200 or a Bruker AC 250 spectrometer. Chemical shifts are quoted in ppm to higher frequency

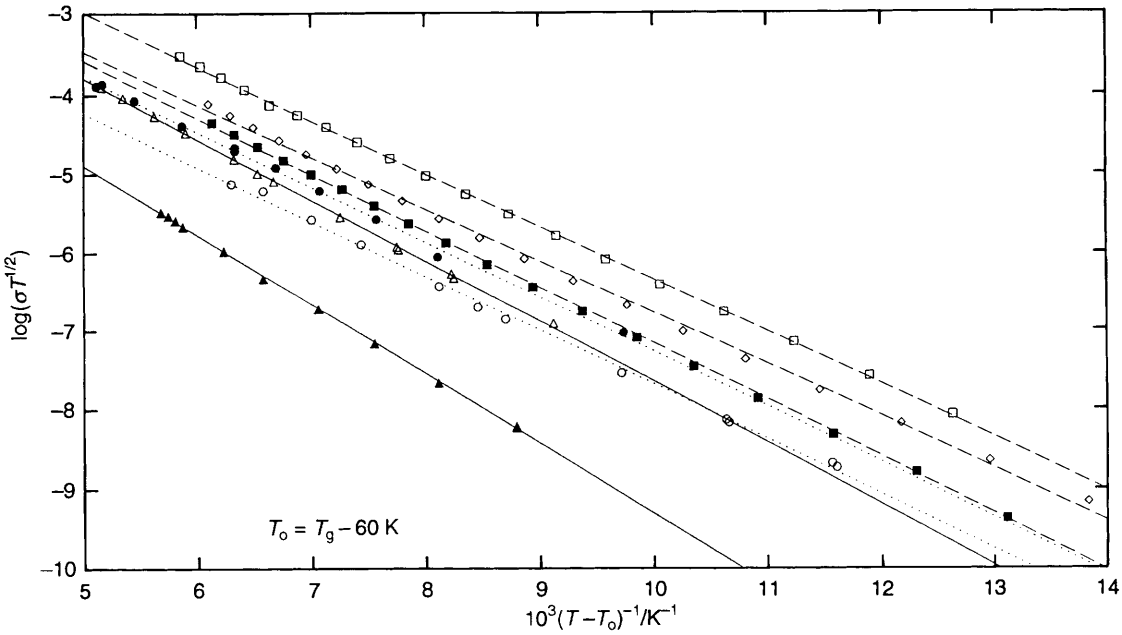


Fig. 8 Variation of conductivity with $T^{-\frac{1}{2}}$ allowing for the effect of T_g (O:Li = 18:1): **(11)**$_n$, (□); **(24)**$_n$, (◇); **(12)**$_n$, (■); **(4)**$_n$, (●); **(18)**$_n$, (△); **(3)**$_n$, (○); **(19)**$_n$, (▲)

of $(CH_3)_4Si$. IR spectra were recorded on a Perkin-Elmer 577 spectrometer as a thin film or as a Nujol mull using NaCl plates. Mass spectra were recorded on a VG 7070E operating in electron impact (e.i.), chemical ionisation (NH_3) or desorption chemical ionisation (d.c.i.). In the latter case samples were presented as methanol or dichloromethane solutions with NH_3 as the impingent gas. Gas chromatographic analyses were performed with a Hewlett Packard HP 5890 gas chromatograph fitted with an SE-30 capillary column using a temperature programme of 30 s at 40 °C increasing to 270 °C at 10 °C min^{-1}, then holding for 10 min. Glass transition temperatures were measured by differential scanning calorimetry with a calibrated Perkin-Elmer DSC-7 (20 °C min^{-1}) and molecular weights were estimated, relative to polystyrene standards, by GPC of a tetrahydrofuran solution of the polymer sample using a Viscotek 200 differential viscometer detector. Bulk ionic conductivities were measured by alternating current impedance spectroscopy using a Solartron 1260 impedance/gain-phase analyser in the frequency range 0.1 Hz to 63 kHz. The polymeric samples were pressed between brass or stainless steel blocking electrodes and a constant thickness (between 0.1 and 1 mm) was maintained using a PTFE spacer. The temperature and atmosphere were controlled by passing heated dry nitrogen gas over the sample cell.

For the ^{13}C NMR titration studies, a known mass—*ca.* 50 mg—of the ligand (*e.g.* **7**, **8**) was dissolved in methanol (*ca.* 1.5 cm^3), and weighed amounts of anhydrous lithium perchlorate added sequentially (*ca.* 2.5 mg) and the NMR spectrum recorded. A plot of the variation of the change in chemical shift for selected ligand resonances was made as a function of the ligand:lithium ratio. The variation of $\Delta\delta_C$ with added salt was fitted by a simple iterative least-squares analysis in Kaleidagraph. Details are available from the authors on request. The effect of added lithium salt (added as the anhydrous trifluoromethylsulfonate salt) on the ^{13}C spectrum of the polymers **11** and **12** was carried out in CD_2Cl_2 solution (in the temperature range −50 to +30 °C), varying the oxygen (ring) to lithium ratio from 18:1 to *ca.* 12:1 in order to allow comparison with the conductivity studies.

Compounds **1a**, **1b**, **2a**, **2b**, **27** and **31**–**33** were prepared as described in the literature.

2-(2-*Methylenepropionyloxymethyl*)-1,4,8,11-*tetraoxacyclotetradecane* **4**. The alcohol **2a** (0.9 g, 3.85 mmol), triethylamine (0.8 g, 8 mmol), and methacryloyl chloride (0.6 g, 5.8 mmol) and a crystal of hydroquinone were dissolved in dry diethyl ether (10 cm^3) and the mixture was stirred for 1 h at room temp. After removal of solvent under reduced pressure the residue was purified by chromatography on alumina (eluent; hexane then 5:1 hexane–ethyl acetate) to yield a colourless oil (1.04 g, 89%) [Found (d.c.i.): 303.1801, $M^+ + 1$. $C_{15}H_{27}O_6$ requires 303.180 87]. This compound was used directly for polymerisation. $\delta_H(C_6D_6)$ 1.75 (4 H, mult., CH_2 ring), 1.85 (3 H, d, CH_3), 3.3–3.8 and 3.85–4.15 (17 H, mult., CH_2O + CHO), 5.30 (1 H, mult., CH *cis* to Me) and 6.11 (1 H, mult., alkene CH); $\delta_C(C_6D_6)$ 18.8 (CH_3), 31.35, 31.45 (CH_2C), 64.9, 66.55, 67.15, 67.8, 70.6, 72.05, 72.82 (CH_2O), 77.55 (CHO), 125.7 (=CH_2), 137.2 (=C–) and 167.1 (CO).

