^{1}H NMR spectroscopic studies of the structures of a series of pseudopolyrotaxanes formed by "threading"

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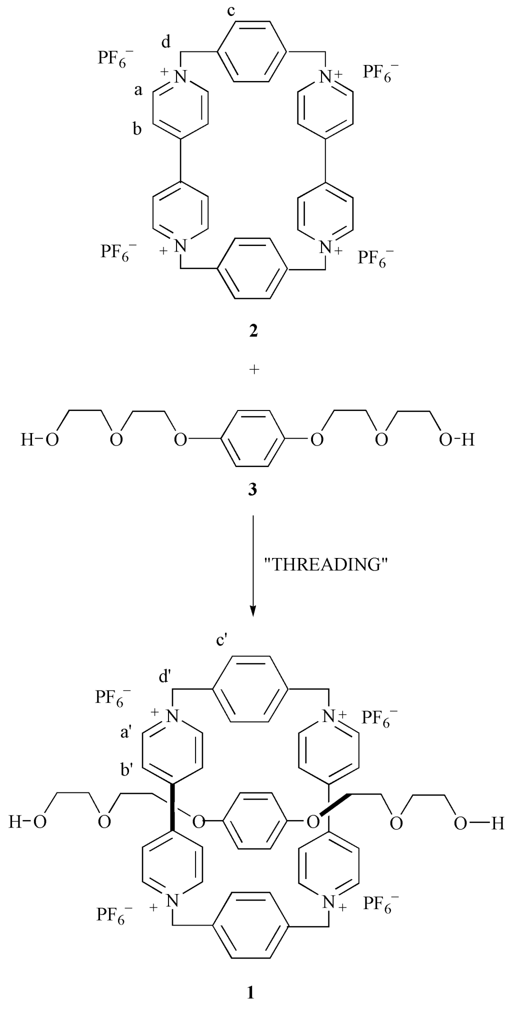
Introduction of the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) **2** into deuterioacetonitrile solutions of linear polymers with hydroquinol or resorcinol ether units linked by ethylene oxide sequences where, in several cases, the latter also contained carboxylic ester groups, led to the formation of pseudopolyrotaxanes. ^{1}H NMR spectroscopic analysis of these solutions at −40 °C shows how the structures of the pseudopolyrotaxanes evolve as the amount of cyclophane introduced into the solution increases. In some cases the pseudopolyrotaxanes have about half the polymer repeat units threaded through cyclophane molecules and they adopt a 'concertina' type of structure as a result of π-stacking. In other cases more than 85% of the repeat units of the polymer are threaded through cyclophane molecules, so that most of the polymer repeat units which are threaded have adjacent repeat units which are also threaded, and to avoid interactions between the cyclophanes the polymer almost certainly exists mainly in an extended conformation.

Until about 20 years ago rotaxanes‡ were rarely obtained in other than trace amounts,[1–3] but since then, based on an ever improving understanding of non-covalent molecular interactions,[3–6] many rotaxanes and pseudorotaxanes‡ have been synthesised.[2,3,6–12] Several types of polyrotaxanes and pseudopolyrotaxanes have also been prepared.[3,10,11,13–16]

One type of rotaxane, extensively studied by Stoddart's research group,[3,7–9] but also by others,[10,15,16] is that where there is a strong π–π interaction between the ring component and the rod component. A simple example is the rotaxane **1** which is formally derived from the π-poor cyclophane **2** and the π-rich hydroquinol (HQ) ether **3**.[7] More complex examples are the rotaxanes formed from cyclophane **2** and the HQ derivatives **4** and **5**, which can adopt the π-stacked structures **6** and **7** respectively:[8] see Fig. 1. X-Ray diffraction studies of this type of rotaxane have shown that the HQ ether unit is generally threaded through the cyclophane **2** at an angle such that the oligo(ethylene oxide) chain passes close to two pyridinium moieties.[8,17,18] Association constant–structure studies indicate that interactions between some of the pyridinium moieties of the cyclophane and the first two ethylene oxide (EO) units of the side chains, or spacer chains, are at least as important in determining the association energy of the complexes as the interactions between the π-rich HQ ether units and the π-poor cyclophanes.[7] Of particular importance in the present work is that with all rotaxanes of this general type, rotaxane formation in solution is easily monitored by ^{1}H NMR spectroscopy as a consequence of the very close juxtaposition of the aromatic rings of both components in the rotaxane. This results, mainly because of ring current effects, in substantial and characteristic changes in the chemical shifts of many of the neighbouring protons.[7,8]



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‡ Rotaxanes have a rod or chain threaded through rings and end-groups that are sufficiently large to prevent the rings from slipping off. Pseudorotaxanes do not have the large end-groups and so can dissociate.

