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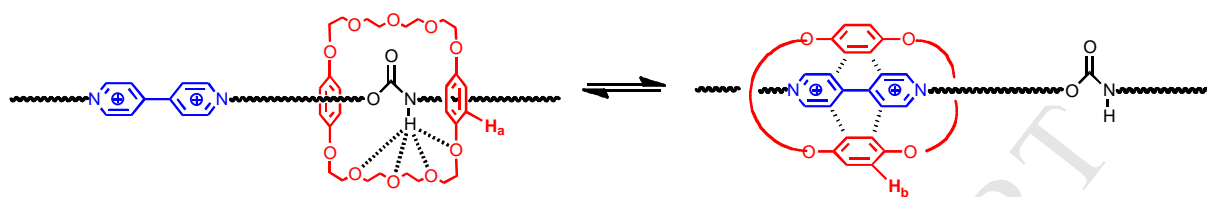
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GRAPHICAL ABSTRACT



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Polymeric Molecular Shuttles: Polypseudorotaxanes & Polyrotaxanes Based On Viologen (Paraquat) Urethane Backbones & Bis(*p*-Phenylene)-34-Crown-10

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ABSTRACT

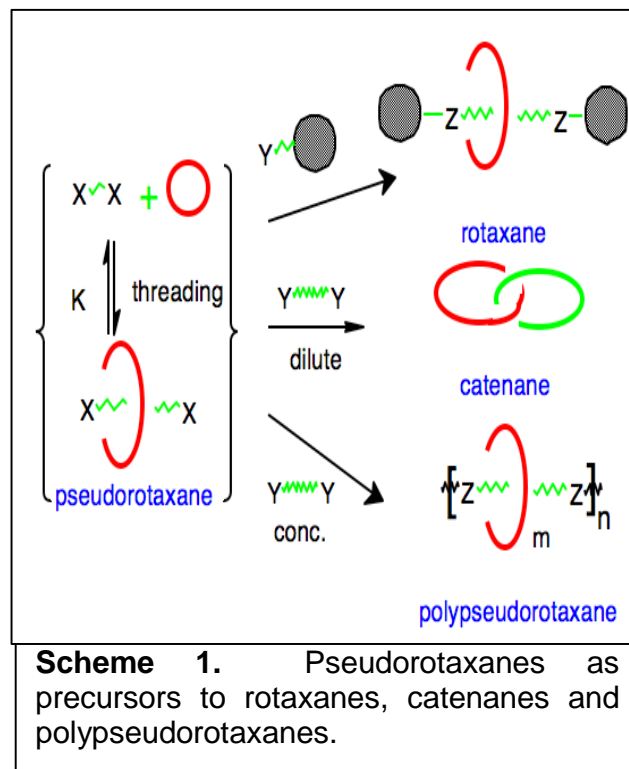
Reaction of di(*p*-isocyanophenyl)methane (MDI, **4**) with N,N'-di(2-hydroxyethyl)- (**1b**) or N,N'-di[2-(2'-hydroxyethoxy)ethyl]- 4,4'-bipyridinium di(hexafluorophosphate) (**1e**) and other diols [oligo(ethylene glycol)s and poly(tetramethylene oxide)s] in the presence of bis(*p*-phenylene)-34-crown-10 (**2**) afforded polyurethane (pseudo)rotaxanes as statistical (**7P** or **7R**) and segmented analogs **10P** (**P** = pseudorotaxane, **R** = rotaxane). In **7R** a bulky alcohol was incorporated at the chain ends and in **13R** a bulky diol as in-chain units to form polyrotaxanes and preclude the possibility of dethreading. The crown ether **2** in **10P** and **13R** was shown by ¹H NMR spectroscopy to be shuttling between the viologen (paraquat) and urethane sites; in DMSO the crown ether prefers the urethane site, probably because of H-bonding with the N-H moieties and complexation of the pyridinium site by the dipolar solvent, while in acetone at low temperatures the viologen site is preferred by the crown ether, with $\Delta H = -6.91$ kcal/mol and $\Delta S = -22.9$ eu for **13R**.

