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Threading/Dethreading Exchange Rates as Structural Probes in Polypseudorotaxanes

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ABSTRACT: First, the complexation of rigid bis(paraquat)-based cyclophane host **1** with linear MDI-based polyurethane guests **2**−**5** prepared from tetra(ethylene glycol) was studied. Through detailed analysis of ^{1}H NMR data, we have shown a relationship between the length of the linear polyurethanes and the fraction of all threaded cyclophanes rapidly exchanging with solution upon the ^{1}H NMR time scale. In other words, the molecular weight of the polymer can be estimated from the proportion of cyclic threaded but exchanging rapidly, i.e., those near the ends, versus those that are threaded but exchanging slowly because they do not have ready access to the ends of the macromolecule; this is essentially an end group analysis. And then in a similar study of branched polyurethanes **7**−**11** derived from tetra(ethylene glycol) and glycerol, it was shown that the cyclophane can be used to determine the (accessible) fraction of the polymer between a branch point and a terminus and the average length between a branch point and a terminus. Third, inclusion of bisphenol A diethoxylate units in linear polyurethanes **12**−**16** provides effective barriers to room-temperature threading and dethreading, allowing a “slippage” method for polyrotaxane synthesis at elevated temperature (60 or 90 °C), yielding polyrotaxanes stable for extended periods in solution at room temperature.

Introduction

Rotaxanes,[1,2] catenanes,[2,3] and knots[4] (Figure 1, a, b, and c, respectively) are now well-known architectures in supramolecular chemistry. One interest in such motifs is to construct molecular devices capable of performing tasks (e.g., molecular switches,[5] sensors,[6] etc.). However, at this point in time, the manufacture of a primitive architecture is still considered an achievement. Another goal for this research is the production of materials with novel properties. It is to these ends that we[7] and others[1e,8] have been investigating polyrotaxanes[2] (Figure 1d,e).[9] Yet another aspect of these interactions that is only beginning to be examined is as analytical probes of molecular structure. To this end, here we report how the kinetics of movement of a cyclophane betray certain structural aspects of the polymer with which it is interacting, some unique to this technique.

Main chain polyrotaxanes can be divided into two categories:[2] (i) *true polyrotaxanes* whose macrocycles are mechanically trapped upon the polymer by the incorporation of blocking groups or stoppers (represented by the filled circles) and cannot dethread (Figure 1e); (ii) *polypseudorotaxanes* whose macrocycles are threaded, but with no steric barriers to prevent dethreading (Figure 1d).

There are five basic routes to produce these architectures; each has favorable and unfavorable attributes. The first two methods involve the production of the polyrotaxane species in the polymerization step; in the latter three it is formed using a preformed polymer.

(a) Polymerization in the presence of a macrocycle (Figure 2a).[2,7a−i,k,8a,b] If one or both of the monomers is a blocking group,[7a,b,d,e,h,8a] then a true polyrotaxane is formed.

(b) Polymerization of a rotaxane (Figure 2b).[2,10] Although simple in principle, the arduous syntheses of functionalized rotaxanes accounts for the sparse representation of this method in the literature.

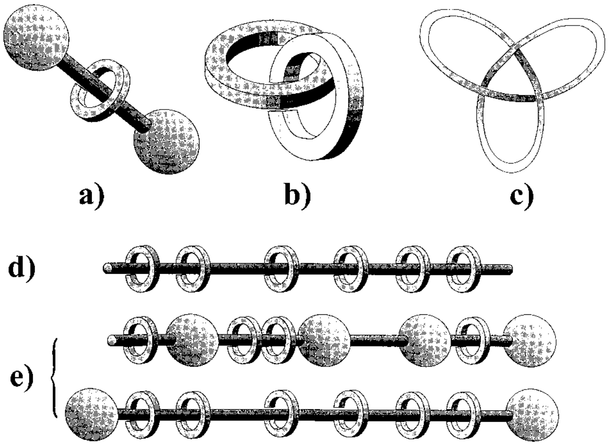

Figure 1. Schematic representations of (a) a rotaxane, (b) a catenane, (c) a knot, (d) a polypseudorotaxane, and (e) true polyrotaxanes.

(c) Clipping (Figure 2c) involves the formation of the macrocycle templated around the polymer. Due to their specific nature, few clipping reactions are available; some have been applied to low molar mass rotaxanes,[1i,2] and by definition to all catenanes,[2,3] but not to polyrotaxanes.

(d) Threading, the simplest method of producing main chain polypseudorotaxanes,[1e,2,7a,l,m,8c,h] involves simply mixing the macrocycle and the polymer (Figure 2d).

(e) In slipping, by raising the temperature, the macrocycle is promoted to higher energy conformations such that it can slip over bulky groups upon the polymer but cannot dethread upon cooling (Figure 2e).[8c] There are few reports of this method even with low molar mass systems[1b,c,l,2] due to the difficulty in matching the sizes of the slippage group and the macrocycle.

In the present paper we will consider the interaction of the bis(paraquat) cyclophane **1**[11] with linear polymers,

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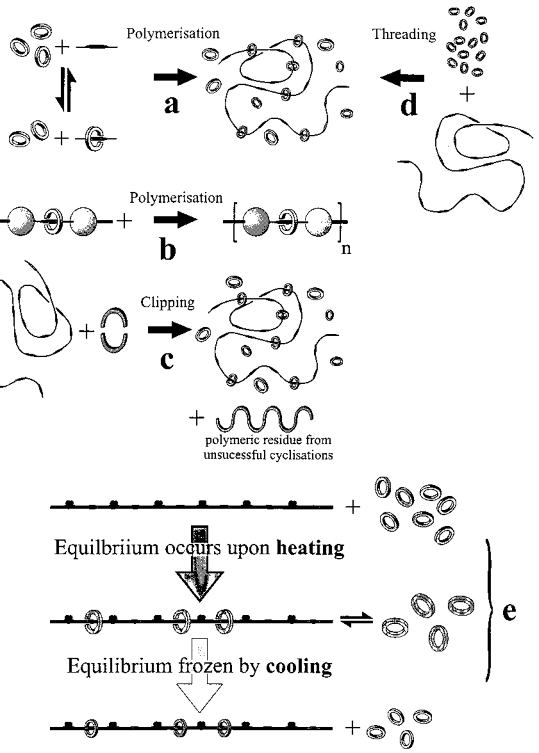


Figure 2. Schematic representations of the principal synthetic routes to polyrotaxanes: (a) polymerization in the presence of a macrocycle, (b) polymerization of a rotaxane, (c) clipping a macrocycle onto a polymer, (d) threading a macrocycle onto a polymer, and (e) slipping macrocycles onto a polymer by heating and then “freezing” them onto the polymer by cooling.

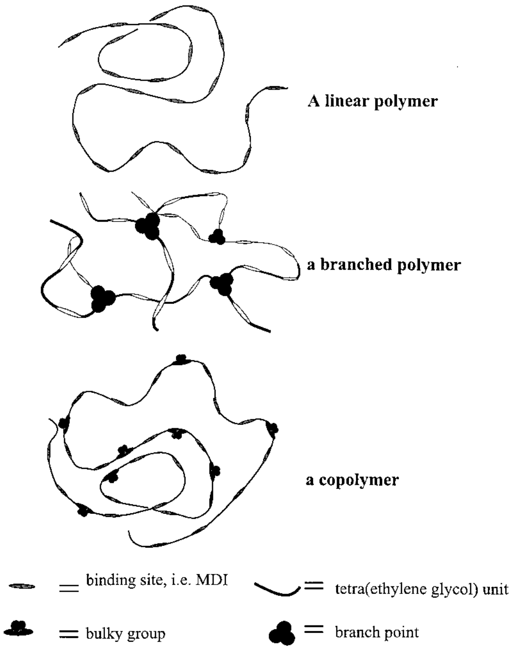


Figure 3. Schematic representations of linear polyurethanes **2**–**5**, **7**, and **12**, branched polyurethanes **8**–**11,** and bisphenol-A-containing polyurethanes **13**–**16**.