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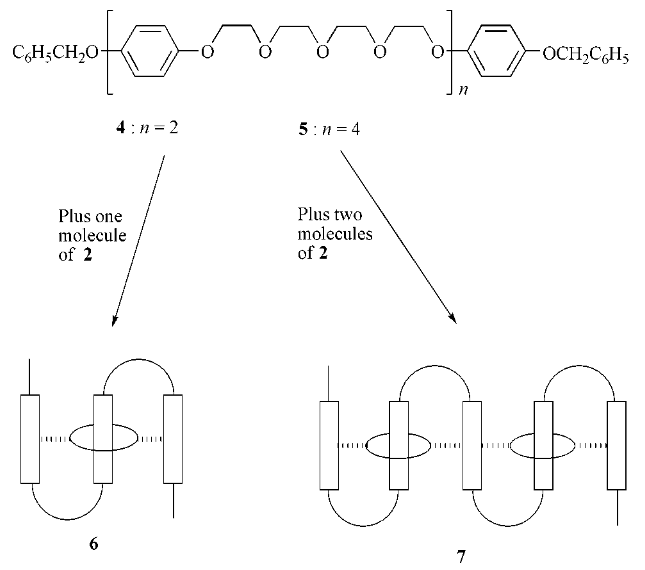

Fig. 1 Some pseudorotaxanes described in the literature (ref. 7) and schematic representations of their structures. In the schematic structures for pseudorotaxanes **6** and **7** the boxes represent HQ units; solid curved lines the tetra(ethylene glycol) linking groups and straight lines the tail units shown in detail in formulae **4** and **5**; the circles cyclophane **2**; and the broken lines π-donor–acceptor interactions.

The present project is concerned with the formation of pseudopolyrotaxanes by "threading" the cyclophane **2** on to polymers **8**–**14**, each of which contains many HQ ether or resorcinol ether moieties linked by various EO-derived units. Information on the substructures present in the pseudopolyrotaxanes was obtained by a careful ^{1}H NMR spectroscopic analysis and the results of this analysis are now reported here. We have briefly reported before on the extent of binding of cyclophane **2** to three of the polymers, but no detailed information was obtained on the substructures produced.[14] This approach to studying rotaxanes, in which the evolution of the proportions of the various substructures present in a pseudopolyrotaxane is determined as more of the cyclic component is added, complements well the more usual type of studies where, typically, rotaxanes are isolated as solids and their structures then determined in great detail by X-ray crystallography. Since our initial report,[14] other researchers[15,16] have used ^{1}H NMR spectroscopy to study the rates at which cyclophane **2** "threads onto" and "dethreads from" some polymers similar in structure to those we have studied.

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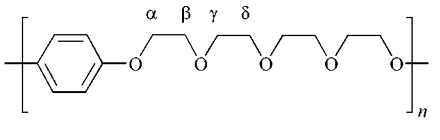

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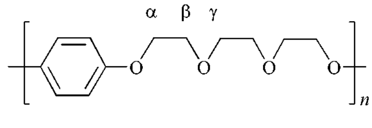

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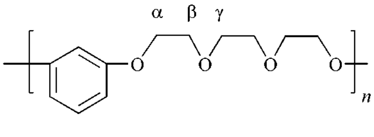

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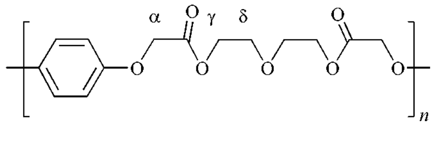

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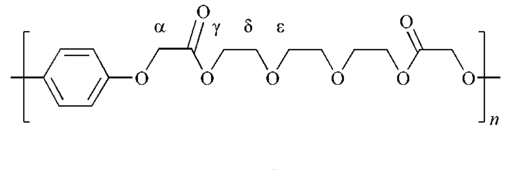

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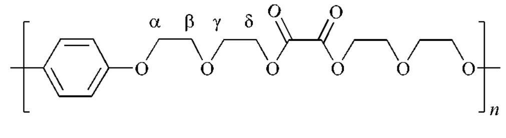

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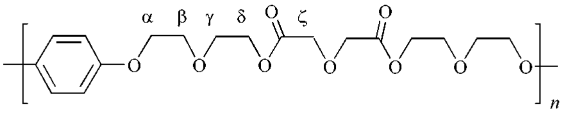
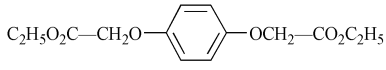


Results and discussion

Polymer synthesis

Polymers **8**–**10** were prepared by reacting the appropriate bis(tosylate) of tri- or tetra-(ethylene glycol) in 1,2-dichlorobenzene with an aqueous tetra-n-butylammonium hydroxide solution of hydroquinol or resorcinol at reflux temperature under phase transfer catalysed conditions. Polyesters **11** and **12** were prepared by reacting the diester **15**[8] with di- or tri-(ethylene glycol) as appropriate in the presence of a catalytic amount of titanium isopropoxide at 150 °C and distilling out the ethanol formed. Polymers **13** and **14** were similarly prepared by reacting diol **3** with dimethyl oxalate or dimethyl diglycolate as appropriate. The reaction yields and the molecular weights of the various polymers, as estimated by gel permeation chromatography (GPC), are summarised in the Table 1. The ^{1}H NMR spectra of the polymers were fully consistent with the assigned structures and the M_n values.