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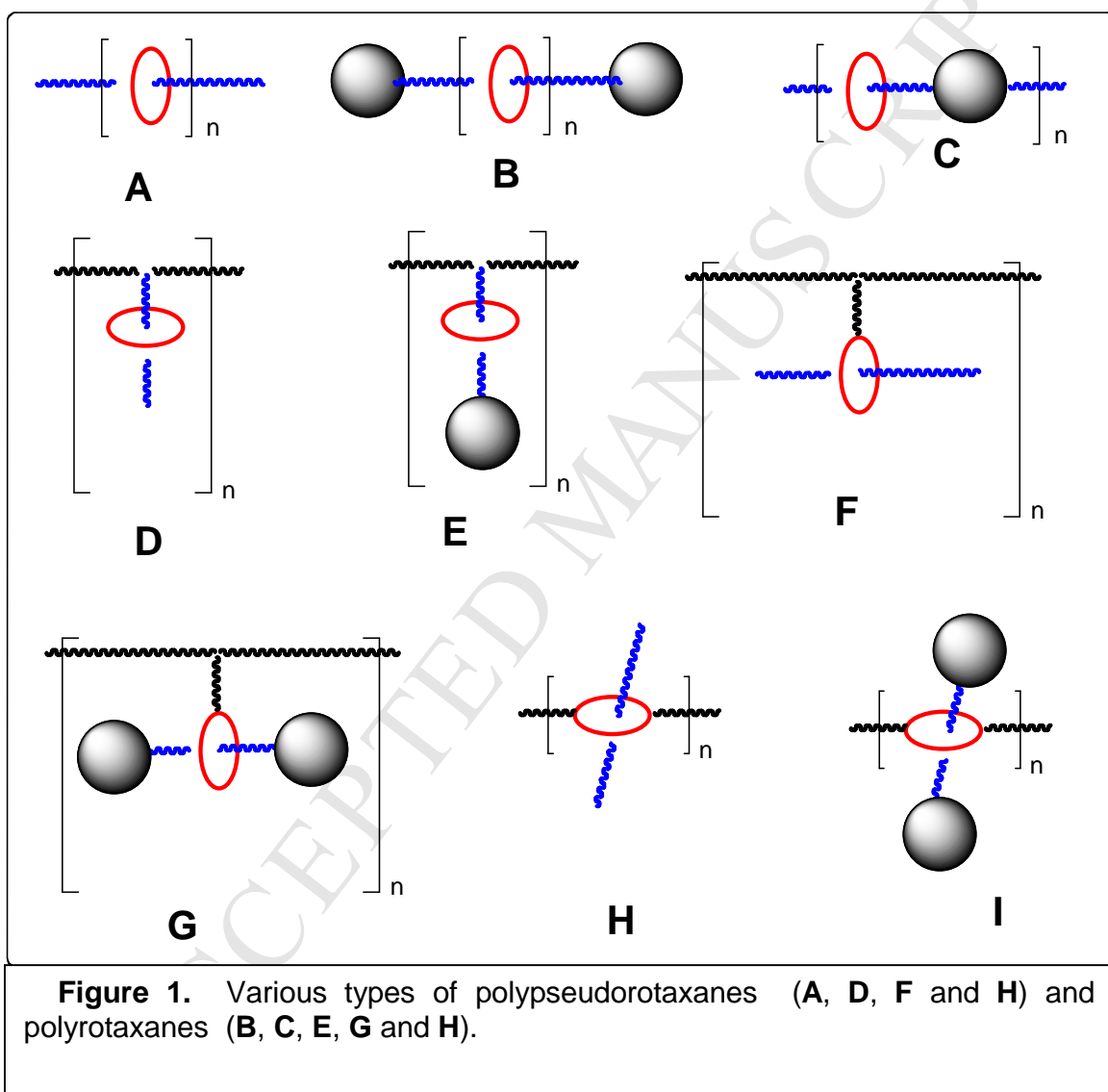
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INTRODUCTION



Pseudorotaxanes, rotaxanes and catenanes (**Scheme 1**) are now part of the lexicon of small molecule chemistry. [1] Pseudorotaxanes consist of cyclic species through which are threaded linear molecules, whereas rotaxanes have bulky groups at the end of the linear species, thus preventing dethreading. And catenanes are interlocked cyclic species. Similarly, a poly(pseudo)rotaxane is a molecular composite comprised of a macromolecule in which macrocycles are threaded by linear segments with no covalent bonds between the two species. [2] Similarly polycatenanes contain catenane units either in the backbone or pendant groups. [10] The mechanical linkages in these compounds lead to novel behavior and opportunities for creative applications. Several types of polyrotaxanes are depicted in **Figure 1**; polypseudorotaxanes do not possess bulky groups to prevent potential diffusional loss of macrocycles, while true polyrotaxanes do possess such “stoppers.” In practice, however, polypseudorotaxanes are relatively stable; in one instance of a statistically formed system of Type A, the half-life was determined to be on the order of one year at 65 °C in solution. [3] All of the architectures represented in **Figure 1** have now been realized in practice. The formation of a

