

Dynamic behaviour of a pseudo[*n*]polyrotaxane containing a bipyridyl-based cyclophane: spectroscopic observations†

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We have shown by ¹H n.m.r. spectroscopy that the equilibrium between the cyclophane 5,12,19,26[tetraazoniaheptacyclo[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2^{21,24}]tetraconta2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,35,37,39-octa-decaene]tetrakis(hexafluorophosphate) (**1**) and the polymer [poly(1-(1,4,7-trioxadecenyl)-4-(11-(1-(5-oxynaphthyl)-1,4,7,11-tetroxaundecenyl))benzene)] (**B:N**)_{*n*} is both rapid and heavily weighted toward the formation of the pseudo[*n*]polyrotaxane at room temperature in both MeCN-d₃ and DMSO-d₆. At room temperature in DMSO-d₆ there is about one ring upon the polymer for each two repeat units of (**B:N**), at higher temperatures more repeat units are required to support one **1**. At temperatures of ca. 243 K in MeCN-d₃ this system self assembles, by π stacking of the electron-rich polymer aromatics and the electron-poor cyclophane aromatics, into very ordered 'rods' that are on average about 10 nm long. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: pseudopolyrotaxane; polymer; cyclophane)

INTRODUCTION

The synthesis of polymers with novel and useful properties is a persistent goal of polymer science, in which the preparation of polyrotaxanes and the analysis of their properties has a place in the hope that this relatively new class of polymers will be of interest. As part of our ongoing studies of such species we now report on certain aspects of the solution behaviour of pseudopolyrotaxanes, studied by dynamic n.m.r. spectroscopy.

There are several types of species that can be made from a polymer and a cyclophane¹. In this study we are only concerned with pseudo[*n*]polyrotaxanes (here *n* – 1 is the average number of cyclophanes per polymer) (*Figure 1*), which consist of a polymer thread with cyclophanes threaded onto it: the polymer is linear and has on its primary structure no functionalities that significantly hinder the movement of the cyclophanes.

A major problem in the synthesis of pseudo[*n*]polyrotaxanes is that it will usually be entropically unfavourable to thread a cyclophane onto a polymer. Gibson and co-workers managed to synthesise polyrotaxanes having linear polyglycol/polyurethanes or polyglycol/polyester backbones with crown ethers as cyclophane components by actually conducting the polymerisation with molten crown as a solvent, thus improving the statistics². Although Gibson's work actually reports some properties of the pseudo[*n*]polyrotaxanes, this method has a synthetic drawback in its need for large amounts of (liquid) crown ethers. A second way in which pseudo[*n*]polyrotaxanes could be synthesised is to choose cyclophanes having strong enthalpies of threading onto the polymer, thus making complexation by threading a more viable approach.

Recent work by Stoddart and co-workers on self assembly has revealed that a very rigid, inflexible 4,4'-bipyridyl (BIPY)-based cyclophane (*Figure 2*: hereinafter the term cyclophane is used to refer to this species as its hexafluorophosphate salt) has strong binding for 1,4-dioxybenzene (**B**)- and 1,5-dioxynaphthalene (**N**)-type binding sites (e.g. $K_{\text{bind}} \sim 5000 \text{ M}^{-1}$ for **1** with 1,4-bis[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene in MeCN at room temperature (*Figure 3*)³. Further, Stoddart and co-workers report two methods for introducing this cyclophane onto a binding site, clipping and threading⁴. Clipping involves the binding site templating the final cyclisation step in the formation of the cyclophane. The process can be remarkably efficient (yields of 70% have been reported in the synthesis of some catenanes)⁵, but when polymers are involved the method suffers from technical problems, mainly concerning the separation of the polymer from the non-cyclic residues of the clipping reaction. The second method, threading, which involves the mixing of preformed cyclophane with the appropriate polymer has an inherent drawback in that is kinetically dependent upon the number of ends of the polymer. Nonetheless, Stoddart and co-workers demonstrated that the complexation of a polyurethane containing **B** units and cyclophane **1** was fast and strong for a polymer with M_n ca. 10.0 kg mol^{-1} . Harada et al. also used this general strategy to produce pseudo[*n*]polyrotaxanes using poly(oxyethylene) (M_n ca. 2.0 kg mol^{-1}) and cyclodextrins⁷, although it is clear that, despite the low molecular weight of the polymer, the process of threading is a much slower and reptatory process for this second system.

With a view to building on this work we have synthesised three types of polymer based on the **B** and **N** binding sites (*Figure 4*) and studied their complexation with the cyclophane **1** (used only as the hexafluorophosphate salt).

In what follows we concentrate upon pseudo[*n*]polyrotaxane solutions based upon the alternating polymer

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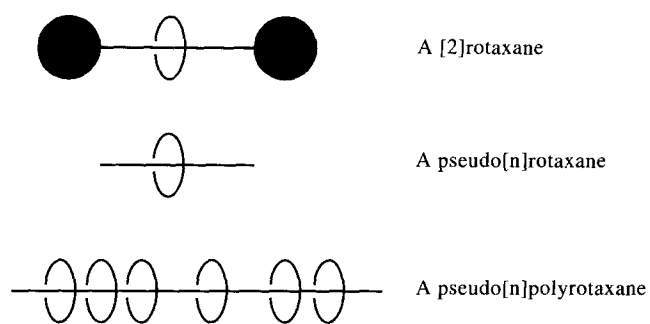


Figure 1 A schematic view of a [2]rotaxane, pseudo[2]rotaxane and a pseudo[n]polyrotaxane

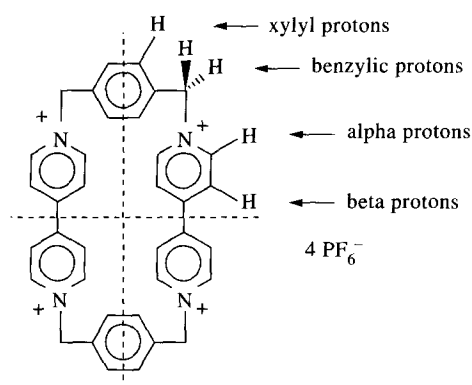


Figure 2 The cyclophane used in this study

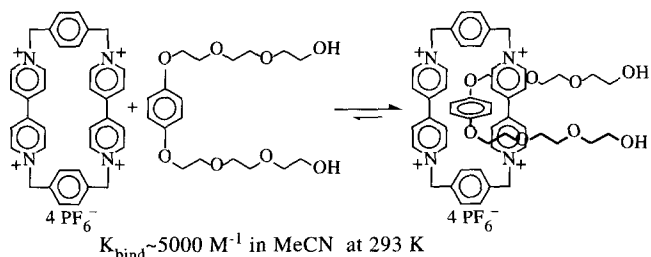


Figure 3 A typical pseudo[2]rotaxane equilibrium. The equilibrium is heavily weighted toward the formation of the pseudorotaxane ($K_{\text{bind}} \sim 5000 \text{ M}^{-1}$ in MeCN)

(B:N)_n because this, most clearly of the three, demonstrates the dynamic processes occurring in these systems. Clearly, the precise values of the binding constants will vary with solvents used: in particular, DMSO is a very polar medium, and the binding constants will presumably be much reduced in this, vis a vis less polar media such as MeCN. In addition, the ¹H n.m.r. spectra from pseudo[n]polyrotaxane solutions containing the (N:N)_n polymer are very complicated due to the reduced symmetry of the cyclophane/naphthalene complex's structure. In a different way, pseudo[n]polyrotaxane solutions containing the (B:B)_n polymer are difficult to analyse due to a less favourable pattern of the changes in chemical shifts observed for complexed and uncomplexed cyclophane protons.

