Synthesis of some new polypseudorotaxanes

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Linear polymers are synthesised which have hydroquinol ether units linked by several ethylene oxide units; in some cases the latter also contain ester groups and introduction of the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) 1 to solutions of the polymers in acetonitrile leads to the formation of polypseudorotaxanes; ^{1}H NMR analysis of these solutions at −40 °C showed that in some cases up to 94% of the hydroquinol ether units were threaded through cyclophanes.

Interest in molecular assemblies of novel topology has increased enormously in recent years.[1–4] Numerous rotaxanes,† pseudorotaxanes† and catenanes have been synthesised.[3] Stoddart's group have exploited the favourable interactions between π-electron-rich moieties such as hydroquinol (HQ) ethers, where the ethers are formally derived from oligoethylene oxides (xEO), and π-electron-poor moieties such as those in the tetracationic cyclophane **1** for the self assembly of many rotaxanes and catananes.[3,5] The interest in molecular assemblies has extended to polymeric systems and various polyrotaxanes and polypseudorotaxanes have been prepared.[3] Polyrotaxanes have, for example, been prepared from polyester **2** and 30-crown-10,[6] and polypseudorotaxanes from polyacrylonitrile and 60-crown-20,[7] and from polymer **3** and β-cyclodextrin.[8] We wish to combine studies of polyrotaxanes and polypseudorotaxanes with our work on the synthesis of macrocycles[9,10] in order to build novel polymeric systems. As a first step we have synthesised polypseudorotaxanes based on polymers with dialkoxyaromatic units linked by several EO groups, plus in some cases ester groups, and Stoddart's cyclophane **1**, and we now report the results. Stoddart *et al.* have previously prepared two types of oligo- or poly-pseudorotaxanes.[11,12] One type was prepared, from compound **4**, which has