main chain polypseudorotaxane of Type A, one of the focuses of this paper, via *in situ* formation of a low molar mass pseudorotaxane is represented in cartoon form in **Scheme 1**. The macrocycle content, defined as macrocycles per repeat unit (m/n), in the polyrotaxane derived from the pseudorotaxane formed *in situ* depends on the driving force for the threading and the stoichiometry.



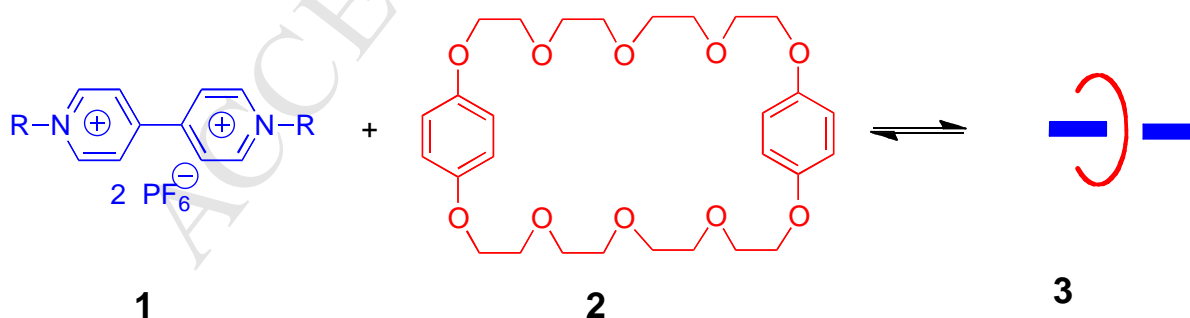
Generally there are two synthetic approaches to achieve the threading that leads to a monomeric pseudorotaxane: statistical and template or host-guest methods. In the statistical threading approach there is negligible enthalpic driving force and entropy plays a major role; the threading efficiency is affected by several variables such as ring size and ring rigidity, chain

length and chain rigidity, ring-chain compatibility, etc., [1] but the equilibrium constant K is small.

On the other hand, the negative enthalpy change for non-covalent bonding (hydrogen bonding, coordination, complexation, electron transfer, etc.) is adopted as a driving force in the host-guest approach. A nearly quantitative threading efficiency can be obtained at high concentrations by this approach if K is sufficiently high. The host-guest or self-assembly approaches can be further classified into two categories. First, a species such as a metal ion may be added into the system to serve as a template; the coordination among the metal ion and both cyclic and linear species is the driving force for the formation of an interlocking system, the pseudorotaxane of **Scheme 1**. [1c,1e,4] Second, direct host-guest complexation between cyclic and linear species may be used as a driving force. In other words, the cyclic and linear species serve as templates for each other via molecular recognition. [1]

For example, with the enthalpic attraction provided by hydrogen bonding interactions of host macrocycles with the diols, we achieved syntheses of Types A, B and C, namely poly(ester-rotaxane)s [3,5] and polyurethane rotaxanes. [6] Other main chain polyrotaxanes of Type B include polyacrylonitrile-based systems through hydrogen bonding of aliphatic crown ethers with the monomer or polymer. [7]

From the point of view of molecular recognition-based templation, an important discovery was made in 1987 when Stoddart and coworkers reported the synthesis and X-ray structure of a threaded host-guest or pseudorotaxane complex **3a** of N,N' -dimethyl-4,4'-bipyridinium (**1a**, “methyl viologen” or “paraquat”) and the aromatic crown ether bis(*p*-phenylene)-34-crown-10 (**2**)(**Scheme 2**). [8] This motif has been widely used in the



a. $R = \text{CH}_3$, b. $R = \text{CH}_2\text{CH}_2\text{OH}$, c. $R = \text{CH}_2\text{COOH}$, d. $R = \text{CH}_2\text{COOCH}_3$, e. $R = (\text{CH}_2\text{CH}_2\text{O})_2\text{H}$