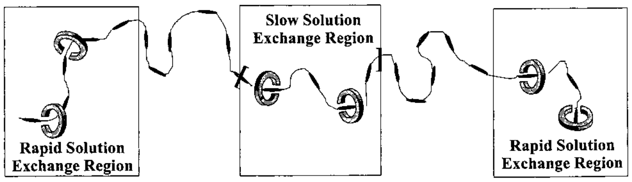
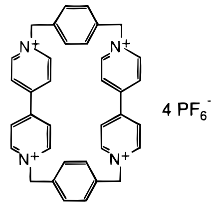


Figure 4. Schematic representation of the extreme cases of exchange rates of threaded macrocyclic components of a polypseudorotaxane with solution. Macrocycles near the ends of the macromolecule undergo rapid exchange on the NMR time scale, while those on host sites located in the interior portions of the linear macromolecule exchange very slowly due to the distance they must traverse and the fact that they cannot pass other threaded macrocycles. In the present systems at ambient temperature macrocycle **1** undergoes rapid exchange with up to ca. three terminal repeat units.

branched polymers, and copolymers of similar constitution (schematically described in Figure 3). All these polymeric structures are based upon a bis(acylaminophenyl)methyl binding site derived from 4,4′-methylenebis(*p*-phenyl isocyanate) (MDI) to which the cyclophane binds strongly ($K_a \sim 100$ M^{-1} in DMSO at 25 °C). In the first two cases the system is observed at equilibrium. Then we will consider a system in which barriers to threading are introduced into the polyurethane backbone; in this case the kinetics of the process are measured as a function of the density of barriers.



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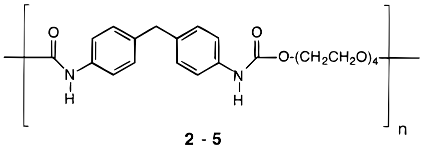

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Results and Discussion

a. Interactions of Cyclophane 1 with Linear Polymers, Effect of Molecular Weight. It is clear that the rate of threading/dethreading of macrocycles from preformed linear macromolecules will be dependent upon the concentration of ends, i.e., in the bulk on the number of ends per unit mass, and hence inversely upon the molecular weight of the polymer. In principle, then, threading rate measurements should yield molecular weight information.

As shown in Figure 4, exchange of cyclics between the threaded state on the interior of a long macromolecule and the free state in solution requires not only that it traverse the length of the polymer backbone but also that any other cyclics between it and the external solution must move out of its way since passage of one ring through another is very unlikely. Therefore, although there are really only two states of the cyclic species to consider, free and bound, because the exchange rate has a topological component, i.e., it depends on the location of the cyclic along the backbone, it is convenient to think of two extreme cases as detected by NMR spectroscopy: (i) *type 1 signals*: with fixed chemical shift corresponding to cyclic units that remain threaded on interior positions along the backbone for longer than the NMR time scale and not time averaged with solution, i.e., those undergoing very slow exchange with free cyclic in solution as a result of the stochastic nature of this process which is limited by the number of chain ends; (ii) *type 2 signals*: time averaged and thus of variable chemical shift, representing cyclics near the ends of the linear macromolecules that undergo rapid exchange (relative to the NMR time scale) between the free state in solution and the threaded state.

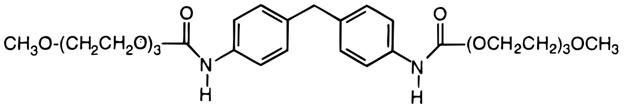
Table 1. Molecular Weights (kg/mol) of Polyurethanes 2−5

polymer	M_n[a]	M_w[a]	M_w/M_n	DP_n[b]
2	2.8	3.4	1.2	6.3
3	4.4	6.4	1.5	9.9
4	11.5	20	1.7	25.9
5	15.2	43	2.8	34.2

[a] Determined by GPC in THF using polystyrene standards. [b] Number-average degree of polymerization based on repeat unit molecular weight of 444.5.

Of course, at intermediate exchange rates, i.e., near the coalescence point, we may expect to observe very broad signals. This situation is somewhat analogous to proton exchange between solvent and molecular sites of different accessibility (acidity), which enables us to assign them on the basis of exchange with D_2O; that is, in a given molecule we may have rapidly exchangeable protons associated with more acidic moieties and protons which essentially do not exchange on the NMR time scale because they are less acidic. The difference in the present case is that the origin of the difference is topological, not chemical. And consideration of the relative amounts of rapidly exchanging and very slowly exchanging cyclics allows us to probe topology, i.e., the length (molecular weight) and proportion of repeat units outside branch points, as we will describe.

Four linear polyurethane samples (**2**−**5**) with different molecular weights were synthesized from MDI and tetra(ethylene glycol) (Table 1, schematically shown in Figure 3) and model monomer **6** from MDI and tri(ethylene glycol) monomethyl ether. The interactions of urethanes **2**−**6** with **1** were studied in the series of DMSO-d_6 solutions summarized in Table 2.



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In the first analysis we will examine the signals from the α protons of **1**, as they stand clear of the rest of the spectrum. Consistent with previous studies,[7m] two types of ^{1}H NMR signals may be observed for macrocycle **1** in these pseudorotaxane solutions. It is instantly obvious from Figure 5 that the nature of the signals obtained for the α protons of **1** in otherwise identical solutions is related to the molecular weight of the polymer; this relationship has never been documented before. Solutions containing polymer **2** ($M_n = 2.8$ kg/mol) and the model monomer **6** do not display a type 1 peak, yet solutions containing polymers **3**−**5** do (at 9.22 ppm). It is therefore empirically observed that the number of cyclophanes that stay upon model system **6** and polymer **2** for longer than the ^{1}H NMR time scale is below the detection limit of the spectrometer, yet there is a measurable population of cyclics that stay upon higher molecular weight polymers **3**−**5** for longer than the ^{1}H NMR time scale. It is possible to use these two data to estimate the speed of movement of the cyclophane.

A very simple model was applied to this system, based on the following rules: (i) There are no interactions between threaded cyclophane moieties.[12] (ii) A cyclophane hops randomly between MDI binding sites. (iii) Hopping into solution is of equal probability as hopping to an adjacent site.[13]

A cyclophane was placed upon the first binding site of the polymer. The cyclophane was allowed to perform one hop, and the probability of the cyclophane leaving the polymer was calculated (50%). This process was repeated until 97% of the cyclophanes had left the polymer (i.e., 3% threaded cyclic taken to be the detection limit of the spectrometer). This procedure was repeated for all sites upon the polymer. The average number of hops to migrate 97% of the cyclophanes off the polymer was then calculated.[14] This occurs for a polyurethane with six sites (equivalent to $M_n \sim 2.8$ kg/mol) in about 60 hops. The ^{1}H NMR time scale appropriate to the α protons is about 4 ms; therefore, we estimate the cyclophane is performing about 15 000 hops/s (equivalent to a velocity of ca. 0.04 mm/s). The cyclophane is moving very quickly. This simulation also predicts that all sites in low molar mass polyurethane **2** are equally occupied (time averaged).

From the chemical shift of the time-averaged type 2 peak it is possible to calculate the fractions of exchanging cyclophane molecules that are instantaneously free and bound.[15] It is, therefore, possible to calculate c, the fraction of all bound cyclophanes that are rapidly exchanging with solution, from f_2, the fraction corresponding to signals of type 2 for rapidly exchanging, but instantaneously bound, cyclics, and f_1, the fraction of very slowly exchanging, but bound, cyclophanes. Since with model diurethane **6** and polymer **2** ($M_n = 2.8$ kg/mol) macrocycle **1** undergoes only rapid exchange, but with polymer **3** ($M_n = 4.4$.kg/mol) signals representing both slow and fast exchange are observed, we estimate that for this system 3000 mass units represents the limit for rapid exchange at ambient temperature. Thus

$$c = f_2/(f_1 + f_2) \approx 3000/M_n$$

and hence

$$M_n \approx 3000/c$$

To check the validity of this equation, the concentration of cyclophane **1** was varied while the polymer repeat unit concentration was kept constant. As shown in Figure 6, the ratio of exchanging to bound cyclic signals, c, the slope, was independent of site occupancy (over the range 0−15%); i.e., the same fractions of all cyclophanes in solution undergo rapid and slow exchange independently of the total cyclophane concentration, and these fractions depend only on the exchange rates which do not vary under these conditions. For model monomer **6** and low molecular weight polymer **2** the slopes are identical and equal to unity. As shown in Figure 4, the cyclic probe is rapidly sampling a constant end segment length, in the present case about three repeat units, regardless of the total length of the polymer. In other words, the cyclic probe enables measurement of the end group concentration for macromolecules longer than ca. 3 kg/mol. Thus, the equation provides a good fit for all data obtained and can be used for determining the M_n of an unknown polymer (with the same repeat unit). However, since the molecular weights of Table 1 are based on polystyrene standards, at this point this equation is not precisely calibrated.