RESULTS AND DISCUSSION

In this system there are cyclophanes in solution, and cyclophanes threaded onto the polymer. They are in dynamic equilibrium, both between being in solution and

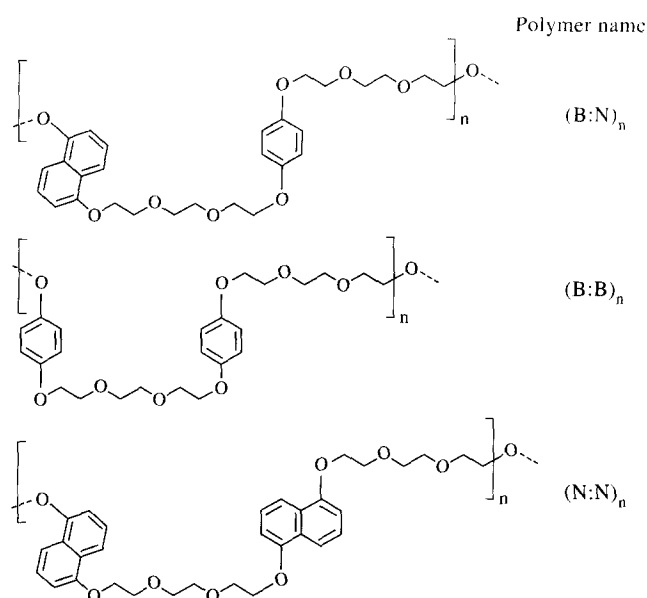


Figure 4 The three polymers that have been studied as the thread component, however, only results from the polymer (B:N)_n are discussed here

complexed on the polymer, and between aromatics along the polymer chain. It is assumed to be sterically impossible for cyclophanes threaded onto the chain to pass each other: in our case this is intuitively obvious given the dimensions and rigid nature of the cyclophane.

We define five types of cyclophane that might be observed by n.m.r. spectroscopy of poly[n]rotaxane and pseudopoly[n]rotaxane solutions.

Type 1: these, for longer than the n.m.r. timescale[†], do not thread themselves onto a polymer, but are actually in exchange.

Type 2: these are in rapid exchange on the n.m.r. timescale, between existence in the solution and being complexed onto a polymer chain.

Type 3: these are mainly complexed onto the polymer, but in exchange between the solution and being complexed by threading onto a polymer chain, with the exchange slow on the n.m.r. timescale. These are the complements of type 1 above.

Type 4: these effectively remain indefinitely on the polymer, but are in rapid exchange between binding sites along the polymer chain.

Type 5: these effectively remain on the polymer indefinitely, and are not in rapid exchange between binding sites along the polymer chain.

This classification is general and should be applicable to all pseudo[n]polyrotaxane solutions. Normally solutions of pseudo[n]polyrotaxanes at ambient temperature will contain only types 1, 2 and 3.

With systems containing the (B:N)_n polymer there is the additional complication that when a cyclophane is on the polymer, it may bind to either a B or an N binding site. Although this will in theory split all of the categories in two, in reality we do not observe this, at least at ambient temperatures (see later) as the discrimination of the n.m.r. experiment is not high enough at room temperature.

[†] A referee points out that this phrase seems slightly inappropriate, but it is the customary one and has considerable history: see, e.g. *J. Chem. Ed.*, 1983, **60**, 933–935.

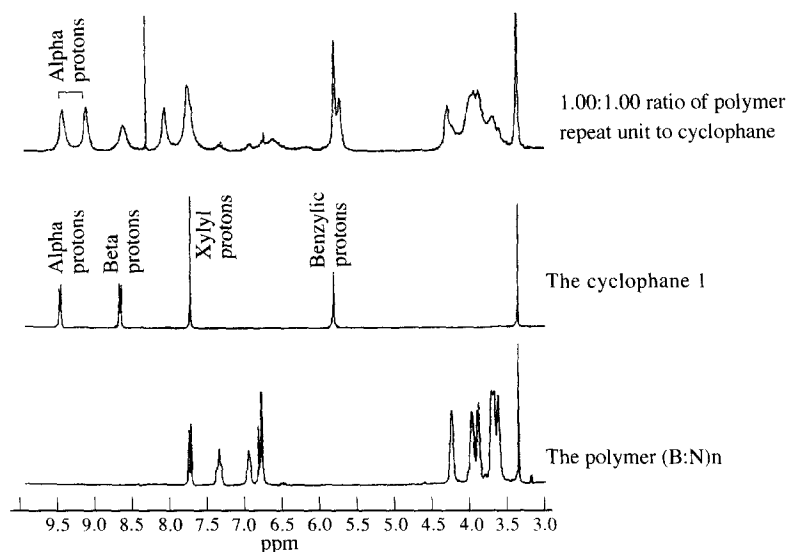


Figure 5 The ^1H n.m.r. spectra (300 MHz, DMSO-d_6) of the polymer $(\text{B:N})_n$, the cyclophane, and a solution containing a molar ratio of the polymer repeat unit to cyclophane of 1.00:1.00

The ^1H n.m.r. spectra of these pseudo[n]polyrotaxanes at ambient temperature are complex, quite often displaying little resemblance to the spectra of the two initial components after mixing in solution. To illustrate this, the ^1H n.m.r. spectra of the cyclophane, the $(\text{B:N})_n$ polymer, and a solution containing a 1.00:1.00 ratio of 1:repeat unit of $(\text{B:N})_n$ in DMSO-d_6 at 295 K are shown in Figure 5. The latter of these shows some of the typical features that we observe in these solutions and which we attribute to complexation, together with dynamic processes that are neither fast or slow on the n.m.r. timescale. The most striking of these are:

The 'disappearance' of the signals between 6.7 and 7.8 δ arising from the polymer aromatic protons

This is not entirely surprising as it is known that signals arising from **B** and **N** both shift several ppm upfield when they reside within the cavity of cyclophane⁸. Further if the rate of hopping from one site to an adjacent one is of the order of the timescale of the spectrometer then the large shift involved could easily result in a broad peak which might be concealed in the baseline. Indeed, Anelli et al.⁹ synthesised a [2] rotaxane which comprised two **B** units and the cyclophane, and is of a very similar nature to this polymer: at room temperature the ^1H n.m.r. spectrum (in acetone- d_6) of this compound displayed no signal attributable to the **B** protons, although it did of course at other temperatures. This, and the fact that the binding energies between **1** and either **B** or **N** units are expected to be of the same order of magnitude prompts us to believe that at this temperature we should not expect to observe different signals for the polymer aromatic protons that are and are not bound by a cyclophane, but rather an average of the two that produces a broad signal: we discuss this in more detail later. The obvious corollary is that if we cannot distinguish whether or not a particular aromatic is within the cavity, then it will be difficult to determine whether it is a **B** or an **N** within the cyclophane. A further complication is the propensity for these systems to form, to a degree, π stacks such as are common in the solid state¹⁰. Additionally, although in solution the changes in chemical shift values ($\Delta\delta$) of the guest aromatic protons that reside alongside the cyclophane are generally small (*ca.* 0.3), they are common

in systems containing three aromatics. This, too, will undoubtedly add to the generally diffuse appearance of the spectra.