Scheme 2. Pseudorotaxane (**3**) formation from paraquats (**1**) and bis(*p*-phenylene)-34-crown-10 (**2**).

intervening decades to self-assemble pseudorotaxane, rotaxane and catenane structures of increasing size and complexity. [1d,1e,1m,1n1u,2b,2c-2h,2j,2n,2r,2u] Based on this motif we reported paraquats with functional groups suitable for incorporation into polymers, namely **1b-1d**. [9] Our previously reported work with polyurethane-based polyrotaxanes utilized only the hydrogen bonding of the urethane linkages with either aliphatic crown ethers [6a-6g] or a lactam [6h] as the driving forces. Here we report for the first time in our laboratories the synthesis of thermoplastic, elastomeric polyrotaxanes containing viologen units in the backbone via adaptation of host-guest complexation of these 4,4'-bipyridinium derivatives with an aromatic crown ether, thus invoking charge transfer and π -stacking interactions in addition to hydrogen bonding and enabling a shuttling of the crown ether between the two distinct sites on the backbone. To our knowledge there are no prior literature reports of such polyurethane rotaxanes based on aromatic crown ethers.

RESULTS AND DISCUSSION

I. Self-Assembly of Pseudorotaxane Monomers

The pseudorotaxane complex **3b** derived from paraquat diol **1b** and BPP34C10 was used as one of the monomers leading to the ionic polyrotaxanes described here. The unique topology of **3**, i.e., the difunctional linear monomer threaded through the ring with its functional groups available from each side of the ring as shown by its crystal structure, [9] makes polyrotaxane formation feasible. Because the threading is essentially quantitative under the high concentrations used in step growth polymerization reactions, the amount of macrocycle incorporated into a polymer can be controlled simply by stoichiometric variation of the monomer feed ratio. Thus, the microstructure of the polyrotaxane may be tailored by designed synthesis. For example, it is possible to make random and block copolymers.

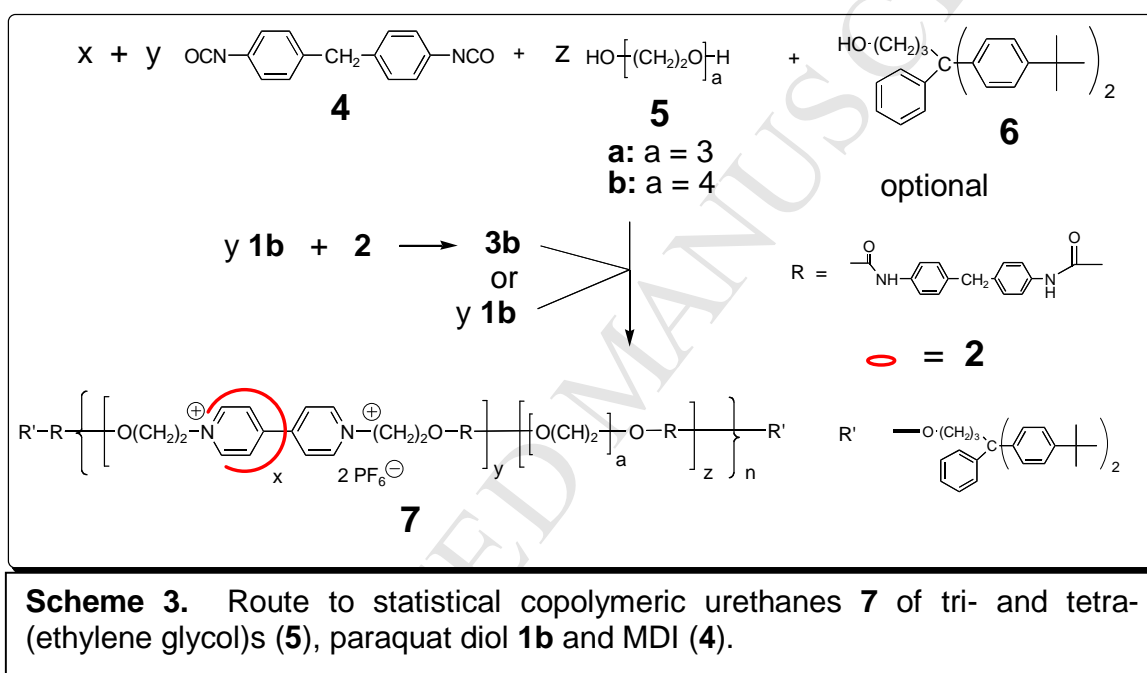
In the schemes that follow we use the designation x/y to indicate the fractions of paraquat or viologen units that are occupied by the crown ether and y/z to indicate the ratio of paraquat based urethane units to urethane units derived from the other diol.