2-(2′-*Methylenepropionyloxymethyl*)-1,4,7,10-*tetraoxacyclododecane* **3**. This was prepared and purified as described for **4** using the alcohol **1a** (1.5 g, 7.3 mmol), methacryloyl chloride (1.1 g, 10.9 mmol) and triethylamine (1.5 g, 14.6 mmol) to yield a colourless oil (2.26 g, 80%) [Found (d.c.i.): 275.1526, $M^+ + 1$. $C_{13}H_{23}O_6$ requires 275.1528]; $\delta_H(CDCl_3)$ 1.87 (3 H, dd, *J* 1, 1.5, CH_3), 3.45–3.9 and 4.0–4.1 (17 H, mult., CH_2O + CHO), 5.51 (1 H, mult., CH *cis* to Me) and 6.03 (1 H, mult.); $\delta_C(CDCl_3)$ 17.92 (CH_3); 63.8, 69.88, 69.93, 70.25, 70.31, 70.42, 70.60, 70.95, (CH_2O), 77.07 (CHO), 125.4 (=CH_2), 135.7 (=C–) and 166.6 (CO).

5-*Benzyloxy*-3-*oxapentanol* **5a**. This was prepared from diethyleneglycol following the benzylation method in ref. 11 and was purified by distillation (b.p. 91–93 °C/0.004 mmHg) to give a colourless liquid (46%); $\delta_H(CDCl_3)$ 2.91 (1 H, br s, OH), 3.56–3.72 (8 H, mult., CH_2O), 4.56 (2 H, s, OCH_2Ph) and 7.33 (5 H, mult., Ph); $\delta_C(CDCl_3)$ 62.2 (CH_2OH); 69.9, 70.9, 73.0, 73.8 (CH_2O); 128.2, 128.3, 128.9 (CHAr) and 138.5 (q, Ar); *m/z* (e.i.) 196 (M^+, 3%), 107 (19), 92 (19) and 91 (100).

6-*Phenyl*-3-*oxahexyl toluene*-p-*sulfonate* **6a**. To a solution of the alcohol **5a** (15 g, 76.5 mmol) in dry pyridine (50 cm^3) was added toluene-*p*-sulfonyl chloride (16 g, 84 mmol) in portions at −5 °C. After 48 h at −15 °C, the mixture was poured onto crushed ice (300 g) and the oily lower layer was dissolved in dichloromethane (300 cm^3), washed with dil. hydrochloric acid (3 × 50 cm^3), dried (K_2CO_3), filtered and solvent removed under reduced pressure to yield a pale yellow oil (24 g, 90%);

$\delta_H(CDCl_3)$ 2.47 (3 H, s, CH_3–Ar), 3.59–3.80 (6 H, mult., CH_2O), 4.22 (2 H, t, CH_2OTs, *J* 4.7), 4.58 (2 H, s, OCH_2Ph), 7.3–7.42 (5 H, mult., Ph), 7.36 (2 H, d, $ArSO_2$) and 7.84 (2 H, d, *J* 8.4, CH–Ar); $\delta_C(CDCl_3)$ 21.47 (Me); 68.52, 69.17, 69.21, 70.63, 73.10 (CH_2O), 127.49 (*p*-CHPh), 127.56 (*m*-CHPh), 128.24 (*o*-CHPh), 137.99 (q, *C*–CH_2O), 127.7, 129.7, 132.8 (ArC) and 144.7 (C–SO_2); ν_{max}(Nujol)/cm^{-1} 1120, 1083 (C–O–C), 1360, 1185 and 1178 (SO_2) [Found (e.i.): 350.2135, M^+. $C_{18}H_{22}O_5S$ requires 350.2139].

3-*Oxahexyl toluene*-p-*sulfonate* **6b**. This was prepared as described for **6a** from the monomethyl ether of diethylene glycol in 83% yield to yield a colourless oil; $\delta_H(CDCl_3)$ 2.44 (3 H, s, CH_3), 3.35 (3 H, s, OMe), 3.48 (2 H, t, CH_2O), 3.58 (2 H, t, CH_2O), 3.69 (2 H, t, CH_2O), 4.17 (2 H, t, CH_2OTs), 7.34 (2 H, d, *J* 8.4, ArH) and 7.95 (2 H, d, ArH); $\delta_C(CDCl_3)$ 21.6 (CH_3), 59.0 (OCH_3), 68.7, 69.3, 70.6, 71.8 (CH_2O); 127.9, 129.8, 132.9 (CH, Ar) and 144.8 (q, Ar).

1-*Benzyloxy*-5-*iodo*-3-*oxapentane* **6c**. To a solution of the toluene-*p*-sulfonate **6a** (24 g, 68 mmol) in dry DMF (100 cm^3) was added potassium iodide (17.1 g, 103 mmol) and the mixture was stirred at room temp. for 14 h. Dichloromethane (25 cm^3) was added, the mixture was filtered, and the solvent was removed under reduced pressure to yield a pale brown oil which was purified by column chromatography on alumina (eluent neat hexane to 5% ethyl acetate–hexane) to yield a colourless oil (17.7 g, 85%) [Found (e.i.): 306.0115. $C_{11}H_{15}O_2I$ requires 306.0117]; $\delta_H(CDCl_3)$ 3.27 (2 H, t, *J* 7.1, CH_2I), 3.6–3.82 (6 H, mult., CH_2O), 4.59 (2 H, s, OCH_2Ph) and 7.30 (5 H, mult., CH arom.); $\delta_C(CDCl_3)$ 2.92 (CH_2I); 69.23, 70.09, 71.31, 73.09 (CH_2O), 127.45 (*p*-CH, Ar), 127.54 (*m*-CH, Ar), 128.20 (*o*-CH) and 137.96 (q).

2-(7-*Benzyloxy*-2,5-*dioxaheptyl*)-1,4,7,10-*tetraoxacyclododecane* **7**. To the alcohol **1a** (0.41 g, 2 mmol) in dry toluene (5 cm^3) was added thallous ethoxide (0.5 g, 2 mmol) under nitrogen. The solvent was removed under reduced pressure and the residue redissolved in acetonitrile (15 cm^3). To this solution was added the iodide, **6c** (0.67 g, 2.2 mmol) and the mixture was heated under reflux for 14 h. After filtration through a short (5 cm) column of alumina (washing with ethyl acetate, 3 × 10 cm^3), the combined eluates were evaporated under reduced pressure and the residue purified by chromatography on alumina (eluent 10–50% ethyl acetate in hexane) to yield a colourless oil (0.56 g, 73%) [Found (d.c.i.): 385.2224, M^+ + 1. $C_{20}H_{33}O_7$ requires 385.2228]; $\delta_H(CDCl_3)$ 3.45–3.55 and 3.64–3.85 (25 H, mult., CH_2O + CHO), 4.59 (2 H, s, $PhCH_2O$) and 7.35 (5 H, mult., arom.); $\delta_C(CDCl_3)$ 69.34, 69.36, 70.01, 70.25, 70.51, 70.56, 70.57, 70.59, 70.79, 70.84, 71.27, 71.59, 73.13 (CH_2O), 78.45 (CHO), 127.47 (*p*-CH), 127.60 (*m*-CH), 128.24 (*o*-CH) and 138.13 (q).