The movement and broadening of the signals due to the cyclophane

(The signals from the protons on the cyclophane have been assigned and checked by COSY and saturation transfer experiments.) There are two unequal signals for each type of proton on the cyclophane, which suggests that there are at least two environments in which the cyclophane can find itself. For simplicity we will restrict the present discussion to the alpha protons as they stand clear of the rest of the spectrum and will serve to make the general points that we wish to emphasise.

The two alpha proton signals are at 9.10 and 9.42 δ , whilst the chemical shift for the alpha protons in a DMSO-d_6 solution containing only cyclophane is 9.48 δ . Thus, one of these signals has a chemical shift similar to that of the free cyclophane, but for two reasons this cannot be due to free cyclophane: firstly the chemical shift is not quite correct, and secondly the peak is very broad compared with the free cyclophane signal. We believe for reasons stated above that hopping between sites is rapid on the n.m.r. timescale at room temperature, and hence we will not see different signals for cyclophanes with **B** or **N** within them, but rather an average signal coming from these two environments. We attribute the signal at 9.10 δ to type 3 cyclophanes, trapped on the polymer for longer than the timescale of the spectrometer, but still moving rapidly between sites, and the signal at 9.42 δ to type 2, which on the n.m.r. timescale are in rapid exchange between being free in solution and bound onto the polymer. Clearly no type 1 signals are observed, as the shift of a type 1 cyclophane signal will be the same as that of free cyclophane. From integration of the alpha protons 52% are type 2 and 48% are type 3 at room temperature in DMSO . It is possible to calculate from these data how many of the type 2 cyclophanes are bound and free at any instant in time. Thus, in this solvent the alpha proton chemical shift for the chain-bound cyclophane is given by the type 3 peak, and the type 2 peak can be treated as a normal coalesced peak: this yields the result that, of the type 2 cyclophanes 82%

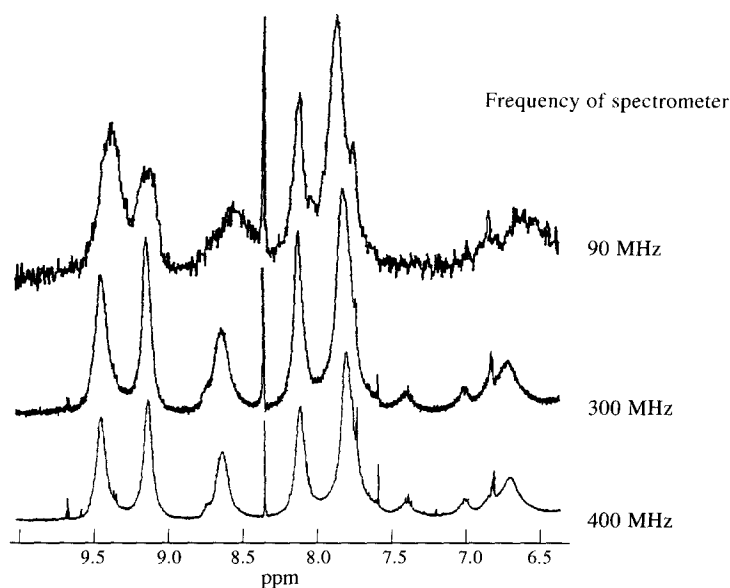


Figure 6 The ^1H n.m.r. spectra (90, 300 and 400 MHz) of a solution (DMSO-d_6) containing a molar ratio of polymer repeat unit to cyclophane of 1.00:1.00

Table 1 The instantaneous number of free and bound cyclophanes at any instant in time, as calculated from measurement off the ^1H n.m.r. spectra (recorded at the shown frequency) of a DMSO-d_6 solution containing a 1.00:1.00 ratio of cyclophane to polymer repeat unit

Frequency of spectrometer (MHz)	Chemical shift of type 2 cyclophanes (δ)	Chemical shift of type 3 cyclophanes (δ)	Fraction of type 2 cyclophanes	Fraction of type 3 cyclophanes	Instantaneous fraction of cyclophanes free in solution ^a	Instantaneous fraction of cyclophanes threaded on the polymer ^a
90 ^b	9.35	9.10	0.62	0.38	0.41	0.59
300	9.41	9.11	0.52	0.48	0.43	0.57
400	9.42	9.12	0.50	0.50	0.44	0.56

^aThe estimated error on these values is 3%

^bBroad overlapping peaks in the 90-MHz spectrum make precise chemical shifts and integrals difficult to measure

are free and 18% are bound at any instant in time. Consequently, for this solution at any instant in time, 43% of the cyclophanes are free in solution and 57% are bound onto the polymer (all $\pm 2\%$).

Clearly it is important to establish this interpretation, and we have done this using n.m.r. spectrometers with different operating frequencies. The number of cyclophanes that are bound and free at any instant in time must be independent of the frequency of the spectrometer: however, the populations of type 2 and type 3 cyclophanes are dependent on the timescale, and hence the frequency of the spectrometer. For coalescence of n.m.r. signals due to the same protons on a particular molecule exchanging between one state and another at a given temperature, the requirement is that the lifetime τ in each state be short enough: for each particular proton type, in the usual rather curt approximation, the explicit condition is:

$$\tau \leq (2^{1/2})(\pi\Delta\nu)^{-1}$$

where $\Delta\nu$ is the chemical shift difference in Hertz between the signals due to that proton in each of the two states. Various other conditions have been suggested, but all¹¹ depend inversely upon $\Delta\nu$. Increasing the frequency of the spectrometer should have the effect of increasing the number of type 3 cyclophanes whilst leaving unchanged the instantaneous populations of free and bound cyclophane. Spectra of the above solution were recorded at 90, 300 and 400 MHz (Figure 6). As our model predicts, the intensity of the type 3 peak increases with frequency but its position

does not change. In contrast the type 2 peak decreases in relative intensity and shifts slightly downfield with increasing field strength. The instantaneous populations of free and bound cyclophane were calculated in each case by the method discussed above (Table 1). At all three frequencies there are, within the errors of measurement of this experiment, identical quantities of bound and free cyclophane.

We therefore conclude that our basic interpretation of this spectrum is correct, and that we are really seeing peaks due to types 2 and 3 cyclophanes and not type 4 and wholly free molecules. It is worth noting that in all of these cases about 20% of the cyclophanes bound to the polymer are in rapid exchange on the ^1H n.m.r. timescale (*ca.* 10^{-3} s). This gives an insight into how fast the exchange is occurring in this equilibrium: i.e. all cyclophanes are moving onto, along and off the polymer in seconds.