five hydroquinol ether moieties, by 'threading' on one or two cyclophanes **1**.[11] The second type was prepared from the copolymer **5**, where the degree of polymerisation (DP) was approximately 9, and an excess of cyclophane **1** with respect to the repeat units.[12] With the former type detailed analysis of ^{1}H NMR spectra provided proof of rotaxane formation;[11] with the latter type the main evidence of rotaxane formation was the expected colour change.[12] We have now assembled poly-pseudorotaxanes starting from polymers **6–10**, which have average DPs of up to 63, and have shown (i) that despite the relatively small number of end = groups present in most cases, polypseudorotaxanes can be rapidly obtained by 'threading' the polymers with cyclophane **1**, and (ii) that it is possible to obtain polypseudorotaxanes where a substantial fraction of the HQ ether units are present as rotaxane moieties and that this can be as high as 94% at −40 °C. Thus, it is possible for cyclophanes **1** to complex to HQ ether units which are adjacent in the polymer chain. This is the first occasion such 'close packing' of this charged cyclophane has been observed.
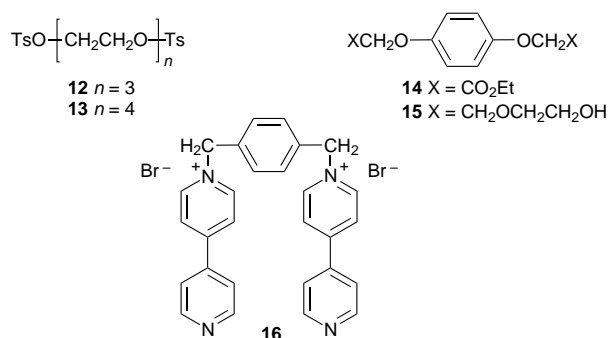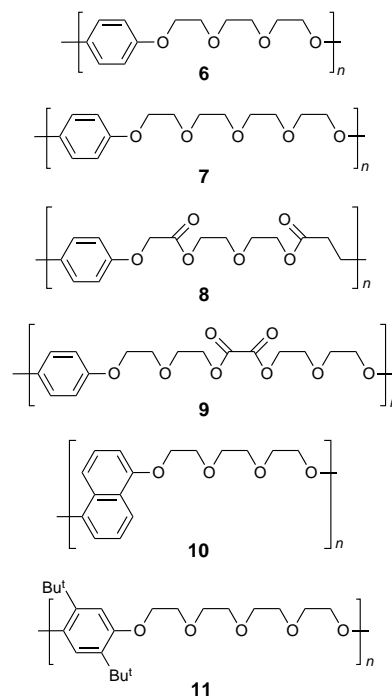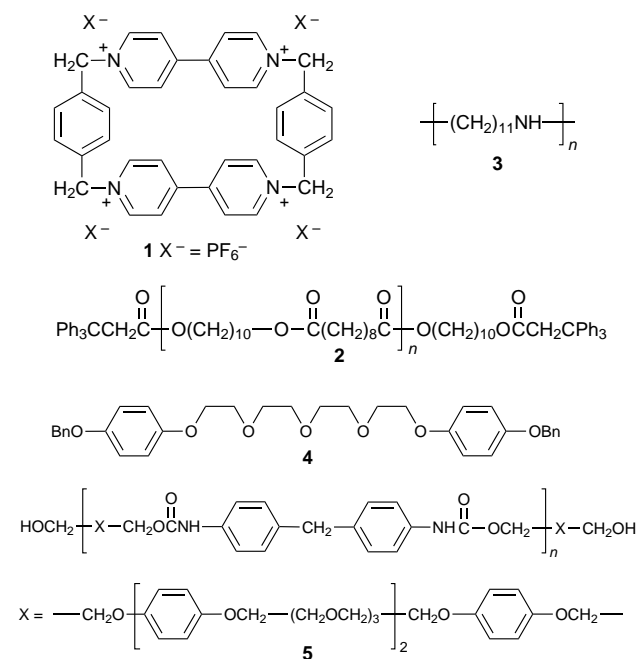
Polymers **6**, **7**, **10** and **11** were prepared by reacting hydroquinol, 1,5-dihydroxynaphthalene (ND) or 2,5-di-*tert*-butylhydroquinol (DBHQ) with the ditosylate of either triethylene glycol (3EO) **12** or of tetraethylene glycol (4EO) **13** (Table 1). Diester **14** and diol **15** were prepared by reacting hydroquinol with ethyl chloroacetate or 2-(2-chloroethoxy)-ethanol respectively in the presence of potassium carbonate in ethanol. Reaction of diester **14** with diethylene glycol (2EO) in the presence of titanium tetraisopropoxide gave polyester **8**. Polyester **9** was similarly prepared from diol **15** and dimethyl oxalate (DMO). The molecular weights of the various polymers were estimated using gel permeation chromatography, Table 1. The ^{1}H NMR spectra of the polymers were consistent with the assigned structures and $\overline{M}_n$ values; no phenolic end-groups were detected.

Attempts to prepare pseudopolyrotaxanes by reacting compound **16** and α,α′-dibromo-*p*-xylene **17** together in acetonitrile in the presence of polymer **6**, *i.e.* by 'clipping',[3] afforded complex mixtures that, by ^{1}H NMR spectroscopy and UV spectroscopy, contained pseudopolyrotaxanes but the latter could not be isolated in a pure state.[13]