2-(7-*Hydroxy*-2,5-*dioxaheptyl*)-1,4,7,10-*tetraoxacyclododecane* **9**. To a solution of the benzyl ether **7** (1.0 g, 2.60 mmol) in aqueous methanol (10%, 20 cm^3) was added toluene-*p*-sulfonic acid (10 mg) and Pearlman's catalyst (palladium hydroxide on carbon, Aldrich) (100 mg) and the mixture was shaken under 3 atm H_2 at room temp. (15 h). After filtering and evaporating the solvent, the residue was purified by chromatography on alumina (0–7 mol% MeOH in ethyl acetate) to yield a colourless oil (726 mg, 95%) [Found: (c.i.): 295.1742, M^+ + 1. $C_{13}H_{27}O_7$ requires 295.1758]; $\delta_H(CDCl_3)$ 3.16 (1 H, br s, OH) and 3.3–3.7 (25 H, mult., CH_2O + CHO); $\delta_C(CDCl_3)$ 61.9 (CH_2OH), 70.41, 70.59, 70.61, 70.88, 70.90, 71.0, 71.21, 71.28, 71.70, 71.89 and 72.9 (CH_2O) and 78.8 (CHO).

2-[7-(2-*Methylenepropionyloxy*)-2,5-*dioxaheptyl*]-1,4,7,10-*tetraoxacyclododecane* **11**. This was prepared as described for **4** using **9** (750 mg, 2.55 mmol), methacryloyl chloride (400 mg, 3.83 mmol) and triethylamine (0.6 cm^3, 4.3 mmol) in dry ether (10 cm^3). The product was purified by column chromatography on neutral alumina (eluent 20–100% ethyl acetate–hexane) to yield a colourless oil (720 mg, 78%); *m*/*z* (c.i.) 380 (M^+ + 18, 46%), 363 (M^+ + 1, 6.5), 78 (100) and 61 (58) (Found: 363.2026, M^+ + 1. $C_{27}H_{31}O_8$ requires 363.2020); $\delta_H(CDCl_3)$ 6.08 (1 H, d, *J* 1, alkene CH), 5.52 (1 H, dq, CH), 4.24 (2 H, mult., CH_2O), 3.82–3.40 (23 H, mult., CH_2O) and 1.89 (34 H, d, *J* 1, CH_3); $\delta_C(CDCl_3)$ 18.21 (CH_3), 63.01, 69.04, 69.81, 70.02, 70.25, 70.30, 70.4, 70.45, 70.50, 70.81, 71.23, 71.31 (CH_2O), 78.2 (CHO), 125.6 (CH_2), 136.0 (q, alkene) and 167.2 (CO).

2-(7-*Benzyloxy*-2,5-*dioxaheptyl*)-1,4,8,11-*tetraoxacyclotetradecane* **8**. This was prepared as described for **7**, from the alcohol **2a** (1 g, 4.27 mmol) and the alkyl iodide **6c** (1.44 g, 4.7 mmol), to yield a colourless oil (1.1 g, 62%), after chromatography on alumina (R_f 0.35; 3:1 ethyl acetate–hexane); *m*/*z* (c.d.i.) 430.2 (M^+ + 18) and 413 (M^+ + 1) (Found: 413.2542, M^+ + 1. $C_{22}H_{37}O_7$ requires 413.254 07); $\delta_H(CDCl_3)$ 1.7–1.85 (4 H, mult., CH_2C) 3.44–3.95 (25 H, mult., CH_2O + CHO), 4.58 (2 H, s, *o*-CH_2Ph) and 7.25–7.38 (5 H, mult., Ph); $\delta_C(CDCl_3)$ 30.22, 30.33 (CH_2C); 65.63, 66.51, 66.54, 66.90, 69.25, 69.69, 70.46, 70.48, 70.66, 70.82, 71.11, 72.35, 73.01 (CH_2O), 77.54 (CHO), 127.35 (*p*-CHAr), 127.49 (*m*-CHAr), 128.13 (*o*-CHAr) and 138.06 (q).

2-(7-*Hydroxy*-2,5-*dioxaheptyl*)-1,4,8,11-*tetraoxacyclotetradecane* **10**. This was prepared as described for **9** by debenzylation of compound **8** (1.1 g, 2.7 mmol) using Pearlman's catalyst (20% palladium hydroxide on carbon, Aldrich) (200 mg), and was purified by chromatography on neutral alumina (eluent 0–1% MeOH–ethyl acetate) to yield a colourless oil (760 mg, 88%); *m*/*z* (d.c.i.) 340.2 (M^+ + 18), 324 (M^+ + 2) and 323 (M^+ + 1) (Found: 323.2074, M^+ + 1. $C_{15}H_{31}O_7$ requires 323.2070); $\delta_H(CDCl_3)$ 1.75–1.81 (4 H, mult., CH_2C) and 3.47–3.79 (26 H, mult., CH_2O + CHO + OH); $\delta_C(CDCl_3)$ 30.14, 30.22, (CH_2C), 61.40 (CH_2OH), 65.67, 66.56, 66.58, 67.05, 69.62, 70.10, 70.61, 70.73, 71.07, 72.13, 72.35 (CH_2O) and 77.50 (CHO).

2-[7-(2-*Methylenepropionyloxy*)-2,5-*dioxaheptyl*]-1,4,8,11-*tetraoxacyclotetradecane* **12**. This was prepared and purified as described for **11** from the alcohol **10** (760 mg, 2.36 mmol) to yield a colourless oil (780 mg, 85%); *m*/*z* (c.i.) 409 (M^+ + 19, 22%), 408 (M^+ + 18, 100), 391 (M^+ + 1, 30) and 113 (9); $\delta_H(CDCl_3)$ 1.7–1.8 (4 H, mult., CH_2C), 1.90 (3 H, dd, *J* 1, 1.5, CH_3), 3.3–4.0 and 4.1–4.2 (25 H, mult., CH_2O + CHO), 5.58 (1 H, mult., HC alkene) and 6.13 (1 H, mult., CH); $\delta_C(CDCl_3)$ 18.2 (CH_3), 30.4 and 30.3 (CH_2C), 64.0, 65.8, 66.6, 66.7, 67.0, 69.1, 69.8, 70.5, 70.8, 71.0, 71.3, 72.4 (CH_2O), 77.6 (CHO), 125.7 (H_2C alkene), 136.0 (alkene) and 167.2 (CO).

2-(6-*Bromohexyloxy*)*tetrahydropyran* **13**. To a solution of dihydropyran (5 g, 60 mmol) and 6-bromohexan-1-ol (5 g, 27.6 mmol) in dry ether (20 cm^3) was added toluene-*p*-sulfonic acid (20 mg) and the mixture was stirred for 30 min. The solution was washed with dil. sodium hydrogen carbonate (2%, 2 × 20 cm^3), dried ($MgSO_4$) filtered and solvent removed under reduced pressure to yield a colourless oil, homogeneous in TLC (6.5 g, 89%) which was used without further purification; $\delta_H(CDCl_3)$ 1.1–1.8 (14 H, mult., CH_2C), 3.13–3.35 (2 H, mult., CH_2O), 3.25 (2 H, t, CH_2Br), 3.5–3.9 (2 H, mult., CH_2O) and 4.42 (1 H, t, *o*-CHO); *m*/*z* (c.i.) 284.1, 282.1 (M^+ + 18) and 267, 265 (M^+ + 1) [Found: (e.i.): 264.0753. $C_{11}H_{21}BrO_2$ (^{79}Br) requires 264.075 49]; $\delta_C(CDCl_3)$ 19.5, 25.28, 25.33, 27.8, 29.4, 30.55, 32.55 (CH_2C), 33.63 (CH_2Br); 62.1, 67.2 (CH_2O) and 98.64 (OCHO).