If equilibrium is defined as the situation when the rate of threading is equal to the rate of dethreading, then the equilibrium constant K can be calculated (Figure 7). K was calculated for solutions containing cyclic **1** and urethane species **2**−**6**. It was found that

Table 2. Compositions of the Solutions (1.00 mL, DMSO-d_6) Used To Study the Interactions of Cyclophane 1 with Species 2−6[a]

sample used	mass polymer/mass **1** (mg/mg)					
2	10.75/1.66	10.75/2.22	10.75/3.33	10.75/4.44	10.75/6.66	10.75/0.00
3	10.75/1.66	10.75/2.22	10.75/3.3	10.75/4.44	10.75/6.66	10.75/0.00
4	11.10/1.66		11.10/3.33		11.10/6.66	4.00/0.00
5	10.75/1.66	10.75/2.22	10.75/3.33	10.75/4.44	10.75/6.66	10.75/0.00
6	13.99/1.66	13.99/2.22	13.99/3.33	13.99/4.44	13.99/6.66	13.99/0.00
1[b]	0.00/1.66	0.00/2.22	3.33	0.00/4.44	0.00/6.66	

[a] Concentrations of **2**, **3**, **5**, **6** = 24.2 mM on MDI repeat unit basis; concentration of **4** = 25.0 mM. Cyclophane concentrations vary from 1.50 to 2.00 to 3.03 to 4.04 to 6.05 mM from left to right. The final column is for control solutions of **2**−**6**, and the bottom row is for control solutions of **1**. [b] Study of these cyclophane standards revealed that the chemical shifts were not concentration dependent over this range.

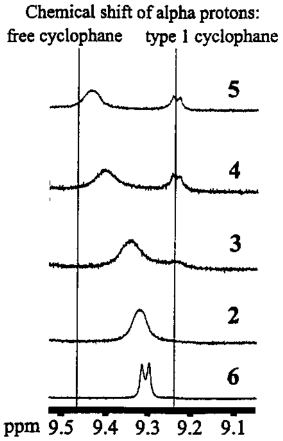


Figure 5. Partial 400 MHz ^{1}H NMR spectra of solutions (DMSO-d_6) containing one of the linear polyurethanes **2**−**5** or the model compound **6** (24.2 mM in MDI-derived binding site) and the cyclophane **1** (3.03 mM). A conspicuous relationship is observed between the molecular weight of the polymer and the signals for the α protons of **1**.

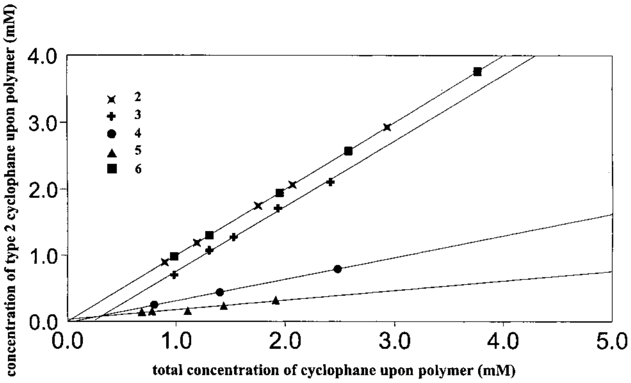
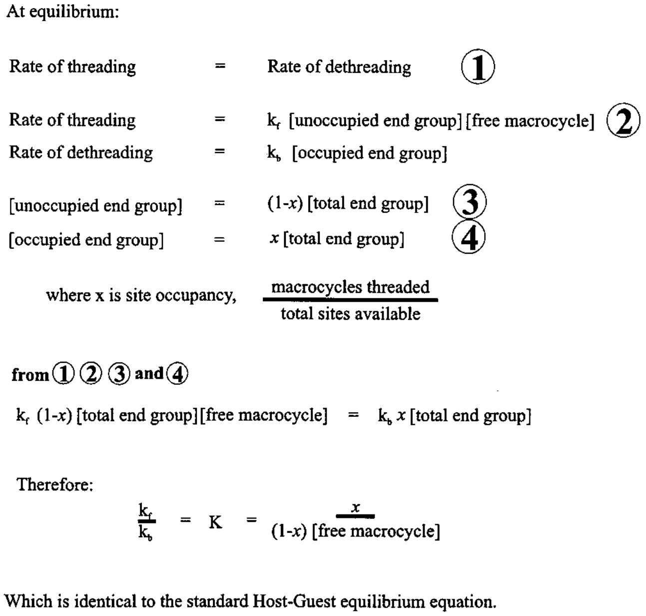


Figure 6. Plots of the concentration of type 2 (rapidly exchanging) cyclophane **1** bound versus total concentration of **1** bound upon the polymer for solutions containing species **2**−**6**. The gradient of each line (*c*) is related to the molecular weight of the polymer. The anomalous results from solutions containing polymer **3** are due to poorly resolved signals from the α protons, making accurate measurements difficult; the central repeat units in the polypseudorotaxane derived from **3** are too far from the ends to be in the rapid exchange limit, but not so far as to cause very slow exchange (Figure 4), and thus signals corresponding to **1** bound to these sites fall in the intermediate exchange rate regime.

the model monomer **6** had a constant and reproducible equilibrium constant, yet the polymeric species displayed an “equilibrium constant” that decreased as M_n increased (Table 3). We attribute this to the following effects. It is expected that to thread multiple cyclophanes onto a long polymer is entropically worse that threading the same number of cyclophanes onto an identical mass of shorter polymer molecules not only based on the total number of particles but also due to conformational constraints on the threaded polymer segments (Figure 8); hence, *K* is expected to decrease as M_n increases. A measure of this nonideality can be obtained by a plot of log(number of moles of **1** per macromolecule in solution) versus Δ*G* (Figure 9). It is found that the plot, containing all data from all polymers, consists of two straight lines, one representing ideal behavior and the other representing nonideal behavior. “Ideal” behavior is observed below 0.35 **1** per macromolecule, and the nonideal line may be described


At equilibrium:

Rate of threading = Rate of dethreading ①

Rate of threading = k_f [unoccupied end group] [free macrocycle] ②

Rate of dethreading = k_b [occupied end group]

[unoccupied end group] = (1-*x*) [total end group] ③

[occupied end group] = *x* [total end group] ④

where x is site occupancy, $\frac{\text{macrocycles threaded}}{\text{total sites available}}$

from ① ② ③ and ④

k_f (1-*x*) [total end group][free macrocycle] = k_b *x* [total end group]

Therefore:

$$\frac{k_f}{k_b} = K = \frac{x}{(1-x)\,[\text{free macrocycle}]}$$

Which is identical to the standard Host-Guest equilibrium equation.

Figure 7. If the equilibrium in a polyrotaxane solution is defined as the state when the rate of threading is equal to the rate of dethreading, then a simple mathematical proof shows this to be numerically the same as the standard host−guest equation.

Table 3. Equilibrium Constants (295 K) Calculated from the ^{1}H NMR Spectra of the Solutions of Table 2

	K (M^{-1})						95%
species	*0.062*[a]	*0.083*	*0.125*	*0.167*	*0.250*	K_{av} (M^{-1})	confidence limits
6	81	80	81	82	80	81	1.6
2	70	73	78	64	71	71	12
3[b]	108	121	75	85	90	96	43
4[c]	54		48		52	51	8
5	41	32	32	34	35	35	9

[a] The figures in italics denote the total number of cyclophanes in solution per repeat unit of polymer. Repeat unit concentrations 24.2 mM for **2**, **3**, **5**, **6**; 25.0 mM for **4**. [b] Measurements from spectra containing this species were hampered by the poorly resolved types 1 and 2 peaks. [c] The number of cyclophanes per repeat unit of polymer is 3% lower in these solutions than indicated in the column headings.

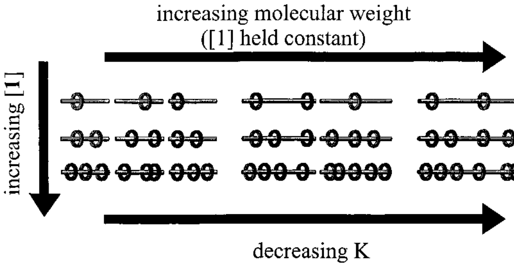


Figure 8. General trends that are observed in these polypseudorotaxane systems: as molecular weight increases, so the equilibrium constant decreases.