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Synthesis of pseudopolyrotaxanes and ^{1}H NMR spectroscopic studies of their structures

In the present study the pseudopolyrotaxanes were prepared in the NMR tube by "threading".[7] This simply involved adding the chosen amount of the cyclophane **2** to a solution of the chosen polymer in deuterioacetonitrile, or, in one case, a mixture of this solvent and deuteriochloroform, at 20 °C. In each case the solution immediately became dark red, indicative of rotaxane formation,[17] and as more cyclophane **2** was added the colour generally became more intense. Movement of the cyclophane **2** onto, off and along the polymer chains is very fast at 20 °C.[15] The rate of "threading" will clearly depend on the concentration of end-groups present, *i.e.* on the molecular weights of the polymers, but in the present work the time taken between mixing the components at 20 °C and recording the spectra at −40 °C appears to be sufficient for the equilibria to be fully established and the molecular weights of the polymers used does not appear to be a factor here.[15] Prior to recording the ^{1}H NMR spectra the solutions were cooled to −40 °C so that the signals became sharp, *i.e.* so that movment of the rings onto, off and along the polymer was slow on the NMR time scale and separate signals were seen for the uncomplexed HQ units and complexed HQ units in various environments.[7,8,17,18]

In the present work the chemical shifts of the uncomplexed cyclophane **2** occurred at δ 5.77 (CH_2N^+), 7.55 (benzene ring), 8.19 (β-proton of pyridinium ring) and 8.87 (α-proton of pyridinium ring). On pseudopolyrotaxane formation these signals broadened and shifted respectively to δ 5.50 (*i.e.* a shift upfield

Table 1 Synthesis and characterisation of polymers **8**–**14**[a]

Polymeric product	Starting materials[b]	Yield(%)	Molecular weight[c]/kg mol^{-1} M_n	M_w	DP[d]
8	HQ + E4BT	36	3500	4700	13
9	HQ + E3BT	83	11 300	19 100	50
10	R + E3BT	53	7800	12 600	35
11	**15** + E2	89	18 600	23 400	63
12	**15** + E3	92	20 500	24 900	65
13	**3** + DMO	47	7100	10 300	21
14	**3** + DMDG	80	2100	4500	6

[a] See Experimental section for details of procedures used. [b] Abbreviations: HQ = hydroquinol; R = resorcinol; E4 = tetra(ethylene glycol); E3 = tri(ethylene glycol); E2 = di(ethylene glycol); BT = bis(tosylate); DMO = dimethyl oxalate; and DMDG = dimethyl diglycolate. [c] Determined by gel permeation chromatography. For polymer **8**–**10** and **14** polystyrene standards were used. For polymers **11**–**13** poly(ethylene glycol) standards were used. [d] The average number of *aromatic units* per chain calculated from the M_n values, *i.e.* the values of '*n*' in the formulae. The actual average number of linkages formed during the syntheses are twice these values.

of +0.27 ppm), 7.70 (−0.15 ppm), 7.70 (+0.49 ppm) and 8.82 (+0.05 ppm): see Fig. 2. In all the spectra of the pseudopolyrotaxanes the chemical shifts due to the cyclophane were within 0.06 ppm of these values.

Most structural information was, however, derived from the signals due to the HQ or resorcinol ether moieties in the polymers. The HQ ether moieties in the polymers were found to be present in one of the four environments shown in Fig. 3. These are conveniently labeled as "free" (**F**), "threaded" (**T**), "alongside" and interacting with one threaded unit (**A**), or were "between" and interacting with two threaded units (**B**). Except where noted below, in whatever pseudopolyrotaxane the **F**, **A** and **B** structures occurred the chemical shifts values were found to be within 0.06 ppm of those given in Fig. 3, values which agree well with those reported for less complex rotaxanes or pseudorotaxanes.[8] A typical spectrum is shown in Fig. 2. The precise signal positions due to the HQ units in **T** environments were difficult to determine because they fall in the δ 3.20–4.70 region that is dominated by the broadened multiplets due to the ethylene oxide-derived spacer units. The percentage of the HQ units in **T** environments was, however, readily determined from the integrals of the signals due to free and complexed cyclophane molecules. By progressively "feeding" more and more cyclophane **2** to the polymer chains it was possible to determine from these various signals how the loading of the cyclophane increased and how the structure of the pseudopolyrotaxanes evolved as the loading increased. The NMR signals were generally broadened because the samples were polymers. This and the fact that the signals due to the various methylene groups in the EO-derived spacer units were complex and overlapping meant it was not possible to glean much useful information from these particular signals about the substructures present in the pseudopolyrotaxanes.