2-[8-(*Tetrahydropyran*-2-*yloxy*)-2-*oxaoctyl*]-1,4,8,11-*tetraoxacyclotetradecane* **15**. This was prepared from the thallous salt of the alcohol, **2a** (0.85 g, 3.63 mmol) and the bromoalkane **13** (1.4 g, 5.4 mmol) as described for **7**. The product was purified by column chromatography on neutral alumina (eluent 0–50% ethyl acetate–hexane) to yield a colourless oil (0.92 g, 60%); *m*/*z* (c.i.) 436.3 (M^+ + 18) and 419.3 (M^+ + 1) [Found (c.i.):

419.3010, $M^+ + 1$. $C_{22}H_{43}O_7$ requires 418.301 02, $M^+ + 1$]; $\delta_H(CDCl_3)$ 1.2–1.75 (18 H, mult., CH_2C), 3.2–4.05 (23 H, mult., CH_2O + CHO) and 4.44 (1 H, t, *o*-CHO); $\delta_C(CDCl_3)$ 19.36, 25.21, 25.66, 25.79, 29.25, 29.40, 30.14 (CH_2C), 30.25, 30.45 (CH_2C ring), 61.89, 65.53, 66.41, 66.43, 66.78, 67.15, 69.62, 70.45, 70.75, 71.15, 72.42 (CH_2O), 77.48 (CHO) and 98.43 (*o*-CHO).

2-(8-*Hydroxy*-2-*oxaoctyl*)-1,4,8,11-*tetraoxacyclotetradecane* **17**. To a solution of the tetrahydropyranyl 'ether' **15** (0.92 g, 2.2 mmol) in methanol (9 cm^3) was added hydrochloric acid (1 mol dm^{-3}; 1 cm^3) and the mixture was stirred at room temp. for 15 h. After removal of solvents, a colourless oil was obtained (0.74 g, 100%) which was used without further purification; *m*/*z* (d.c.i.) 352.2 ($M^+ + 18$) and 335.2 ($M^+ + 1$) (Found: 335.2433, $M^+ + 1$. $C_{17}H_{35}O_6$ requires 335.2435).

2-[8-(2-*Methylenepropionyloxy*)-2-*oxaoctyl*]-1,4,8,11-*tetraoxacyclotetradecane* **19**. This was prepared as described for **11** using the alcohol **17** (0.74 g, 2.2 mmol), and was purified by column chromatography on neutral alumina (eluent 0–10% ethyl acetate–hexane) to yield a colourless oil (0.63 g, 71%); R_f 0.75 in 3:1 hexane–ethyl acetate; *m*/*z* (d.c.i.) 420.3 ($M^+ + 18$) and 403.3 ($M^+ + 1$) (Found: 403.26910. $C_{21}H_{39}O_7$ requires 403.269 72, $M^+ + 1$); $\delta_H(CDCl_3)$ 1.1–1.25 and 1.35–1.60 (8 H, mult., CH_2 chain), 1.7–1.85 (4 H, mult., CH_2 ring), 1.93 (3 H, dd, *J* 1, 1.5, CH_3), 3.2–4.2 (21 H, mult., CH_2O + CHO), 5.30 (1 H, mult., HC alkene) and 6.21 (1 H, dq, *cis* to carbonyl CH); $\delta_C(CDCl_3)$ 18.92 (CH_3), 26.52, 26.60, 29.38, 30.43 (CH_2C chain), 31.51, 31.69 (CH_2 ring), 65.13 (CH_2CO_2), 66.58, 67.34, 67.36; 67.80, 70.57, 71.90, 71.91, 72.35, 73.86 (CH_2O), 78.78 (CHO), 125.23 (CH_2 alkene), 137.56 (q, alkene) and 167.39 (CO).

2-[8-(*Tetrahydropyran*-2-*yloxy*)-2-*oxaoctyl*]-1,4,7,10-*tetraoxacyclododecane* **14**. This was prepared and purified as described for **15**, from the thallous salt of the alcohol **1a** (1.5 g, 7.3 mmol) and the alkyl bromide **13** (2.3 g, 8.75 mmol) to yield a colourless oil (1.86 g, 65%); R_f (Al_2O_3, EtOAc) 0.60; *m*/*z* (d.c.i.) 408.3 ($M^+ + 18$) and 391.3 ($M^+ + 1$) (Found: 391.2624, $M^+ + 1$. $C_{20}H_{39}O_7$ requires 391.262 54, $M^+ + 1$); δ_H ($CDCl_3$) 1.1–1.2 and 1.25–1.50 (14 H, mult., CH_2C), 3.4–3.65 (23 H, mult., CH_2O + CHO) and 4.34 (1 H, t, *o*-CHO); $\delta_C(CDCl_3)$ 19.13, 25.00, 25.44, 25.57, 29.05, 29.18 and 30.24 (CH_2C), 61.66, 66.93, 69.67, 69.83, 70.13, 70.14, 70.15, 70.32, 70.40, 71.00, 71.26 (CH_2O), 78.07 (CHO) and 92.21 (OCHO).

2-(8-*Hydroxy*-2-*oxaoctyl*)-1,4,7,10-*tetraoxacyclododecane* **16**. This was prepared as described for **17** using **14** (1.86 g, 4.77 mmol), and the product, a colourless oil (1.46 g, 100%) was used without further purification; *m*/*z* (d.c.i.) 314 ($M^+ + 18$), 308 ($M^+ + 2$) and 307 ($M^+ + 1$) (Found: 307.2124, $M^+ + 1$. $C_{15}H_{31}O_6$ requires 307.212).

2-[8-(2-*Methylenepropionyloxy*)-2-*oxaoctyl*]-1,4,7,10-*tetraoxacyclododecane* **18**. This was prepared as described for **11** using the alcohol **16** (0.78 g, 2.5 mmol) and was purified by column chromatography on neutral alumina (eluent 0 to 20% ethyl acetate in hexane) to yield a colourless oil (0.73 g, 75%); $\delta_H(CDCl_3)$ 1.37 and1.57–1.72 (8 H, mult., CH_2C), 1.93 (3 H, dd, *J* 1 and 1.5), 3.39–3.43, 3.66–3.82 and 4.10–4.16 (21 H, mult., CH_2O + CHO), 5.54 (1 H, dq, HC alkene) and 6.09 (1 H, dq, HC *cis* to carbonyl); $\delta_C(CDCl_3)$ 18.32 (CH_3), 25.74, 25.81, 28.55, 29.48 (CH_2C), 64.66 (CH_2CO_2), 70.23, 70.36, 70.66, 70.67, 70.68, 70.85, 70.93, 71.46, 71.78 (CH_2O), 78.62 (CHO), 125.17 (CH_2 alkene), 136.47 (q, alkene) and 167.50 (CO); *m*/*z* (d.c.i.) 392.2 ($M^+ + 18$) and 375 ($M^+ + 1$).