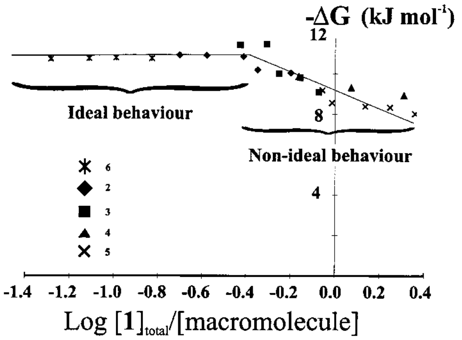


Figure 9. Plot of $-\Delta G$ vs log(number of moles of **1** per macromolecule in solution) gives an indication of the ideal and nonideal behavior in polypseudorotaxanes derived from **1** and polyurethanes **2**–**5**.

by the formula

$$\Delta G = [-3.0 \times 10^{-4} \log([\mathbf{1}]_{\text{total}}/[\text{macromolecule}]) + 9100]\ \text{kJ/mol}$$

A contributing factor may also be the polyelectrolyte effect; as increasing proportions of cyclophane **1** are threaded, the resultant electrostatic repulsion of charge centers leads to a free energy penalty.

b. Interaction of Cyclophane 1 with Linear Polymers, the Effect of Temperature. There are two important trends observed with temperature. The first is with respect to the signal from the protons of **1**; the second is with respect to the signals observed for the aromatic protons of the MDI-derived guest units. As the solutions are heated, the cyclophanes move faster, and the equilibrium shifts in favor of the dissociated species. The increasing speed of the cyclophane movement can be observed as an increase in size of the rapidly exchanging type 2 peak (downfield, time-averaged signal of variable chemical shift, ca. 9.4 ppm) at the expense of the very slowly exchanging type 1 peak (upfield, 9.22 ppm, representing slow exchange between threaded and solution states) for the α protons of **1** (Figure 10).

Again, although there are really only two individual states for the MDI units, threaded or not threaded, the NMR spectra will reveal information about the exchange rates between these two states. In principle, the signals for the aromatic protons of the MDI-derived guest units can be categorized as follows: (i) *type A*—for MDI units away from the ends of the macromolecule that bind cyclophanes for longer than the ^{1}H NMR time scale; (ii) *type B*—time-averaged, corresponding to MDI units near the ends of the macromolecules that experience the effect of a cyclophane during the ^{1}H NMR time scale; (iii) *type C*—those corresponding to MDI units that do not bind a cyclophane during the ^{1}H NMR time scale.

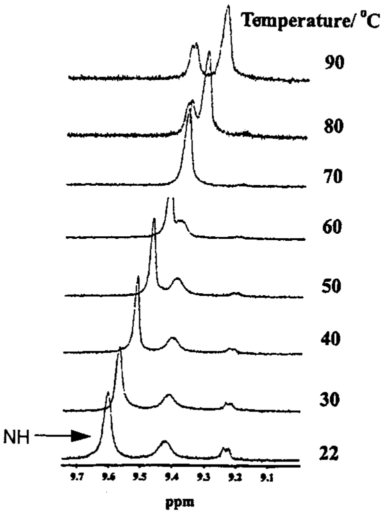


Figure 10. Partial ^{1}H NMR spectra (400 MHz) of a solution (DMSO-d_6) containing polyurethane **5** (24.2 mM in MDI-derived binding site) and cyclophane **1** (3.03 mM). As the temperature increases, the type 1 peak at 9.22 ppm (for **1** bound on the NMR time scale) decreases in size but does not change its chemical shift, while the type 2 peak (rapidly exchanging) at ca. 9.4 ppm increases in size and shifts slightly upfield, as it now represents a larger fraction of bound **1**. The large signal that moves from 9.62 to 9 9.27 δ is due to the N–H of **5**.

Type A MDI-derived units were not observed due to the rapid movement of the cyclophane; further, it was not possible to determine the chemical shift of this environment as the solvent precluded low-temperature study.

It should be stressed that the time scale appropriate to the MDI-derived protons is considerably longer than that of the α protons of the cyclophane.[16] Therefore, although the cyclophane signal may be time-averaged over all sites and in solution, this does not mean that all the MDI-derived sites will be type B. Experimentally at ambient temperature the MDI signals are of types B (δ = 6.98, 7.25, broad) and C (δ = 7.06, 7.33, sharper) for low molecular weight **2** and **3** (Figure 11)**.** At ambient temperature the exchange rate is comparable to the NMR sampling rate, yielding broad type B signals. However, at 90 °C, due to more rapid motion, essentially only relatively sharp type B signals (δ = 7.02, 7.29 ppm) are observed for polymers **2** and **3** (Figure 12)**.** For higher molecular weight **4** and **5**, both types B and C signals are observed at both ambient temperature and 90 °C (Figures 11 and 12). At ambient temperature the signals for the exchanging units are detected as upfield shoulders or signal broadening that diminishes with increasing molecular weight. At 90 °C the type B signals comprise the broad upfield components, and the type C signals are distinguished on the basis of the vicinal coupling which affords the expected doublets downfield from the type B signals. As the molecular weight increases (**4** to **5**), the broad upfield type B signals move downfield, as expected on the basis of time averaging of a smaller fraction of total MDI sites.

K was calculated at various temperatures (Table 4) using the chemical shifts of the α protons of **1** in solutions containing the polyurethanes (24.2 mM in MDI-derived guest site) and **1** (3.03 mM). When no type 1 cyclophane peak was observed, its chemical shift was estimated by extrapolation from known points. The chemical shift of free **1** was measured at the appropriate

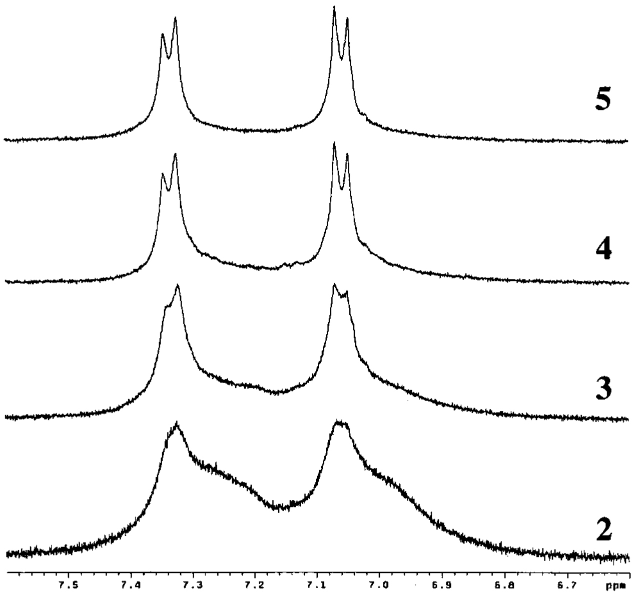


Figure 11. Partial ^{1}H NMR spectra (400 MHz) of solutions (DMSO-d_6) containing polyurethanes **2**−**5** (24.2 mM in MDI-derived binding site) and cyclophane **1** (3.03 mM) at ambient temperature. The signals at 7.06 and 7.33 ppm of type C (due to MDI units not accessed by cyclophane **1**) increase relative to the broad, time-averaged upfield signals of type B (due to MDI units that are complexed by **1**) as molecular weight increases (**2** to **5**).

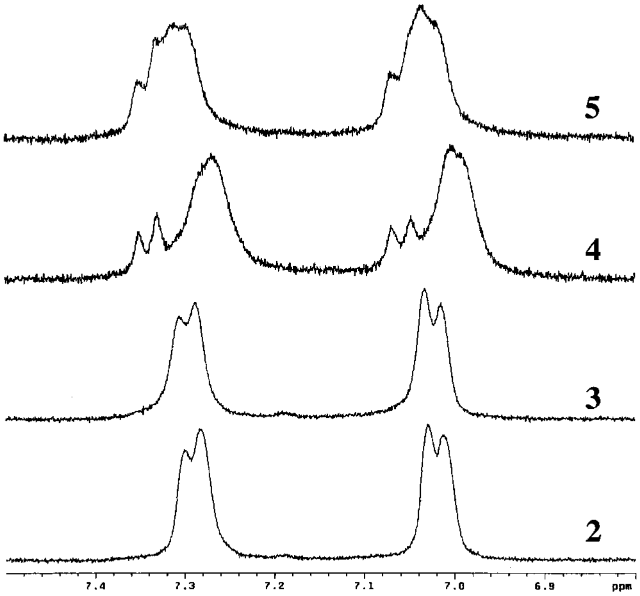


Figure 12. Partial ^{1}H NMR spectra (400 MHz) of solutions (DMSO-d_6) containing polyurethanes **2**−**5** (24.2 mM in MDI-derived binding site) and cyclophane **1** (3.03 mM) at 90 °C. Type C signals are not observed for low molecular weight **2** and **3**, but both types B and C signals are observed for higher molecular weight **4** and **5**.