The structure of binding sites

It is known that one **B** unit can support a cyclophane, as single site rotaxanes have been synthesised with this general structure¹²; however, it has also been shown that in systems where the guest is of a very similar nature to the polymer in this study, but containing only five binding sites, that not all of the binding sites can be occupied¹³. Logically there must be a lower limit to the number of aromatic units upon the polymer required to support one cyclophane. We have attempted to obtain this figure by measurements of the $\Delta\delta$ values of the alpha protons' ^1H n.m.r. signals and of the

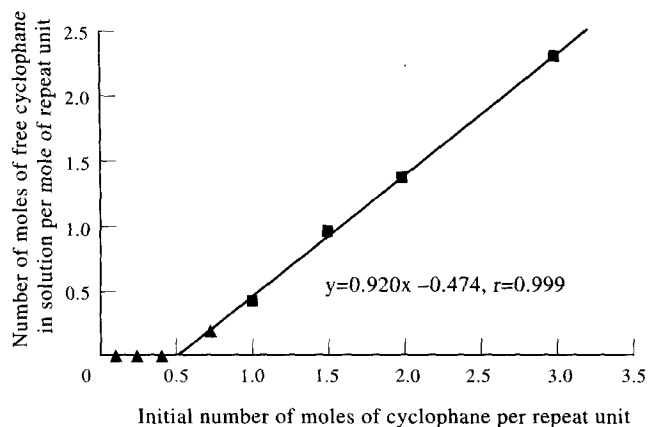


Figure 7 A plot that shows the 'saturation' of the polymer occurring when there is approximately one cyclophane for every two polymer repeat units in solution

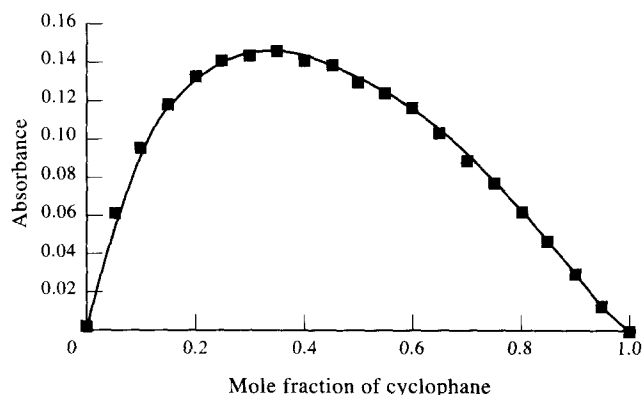


Figure 8 A Job plot showing the variation in intensity of the charge transfer absorption arising from the cyclophane threading on the polymer (see text). The maximum is at a mole fraction of cyclophane of ca. 0.35. This implies that the stoichiometry of the complex is about one cyclophane for every two polymer repeat units

charge transfer absorption of these solutions. We discuss firstly the n.m.r. method.

To establish this number we make the modelling assumption that the binding between the polymer and the cyclophane is very strong, and thus that a cyclophane will remain in solution only if there is no space left for it on the polymer. This would mean that we can essentially titrate the two components to ascertain how many aromatics are required to support one cyclophane. Eight solutions containing various ratios of polymer repeat unit (polymer $M_n = 5.0 \text{ kg mol}^{-1}$) to cyclophane were prepared in DMSO-d_6 . In each case the number of moles of cyclophane per mole of repeat unit that were instantaneously free in solution was calculated and these values were plotted against the initial number of moles of cyclophane per mole of repeat

unit added to that particular solution (Figure 7). The graph's appearance is consistent with a strong binding constant. If the binding were infinitely strong, then once the chain has been saturated, this graph should have a gradient of 1: experimentally the gradient of the 'post saturation' line is 0.92, which implies that, as we add more cyclophane to the solution, so we get more cyclophanes binding to the polymer, as expected for an equilibrium. From the intercept on the initial ratio axis we estimate that the number of repeat units required to accommodate one cyclophane is 2.0 (or 4.0 aromatic units) assuming whole numbers to be appropriate here.

Rotaxane-like systems of this kind are known to display a charge transfer absorption with a λ_{max} of 465 and 525 nm, respectively, when a **B** or **N** resides inside the cavity of the cyclophane¹⁴; consequently all these pseudo[n]polyrotaxanes are highly coloured (deep red or purple) in both solution and the solid state. We have used this property of the system to verify the value of the number of polymer repeat units required to complex one cyclophane obtained above. Solutions for a Job plot¹⁵ were prepared with an additive concentration of $2 \times 10^{-3} \text{ M}$. The absorbances of these solutions were measured at 490 nm (the average charge transfer maximum for all these solutions occurred at $490 \pm 13 \text{ nm}$). The resultant Job plot (Figure 8) had a maximum at a mole fraction of cyclophane of approximately 0.35 which means that the complex formed in this solution has about 1.9 repeat units for each cyclophane. This result is very similar to that calculated from the n.m.r. spectroscopy data.

This result is also consistent with the broad n.m.r. signal observed for the aromatic protons on the polymer at approximately 6.7δ in the pseudo[n]polyrotaxane spectrum (Figure 5). The weighted average of the aromatics' signals for uncomplexed polymer is approximately 7.1δ . The signals from an aromatic within the cavity shift about 3δ upfield (an approximate weighted average for all known shifts (see Table 2) of these protons on their inclusion in the cyclophane) and we have shown that there is about one cyclophane for every four aromatics. This implies that in the exchanging n.m.r. situation we expect a broad singlet shifted about 0.75δ upfield from the weighted average of all signals for the polymer, which corresponds approximately with what is observed in the pseudo[n]polyrotaxane spectrum of Figure 5.

It is interesting that the occupancy of this polymer is so low (approximately five cyclophanes per polymer) when the binding constant between the host and unpolymerised guest is large, especially as Harada *et al.*⁷ report that with PEG ($M_n = 3.3 \text{ kg mol}^{-1}$, i.e. about half the molecular weight of the polymer in this experiment, albeit about the same chain length) they find approximately 20 α -cyclodextrins per polymer. Nonetheless the result is consistent with work conducted by Stoddart and co-workers who showed that, when clipping was attempted on a capped linear species, similar to the polymer used in this study but containing only

Table 2 The chemical shifts of the aromatic protons upon the polymer in different environments

	Chemical shift of B (δ)	Chemical shift of the aromatic protons on the naphthalene unit (δ)		
		N-2, N-6 protons	N-3, N-7 protons	N-4, N-8 protons
Chemical shifts of the free polymer (B : N) _n at 298 K	6.78	6.96	7.36	7.73
Chemical shift for the aromatic polymer protons in the pseudo[n]polyrotaxane solution in DMSO at 353 K	6.78	6.92	7.25	7.42
Typical δ value on inclusion in the cyclophane	3.5	6.2	6.0	2.4

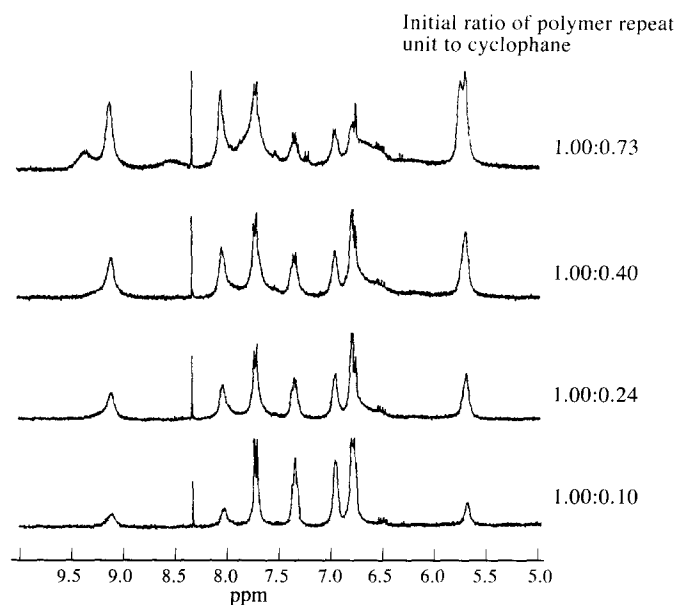


Figure 9 The ^1H n.m.r. spectra (300 MHz, DMSO-d_6) of solutions that contain the polymer with an increasing concentration of cyclophane. Eventually there is enough cyclophane in solution to give a type 2 and a type 3 peak

five aromatic units, only the [2]rotaxane was isolable⁶. The most likely reason for this relatively low occupancy is the electrostatic repulsion between these tetracationic cyclophanes.