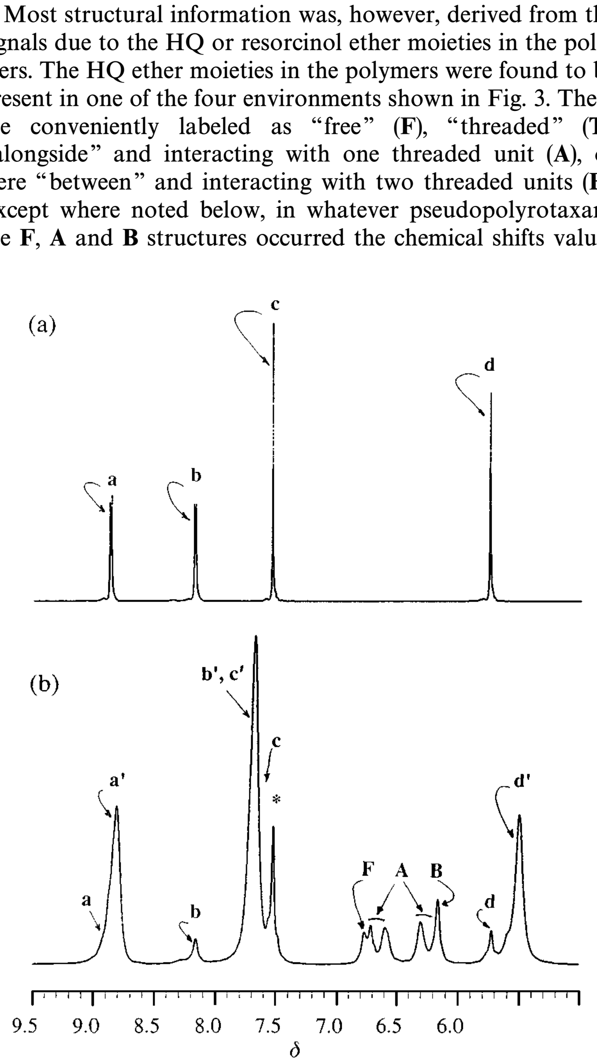
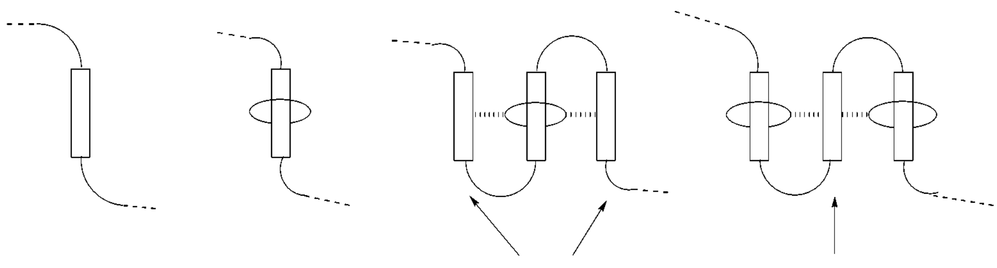


Fig. 2 Typical ^{1}H NMR spectra: (a) the spectrum for cyclophane **2** in CD_3CN at ambient temperature; (b) the spectrum for the pseudopolyrotaxane formed from polymer **9** plus 22 mol% of cyclophane **2** in $CD_3CN : CDCl_3$ (3 vols. : 1 vol.) at −40 °C in the region δ 5.0 to 9.5. The assignments are labeled using the letters "a" to "d" as shown in formula **2**, "a′" to "d′" as shown in formula **1**, and the letters **F**, **A**, and **B** for the HQ moieties in the various environments shown in Fig. 3. The signal for the HQ moieties in the **T** environment were part of the envelope between δ 3.4 and 4.2. * indicates signal from $CHCl_3$ in solvent.

Pseudopolyrotaxanes formed from polymer 8 and cyclophane 2. The NMR spectra of the pseudopolyrotaxanes obtained from polymer **8**, which has four EO units between the HQ moieties, clearly contained signals due to the presence of HQ moieties in **F**, **T**, **A** and **B** environments. The results obtained by progressively "feeding" more and more of the cyclophane **2** are shown graphically in Fig. 4. It is evident that up to a cyclophane "feed" of *ca.* 50% nearly all the added cyclophane becomes bound to the polymer. Up to *ca.* 10% of threading, for each HQ residue that threads through a cyclophane two other HQ residues are in an **A** environment, so that the principal substructure present is that shown schematically in Fig. 5(a). Clearly it would only be possible to have the HQ units present entirely in this substructure up to a loading of 33% and as this level of loading is approached the HQ residues are increasingly shared, *i.e.* the fraction of HQ residues in a **B** environment increases. The main substructure present then becomes of the general type of π-stacked structure shown in Fig. 5(b). It is not possible to be more precise about this π-stacked structure than this because one **B** may simply be flanked by two **T** units, when the **B** : **T** ratio will be 1.0 : 2.0, or the **B** and **T** units may alternate over many units, when the **B** : **T** ratio will tend to 1.0 : 1.0. Also the sequence of **B** and **T** units may end with an **F** or an **A** unit. At still higher "feeds" the fraction of HQ residues threaded progressively increases and at 100% feed *ca.* 65% of the HQ residues are threaded. It eventually reaches a plateau at *ca.* 74%. Clearly as the loadings begin to exceed *ca.* 50%, then increasingly *adjacent* HQ units must be threaded through cyclophane molecules. The fact that the loadings achieved tend towards a plateau of *ca.*



	Free	Threaded	Alongside	Between
ENVIRONMENTS :	Free	Threaded	Alongside	Between
^{1}H NMR SIGNALS :	Singlet	Singlet	Distorted A_2B_2 system	Singlet
	δ6.80	δ*ca.* 3.4 - 4.6	δ6.30 and 6.48 for polymer **8** and δ6.25 and 6.65 for polymer **9**	δ6.16

Fig. 3 Environments for HQ units that can be detected by ^{1}H NMR spectroscopy and the corresponding chemical shifts as measured in the present work. All spectra were measured for solutions at −40 °C. The positions of the signals for HQ units in **T** environments were not easily determined accurately as they lie under the broad multiplets due to the spacer chains. The actual shift values given agree closely with those reported in ref. 8 for similar structures in non-polymeric systems.