Table 4. Equilibrium Constants Calculated from the ^{1}H NMR Spectra of Solutions of Polyurethanes (24.2 mM Repeat Unit)[a] and 1 (3.03 mM) at Various Temperatures

	K (M^{-1})[b]				
temp (°C)	2	3	4	5	6
21	100	60	34	26	95
30	77	47	28	20	73
40	57	34	21	16	56
50	44	25	19	11	42
60	37	23	13	*c*	32
70	28	*c*	*c*	*c*	*c*
80	*c*	16	12	8	24
90	*c*	14	10	6	15

[a] For **2**, **3**, **5**, **6**; 25.0 mM for **4**. [b] Relative errors estimated based on the values in the first row of this table and the corresponding fourth column of Table 3 (0.125 cyclophanes per repeat unit): **2**, ±12%; **3**, ±12%; **4**, ±17%; **5**, ±10%; **6**, ±8%. [c] These equilibrium constants could not be calculated because the NH peak of the polymer could not be distinguished from the type 2 peak of **1**.

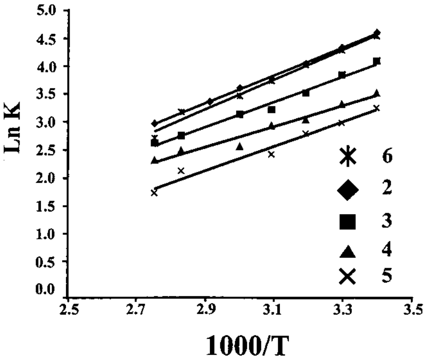


Figure 13. Van't Hoff plots of solutions (DMSO-d_6) containing cyclophane **1** (3.03 mM) and urethane guests **2**−**6** (24.2 mM in MDI-derived binding site).

Table 5. Thermodynamic Constants Measured from Van't Hoff Plots

sample	r^2 [a]	$\Delta H°$ (kJ/mol)[b]	$\Delta S°$ (J/(mol deg))[b]
6	0.986	−22.5 ± 2.1	−38.1 ± 6.5
2	0.997	−21.5 ± 1.0	−34.8 ± 3.3
3	0.984	−18.7 ± 2.8	−30.0 ± 8.7
4	0.966	−15.7 ± 3.8	−24.3 ± 11.6
5	0.977	−17.9 ± 1.8	−34.3 ± 5.8

[a] Square of least-squares correlation coefficient obtained using the values for K given in Table 4. [b] Values are from least squares fits of K from Table 4. Estimates of error as ± values are the standard errors calculated for the least-squares fit of the values of Table 4 and additionally for each point values corresponding to the relative errors given in Table 4, footnote *a*, i.e., three points for each temperature corresponding to the observed value and the estimated maximum and minimum values. These are viewed as extreme limits for the errors.

temperature and concentration. Van't Hoff plots were constructed (Figure 13); all yielded straight lines. The physical constants for these systems were calculated (Table 5). Although it is found that $\Delta G_{\mathrm{binding}}$ is dependent upon the length of the polymer (this is molecular recognition of polymers), $\Delta H_{\mathrm{binding}}$ and $\Delta S_{\mathrm{binding}}$ do not appear to be simply related to the length of the polymer. (We might naively expect ΔH to be constant throughout these systems and $-\Delta S$ to increase with molecular weight.) This may be attributed to a poor extrapolation due to too few data points over too narrow a range, or ΔH being a result of two effects (e.g., site occupancy and temperature), such that each varies linearly over this data range, but prevent the desired separation of the variables.

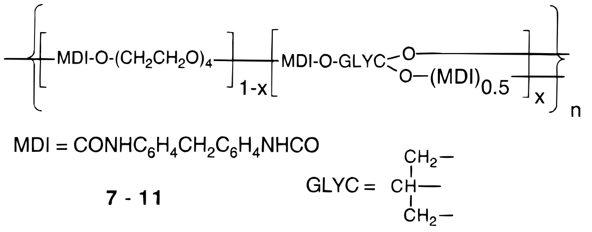
c. Interaction of Cyclophane 1 with Branched Polymers. In any branched polymeric system, it is sterically impossible for a threaded cyclic molecule to pass a branch point. Polymers **7**−**11** were synthesized by incorporating different amounts of a glycerol branch point (Table 6), such that the branched polymers were completely soluble in THF, i.e., below the gel point. It is expected that with a polymer with one or no branch points the cyclophane has access to all of the binding sites. As the number of branch points increases, the number of sites the cyclophane is forbidden from accessing (between any two branch points) increases.

Table 6. Stoichiometric Compositions and Molecular Weights (kg/mol) of the Branched Polyurethanes 7−11

polymer	*x*	M_n[a]	M_w[a]	DP_n[b]
7	0.000	11.4	22	25.7
8	0.014	12.2	25	27
9	0.032	12.0	26	27
10	0.060	12.2	32	27
11	0.120	14.6	81	32.7

[a] Determined by GPC in THF using polystyrene standards. [b] Number-average degree of polymerization based on repeat unit molecular weights of 444.5 and 455.4 for TEG and GLYC units, respectively.

Solutions were prepared (Table 7) and studied by ^{1}H NMR spectroscopy. There was a relationship between the proportion of branching unit incorporated into the polymer and the nature of the signal obtained from **1**; as expected, as the percentage of branch points was increased, the type 1 (bound) signal observed for **1** decreased and the type 2 (exchanging) signal increased, and its chemical shift tended toward that of the free **1**. Using the observed empirical formula $M_n \sim 3000/c$, it is possible to estimate the average length between a branch point and a terminus. As the amount of the branching unit in the polymer increases, so the fraction of rapidly exchanging macrocycles out of all threaded macrocycles, *c*, becomes larger, or to put it another way, the average distance between a branch point and a terminus becomes shorter. Polymers **7−11** behave as if they were linear polyurethanes with average lengths of 19, 18, 16, 13, and 10 repeat units, respectively. The greatest distance a cyclophane can be from a terminus is in the middle of a linear polymer or at a branch point for a cross-linked system; this will be numerically half of the above values, i.e., 9.5, 9.0, 8.0, 6.5, and 5.0 repeat units.

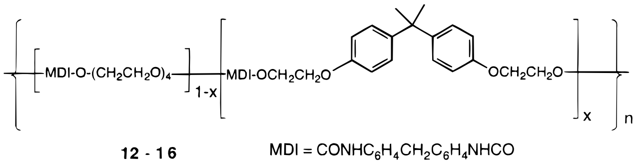


7 - 11

Another, more direct attribute of these polymers can be measured. It is first necessary to assign a new category of NMR signal for MDI-derived units: type D, for those units between branch points that the cyclophane is forbidden from accessing. The chemical shift of this signal should be identical to the type C signal for unaccessed MDI-derived units in simple linear polyurethanes ($\delta = 7.08, 7.35$). At ambient temperature even in low molecular weight linear polyurethanes **2** and **3** both types B and C signals are observed (Figure 11). However, at elevated temperature for linear polyurethanes **2** and **3** only type B signals are observed (Figure 12), but higher molecular weight **4** and **5** still exhibit signals of both types B and C.

The spectra of solutions containing **1** (6.05 mM) and polymers **7−11** (24.2 mM in MDI-derived guest site) were recorded at 90 °C (Figure 14). In linear polymer **7**, only a small amount of type C signal was observed. It is therefore logical that branched polymers **8−11** should have very little or no type C peak; therefore, the peaks observed in these spectra with chemical shifts identical to type C signals for MDI-derived units (Figure 12, ca. 7.08, 7.35 ppm) are type D signals from MDI units that cannot be accessed by the cyclophane. The fraction of inaccessible MDI units (as determined by the integrals of these signals) in solutions containing polymers **7−11** and **1** at 90 °C increases with the fraction of branch point in the polymer (Figure 15), as expected. This is the first time the fraction of dangling ends in branched polymers has been measured directly with this type of probe. Therefore, this technique provides a relatively simple spectroscopic probe to estimate the fraction of such "internal" sites in branched polymers.

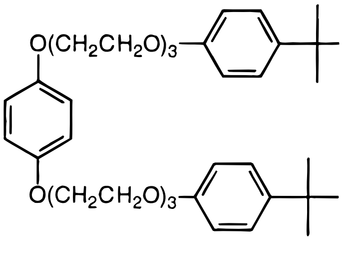
d. Slippage: Interaction of Cyclophane 1 with Copolymers Containing Bisphenol A Units. Copolymers **12−16** (Table 8) were synthesized from MDI, tetra(ethylene glycol), and bisphenol A (BPA) diethoxylate, incorporating varying mole fractions *x* of the BPA moiety.



12 - 16

The solutions summarized in Table 9 were studied by ^{1}H NMR spectroscopy. For reference, when cyclophane **1** is mixed in solution with the bis(*tert*-butylphenyl) ether **17** at room temperature, it takes about 20 min to establish equilibrium.[17] Since virtually no change relative to **1** alone was observed in the signals for the α protons of **1** in solutions containing polymers **15** and **16** over 3 days at room temperature, it is clear that the BPA units in these polymers prevent threading. For **1** to move over the bulky BPA moiety requires an activation energy in excess of that which the molecules have at room temperature.