II. Syntheses of Model Polymers and Poly(pseudo)rotaxanes According to the Generic Approach of Scheme 1.

A. Copolymeric Urethanes of Tri- and Tetra-(ethylene glycol)s and Paraquat Diol **1b**.

Our early work focused on the use of tri- and tetra-(ethylene glycol)s to prepare statistical copolymeric urethanes from paraquat diol **1b**. In the first approach, shown in **Scheme 3**, all of

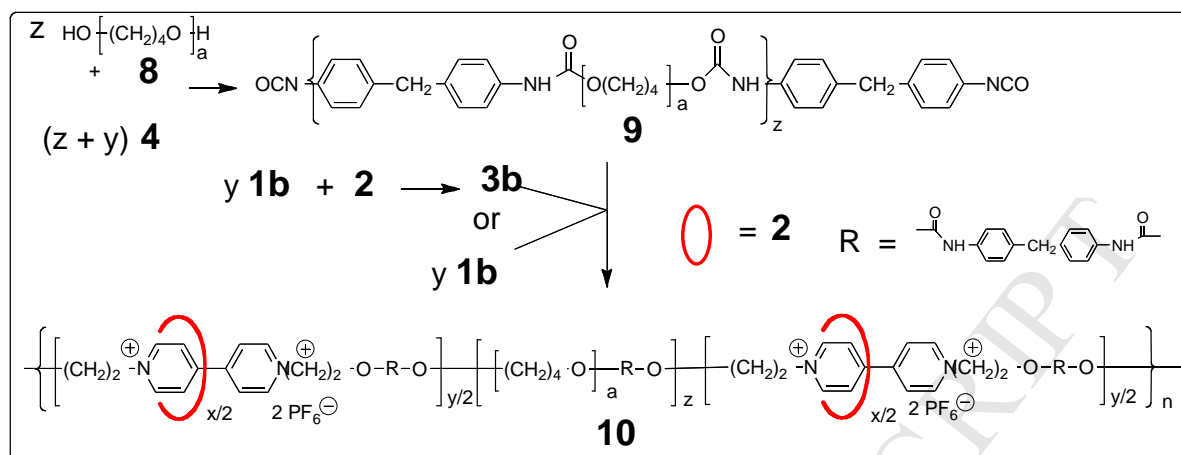
the reactants, the paraquat diol **1b**, 4,4'-diphenylmethane diisocyanate (MDI, **4**), the glycol **5**, and in the case of the (pseudo)rotaxanes, bis(*p*-phenylene)-34-crown-10 (**2**), were mixed simultaneously and polymerization was allowed to proceed in acetonitrile or acetonitrile-diglyme. Pseudorotaxane **3b** was formed *in situ* when both **1b** and **2** were present. The monofunctional blocking group alcohol **6** [10] was included in the original mixtures in some cases and added near the end of the polymerization in other cases to form structures of Type B (**Figure 1**). This approach produces a statistical copolymer of the two types of urethane repeat units, the oligo(ethylene glycol) as the soft units and the paraquat units as harder components..



Experimental conditions and results are summarized in **Table 1**.

B. Segmented Copolymeric Urethanes of Poly(tetramethylene oxide)s and Paraquat Diols **1b** and **1e**.

Moving on to a system more typical of commercial polyurethanes, the standard two-step synthetic method leading to segmented polyurethane elastomers was used (**Scheme 4**). In the first step, a prepolymer was prepared *in situ* from oligomeric poly(tetramethylene oxide) (PTMO, **8**) and MDI (**4**). Three different molecular weight PTMOs [MW = 650 (**8**, a = 8.76), 1000 (**8**, a = 13.6), 2000 (**8**, a = 27.5)] were used as soft segments in order to observe variation of properties with the segmental length. The hard segments of the polyrotaxanes and the model polymers



Scheme 4. Route to segmented copolymeric urethanes **10** from MDI (**4**), PTMOs (**8**) and paraquat diol **1b**. In polypseudorotaxane **10P** crown ether **2** was the cyclic component. The model polymers **10M** contained no cyclic species.