The occupancy of the chain before saturation

We believe that for the present polymers the rate-determining step in inter-aromatic hopping for the cyclophane is leaving the guest aromatic prior to diffusing to the next site. For simplicity in the discussion, although this is clearly unrealistic, we will in addition assume that the probability of hopping into solution from the end site is approximately the same as that of hopping to an adjacent site from a position within the chain. Consider a polymer chain with one cyclophane upon it. The only factor that will define whether the cyclophane is type 2 or type 3 will be whether it is travelling fast enough to make it off the end of the chain within the n.m.r. timescale. It has been shown that the rate that cyclophanes move between aromatic sites on a rotaxane of similar architecture to the polymer used here is about 2500 hops per second¹⁰. We will assume this is similar to the rate of hopping in our polymer, and further we will assume that the motion is a random walk. The chemical shifts of a protons on free and bound cyclophanes in DMSO-d_6 at ambient temperature are 9.48 and 9.10 δ , respectively, and hence the frequency difference between these two states is about 114 Hz on a 300 MHz (152 on a 400 MHz) spectrometer. Therefore a cyclophane must move from being on the polymer to free in solution in approximately 4×10^{-3} s (3×10^{-3} s at 400 MHz) to be observed as type 2 via the signal from the alpha protons. This would imply that for a 300 MHz spectrometer a cyclophane must move from being bound to the polymer to being free in solution within approximately 10 hops (seven at 400 MHz) to be observed as type 2. The polymer used in these experiments had a number average molecular weight of approximately 5.0 kg mol^{-1} , corresponding to approximately 20 aromatic units. This would imply that for this polymer, even without impedance by other cyclophanes, both type 2 and 3 cyclophanes would be found. In the simplest instance, where there is only one cyclophane per chain, we may estimate the percentages of type 2 and 3 cyclophanes at very

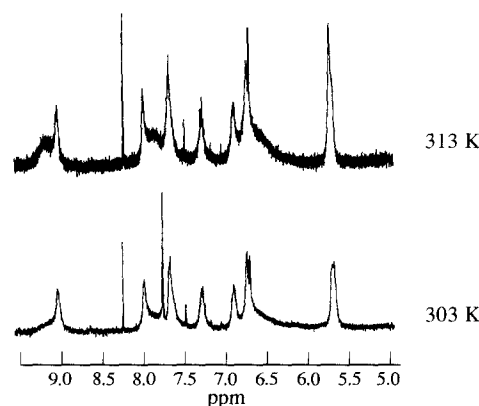


Figure 10 A 10 K increase in temperature of the solution (DMSO-d_6) containing a molar ratio of polymer repeat unit to cyclophane of 1.00:0.40 clearly resolves the peak at 9.1 δ into a type 2 and 3 peak on the ^1H n.m.r. spectrum (400 MHz). The increase in the signal to noise ratio upon the upper trace is caused by a different processing method.

low concentration by a crude model. We will assume that there is only one cyclophane per chain, and that it starts in a random position on the polymer, if the cyclophane leaves the polymer in 10 random hops then it will be type 2 and if it does not then it is type 3. We thus expect about 20% to be type 2 and 80% to be type 3 at room temperature for the polymer with $M_n = 5.0 \text{ kg mol}^{-1}$.

In order to investigate this, four solutions, each containing the same amount of polymer ($M_n \approx 5.0 \text{ kg mol}^{-1}$) with, respectively, 0.10, 0.24, 0.40 and 0.73 molar equivalents of cyclophane per repeat unit of polymer were prepared in DMSO-d_6 and their ^1H n.m.r. spectra recorded at 300 MHz (Figure 9).

At the lowest concentration of cyclophane (approximately one cyclophane for every 10 repeat units or 20 aromatic sites) we only see one (broad) peak for the alpha protons, at 9.10 δ . The shift of the maximum in this peak is similar to that of the type 3 signal in Figure 5 but we now attribute it differently. As the association between the cyclophane and binding site is strong (the binding constant between the typical monomer and cyclophane is approximately 1000 M^{-1}) we expect most of the cyclophanes to

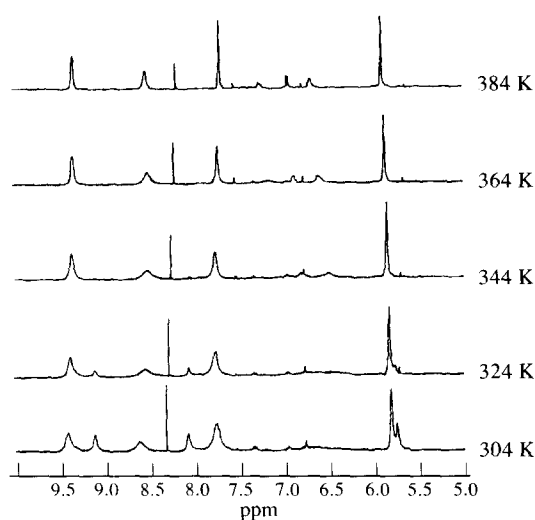


Figure 11 The ^1H n.m.r. spectra (400 MHz) of a solution (DMSO-d_6) containing a molar ratio of polymer repeat unit to cyclophane of 1.00:1.00 at temperatures between 304 and 384 K

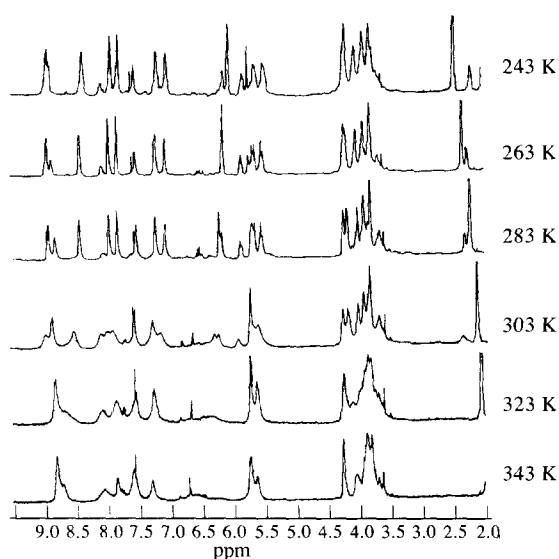


Figure 12 The ^1H n.m.r. spectra (400 MHz) of a solution (MeCN-d_3) containing a molar ratio of polymer repeat unit to cyclophane of 1.00:1.00 at temperatures between 243 and 343 K

reside on the polymer. As the concentration of the cyclophane is increased so more cyclophanes reside on the chain and the alpha signal remains at 9.10 δ , but increases in intensity. As the concentration of cyclophane is increased still further the peak develops a shoulder which eventually splits from the main peak. This is the type 2 signal which can only now be clearly distinguished from the type 3 as there is now a substantial amount of free cyclophane.