However, upon heating these solutions to 90 °C, there is an instantaneous change and a very dramatic dependence of the ^{1}H NMR signal obtained for **1** upon *X* (Figure 16). Namely, as the proportion of BPA units increases (**12** to **16**), the fraction of bound cyclics represented by the type 1 signal decreases to near zero, and the signal for exchanging cyclics increases and shifts toward the chemical shift of unthreaded **1**, indicating greatly diminished complexation/threading.



17

With respect to MDI-derived signals only types B (exchanging) and D (inaccessible) are observed.[18] Quantitative analyses of these signals as outlined above affords estimates of the accessible fraction of MDI-derived sites (between a terminus and a BPA unit): 0.86,[17] 0.43, 0.19, 0.09, and 0.05 for polyurethanes **12−16,** respectively.

If it is assumed that species **13−16** are random copolymers, the average number of MDI-derived guest sites accessible (between a terminus and the first BPA

Table 7. Compositions of Solutions (1.00 mL, DMSO-d_6) Used To Study the Interaction of Cyclophane 1 with Polyurethanes 7−11[a]

polymer	mass polymer/mass **1** (mg/mg)					
7	10.75/1.66	10.75/2.22	10.75/3.33	10.75/4.44	10.75/6.66	10.75/0.00
8	10.75/1.66	10.75/2.22	10.75/3.33	10.75/4.44	10.75/6.66	10.75/0.00
9	10.75/1.66	10.75/2.22	10.75/3.33	10.75/4.44	10.75/6.66	10.75/0.00
10	10.75/1.66	10.75/2.22	10.75/3.33	10.75/4.44	10.75/6.66	10.75/0.00
11	10.75/1.66	10.75/2.22	10.75/3.33	10.75/4.44	10.75/6.66	10.75/0.00
1[b]	0.00/1.66	0.00/2.22	0.00/3.33	0.00/4.44	0.00/6.66	

[a] Concentrations of **7**−**11** = 24.2 mM on MDI repeat unit basis. Cyclophane concentrations vary from 1.50 or 2.00 to 3.03 to 4.04 to 6.05 mM from left to right. The final column is for control of solutions **7**−**11,** and the bottom row is for control solutions of **1**. [b] Study of these cyclophane standards revealed that the chemical shifts were not concentration dependent over this range.

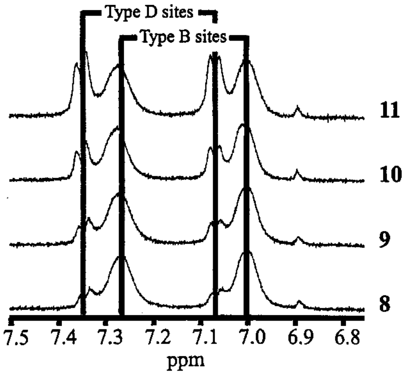


Figure 14. Partial 400 MHz ^{1}H NMR spectra of solutions (DMSO-d_6) of branched polyurethanes **7**−**11** (24.2 mM in MDI-derived binding site) and cyclophane **1** (6.05 mM) at 90 °C. The doublets at ca. 7.35 and 7.08 δ are of type D (due to protons of MDI units that are inaccessible to threading), while the broad singlets at ca. 7.28 and 7.01 δ are of type B (due to protons of MDI sites accessed by macrocycle **1**). The clear relationship between the amount of branching unit in the polymer and the ratio of the signals for types B and D protons can be seen.

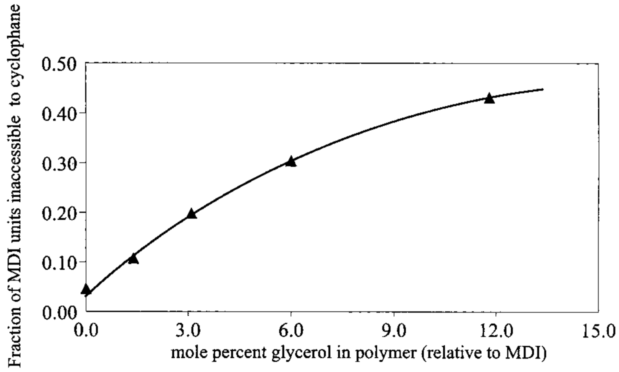


Figure 15. Plot of the fraction of branched polyurethanes **7**−**11** inaccessible to cyclophane **1** versus *x*, the mole fraction of glycerol incorporated.

unit) = 1/*X* and the fraction of accessible sites = (1/*X*)/(*n*/2), where *n* is the average number of units per macromolecule. Thus, polyurethanes **13**−**16** have, on average, 8, 4, 2, and 1 binding sites between an end group and the first BPA unit. Indeed, this trend can be qualitatively observed in Figure 16. For polymeric termini longer than ca. three MDI repeat units a fraction of complexation will involve slow exchange with interior units; a diminishing type 1 signal for the very slowly exchanging cyclics is thus expected and indeed observed in polymers **12**−**16** as the proportion of BPA units increases. The second equation predicts the fraction of binding sites accessible to the cyclophane as 1.00:0.42:0.20:0.07:0.04 for polymers **12**−**16**, which are in close correlation to those measured from the signals from the MDI protons at 90 °C.

Table 8. Stoichiometric Compositions and Molecular Weights (kg/mol) of Polyurethanes 12−16

polymer	*x*	M_n[a]	M_w[a]	DP$_n$[b]
12	0.000	18.8	46.9	42.3
13	0.125	17.2	44.4	38.3
14	0.250	17.8	46.9	39.3
15	0.500	23.9	65.9	51.8
16	1.00	21.1	54.0	44.1

[a] Determined by GPC in THF using polystyrene standards. [b] Number-average degree of polymerization based on repeat unit molecular weights of 444.5 and 478.5 for TEG and BPA units, respectively.

The kinetics of threading of **1** onto polyurethanes **12**−**16** were examined at 60 °C. As seen in Figure 17 **12**, which has no BPA units, reaches equilibrium essentially instantaneously (0 days) and achieves an MDI site occupancy of 4.86% (±0.05%), corresponding to $K = 27.7 \pm 0.7$ M^{-1} and ca. two cyclophanes per macromolecule. As the fraction *X* of BPA units increases, the fraction of instantaneous threading is dramatically reduced. As the fraction of BPA units increases, at day zero the system is further from equilibrium. As a result, somewhat counterintuitively, the initial rate of threading actually increases with *X*, because at low values of *X*, the overall rate of threading contains a significant contribution from the reverse process, dethreading.

The BPA homopolymer **16** contains one MDI unit between each pair of slippage stoppers and essentially no dangling MDI ends and therefore an undetectable level of instantaneous threading. In this case the initial threading rate corresponds to the rate of occupation of the MDI unit between the ultimate pair of BPA units, i.e.,

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k_{\mathrm{f}}[\mathrm{ends}][\mathbf{1}]$$

Since the concentration of chain ends remains constant, the data from days 0−5 were analyzed as pseudo-first-order kinetics:

$$\ln\{[\mathbf{1}]/[\mathbf{1}]_0\} = -k_{\mathrm{f}}[\mathrm{ends}]t$$

The chain end concentrations were calculated from the M_n values and masses of polyurethane samples (Table 10). The rate constant derived from this treatment was 15 M^{-1}/day. Assuming that $K = k_f/k_r = 27.7$ M^{-1}, $k_r = 0.54$/day.[19,20]

Estimates of the times required to reach 4.86% MDI occupancy for the various polyurethanes were made by extrapolating the fitted data to 4.86% MDI occupancy (Table 10).[20] The BPA homopolymer **16** would require nearly 3 years! Even **13** containing only 12.5 mol % BPA units would require more than 6 months. Of course, it may be that the binding constant for the BPA−MDI unit

Table 9. Compositions of the Solutions (1.00 mL, DMSO-d_6) Used To Study the Interaction of Cyclophane 1 with Polyurethanes 12−16[a]

polymer	mass polymer/mass **1** (mg/mg)					
12	10.75/1.66	10.75/2.22	10.75/3.33	10.75/4.44	10.75/6.66	10.75/0.00
13	11.38/1.66	11.38/2.22	11.38/3.33	11.38/4.44	11.38/6.66	11.38/0.00
14	12.01/1.66	12.01/2.22	12.01/3.33	12.01/4.44	12.01/6.66	12.01/0.00
15	13.29/1.66	13.29/2.22	13.29/3.33	13.29/4.44	13.29/6.66	13.29/0.00
16	15.83/1.66	15.83/2.22	15.83/3.33	15.83/4.44	15.83/6.66	15.83/0.00
1[b]	0.00/1.66	0.00/2.22	0.00/3.33	0.00/4.44	0.00/6.66	

[a] Concentrations of **12**−**16** = 24.2 mM on MDI repeat unit basis. Cyclophane contrations vary from 1.50 to 2.00 to 3.03 to 4.04 to 6.05 mM from left to right. The final column is for control solutions of **12**−**16,** and the bottom row is for control solutions of **1**. [b] Study of these cyclophane standards revealed that the chemical shifts were not concentration dependent over this range.