74% suggests that while having two adjacent HQ units threaded is energetically acceptable in the present system, having three is significantly more difficult, possibly because the four EO spacer between the HQ units is not sufficient to fully insulate one HQ unit from the next. Thus, there may be electrostatic and/or steric repulsions which become very important in this system when three adjacent HQ units are threaded. It is interesting to note that although at certain loadings a particular substructure may be dominant, in general there is always more than one type of structure present. For example, at 50% feed 36% of the remaining HQ residues are in an **A** environment and 48% in a **B** environment. At the same time 8% of all the HQ units are still "free". Finally with this polymer it should be noted that the signal due to the HQ units in the **A** environment appears at all loadings as two multiplets of equal intensity centred at δ 6.30 and 6.48 due to an A_2B_2 system. The non-equivalence is almost certainly due to the fact that the **A** units do not sit symmetrically over the cyclophane aromatic rings.

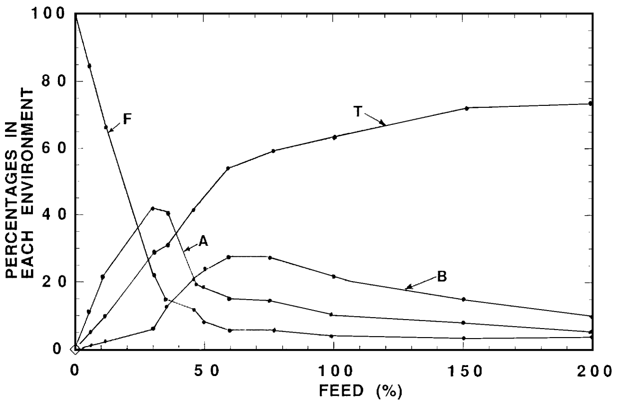


Fig. 4 Plots of the percentage of the HQ units in polymer **8** (7.5 × 10^{-2} M in CD_3CN at −40 °C) in **F**, **T**, **A** and **B** environments *vs.* the percentage feed of cyclophane **2**.

Pseudopolyrotaxanes formed from polymer 9 and cyclophane 2. The NMR spectra of the pseudopolyrotaxanes obtained from polymer **9**, which has only three EO units between the HQ moieties, also clearly contained signals due to HQ units in **F**, **T**, **A** and **B** environments, and the results obtained by progressively "feeding" more and more of the cyclophane **2**

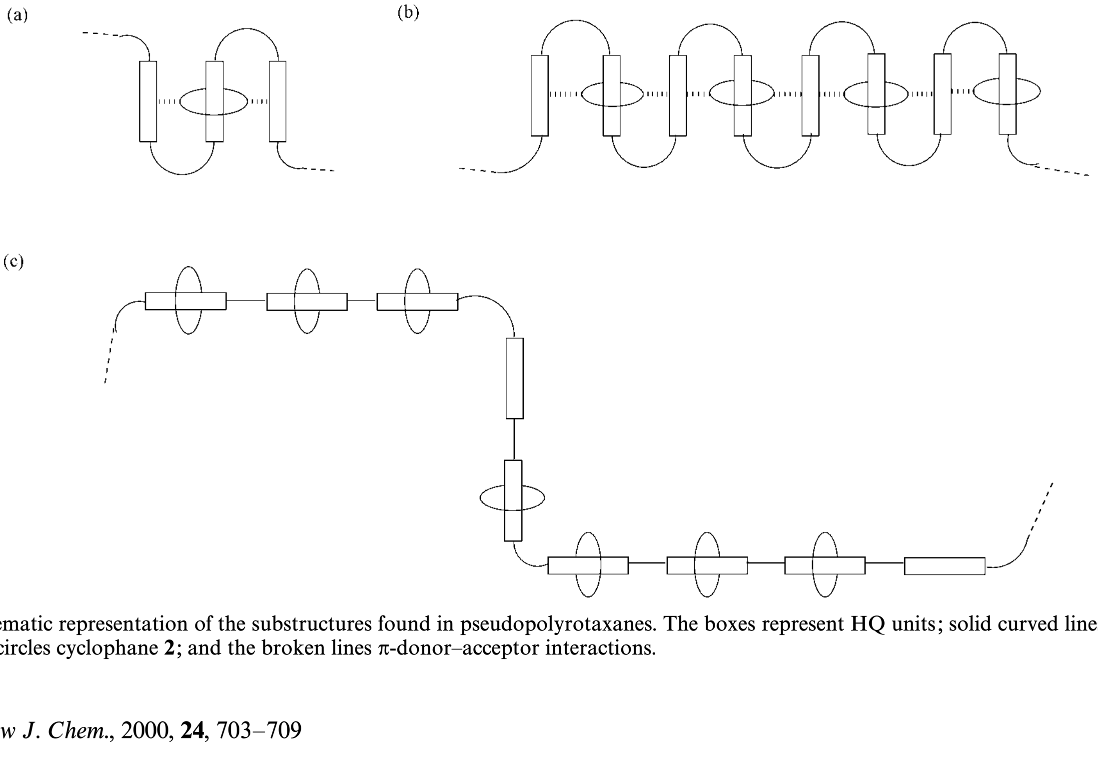


Fig. 5 Schematic representation of the substructures found in pseudopolyrotaxanes. The boxes represent HQ units; solid curved lines the linking groups; the circles cyclophane **2**; and the broken lines π-donor–acceptor interactions.