3-*Benzyloxymethyl*-3-*methyl*-1,5,8,11-*tetraoxacyclotridecane* **20**. A 2 dm^3 flask fitted with a condenser, dropping funnel and argon inlet was flushed with argon and then charged with *tert*-butanol (500 cm^3) and lithium (2.4 g, 0.34 mol) and the mixture was heated at 30 °C until all the lithium had dissolved.

A solution of the diol **36** (35 g, 0.17 mol) in *tert*-butanol (380 cm^3) was added dropwise and then the ditoluene-*p*-sulfonate (76.33 g, 0.17 mol) was added and the mixture was kept at 60 °C for 72 h. The *tert*-butanol was then removed under reduced pressure and the brown residue was taken up in chloroform (500 cm^3) and washed sequentially with HCl (1 mol dm^{-3}; 2 × 300 cm^3), saturated sodium hydrogen carbonate (400 cm^3), 10% sodium hydroxide (250 cm^3) and water (500 cm^3). The chloroform was then evaporated to give a dark oil which was purified by column chromatography (alumina, 6:1 hexane–EtOAc) which gave a clear, colourless oil (23.94 g, 44%); $\delta_H(CDCl_3$, 400 MHz) 7.32–7.22 (5 H, m, ArH), 4.48 (2 H, s, $ArCH_2$), 3.72–3.58 (12 H, m, CH_2O), 3.41 (2 H, d, *J* 8, CHHO), 3.37 (2 H, d, *J* 8, CHHO), 3.34 (2 H, s, CH_2Br) and 1.00 (3 H, s, CH_3); $\delta_C(CDCl_3)$, 138.76 (s, C arom.), 127.1 (d, C arom.), 127.0 (d, C arom.), 73.9, 73.1, 71.5, 70.0, 69.7, 69.6 (CH_2O), 40.5 (q, C) and 17.6 (CH_3); *m*/*z* (CI) 342 ($M^+ + 18$, 62%) and 325 ($M^+ + 1$, 100) (Found: C, 66.3; H, 8.2. $C_{17}H_{26}O_5$ requires: C, 65.81; H, 8.39%).

3-*Hydroxymethyl*-3-*methyl*-1,5,8,11-*tetraoxacyclotridecane* **21**. The benzyl ether, **2** (14.6, 0.045 mol) was debenzylated as described for **9**. A clear, yellow oil was obtained which was distilled onto a cold finger (75 °C/< 0.002 mmHg) to give a colourless oil (7.8 g, 75%); $\delta_H(CDCl_3$, 400 MHz) 3.72–3.48 (18 H, m, CH_2O), 3.23 (1 H, br s, OH) and 0.82 (3 H, s, CH_3); $\delta_C(CDCl_3$, 100 MHz) 72.8, 69.8, 69.6, 69.5, 69.4 (CH_2O), 40.1 (q, C) and 17.3 (CH_3); *m*/*z* (CI) 252 ($M^+ + 18$, 20%) and 235 ($M^+ + 1$, 100).

3-(7-*Benzyloxy*-2,5-*dioxaheptyl*)-3-*methyl*-1,5,8,11-*tetraoxacyclotridecane* **22**. The alcohol **21** (3.40 g, 14.6 mmol) and the toluene-*p*-sulfonate **6a** (5.61 g, 16 mmol) were dried overnight under vacuum. The reaction was carried out under argon and THF (50 cm^3) (distilled over Na) was added, followed by freshly washed sodium hydride (0.6 g, 25 mmol). The mixture was heated to 70 °C under argon for 4 h and then ethanol (0.18 g, 4 mmol) was added. The heating was continued for a further 4 h and then the mixture was allowed to cool before HCl (2 mol dm^{-3}, 15 cm^3) was added. The tetrahydrofuran and water were removed under reduced pressure leaving a brown residue which was taken up in sodium hydrogen carbonate solution (10%, 15 cm^3) and CH_2Cl_2 (25 cm^3). A 10% solution of sodium hydroxide was added dropwise until the pH of the aqueous layer was > 10.5 and then the organic layer was separated. The aqueous layer was then further extracted with CH_2Cl_2 (2 × 25 cm^3) and the combined organic layers were washed with water (10 cm^3) which was itself extracted with CH_2Cl_2 (2 × 10 cm^3). All the organic layers were combined and the solvent removed under reduced pressure to leave a brown oil (5.72 g) which was purified by column chromatography (alumina, 0–0.5% methanol–CH_2Cl_2) to give a colourless oil (4.74 g, 79%); δ_H ($CDCl_3$) 7.40–7.20 (9 H, m, ArH), 4.57 (2 H, s, CH_2Ar), 3.75–3.52 and 3.42–3.28 (26 H, m, CH_2O) and 0.95 (3 H, s, CH_3); $\delta_C(CDCl_3)$ 138.8, 128.8, 128.2, 128.0 (A), 75.4, 73.7, 72.2 (2 C), 71.7, 71.2, 70.9, 70.7 (2 C), 70.4 (4 C), 69.9 (CH_2O), 41.1 (q) and 18.1 (CH_3); *m*/*z* (d.c.i.) 430 ($M + NH_4^+$, 5%), 413 ($M^+ + 1$, 8), 106 (28), 108 (24) and 44 (100) (Found: C, 64.6; H, 9.2. $C_{22}H_{36}O_7$ requires: C, 64.1; H, 8.80%).

3-(7-*Hydroxy*-2,5-*dioxaheptyl*)-3-*methyl*-1,5,8,11-*tetraoxacyclotridecane* **23**. The monobenzyl ether **22** (4.70, 11.4 mmol) was debenzylated as described for **9** to give a very pale yellow oil (3.63 g, 99%); $\delta_H(CDCl_3)$ 3.75–3.53 and 3.45–3.30 (26 H, m, CH_2O), 3.10 (1 H, br s, OH) and 0.95 (3 H, s, CH_3); $\delta_C(CDCl_3)$ 75.4, 72.8, 72.1 (2 C), 71.6, 70.7, 70.6 (2 C), 70.3 (4 C, CH_2O), 62.2 (CH_2OH), 41.1 (1, c) and 18.1 (CH_3); *m*/*z* (d.c.i.) 340 ($M + NH_4^+$, 25%), 321 ($M^+ + 1$, 100), 133 (11) and 73 (16) (Found: C, 56.3; H, 9.85. $C_{15}H_{30}O_7$ requires: C, 55.9; H, 9.38%).