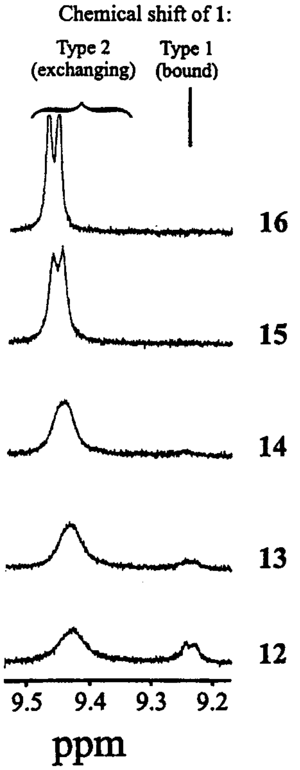


Figure 16. Partial 400 MHz ^{1}H NMR spectra of solutions (DMSO-d_6) of polyurethanes **12**−**16** (24.2 mM in MDI-derived binding site) and cyclophane **1** (6.05 mM) at 90 °C.

differs from that of the TEG−MDI unit, but the relatively long times required for the production of such polyrotaxanes by slippage under these conditions is not in doubt. However, for practical larger scale syntheses the use of higher concentrations, by factors of 100−1000, would allow the threading rates to be increased by factors of 10^4−10^6, meaning that this approach is probably practical in this system.[19] Approaches in which only the ends of the polymers are capped with cumylphenol units could also be used to avoid the kinetic limitations of multiple barriers. These methods are under consideration in our laboratory.

Conclusions

We have shown that the dynamics of threading/dethreading of the bis(paraquat) cyclophane **1** reveal aspects of the polymer with which it is interacting in solution. The ^{1}H NMR signals observed for **1** when it is interacting with a linear polymer provide a novel method of determining M_n values. When **1** is complexed with a branched polymer, the cyclophane interacts with all the MDI-derived binding sites up to the first branch point (which it is sterically forbidden from passing). This behavior can be used to deduce the ratio between the number of units between two branch points (inaccessible to threading) and the number between a branch point and a terminus (accessible to threading); the average length between a branch point and a terminus can also be determined. A similar behavior is observed when the cyclophane interacts with a copolymer in which one of the units is large enough to prevent **1** from passing. Incorporation of bulky BPA units in the polymer backbone results in dramatically retarded threading/dethreading kinetics, making the elevated temperature slippage approach to these systems practical.

Experimental Section

Chemical reagents were used as supplied by Aldrich, unless otherwise stated. ^{1}H NMR spectra were recorded on a Varian Unity 400 spectrometer (400 MHz); each of the three sets of solutions (linear polymers, branched polymers, and copolymers) were prepared using one bottle of DMSO-d_6. GPC was performed with an ISCO machine using PLgel 5 mm MIXED-D (300 × 7.5 mm) columns and Polymer Laboratories EasiCAL PS-2 polystyrene standards and THF as solvent. All ^{1}H NMR solutions were prepared by mixing known volumes of carefully prepared volumetric solutions of **1** in MeCN and the polymeric species in THF. The volatile solvents were then removed under a stream of N_2, and the residue was dissolved in 1.00(0) mL of DMSO-d_6.

5,12,19,26-Tetraazoniaheptacyclo[24.2.2.2^{2,5}.2^{7,10}.2^{12,15}.2^{16,19}.2^{21,24}]tetraconta-2,4,7,9,12,14,16,18,21,23,26,28,29,31,33,-35,37,39-octadecaene] tetrakis(hexafluorophosphate) (**1**). 4,4′-Bipyridine (3.00 g, 19.2 mmol) and α,α′-dichloro-*p*-xylene (3.36 g, 19.2 mmol) and hydroquinone bis(2-hydroxyethyl) ether (25.0 g, 126 mmol) were placed in a sealed round-bottomed flask and dissolved in 100 mL of dimethylformamide (DMF). The solution was allowed to stir at room temperature for 2 weeks. The brown solid was filtered and recrystallized once from water. The red needle crystals were dissolved in water (80 mL) and continuously extracted with dichloromethane for 3 days. NH_4PF_6 (3.0 g, 18 mmol) was added to the light yellow aqueous phase, and the white precipitate was filtered and dried, 769 mg (7.3%, reported[13] 12% after column chromatography), decomposition 275 °C, reported[13] deccomposition > 275 °C. ^{1}H NMR (DMSO-d_6), δ: 9.451, (8H, d, J = 6.5 Hz), 8.650, (8H, d, J = 6.5 Hz), 7.713 (8H, s), 5.808 (8H, s): ^{13}C NMR (DMSO-d_6), δ: 127.360, 130.447, 136.918, 145.399, 148.312, 149.435.

General Procedure for Polymers 2−5. Polymer 2. Tetra(ethylene glycol) was dried in a flask heated at ca.160 °C under a stream of N_2 for 2 days. Of this, 1.611 g (8.30 mmol) was weighed into a glass vial, and 20 mL of DMF (sieve dried) was added: MDI (1.869 g, 7.476 mmol) was added and the mixture stirred and heated at 80 °C for 24 h. The volume of the solution was reduced to ca. 5 mL under vacuum, and it was precipitated into methanol (MeOH, 200 mL). The precipitate was removed and dried under a vacuum. Polymer **2** (860 mg, 25%) was obtained as a white solid. ^{1}H NMR (DMSO-d_6), δ: 9.636 (2H, s) 7.346, (4H, d, J = 8.4 Hz), 7.069 (4H, d, J = 8.4 Hz), 4.154 (4H, s), 3.760 (2H, s), 3.44−3.65 (12H, m).

Model Compound 6. A solution of tri(ethylene glycol) monomethyl ether (1.19 g, 7.27 mmol) and MDI (0.865 g, 3.46

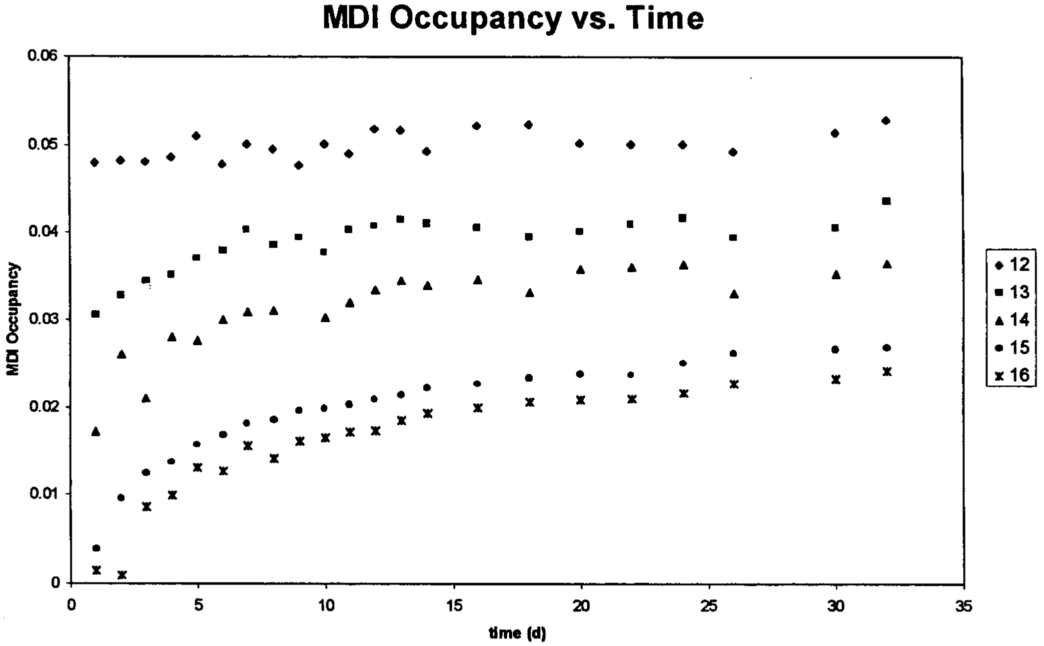


Figure 17. Kinetics of threading of polyurethanes **12**−**16** (24.2 mM in MDI repeat unit) by cyclophane **1** (3.03 mM) in DMSO-d_6 at 60 ± 5 °C in sealed tubes as measured by ^{1}H NMR spectroscopy.