To obtain an estimate of the amount of type 2 and 3 cyclophanes at room temperature a variable temperature n.m.r. study was conducted on the solution containing a ratio of polymer repeat unit to cyclophane of 1.00:0.40 (Figure 10). The signal arising from the alpha protons at ambient temperature is a broad singlet with a slight shoulder to low field: the spectrum recorded at 313 K (only a 10 K increase in temperature) displays a broad doublet of approximately equal intensity, both possessing chemical shifts similar to that of type 3 cyclophanes. If we assume that change in the populations of type 2 and 3 is modest over this 10 K range we can gain some idea of the populations of

type 2 and 3 cyclophanes at room temperature. This implies that in this solution at room temperature, approximately half of the cyclophanes are type 2, but mostly bound to the polymer, and half are type 3. This is only broadly consistent with the approximation from our model which predicts that about 20% will be type 2 and 80% will be type 3 at a low concentration of cyclophane. This model of course, takes little account of the molecular weight distribution of the polymer, though this must certainly contribute to the general difficulty in precise interpretation of these spectra.

Temperature effects

The solutions discussed so far used DMSO (m.p. ca. 15°C) as a solvent. This makes low-temperature n.m.r. spectroscopy on these solutions impossible. The usual solvents used for low-temperature studies on rotaxanes similar to these systems are MeCN-d_3 ¹⁶ and acetone-d_6 ¹⁷ and, though the polymer is almost wholly insoluble in MeCN-d_3 , the pseudo[n]polyrotaxane systems containing more than ca. 0.5 molar equivalents of cyclophane per repeat unit do have an appreciable solubility in this solvent. We have conducted an n.m.r. study of this system over the temperature range 304–384 K in DMSO-d_6 and 243–353 K in MeCN-d_3 , both solutions having the same initial concentration of cyclophane (14.3 mM) and polymer repeat unit (14.3 mM) (polymer $M_n = 5.0 \text{ kg mol}^{-1}$). The n.m.r. spectra of the DMSO solution between 304 and 384 K are shown in Figure 11, and those of the MeCN solution between 243 and 353 K in Figure 12.

Firstly we discuss the DMSO spectra, and as before confine our initial discussion to the alpha protons. At room temperature there are two signals which are attributed to type 2 and 3 cyclophanes, at 9.42 and 9.11 δ , respectively. As the temperature increases so the type 2 peak increases in size and shifts downfield, whilst the type 3 peak, although it displays no appreciable change in its chemical shift, decreases in size. This indicates that as we increase the temperature so there are less cyclophanes bound per aromatic unit and that more cyclophanes are in rapid exchange on the n.m.r. timescale.

The position of the type 2 signal is determined by the chemical shift and population of the free and bound cyclophane at that temperature. The type 3 signal does not shift with temperature: however, the chemical shift of the alpha protons on the free cyclophane does change slightly with temperature (we measured a shift of 0.08 δ between 295 and 373 K, and have taken this into account in subsequent calculations). This temperature dependence does not change the obvious trend whereby as the temperature is increased so more cyclophanes are type 2, and hence exchanging with solution on the n.m.r. timescale. There are two complementary explanations for this observation. Firstly, as the temperature is increased the cyclophanes move faster and more of them will be able to escape from the chain over the n.m.r. timescale; and secondly, as the temperature is increased, the equilibrium shifts away from complexation. At approximately 380 K all the cyclophanes are type 2, yet still there is a reasonable proportion of the cyclophanes bound to the polymer (ca. 26% from the position of the type 2 alpha peak).

At 384 K the spectrum is sufficiently resolved for sensible conclusions to be drawn from the position of other peaks. There are four signals in the region that would be expected for the aromatic's protons on the polymer: these signals have been assigned in Table 2. The chemical shift of the B units is unchanged from the signal for the free polymer, but

all of the protons on the N unit do display appreciable shifts. These results demonstrate that even at these higher temperatures there are still cyclophanes upon the polymer; that they do not remain upon the polymer for periods longer than the n.m.r. timescale, and that whilst upon the polymer they spend most of their time upon the N sites.

It is important to realise that these systems do have a significant dependence upon the solvent. Several cases have been reported where a change in preference for a particular binding site, or a increase in binding strength have been witnessed upon changing the solvent from DMSO to the much less polar MeCN¹⁸.

Consider now the spectra obtained in MeCN-d₃ between 243 and 353 K. Initially we discuss the signals from protons on the cyclophane. When an N is 'frozen' within the cavity of the cyclophane the degenerate states for the cyclophanes' protons are split due to the descent in symmetry from D_{2h} to C_{2h} . The spectrum at 243 K shows clearly the dissymmetrisation of the cyclophane, with the pairs of signals attributed to alpha, beta and xylyl protons being observed at 8.91 and 8.35 δ , 7.17 and 7.02 δ and 7.92 and 7.80 δ , respectively (confirmed by COSY for the alphas and betas). The integration of these signals shows that 85% of the cyclophanes are upon N sites. The remaining set of signals arises from cyclophane protons on the small portion of type 2 cyclophanes existing at this temperature (ca. 15%); although the set of peaks we observe here are virtually identical to those of free cyclophane in MeCN (e.g. both show a chemical shift for the alpha proton of 8.88 δ) we still assign this peak as type 2, since with the higher temperature spectra we can see this peak broaden and move as expected for a type 2 peak. The fact that there is a type 2 peak at all is peculiar; we believe that this may be due to some of the terminal aromatics being unable to bind a cyclophane strongly, and this reasonable supposition broadly fits the results obtained (a first-order approximation gives $M_n = 5.0 \text{ kg mol}^{-1} = 20$ aromatic units, two of these must be terminal $\sim 10\%$); however, we have been unable to locate the corresponding polymer aromatic signals due to the general noise of the spectrum. A second reason could be that this is just an entropy effect.

Only one set of naphthalene proton signals are observed on the spectrum acquired at 243 K; they display chemical shifts that are consistent with this aromatic unit residing exclusively inside the cavity of the cyclophane (N-2, N-6; N-3, N-7; N-4, N-8 of 6.12; 5.81; 2.17 δ versus 6.68; 6.03; 2.49 δ in MeCN at 298 K for a catenane in which the N site is known to reside essentially inside the cavity of the cyclophane, although these values are not identical they are similar)¹⁹.

Having established that the cyclophane resides almost entirely upon the naphthalenes, we may now discuss the B signal. This is a sharp singlet at 6.02 δ and has a shift that is considerably different from that of free B (approximately 6.83 δ). Work conducted by Stoddart and co-workers on smaller molecular species suggests that this shift is consistent with the B unit being sandwiched between two cyclophanes (the reported chemical shifts for a B unit alongside a cyclophane are 6.60 and 6.42 δ : and when it is sandwiched between two cyclophanes a singlet at 6.22 δ —both values are in acetone-d₆ at 233 K)²⁰.