3-*Methyl*-3-[7-(2-*methylenepropionyloxy*-2,5-*dioxaheptyl*]-1,5,8,11-*tetraoxatridecane* **24**. This was prepared and purified as

described for **11** from the alcohol **23** (1.9 g, 5.9 mmol), to yield after column chromatography on neutral alumina (eluent: 0–0.5% MeOH–CH_2Cl_2) a colourless oil, R_f [Al_2O_3, 0.5% MeOH–CH_2Cl_2] 0.31 (1.27 g, 55%); *m/z* (d.c.i.) 408 (M^+, 18, 48%) and 391 ($M^+ + 1$, 100); $\delta_H(CDCl_3)$ 0.95 (3 H, s, CH_3), 1.95 (3 H, dd, CH_3), 3.32–3.42 (6 H, mult., CH_2O), 3.55–3.78 (18 H, mult., CH_2O), 4.29 (2 H, t, CH_2OC), 5.57 (1 H, dq, CH alkene) and 6.14 (1 H, br s, CH *cis* to CO); $\delta_C(CDCl_3)$ 17.71 (CH_3), 18.41 (CH_3) and 40.70 (q, ring), 64.10 (CH_2OCO), 69.23, 69.81, 69.90, 70.01, 70.04, 70.28, 78.31, 70.50, 70.31, 71.71, 71.73 and 75.0 (CH_2O). The product was stabilised with 0.01% of 4-methoxyphenol prior to polymerisation and was stored in the dark at −20 °C, under argon.

2-*Benzyloxymethyl*-1,4,7,11-*tetraoxacyclotridecane* **25**. A 250 cm^3 three-necked flask was flushed with N_2 and charged with *tert*-butanol (200 cm^3) and lithium (0.12 g, 17 mmol). After stirring overnight to dissolve the lithium, 3-benzyloxypropane-1,2-diol (3.08 g, 17 mmol) and the ditoluene-*p*-sulfonate **32** (8 g, 17 mmol) was added and the mixture was stirred for 120 h with more lithium (two portions of 0.12 g) being added after 24 and 48 h. The *tert*-butanol was removed under reduced pressure to leave a brown residue to which was added HCl (2 mol dm^{-3}; 12 cm^3) which brought the pH to 4. The mixture was then extracted with dichloromethane (5 × 40 cm^3) and the combined extracts were dried (K_2CO_3), filtered and concentrated on a rotary evaporator to yield a pale-orange oil. This was purified by column chromatography (alumina, hexane–EtOAc, 3:1) to give a colourless oil (2.4 g, 46%); $\delta_H(CDCl_3)$ 7.30–7.18 (5 H, m, ArH), 4.48 (2 H, s, CH_2Ph), 3.80–3.39 (17 H, m, CH_2O + CHO) and 1.72 (2 H, tt, $CH_2CH_2CH_2$); $\delta_C(CDCl_3)$ 137.9, 127.9, 127.1 (AC), 77.9 (CH), 72.9 (CH_2Ph), 71.2, 70.1, 69.8, 69.7, 69.3, 68.9, 65.6, 65.3 (CH_2O) and 29.8 ($CH_2CH_2CH_2$); *m/z* (CI) 328 ($M^+ + 18$, 43%), 311 ($M^+ + 1$, 100), 133 (27), 94 (45) and 92 (42) (Found: C, 65.4; H, 8.6%. $C_{17}H_{26}O_5$ requires: C, 65.8; H, 8.39%).

2,3-*Bis*(*benzyloxymethyl*)-1,4,7,10-*tetraoxacyclododecane* **26**. Lithium (0.08 g, 11.4 mm) was stirred under an argon atmosphere in *tert*-butanol (200 cm^3) at 60 °C for 4 h, after which it had dissolved to give a pale solution. To this was added the diol **33** (3 g, 0.01 mol), and 1,8-ditosyloxy-3,6-dioxaoctane (4.55 g, 0.01 mol) and lithium bromide (0.9 g, 0.01 mol) and the mixture was stirred at 60 °C for 72 h with further addition of lithium (2 portions, total 0.10 g, 0.014 mol) at 24 and 48 h. The mixture was allowed to cool and then the *tert*-butanol was removed under reduced pressure to give a dark oil which was purified as described for **23** to give a colourless oil (1.05 g, 25%); $\delta_H(CDCl_3)$, 7.26–7.15 (10 H, m, ArH), 4.50 (2 H, d *J* 12, CHHPh), 4.42 (2 H, d, *J* 12, CHHPh) and 3.88–3.37 (18 H, m, CH_2O and CHO); $\delta_C(CDCl_3)$ 138.0, 128.0, 127.3, 127.2 (A), 80.0 (CHO), 72.0, 70.7, 70.3, 69.8 and 69.6 (CH_2O); *m/z* (CI) 434 ($M^+ + 18$, 40%) and 417 ($M^+ + 1$, 8) (Found: C, 68.9; H, 7.9. $C_{24}H_{32}O_6$ requires: C, 69.2; H, 7.75%).

2,3-*Bis*(*benzyloxymethyl*)-1,4,7,11-*tetraoxacyclotridecane* **28**. Lithium (0.34 g, 48.6 mmol) was dissolved in *tert*-butanol (220 cm^3), following heating to reflux for 20 h under argon, to give a clear solution. The diol **33** (4.5 g, 15 mmol), 1.9-dichloro-3,7-dioxanonane, **31** (3.0 g, 15 mmol) and lithium bromide (1.4 g, 16.1 mmol) were added and the mixture was stirred at 80 °C for 14 days after which the product was isolated as described for **23**. A pale orange oil was isolated which was purified by column chromatography (alumina, hexane–ethyl acetate, 3:1) to give a colourless oil (0.67 g, 10%); $\delta_H(CDCl_3)$, 7.36–7.22 (10 H, m, ArH), 4.51 (2 H, d, *J* 12, CHHPh), 4.44 (2 H, d, *J* 12, CHHPh), 3.92–3.38 (18 H, m, CH_2O and CHO) and 1.78 (2 H, tt, $CH_2CH_2CH_2$); $\delta_C(CD_3OH)$ 139.6, 129.4, 128.9, 128.7 (A), 81.4 (CH), 74.2, 71.3, 70.4, 70.39, 66.3 (CH_2O) and 30.8 (CH_2) (Found: M, 430.238 23. Calc. for $C_{25}H_{34}O_6$; *M*, 430.235 54).

2-(2,5,8-*Trioxanonyl*)-1,4,7,10-*tetraoxacyclododecane* **29**. To the [12]-ring alcohol **1a** (0.95 g, 4.63 mmol) and the toluene-*p*-sulfonate, **6b** (1.40 g, 5.10 mmol) under dry argon was added THF (15 cm^3) and sodium hydride (0.2 g, 8.3 mmol) and the mixture was stirred at room temp. for 120 h and then heated to reflux for 1 h. It was allowed to cool and HCl (2 mol dm^{-3}; 5 cm^3) was added slowly. The THF and water was removed under reduced pressure and saturated sodium hydrogen carbonate solution (5 cm^3) was added to the residue. A solution of NaOH (10%) was added until the solution was alkaline and it was then extracted with CH_2Cl_2 (3 × 20 cm^3). The combined extracts were washed with water (10 cm^3) which was itself then washed with CH_2Cl_2 (10 cm^3). The combined organic extracts were evaporated to give a brown oil which was purified by column chromatography (alumina, 0–3% methanol–CH_2Cl_2) to give a clear, colourless oil (0.81 g, 57%); $\delta_H(CDCl_3)$ 3.88–3.38 (28 H, m); $\delta_C(CDCl_3)$ 78.2, 71.6, 71.3, 71.0, 70.5, 70.3, 70.27, 70.2, 70.17, 70.0, 69.8 (CH_2O) and 58.6 (OCH_3); *m/z* (CI) 326 ($M^+ + 18$, 100%) and 309 ($M^+ + 1$, 29) (Found: C, 52.1; H, 9.0. $C_{14}H_{28}O_7 \cdot H_2O$ requires: C, 51.5; H, 9.21%).