Polypseudorotaxanes were successfully prepared by 'threading', *i.e.* cyclophane **1** was prepared [from **16** and **17**][14] and purified, then it was added progressively to solutions of the polymers in acetonitrile at 20 °C. In each case the solution immediately became dark red, indicative of rotaxane formation, and as more cyclophane **1** was added the colour generally became more intense as monitored by UV spectroscopy. The solutions were analysed by ^{1}H NMR spectroscopy at −40 °C.‡ At this temperature 'shuttling' of the threaded cyclophane was slow on the NMR timescale. In general the signals due to the starting polymer and the free cyclophane **1** were observed to decrease or disappear and signals characteristic of the rotaxane moiety, *i.e.* the HQ ether groups residing in the centre of the cyclophane plus the encircling cyclophane, appeared. The extents of 'threading' achieved with the various polymers are summarised in Fig. 1. It is evident in the cases of polymers **6**, **7** and **9** that up to the point when *ca.* 35% of cyclophane **1** has been added, essentially all the added cyclophane **1** becomes threaded. With polymer **6** the loading achieved, *i.e.* the percentage of HQ ether repeat units that are threaded, reaches a plateau at *ca.* 50% whilst with polymer **7** it reaches a plateau at *ca.* 70%. This latter percentage implies that a substantial fraction of the adjacent HQ ether units in the polymer chain are present as rotaxane moieties. Presumably with polymer **6**, which has only a 3EO spacer unit, such close proximity of the cyclophane rings is seriously inhibited because it results in electrostatic and/or steric interactions between the solvated cyclophanes. The presence of the ester linkage in polymer **8** clearly has an unfavourable effect on the 'threading' because the loading of this polymer, which formally has a 4EO spacer, reaches a plateau at *ca.* 55%, *i.e.* significantly lower than with polymer **7**. Polyester **9** on the other hand, which formally has a 5EO spacer, loads up to *ca.* 94%. Since this polymer has on average 21 HQ units in the chain, the result implies that on average each chain has 20 threaded rings. Similarly polyester **8** has on average, at maximum loading, 37 threaded rings per chain, *i.e.* is a [38]pseudopolyrotaxane. Polymer **10** also threads rapidly but the mixture obtained only dissolved in [^{2}H$_6$]DMF or [^{2}H$_6$]DMSO at *ca.* 100 °C. At this temperature the ^{1}H NMR spectrum in [^{2}H$_6$]DMF was broad and whilst it was clear 'threading' occurred an accurate analysis was not possible. As expected on steric grounds, polymer **11** did not thread at all.

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Table 1 Synthesis and characterisation of polymers **6–11**

Polymeric product	Starting compounds[a]	Yield (%)	Molecular weight[b]		
			$\overline{M}_n$	$\overline{M}_w$	$\overline{DP}$[c]
6	HQ + **12**	83	11 300	19 100	50
7	HQ + **13**	36	3500	4700	13
8	**14** + 2EO	89	18 600	23 400	63
9	**15** + DMO	47	7100	10 300	21
10	ND + **12**	77	7500	15 600	20
11	DBHQ + **13**	61	6600	13 200	17

[a] See text for abbreviations. [b] Determined by gel permeation chromatography. For polymers **6**, **7**, **10** and **11** polystyrene standards were used. For polymers **8** and **9** polyethylene glycol standards were used. [c] The average number of aromatic units per chain calculated from the $\overline{M}_n$ values, *i.e.* the values of *n* in formulae **6–11**. The actual average number of linkages formed during the syntheses are twice these values.
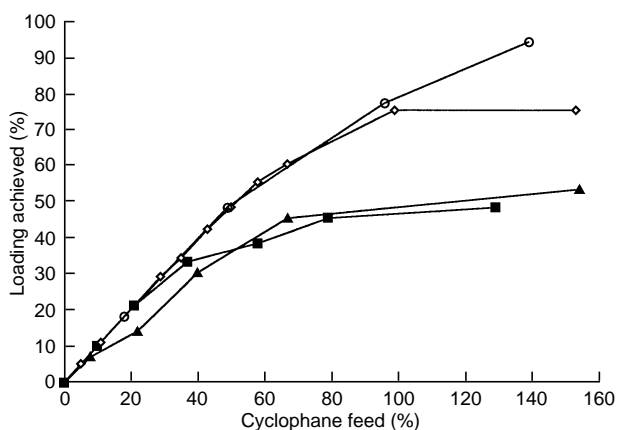
Fig. 1 Loading of cyclophane **1** achieved with various polymers in CD$_3$CN at −40 °C as a function of the cyclophane **1** feed. Polymer **6** —■—; **7** —◇—; **8** — ▲ —; **9** —○—. The cyclophane feed is the amount (mol%) of cyclophane added to the reaction mixture per polymer repeat unit.

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