Taken together, the results imply that at 248 K the structure of the pseudo[n]polyrotaxane consists of a cyclophane upon almost every naphthalene (85% from the integrations of the alpha protons) with the system coiled so that a nearly continuous Π stack is formed with a B unit

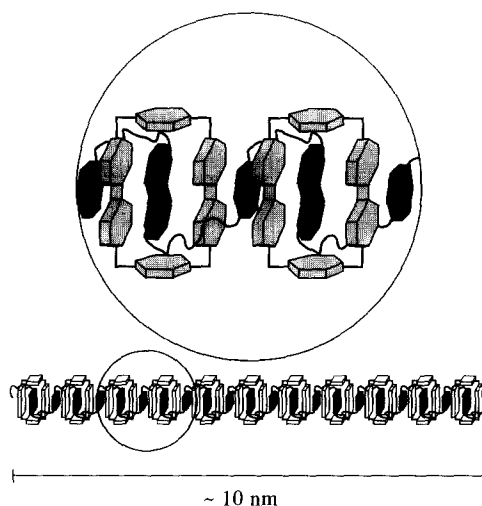


Figure 13 The very ordered 'rod' arrangement that is formed in a solution (MeCN-d₃) containing the polymer (B:N)_n and the cyclophane at lower temperatures

being sandwiched between two adjacent cyclophanes (Figure 13). Such structures have been reported before for small molecules²¹, but this is the first time such a structure has been reported in a polymer. This is the first nanoscale (ca. 10 nm) self assembly of an initially flexible polymer into a known supramolecular (rodlike) conformation.

The spectra at higher temperatures imply the following processes. Firstly comes the slow erosion of the Π stacking motif, for which the chemical shift of the B signal acts as a marker. The shift downfield from 6.02 to 6.28 δ from 243 to 303 K is wholly consistent with this process, for if the cyclophane was actually spending more time upon the B units then an upfield shift should be observed. A second process which can be observed between 303 and 323 K is the symmetrisation of the cyclophane. The established process by which this occurs is that the naphthalene moves out of the cyclophane (using the cyclophane as a frame of reference), rotates 180° and then moves back into the cyclophane²². Our results would indicate that at temperatures slightly above that at which the system has enough energy for this process to occur fairly rapidly, the cyclophanes begin to migrate quickly up and down the chain, since by 353 K a large portion of the cyclophanes are in rapid exchange with the solution. This observation is consistent with the earlier supposition that the rate-determining step in inter-site hopping is the leaving of the guest aromatic.

Effects of polymer length

Polymers were prepared with molecular weights of 3.1, 5.0 and 12.0 kg mol⁻¹ (M_w/M_n 2.1, 2.5 and 3.6, respectively) as determined by g.p.c. versus poly(methylmethacrylate) standards. Solutions containing identical initial concentrations of polymer repeat unit (14.3 mM) and cyclophane (14.3 mM) were prepared in DMSO-d₆ for these three polymers. The spectra are consistent with our model of how these systems behave in solution. As the concentrations of repeat unit and cyclophane are identical in all these solutions, it is reasonable to expect that there should be the same number of cyclophanes upon sites in all these solutions at any moment in time, since this is largely governed by thermodynamic considerations, and indeed this is substantially what we observe (Table 3). (It is, however,

Table 3 The effect of polymer molecular weight on the relative amounts of type 2 and type 3 cyclophanes, and the instantaneous percentage of free and complexed cyclophanes, as calculated from measurement off the ^1H n.m.r. spectra (300 MHz) of a DMSO- d_6 solution containing a 1.00:1.00 ratio of cyclophane to polymer repeat unit (of the molecular weights shown)

Temperature (K)	M_n of polymer used (kg mol^{-1})	Type 2 shift (δ)	Type 3 shift (δ)	Type 2 peak integral	Type 3 peak integral	Total complexed cyclophane (%) ^a	Total free cyclophane (%) ^a
295	3.1	9.400	9.113	64	36	49	51
295	5.0	9.418	9.105	55	45	54	46
295	12.0	9.420	9.104	49	51	59	41

^aThe estimated error on these values is 3%

worth noting that the amount of cyclophanes that are at any instant bound to the polymer in these solutions declines somewhat with molecular weight. This would be the expected effect if the end groups of the polymer did not complex cyclophanes as strongly as sites in the middle of the polymer chains.)

It is interesting that in solutions containing enough cyclophanes to essentially saturate the polymer, the number of cyclophanes that are type 2 but polymer bound should display a linear relationship to the number of ends. Consequently, as the molecular weight of the polymer is increased (although the mass added to the solution is not) and the number of ends inevitably decreases, so we observe a smaller portion of the cyclophanes that are polymer bound and type 2.

A variable temperature 400 MHz study also supports the idea that we are measuring the populations of the fast exchanging and slow exchanging cyclophanes by the integration and position of the alpha protons' signals. As expected, the polymer with M_n of 3.1 kg mol^{-1} loses its type 3 peak first between 324 and 344 K, the polymer with M_n of 5.0 kg mol^{-1} loses its type 3 peak between 344 and 364 K and the longest polymer with M_n of 12.0 kg mol^{-1} , loses its type 3 peak last, between 364 and 384 K. At each temperature studied the three solutions showed a very similar fraction of free and complexed polymer; these generally fell away as the temperature increased.

CONCLUSIONS

We have shown that the complexation between the polymer and the cyclophane used in this study is both strong and rapid in DMSO and in MeCN at room temperature, and set forth a general method for the interpretation of the ^1H n.m.r. spectra of these species. We note that Gibson et al., working upon systems with a polymer containing 4,4'-bipyridyl units and bisparaphenylene 34 crown 10²³, has observed a pattern of behaviour in the ^1H n.m.r. spectra of these species similar to that documented in this report. Although these effects are clearly related it is not clear whether they are due to identical processes. In some ways this rapid threading is the most interesting property of this system: Gibson and co-workers, who have reported work with pseudo[n]polyrotaxanes with polymers of M_n ca. 10 kg mol^{-1} and crown ethers state that the dethreading process in these systems takes place over days in a melt²⁴; whilst Harada et al.⁷ who worked with poly(oxyethylene) (M_n ca. 3 kg mol^{-1}) and α -cyclodextrins implies a threading time of hours; finally Wenz and Keller report that in poly(iminoundecamethylene) with M_n ca. 15 kg mol^{-1} a threading time for α -cyclodextrin of about an hour was observed by viscometry²⁵ (apparently, none of these polymers possessed groups that could hinder the movement of the ring component, although in Gibson's case hydrogen bonding may have been a factor

in some examples). Our system shows complexation which is very much more facile than these others. We attribute these differences to two factors that are largely absent in the studies above: firstly there is a specific, strong binding between the cyclophane and the polymer in this study and, secondly, the cyclophane has a very rigid hole in it. It is reasonable that a rigid cyclophane will generally progress along a polymer far more quickly than one that is entropically hindered by many configurations, and indeed this is largely what has been observed with the very rigid cyclophane used in this study moving faster than the slightly less rigid cyclodextrins which in turn move faster than the conformationally very flexible crown ethers. The strength of complexation is very dependent on the temperature and solvent: as the temperature increases so the strength of complexation decreases, whilst at lower temperatures we find evidence for a novel, highly ordered, nanometer-scale π stacked arrangement in solution. Stronger complexation in MeCN than in DMSO is reflected by a higher chain occupancy in MeCN which is almost certainly due to the lower polarity of this solvent.

After this paper was submitted, a further publication reporting work on systems very similar to those studied here appeared²⁷. We regard the results in this publication, where they bear directly upon our study, as being generally supportive of our model.

EXPERIMENTAL

^1H and ^{13}C n.m.r. spectra were recorded on Jeol FX90, Bruker AC300 and AMX400 machines. Mass spectrometry was performed on a VG Zabspec machine. Gel permeation chromatography was conducted by comparison with polymethylmethacrylate standards on a Waters machine using *N*-methylpyrrolidinone as a solvent.