2-(2,5,8-*Trioxanonyl*)-1,4,8,11-*tetraoxacyclotetradecane* **30**. The [14]-ring alcohol **2a** (1.0 kg, 4.63 mmol) and the toluene-*p*-sulfonate **6b** (1.40 g, 5.10 mmol) were added to a dried two-necked flask under argon and dry THF (25 cm^3) and sodium hydroxide (0.2 g, 8.3 mmol) were added. The mixture was heated to reflux for 3 h and stirred at room temp. for 16 h before HCl (2 mol dm^{-3}; 8 cm^3) was added slowly to quench the reaction. The product was isolated as described for the [12]-ring analogue, **29**, and the resulting dark oil was purified by column chromatography (alumina, 0–3%, MeOH–CH_2Cl_2) to give a colourless oil (0.94 g, 60%); $\delta_H(CDCl_3)$ 4.00–3.37 (28 H, m, CH_2O and CH_3O) and 1.86–1.71 (4 H, m, $CH_2CH_2CH_2$); $\delta_C(CDCl_3)$ 77.7, 72.5, 71.9, 71.3, 71.0, 70.8, 70.54, 70.5, 69.9, 67.1, 66.7, 66.67, 65.8 (CH_2O), 59.9 (OCH_3), 30.3 and 30.2 ($CH_2CH_2CH_2$); *m/z* (CI) 354 ($M^+ + 18$, 100%), 337 ($M^+ + 1$, 28) and 240 (30) (Found: C, 57.0; H, 10.0. $C_{16}H_{32}O_7$ requires: C, 57.2; H, 9.5%).

2,2-*Dimethyl*-5-*hydroxymethyl*-5-*methyl*-1,3-*dioxane* **34**. 1,1,-1-Tris(hydroxymethyl)ethane (60 g, 0.5 mol), 2,2-dimethoxypropane (57.2 , 0.55 mol), toluene-*p*-sulfonic acid (460 mg) and chloroform (230 cm^3) were placed in a 1 dm^3 flask which was fitted with a Soxhlet extractor containing 4 Å molecular sieves. The mixture was heated at reflux for 17 h with one change of sieves and then it was cooled, stirred with moist sodium carbonate and then filtered. The solvent was removed under reduced pressure to leave a colourless oil (77 g, 96%); $\delta_H(CDCl_3)$ 3.70 (d, *J* 11.6, CHH), 3.67 (s, CH_2OH), 3.62 (d, *J* 11.7, CHH), 2.83 (s, br, OH), 1.44 (s, CH_3), 1.40 (s, CH_3) and 0.83 (s, CH_3); *m/z* (d.c.i.) 161 ($M^+ + 1$, 100%), 145 (15), 58 (15) and 59 (8).

2,2-*Dimethyl*-5-*benzyloxymethyl*-5-*methyl*-1,3-*dioxane* **35**. The alcohol, **34** (77 g, 0.48 mol), ground sodium hydroxide (30 g, 0.75 mol), tetrabutylammonium hydrogen sulfate (6.22 g, 0.018 mol) and THF (250 cm^3) were mixed under an N_2 atmosphere. The mixture was stirred mechanically while a solution of benzyl chloride (64 cm^3, 70.4 g, 0.55 mol) in THF (250 cm^3) was added. The mixture was then heated under a reflux for 20 h. It was then allowed to cool and water (400 cm^3) and chloroform (300 cm^3) added. The organic layer was separated and solvent removed to give a pale brown oil. This was distilled under vacuum through a 20 mm vigreux column to yield a colourless oil (84.78 g, 70%), (b.p. 87–91 °C/0.002 mmHg); $\delta_H(CDCl_3$, 250 MHz), 7.28–7.35 (5 H, m, ArH), 4.52 (2 H, s, $ArCH_2$), 3.72 (2 H, d, *J* 11.6), 3.54 (2 H, d, *J* 11.6), 3.46 (2 H, s, CH_2OBr), 1.41 (3 H, s, CH_2), 1.38 (3 H, s, CH_3) and 0.89 (3 H, s, CH_3); *m/z* (d.c.i.) 251 ($M^+ + 1$, 100%), 193 (43), 158 (46) and 91 (43).

2-*Benzyloxymethyl*-2-*methylpropan*-1,3-*diol* **36**. The isopropylidene derivative **35** (83 g, 0.33 mol) was heated to reflux with conc. HCl (45 cm^3) and methanol (450 cm^3) for 17 h. The

methanol and water was then distilled off at atmospheric pressure and fresh methanol (450 cm^3) and conc. HCl (45 cm^3) was added and the solution heated at reflux for a further 17 h. Methanol and water were evaporated to leave a yellow oil which was filtered and dried under vacuum during which it solidified to a solid which was recrystallised from toluene–hexane (35.53 g, 51%), m.p. 44.5 °C (Found: C, 68.3; H, 8.5. $C_{12}H_{10}O_3$ requires: C, 68.6; H, 8.61%); $\delta_H(CDCl_3$, 200 MHz), 7.45–7.25 (5 H, m, ArH), 4.50 (2 H, s, $ArCH_2$), 3.69 (2 H, d, *J* 10.8, CHHOH), 3.56 (2 H, d, *J* 10.8, CHHOH), 3.45 (2 H, s, CH_2OBr), 2.94 (2 H, br s, OH) and 0.82 (3 H, s, CH_3); *m/z* (c.i.) 228 ($M^+ + \overset{+}{N}H_4$, 23%), 211 (100) ($M^+ + 1$), 108 (33) and 91 (46).

General Method of Polymerisation.—(*a*) The methacrylate **4** (1.04 g, 3.44 mmol) was dissolved in freshly distilled butan-2-one and azabisisobutyronitrile (AIBN) (4.4 mg, 0.42 weight % of monomer) was added under argon. The solution was degassed by three freeze–thaw cycles and was then heated at 85 °C (bath temperature) under argon until TLC analysis revealed that no further monomer remained (typically 15 h). A crystal of hydroquinone or 4-methoxyphenyl was added (*ca.* 1 mg) and the cooled reaction mixture was added slowly to hexane (50 cm^3). After allowing the precipitated polymer to settle, the solvent was decanted off and the polymer was redissolved in acetone (3 cm^3). This solution was added slowly to hexane (30 cm^3) and the reprecipitated polymer was recovered and the process repeated. The washed polymer was dried under vacuum (0.01 mmHg/40 °C) to leave a colourless brittle foam (0.66 g, 63%); M_n (GPC) 28 000, M_w 39 000, M_w/M_n 1.39; T_g 304 K; $\delta_C(CD_2Cl_2)$ 17.0, 18.84 (br, Me, rr + mr diads), 30.72, 30.88 (CH_2C ring), 45.03 (br, qc, rr), 45.39 (br, qc, mr diad), 54 (br, CH_2), 64.9 (br, CH_2O), 65.88, 66.0 (br, CH_2O), 66.8 (strong, CH_2O), 67.61 (CH_2O), 70.11, 71.3, 71.75, 72.04 (CH_2O); 76.54, 76.64 (ratio = 2:1; CHO, mr + rr diads), 176.6 (br, mm diad), 177.4 (br, rm diad, major) and 177.7 (br, rr diad).