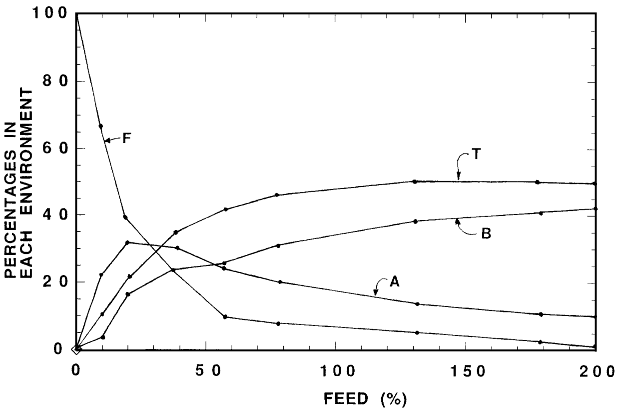


Fig. 6 Plots of the percentage of the HQ units in polymer **9** (7.5 × 10^{-2} M in CD_3CN : $CDCl_3$ (3 vols : 1 vol) at −40 °C) in **F**, **T**, **A** and **B** environments *vs.* the percentage feed of cyclophane **2**.

are shown graphically in Fig. 6. In general the results are similar to those obtained with polymer **8** and although their interpretation is also very similar, there are some important and clear differences. Thus, up to a feed of *ca.* 40% nearly all the cyclophane is bound. Also, as the feed of cyclophane increases, first the substructure shown in Fig. 5(a) dominates followed by that in 5(b), but with this particular polymer the loading plateaus at only 50%. This suggests that in this system the closer proximity of the HQ units discourages adjacent HQ units from threading. The net effect is that at a feed of 180%, for example, the fraction of the HQ units in **B** environments is approximately 80–90% of those in **T** environments and thus most of the polypseudorotaxane has a substructure of the type 5(b), *i.e.* the polymer is mainly a π-stacked "concertina" structure. It is interesting to note that even when the plateau is reached at a feed of 100%, *ca.* 5% of the HQ units are still "free". Again the signals due to the HQ units in the **A** environment appear at all loadings as an A_2B_2 system, this time centred at δ 6.25 and 6.65.

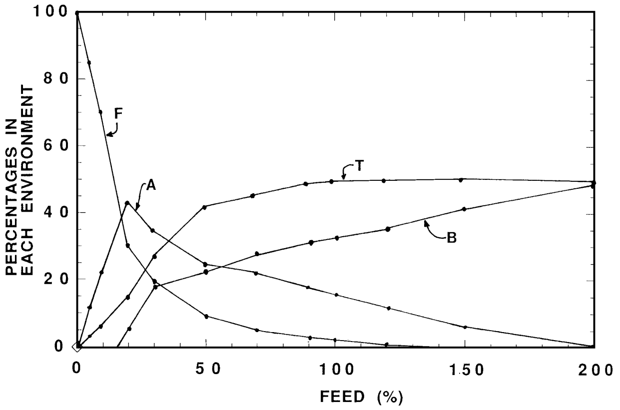


Fig. 7 Plots of the percentage of the resorcinol units in polymer **10** (8.5 × 10^{-2} M in CD_3CN at −40 °C) in **F**, **T**, **A** and **B** environments *vs.* the percentage feed of cyclophane **2**.

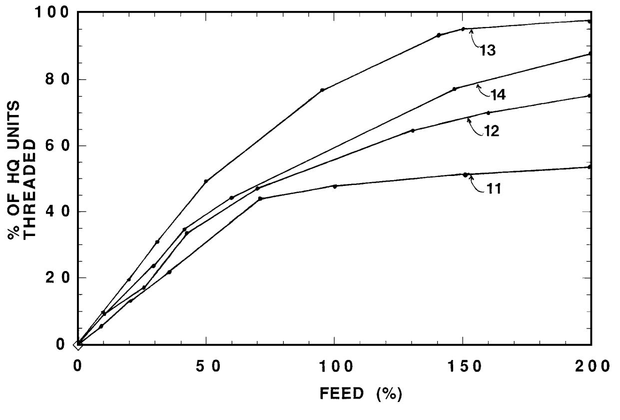
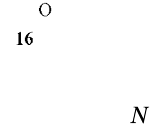


Fig. 8 Plots of the percentage of HQ units in **T** environments in various polymers **11** to **14** *vs.* the percentage feed of cyclophane **2**. The remainder of the HQ units were in **F** environments. There was no evidence for any HQ units in **A** or **B** environments. The polymer concentrations were 6.4 × 10^{-2} M in CD_3CN at −40 °C.

Pseudopolyrotaxanes formed from polymer 10 and cyclophane 2. The results obtained with polymer **10**, which has three EO units between resorcinol moieties, are very similar to those obtained with polymer **9**. They are shown graphically in Fig. 7. Again as the feed of cyclophane **2** increases, first the substructure shown in Fig. 5(a) dominates followed by that in 5(b), the loading plateauing at only 50%.