1,4-Bis[2-(2-(2-bromoethoxy)ethoxy)ethoxy]benzene

A solution of triethylene glycol dibromide (100 g, 362 mmol) in MeCN (200 cm^3) was added to potassium carbonate (100 g, 714 mmol) and refluxed under nitrogen for 4 h. Hydroquinone (13.3 g, 121 mmol) was added whilst maintaining the nitrogen atmosphere and the suspension refluxed for a further 12 h. On cooling the suspension was filtered and the residue was washed with CH_2Cl_2 (200 cm^3). The organic phases were combined and the solvent removed under vacuum. The residual oil was separated into fractions by recrystallisation from EtOEt/60–80 pet. ether. This yielded:

triethylene glycol dibromide (30.5 g, 31% recovery): ^1H n.m.r. (300 MHz CDCl_3) (see above).

1,4-bis[2-(2-(2-bromoethoxy)ethoxy)ethoxy]benzene (15.2 g, 25%); m.p. 34–35°C, m/z (positive-ion FABMS) 500 for M^+ , ^1H n.m.r. (300 MHz CDCl_3) δ_{H} 3.47 (t, $J = 6$ Hz, 4H), 3.67–3.88 (m, 16H), 4.08 (t, $J = 5$ Hz, 4H), 6.83

Table 4 The solutions studied by ^1H n.m.r. spectroscopy: 0.700 cm^3 of deuterated solvent was used to prepare these solutions

Ratio of cyclophane to polymer repeat unit	Molecular weight of polymer used (kg mol^{-1})	Degree of polymerisation of polymer	Initial concentration of polymer repeat unit (mM)	Initial concentration of cyclophane (mM)
0.10:1.00 ^a	5.0	10.0	16.5	1.7
0.24:1.00 ^a	5.0	10.0	16.5	4.0
0.40:1.00 ^a	5.0	10.0	16.5	6.6
0.73:1.00 ^a	5.0	10.0	16.5	12.0
1.00:1.00 ^a	5.0	10.0	14.3	14.3
1.50:1.00 ^a	5.0	10.0	14.3	21.5
2.00:1.00 ^a	5.0	10.0	14.3	28.6
3.00:1.00 ^a	5.0	10.0	14.3	42.9
1.00:1.00 ^a	3.1	6.2	14.3	14.3
1.00:1.00 ^a	12.0	24.1	14.3	14.3
1.00:1.00 ^b	5.0	10.0	14.3	14.3

^aSolvent used was DMSO- d_6 ^bSolvent used was MeCN- d_3

(s, 4H), ^{13}C n.m.r. (75.5 MHz, CDCl_3) δ_{C} 30.3, 68.1, 69.9, 70.6, 70.8, 71.3, 115.6, 153.1.

1,11-bis(4-(2-(2-[2-bromoethoxy] ethoxy) ethoxy) phenoxy)-3,6,9-trioxaundecane (10.6 g 11%) ^1H n.m.r. (300 MHz CDCl_3) δ_{H} 3.48 (t, $J = 7$ Hz, 4H), 3.69–3.79 (m, 12H), 3.74 (t, $J = 5$ Hz, 12H), 4.08 (t, $J = 5$ Hz, 8H), 6.83 (s, 8H.), ^{13}C n.m.r. (75.5 MHz, CDCl_3) δ_{C} 30.3, 68.1, 69.9, 70.0, 70.6, 70.8₍₂₎, 70.8₍₇₎, 71.3, 115.6, 153.1₍₂₎, 153.1₍₈₎.

Higher oligomers, 30 g unanalysed.

[Poly(1-(1,4,7-trioxadecenyl)-4-(11-(1-(5-oxynaphthyl)-1,4,7,11-tetroxaundecenyl)benzene)] (**B:N**)_n

Powdered, oven-dried potassium carbonate (15.0 g, 107 mmol) was placed in an oven-dried flask containing DMF (100 cm^3) and toluene (20 cm^3) and was degassed under nitrogen for 24 h at 100°C whilst being stirred. 1,5-Dihydroxynaphthalene (2.5949 g, 16.20 mmol) was added whilst maintaining the nitrogen atmosphere, the temperature was kept at 100°C for a further 2 h. The temperature was raised to 120°C and the toluene was removed using a Dean Stark apparatus. A solution of 1,4-bis[2-(2-(2-bromoethoxy)ethoxy)ethoxy]benzene (8.0995 g, 16.20 mmol) in degassed DMF (30 cm^3) was added dropwise over 20 min. The reaction was stirred at 120°C for a further 4 h. On cooling the reaction mixture was filtered and the filtrate poured dropwise into methanol (700 cm^3) whilst being stirred vigorously. The yield of polymer precipitated, as a brown solid, was 7.87 g (98%). ^1H n.m.r. (300 MHz d_6 DMSO- d_6) δ_{H} 3.57–3.75 (br m, 12H), 3.82–4.01 (br m, 8H), 4.22 (br s, 4H), 6.78 (br s, 4H), 6.96 (br s, 2H), 7.36 (br m, 2H), 7.73 (d, $J = 9$ Hz, 2H). The calculated molecular weight of the polymer from the integrals of the phenolic end groups *versus* those from the rest of the polymer gave a molecular weight of ca. 3.0 kg mol^{-1} for the polymer. The M_n for the polymer by g.p.c. was 3.1 kg mol^{-1} with a M_w/M_n of 2.1.

A solution of triethylene glycol dibromide (0.500 g, 1.81 mmol) in degassed DMF (5.00 cm^3) was prepared. The polymer (2.001 g, 4.01 mmol of repeat units) was dissolved in degassed DMF (20 cm^3) and 1.00 g of oven-dried potassium carbonate was added. A portion of the triethylene glycol dibromide solution (1.85 cm^3) was added and the reaction was stirred and heated at 100°C under a nitrogen atmosphere for 4 h. After cooling the reaction was poured dropwise into methanol (200 cm^3). The precipitate was

removed by filtration and dried under a vacuum to yield 2.12 g (97%) of chain extended polymer as a light brown sticky powder. The ^1H n.m.r. spectrum of the polymer was unchanged, except for the absence of the phenolic end group signal. G.p.c. yielded a weight of 5.0 kg mol^{-1} for the polymer and a M_w/M_n of 2.5. Further precipitation of a portion of this polymer into MeOH yielded a polymer with a M_n , as determined by g.p.c., of 12.0 kg mol^{-1} and a M_w/M_n of 3.6, the ^1H n.m.r. spectrum of this polymer appeared unchanged.

The cyclophane **1** was synthesised according to literature methods^{26,27}. ^1H n.m.r. (300 MHz MeCN) δ_{H} 5.74 (s, 8H), 7.53 (s, 8H), 8.17 (d, $J = 7$ Hz, 8H), 9.87 (d, $J = 7$ Hz, 8H), ^{13}C n.m.r. (75.5 MHz, MeCN) δ_{C} 65.7, 128.3, 131.4, 137.0, 146.3, 150.4.

Solutions for analysis by ^1H n.m.r. spectroscopy were prepared by removal of solvents from carefully dispensed quantities of solutions of the cyclophane in MeCN and the polymer in CHCl_3 . This material was then dissolved in a volumetrically measured quantity of the appropriate solvent. The solutions that were prepared are summarised in Table 4.

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