This method was also used for the polymerisation of **3**, **11**, **12**, **18**, **19** and **24**. Similar molecular weight distributions were found in all cases {*e.g.* [poly(**24**)]: M_n 13 000, M_n 19 100, M_w/M_n 1.47}, and glass transition temperatures are given in Table 1, in the absence and presence of added anhyd. lithium trifluoromethanesulfonate [added as a solution in anhyd. acetone, followed by removal of solvent (0.01 mmHg) prior to thermogravimetric analysis].

(*b*) In the case of **4** an alternative method of polymerisation (redox initiation) was attempted and gave much higher molecular weight polymer.

To a suspension of the methacrylate **4** (2.34 g, 7.7 mmol) in degassed water (70 cm^3) was added potassium persulfate and ferrous sulfate (0.032 mmol respectively) at 4 °C, and the mixture was allowed to warm to room temp. over 15 h. The aqueous solution was decanted and the polymer redissolved in acetone (15 cm^3), filtered and the polymer reprecipitated by addition of water (100 cm^3). The washed polymer was redissolved in acetone (10 cm^3) and precipitated by addition of hexane (50 cm^3). The supernatant was decanted off and the polymer washed with hexane (2 × 10 cm^3), and dried *in vacuo* (0.01 mmHg/30 °C) to leave a clear film (0.35 g, 31%); M_n 2 × 10^5, M_w 8 × 10^5, M_z 1.25 × 10^6.

Appendix

Derivation of a 1:1 *Binding Model.*—

$$Li + L \overset{K}{\rightleftharpoons} LiL \qquad K_1 = \frac{[LiL]}{[L][Li]}$$

$$\delta_0 = \frac{\delta_0[L] + \delta_1[LiL]}{[L] + [LiL]} \qquad \text{at equilibrium}$$

where δ_0 = ^{13}C chemical shift in the absence of added Li^+, and δ_1 = ^{13}C chemical shift of the 1:1 complex, but [L] + [LiL] = $[L]_{int}$, where $[L]_{int}$ = initial concentration of ligand

$$\Rightarrow \qquad \delta_0 = \frac{\delta_0[L] + \delta_1[LiL]}{[L]_{int}}$$

$$= \frac{\delta_0([L]_{int} - [LiL]) + \delta_1[LiL]}{[L]_{int}}$$

$$= \frac{[LiL](\delta_1 - \delta_0) + [L]_{int}\delta_0}{[L]_{int}}$$

$$= \frac{[LiL](\delta_1 - \delta_0)}{[L]_{int}} + \delta_0$$

$$\Rightarrow \qquad \Delta\delta_0 = \frac{[LiL](\delta_1 - \delta_0)}{[L]_{int}}$$

expressing [LiL] in terms of known quantities:

$$K_1 = \frac{[LiL]}{([L]_{int} - [LiL])([L]_{int} M - [LiL])}$$

where $M = [Li]_{int}/[L]_{int}$ = quantity measured

$$\Rightarrow \quad K_1\{[L]_{int}^2 M - [L]_{int} M[LiL] - [L]_{int}[LiL] + [LiL]^2\} = [LiL]$$

$$K_1[LiL]^2 - (1 + K_1[L]_{int} + K_1[L]_{int}M)[LiL] + K_1[L]_{int}^2 M = 0$$

solving for a quadratic in [LiL]

$$[LiL] = \left(1 + \frac{K_1[L]_{int} + K_1[L]_{int} M}{2K_1}\right) \pm \sqrt{\frac{(1 + K_1[L]_{int} + K_1[L]_{int} M)^2 - 4K_1^2[L]_{int}^2 M}{2K_1}}$$

$$\Rightarrow \quad \Delta\delta_0 = \frac{(\delta_1 - \delta_0)}{2K_1[L]_{int}}\left\{(1 + K_1)[L]_{int} + K_1[L]_{int} M \pm \sqrt{(1 + K_1[L]_{int} + K_1[L]_{int} M)^2 - 4K_1^2[L]_{int}^2 M}\right\}$$

Points on the graphs are experimental values ($\Delta\delta_0$ *versus* *M*) and curves are those calculated by a general curve fitting procedure to the above equation, giving values of the equilibrium constant, K_1 and ^{13}C chemical shift of the 1:1 complex, as shown in Table 1.

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References

1 D. E. Fenton, J. M. Parker and P. V. Wright, *Polymers*, 1975, **14**, 589.

2 M. B. Armand, *Ann. Rev. Mater. Sci.*, 1986, **16**, 245; M. Gauthier, M. Armand and D. Muller, in *Electroresponsive Molecular and Polymeric Systems*, ed. T. A. Skotheim, Marcel Dekker, New York, 1988, pp. 41–87.
3 J. M. G. Cowie and K. Sadaghianizaden, *Makromol. Chem. Rapid Commun.*, 1988, **9**, 387.
4 J. M. G. Cowie and H. H. Wu, *Macromolecules*, 1988, **21**, 2116; J. M. G. Cowie and H. H. Wu, *Br. Polym. J.*, 1988, **20**, 515.
5 G. Shoham, W. N. Lipscomb and U. Olsher, *J. Chem. Soc., Chem. Commun.*, 1983, 208.
6 P. Jutzi, M. Meyer, H. V. Rasika Dias and P. P. Power, *J. Am. Chem. Soc.*, 1990, **112**, 4041.
7 F. Pauer, J. Raha and D. Stalke, *J. Chem. Soc., Chem. Commun.*, 1991, 1477.
8 R. Kataky, P. E. Nicholson and D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 1990, 321.
9 L. Collie, D. Parker, C. Tachon, H. V. St. A. Hubbard, G. R. Davies, I. M. Ward and S. C. Wellings, *Polym. Commun.*, 1993, **34**, 1541.
10 T. Miyazaki, S. Yanagida, A. Itoh and M. Okadhara, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2005.
11 Prepared from diethylene glycol by benzylation ($PhCH_2Br$/MaOH/THF/Bu_4NHSO_4), according to the method of H. H. Freedman and R. A. Dubois, *Tetrahedron Lett.*, 1975, **38**, 3251.
12 J. C. Randall, *Polymer Sequence Determination*, Academic Press, London, 1977.
13 M. Andrei J. M. G. Cowie and P. Prosperi, *Electrochim. Acta*, 1992, **37**, 1545.

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