Pseudopolyrotaxanes formed from polyesters 11-14 and cyclophane 2. The results obtained with the polyesters **11**–**14** were quite different from those already discussed. Thus, the NMR spectra of all the pseudopolyrotaxanes obtained from these polymers, which formally have four, five, or six EO-derived units between the HQ moieties, showed only signals due to HQ units in **F** or **T** environments. There was no evidence at all for HQ units in **A** or **B** environments. Hence the HQ units which are not threaded do not appear to π-stack. Presumably it is more important energetically for the EO units to interact with the pyridinium moieties on the cyclophane than it is for the HQ units to π-stack and that when the EO units interact it is no longer easy for the remaining chain to coil round so that the next HQ unit can adopt an **A** environment. The results obtained by progressively "feeding" more and more of the cyclophane **2** to these various polyesters are shown graphically in Fig. 8. Several points merit comment. First, whilst up to a feed of *ca.* 40% the percentage take up of cyclophane **2** by the polymer is high, for polymers **11**, **12** and **14** it is not quite as high as it is with polymers **8**–**10** and **13**. This no doubt reflects the fact that the binding energy is higher with polymers **8**–**10** due to the additional binding interactions resulting from the HQ units in environments **A** and **B**. Second, at the higher feed levels the loadings achieved with polymers **13** and **14** are higher than 85%. Thus, with these spacers of five and six EO units there is no problem in threading almost every HQ unit through a cyclophane molecule as indicated in Fig. 5(c). Third, whilst polymers **11** and **12** can have >50% of the HQ units threaded, they do not accept the cyclophane molecules as readily as polymers **13** and **14**. Since polymer **12**, like polymer **13**, has spacers of five EO units, this suggests that it is the position of the ester link which affects the extent of binding. Stoddart *et al.* recently noted that an ester link at this position in a non-polymeric compound analogous to polymers **11** and **12** reduced the association constant from 3800 M^{-1} at 25 °C to 520 M^{-1}.[9] The difference appears to be due to a reduction in the strength of the interaction of the EO chain with the pyridinium moiety.[9] It is to be expected that when the ester linkage is further removed from the HQ units, as it is in polymers **13** and **14**, that it will have less effect on the binding energy. It is interesting to note with polymers **13** and **14** that the ester linkages probably have the conformations shown in formulae **16** and **17**. These have each ester link in the preferred[9,19] antiperiplanar conformation and, in the case of the oxalate, the transoid arrangment of the carbonyl groups that minimises the repulsions of their dipoles. These preferred extended planar conformations will serve to discourage the formation of π-stacked structures.



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Conclusions

These studies show how in a series of polymers with HQ moieties the length of the EO spacer units, the presence or absence of ester linkages in these spacer units and, when they are present, their precise location, affects the ease of formation and structure of the pseudopolyrotaxanes formed by threading cyclophane **2**. Thus, in the case of polymer **9** it is possible to have a pseudopolyrotaxane with essentially half the polymer repeat units threaded through cyclophane molecules and which substantially adopt a 'concertina'-like structure as a result of π-stacking, whereas in the case of polymer **13** it is possible to have a pseudopolyrotaxane with no π-stacking and more than 90% of the polymer repeat units threaded through cyclophane molecules. The fact that many of the present polymers can have cyclophanes threaded onto a significant fraction of the polymer repeat units is of particular interest and has not been noted before for any rotaxanes of the general type **1**, *i.e.* involving aromatic ethers and cyclophane **2**.

Experimental

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1710 FT-IR instrument for KBr disks. Except where indicated otherwise ^{1}H NMR spectra were recorded on a Varian Unity 500 MHz spectrometer for solutions of 10 mg of the polymer sample in 1 ml of deuterioacetonitrile at 23 °C. Spectra were referenced by setting the CHD_2CN residual proton signal to δ 1.94. GPC analyses were carried out using a series of four PLgel 30 cm mixed E columns. The eluant was tetrahydrofuran and the detector a Waters 401 RI detector. The apparatus was calibrated using a series of polystyrene standards.

Chemicals

The following compounds were prepared by literature procedures: **2**,[17] **3**,[7] **15**,[8] and the bis(tosylate) of tri(ethylene glycol).[7] All these products had satisfactory mps and FT-IR and ^{1}H NMR spectra. The bis(tosylate) of tetra(ethylene glycol) was purchased from the Aldrich Chemical Company.

Reaction procedure for the synthesis of polymers 8–10

The following procedure for the synthesis of polymer **9** is typical. The results of other syntheses are summarised in Table 1.

A mixture of hydroquinone (2.00 g, 18.2 mmol), tri(ethylene glycol) bis(p-tosylate) (8.34 g, 18.2 mmol), 1,2-dichlorobenzene (75 ml) and water (25 ml) was vigorously stirred. Nitrogen gas was bubbled through the solution for 30 minutes in order to purge it of any oxygen, then tetra-n-butylammonium hydroxide (23.57 g, 36.4 mmol as a 40 wt% solution in water) was added, whilst maintaining the nitrogen flow, and the reaction vessel sealed under a positive pressure of nitrogen and stirred at *ca.* 100 °C for 5 days. The resulting polymer was precipitated into methanol and collected by filtration, then reprecipitated from chloroform into methanol, collected and dried. Yield: 3.42 g (83%).

Reaction procedure for the synthesis of polyesters 11–14

The following procedure for the synthesis of polymer **11** is typical. The results of other syntheses are summarised in Table 1.

Diester **15** (2.00 g, 7.1 mmol), di(ethylene glycol) (0.752 g, 7.1 mmol) and titanium isopropoxide (40 mg, 0.14 mmol) were heated together without solvent at 100 °C under a flow of nitrogen for 1 day. The apparatus was then set up for distillation to remove the ethanol by-product. The mixture was heated at 150 °C under nitrogen for 1 day and finally at 150 °C under vacuum (0.5 mmHg) for 3 days. The resulting oil was allowed to cool, chloroform was added and the mixture was allowed to stand for 18 hours to allow it to dissolve fully. The polymer was precipitated into THF, collected by filtration and then dried under vacuum. Yield: 1.93 g (89%).