Table 10. Kinetics of Threading Polymers 12−16 by Cyclophane 1 at 60 °C in DMSO-d_6[a]

system	X	[end][b] (mM)	t_{eq}[c] (years)
1/12	0.000	1.14	*d*
1/13	0.125	1.32	0.58 ± 0.08
1/14	0.250	1.35	0.79 ± 0.08
1/15	0.500	1.11	2.52 ± 0.22
1/16	1.00	1.50	2.90 ± 0.22

[a] Concentration of MDI repeat units = 24.2 mM; [**1**] = 3.03 mM. [b] End group concentration, calculated from mass of polymer (Table 9) and M_n (Table 8). [c] Time to reach equilibrium value of 4.86% of MDI units occupied by cyclophanes by extrapolation of logarithmic fits of the kinetic data of Figure 17, i.e., % occupancy = ce^{bt}, in which c and b are fitted parameters. Errors were estimated by the intercepts of the logarithmic fit within the standard deviations on the value of 4.86%, i.e., at 4.81% and 4.91%. [d] Equilibrates upon mixing.

mmol) in diglyme (25 mL) was heated at 90 °C for 7 h. The solution was cooled and concentrated by rotoevaporation. The compound was isolated by column chromatography using first an ethyl acetate/hexanes (50:50 v/v) mixture followed by ethyl acetate alone. The ethyl acetate fractions contained 1.62 g (81%) of desired product, an oil. ^{1}H NMR (400 MHz, ambient T, CDCl$_3$), d: 7.25 (4H, d, J = 8.4 Hz), 7.05 (4H, d, J = 8.4 Hz), 4.27 (4H, m), 3.84 (2H, s), 3.69 (4H, m), 3.63 (12H, m), 3.51 (4H, m), 3.33 (3H, s); ^{13}C NMR (100 MHz), d: 171.1, 150.4, 136.2, 135.9, 129.3, 118.8, 71.9, 69.4, 64.1, 60.3, 59.0, 40.5, 21.0, 14.1. FAB MS: positive 601 (M + Na)$^+$, 617 (M + K)$^+$; negative 577 (M − H)$^-$.

General Procedure for Branched Polymers 7−11. Polymer 11. Into a flask of known weight were placed tetra(ethylene glycol) (11.0409 g, 56.91 mmol), DMF (30 mL), and toluene (30 mL), and water was removed azeotropically at relux using a Dean−Stark apparatus for 24 h, after which time the toluene was distilled off. It was calculated that the mass of tetra(ethylene glycol) per gram of solution was 282.0 mg. MDI (5.9437 g, 237.8 mmol) was dissolved in azeotropically dried DMF (20 mL). To a flask containing glycerol (44.10 mg, 0.479 mmol) was added the MDI solution (3.36 mL, containing 1.00 g, 4.00 mmol), and the solution was heated in a sealed vessel for for 20 min at 80 °C. The tetra(ethylene glycol) solution (2.421 g containing 0.683 g, 3.52 mmol) was then added. The solution was heated at 80 °C for 24 h, after which time it was precipitated dropwise into MeOH (200 mL) to yield a swollen, rubberlike material. This was dissolved in THF (2 mL) to give a very viscous liquid which was spread into a film and dried under a vacuum to afford a white solid. ^{1}H NMR (DMSO-d_6), δ: 9.632, (2H, s), 7.345, (4H, d, J = 8.0 Hz), 7.099, (4H, d, J = 8.0 Hz), 4.152 (3.3H, s), 5.19−5.22 (0.13H, m), 4.39−4.43 (0.24H, m), 4.23−4.30 (0.25, m), 3.3−3.8 (integration hampered by H$_2$O peak, m).

General Method of Preparation for Copolymers 12−16. Polymer 16. Tetra(ethylene glycol) (8.736 g, 45.0 mmol) was placed in a flask of known weight with DMF and toluene. The mixture was heated at reflux, and water was removed azeotropically with a Dean−Stark apparatus for 24 h, after which time the toluene was removed. A similar procedure was used to dry a solution of bisphenol A ethoxylate (average M_n 404, 8.4357 g, 20.88 mmol). MDI (0.611 g, 2.44 mmol) was weighed into a flask, and the bisphenol A ethoxylate solution (16.6706 g of solution, 0.9874 g, 2.44 mmol) was added. The reaction vessel was sealed and heated for 24 h at 60 °C. The solution was precipitated into MeOH (200 mL) to give a swollen, rubberlike material. This was dissolved in THF (ca. 2 mL) and dried as a film. The yield of **16** was 1.11 g (70%), obtained as a white solid. ^{1}H NMR (DMSO-d_6) δ: 9.64−9.69 (2H, m), 7.348, (4H, d, J = 8.0 Hz), 6.95−7.12 (8H, m), 6.77−6.85, (4H, m), 4.358 (1H, br s), 4.12−4.22 (4H, m), 3.95−4.08 (3H, m), 3.42−3.80 (14H, m), 1.35 (6H s).

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References and Notes

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(12) A reasonable assumption given the low site occupancy of these polyrotaxanes, typically between 0 and 15%; a similar assumption was made by Wenz et al. in their treatment of a cyclodextrin-based polyrotaxane.[8c]

(13) It is our belief that the rate-determining step is departure from the guest site; a similar assumption was made by Wenz et al. in their treatment of a cyclodextrin-based polyrotaxane.[8c]

(14) Copies of the program available from: P. E. Mason, 77 Park Rd, Loughborough, Leics, LE11 2HD; e-mail masonpe@aol.com.

(15) Using the normal formula for a time-averaged peak: fraction of type 2 peak that is bound to the polymer at any instant in time $= f_2 = (\delta_2 - \delta_{\mathrm{free}})/(\delta_{\mathrm{bound}} - \delta_{\mathrm{free}})$, in which δ_2 and δ_{free} are the chemical shifts of the type 2 peak and the free cyclophane, respectively, and δ_{bound} is taken as equal to the chemical shift of the type 1 peak.

(16) This follows from the Eyring expression, $\tau \propto (1/\Delta\upsilon)$ and the fact that the chemical shift difference for the MDI protons in the bound and unbound states is less than that of the cyclophane protons in bound and unbound states.

(17) Mason, P. E. Ph.D. Thesis, Birmingham University, Birmingham, B16 2TT, England, 1997.

(18) However, type C was observed for polymer **12**; this is not surprising since the type C site can only be observed in the middle of longer polymers, because exchange with the ends of the polymer is always fast. At 90 °C, type C sites are still observed for polymers longer than ca. 10 kg/mol. It is therefore a reasonable assumption that although about 15% of the MDI sites are type C in polymer **12** ($M_n = 18.8$ kg/mol), no type C sites are observed in polymer **13**−**16**.

(19) Wenz et al. reported that threading of α-cyclodextrin (present in excess) onto poly[(*N*,*N*-dimethylammonio)hexamethylene-(*N*,*N*-dimethylammonio)decamethylene dibromide] ("polyionene-6,10") required 2 years at 25 °C in water to reach 55% occupancy but only 4 days for complete occupancy at 80 °C.[8c] In this system the two methyl substituents on the nitrogen atoms provide steric barriers. Based on a simulation called "ABAKUS" at 25 °C, $K = 223$ M^{-1}, $k_{\mathrm{f}} = 270$ M^{-1} day^{-1}, and $k_{\mathrm{r}} = 1.21$ day^{-1}; at 60 °C, $K = 185$ M^{-1}, $k_{\mathrm{f}} = 8.9 \times 10^3$ M^{-1} day^{-1}, and $k_{\mathrm{r}} = 48$ day^{-1}; and at 80 °C, $K = 132$ M^{-1}, $k_{\mathrm{f}} = 3.82 \times 10^4$ M^{-1} day^{-1}, and $k_{\mathrm{r}} = 289$ day^{-1}. Thus, the kinetics of the present system are considerably slower, as expected and indeed desired for a slippage system.

(20) The ABAKUS simulation was applied to **16**; however, because the final degree of threading is unknown, the assumption that $K = 27.7$ M^{-1} was required, making this treatment no better than the simple analysis given in the text. The ABAKUS treatment could not be confidently used for **13**−**15** for two reasons: (1) again *K* is not known, and (2) the number and type of binding sites between BPA units vary. The latter problem is significant because ABAKUS was designed for a system with only a single guest site between blocking groups and assumes that a cyclic must hop to the next inward site before another ring can thread; with the copolymers **13**−**15** this is not required.

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