^{1}H NMR spectra of polymers 8–14

The carbon atoms in the spacer chains are conveniently labelled, starting from the aromatic ring, with Greek letters. See the respective formulae for the labelling.

Polymer **8**: δ 3.50–3.65 (8H, br m, γ- and δ-OCH_2), 3.70 (4H, m, β-OCH_2), 4.02 (4H, br m, α-OCH_2), and 6.78 (4H, s, ArH).

Polymer **9**: δ 3.60 (4H, br m, γ-OCH_2), 3.71 (4H, br m, β-OCH_2), 3.96 (4H, br m, α-OCH_2), and 6.80 (4H, s, ArH).

Polymer **10**: δ 3.58 (4H, br m, γ-OCH_2), 3.73 (4H, br m, β-OCH_2), 3.98 (4H, br m, α-OCH_2), 6.50–6.55 (3H, br m, ArH) and 7.10–7.15 (1H, br m, ArH).

Polymer **11**: δ 3.70 (4H, br m, δ-OCH_2), 4.35 (4H, br m, γ-OCH_2), 4.60 (4H, br s, α-OCH_2CO), and 6.85 (4H, s, ArH).

Polymer **12**: δ 3.63 (4H, br m, ε-OCH_2), 3.73 (4H, br m, δ-OCH_2), 4.38 (4H, br m, γ-OCH_2), 4.62 (4H, br s, α-OCH_2CO) and 6.85 (4H, s, ArH).

Polymer **13**: δ 3.75 (8H, br m, β- and γ-OCH_2), 4.07 (4H, br m, α-OCH_2), 4.47 (4H, br m, CH_2OCO) and 6.85 (4H, s, ArH).

Polymer **14**: δ 3.67 (4H, br m, γ-OCH_2), 3.73 (4H, br m, β-OCH_2), 3.99 (4H, br m, α-OCH_2), 4.17 (4H, br s, ζ-OCH_2), 4.22 (4H, br m, δ-OCH_2) and 6.83 (4H, s, ArH).

^{1}H NMR spectra of pseudopolyrotaxanes

These spectra were recorded on a Varian Unity 500 MHz spectrometer. For each spectrum a solution was prepared by adding carefully weighed samples of the polymer and cyclophane to 0.75 ml of solvent at 20 °C. Except in the case of polymer **9** the solvent was deuterioacetonitrile. For solubility reasons, with polymer **9** the solvent was a mixture of deuterioacetonitrile (3 vols.) and deuteriochloroform (1 vol.). The polymer concentrations were as follows: polymer **8**, 7.5×10^{-2} M; polymer **9**, 7.5×10^{-2} M; polymer **10**, 8.5×10^{-2} M; polymer **11**, 6.4×10^{-2} M; polymer **12**, 6.4×10^{-2} M; polymer **13**, 6.4×10^{-2} M; and polymer **14**, 6.4×10^{-2} M. The spectra were recorded after the solutions had been cooled to −40 °C. In most cases the spectra were measured once. The signals were broadened and typically had a width at half height of *ca.* 35 Hz. See Fig. 2 for a typical spectrum.

The signals of the free cyclophane and the cyclophane threaded over HQ or resorcinol units occurred, within 0.06 ppm, at the positions indicated in the text. HQ signals appeared at the positions indicated in Fig. 3. The signals due to the EO units in the free and threaded units in HQ-containing polymers formed broad overlapping multiplets in the region δ 3.0–4.7.[8] The precise positions due to HQ units in **T** environments were difficult to determine because they also fall in this region. However, the percentages were readily determined from the integrals due to free and complexed cyclophane molecules. The percentages of the aromatic units present in each environment are probably within 3% of the values shown in Figs. 4 and 6–8.

Interpretation of the spectra obtained for the pseudopolyrotaxanes formed from polymer **9** was much more difficult, because not only could the signals due to the aromatic protons potentially occur in **T**, **A** and **B** environments, but for each type of environment the signals due to the four aromatic protons might occur at different positions. The signals due to the cyclophane threaded over the resorcinol units still occurred at the positions quoted in the text for those threaded over HQ units and from the integrals for the free and threaded cyclophane the percentages of resorcinol units in **F** and **T** environments could easily be estimated. Careful analysis of the integrals due to the aromatic protons indicated that some signals were present in the complex δ 3.0–4.1 region (due mainly to the EO units) and the complex δ 5.4–6.0 region (due substantially to the cyclophane). The only clear easily-integrated signal was that at δ 6.5 and this increased in size as the percentage of **T** increased. This was assumed, on the basis of predicted shifts, to be due to H-5 of the resorcinol ring in a **B** environment: the predicted shifts suggested that the other protons in **B** environments would be in the complicated δ 5.4–6.0 region. This assumption allowed the percentage of resorcinol units present in **B** environments to be estimated. The percentages in **A** environments were then estimated by difference, recognising that the signal due to the H-5 proton in a **T** environment occurs at very high field.[8] Despite these difficulties of estimating the percentages of the resorcinol units in each environment, the results, plotted in Fig. 7, show a close resemblance to the results obtained for polymer **9**, which are plotted in Fig. 6.

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