consisted of MDI-rotaxane and MDI-paraquat linkages, respectively. The prepolymer was terminated with isocyanate groups by using an excess of MDI (molar ratio MDI (**4**)/PTMO (**5**) = $z+y/y \geq 2$). The second step was chain extension, by use of the pseudorotaxane **3b** prepared *in-situ* or **1b** itself to link prepolymer segments, resulting in high molecular weight polymers, either polypseudorotaxanes or the corresponding model polymers, respectively. To ensure quantitative threading, a slight excess of BPP34C10 (**2**) was used (**Table 2**). The polymerizations were carried out in mixtures of acetonitrile and diglyme. Because of differences in solubility of PTMOs, the volume ratio of acetonitrile to diglyme was different for each case: 2.5 for PTMO-650 systems, 1.3 for PTMO-1000 system and 0.8 for PTMO-2000 system. No blocking groups or stoppers were used in these systems, so all the products were of Type A (**Figure 1**).

proton NMR after purification. The fact that x/y values in the polyrotaxanes are close to unity indicates that threading efficiencies are nearly quantitative.

Table 1

Statistical Polyurethane Copolymers & Rotaxanes 7 Made According To Scheme 3

Polymer	Molar Feed Ratios					Polymer Composition		
	1b	2	4	5 (a or b)	6	x/y ^a	y/z ^a	DP _n ^a
7M1	0.420	0	1.00	a: 0.570	0	0	0.74	---
7R1	0.432	0.532	1.00	a: 0.558	0.0198 ^c	1.0	0.80	412
7M2	0.639	0	1.00	b: 0.351	0	0	1.8	---
7R2	0.443	0.398	1.00	a: 0.547	0.0099 ^c	0.83	0.79	128
7M3	0.910	0	1.00	b: 0.0799	0.058 ^b	0	9.1	87.5
7R3	0.905	1.36	1.00	b: 0.0852	0.058 ^b	0.80	10	67.5

^a By ¹H NMR spectroscopy. ^b Added after 2 days. ^c Added at the beginning.

Table 2

Segmented Polyurethane Copolymers & Pseudorotaxanes 10 Made According To Scheme 4

Polymer	Molar Feed Ratios					Polymer Composition			
	1b	2	4	a of 8	8	x/y ^a	y/z ^a	[η] ^b (dL/g)	M _w ^c (kDa)
10M1	0.494	0	1.00	8.76	0.506	0	0.98	0.258	105
10P1	0.498	0.576	1.00	8.76	0.502	0.98	0.99	0.230	153
10M2	0.449	0	1.00	13.6	0.551	0	0.82	0.351	143
10P2	0.405	0.489	1.00	13.6	0.595	0.98	0.68	0.433	250
10M3	0.620	0	1.00	27.5	0.380	0	1.6	0.408	---
10P3	0.631	0.757	1.00	27.5	0.369	0.81	1.7	0.400	500
10M4	0.500	0	1.00	27.5	0.500	0	1.0	0.408	286
10P4	0.500	0.618	1.00	27.5	0.500	1.0	1.0	0.400	333
10P5 ^d	0.500	---	1.00	27.5	0.500	0.45	1.0	---	---

^a By ¹H NMR spectroscopy. ^b In 60 mM LiBr/N-methylpyrrolidinone, 31 °C. ^c By LALLS 60 mM LiBr/N-methylpyrrolidinone. ^d Prepared by mixing **10M4** with 10 equivalents of **2** in 3:1 acetone:dichloromethane for 7 days at 23 °C.

III. Polyrotaxane Synthesis by Self Assembly from Preformed Linear Polymer and Macrocycle

An alternate approach to main chain polyrotaxane synthesis is the equilibration of preformed linear macromolecules and preformed macrocycles. [1,6f] The attractive feature of this methodology is its enablement of property modification of preformed linear polymers. The enthalpic driving force for threading provided by complexation of 4,4'-bipyridinium units and BPP34C10 (**2**) made the present systems ideal test cases for this methodology. Threading of preformed polyethers and polyesters containing electron rich aromatic rings by cyclobis(paraquat-*p*-phenylene), a cyclic species containing two paraquat moieties, has been reported. [11]

Thus model ionomeric polyurethane **10M4**, $a=27.5$, $x = 0$, a nearly colorless material, was equilibrated in acetone:dichloromethane (3:1, v:v) for five days with ten equivalents (based on bipyridinium units) of BPP34C10 (**2**). During the equilibration the solution became red

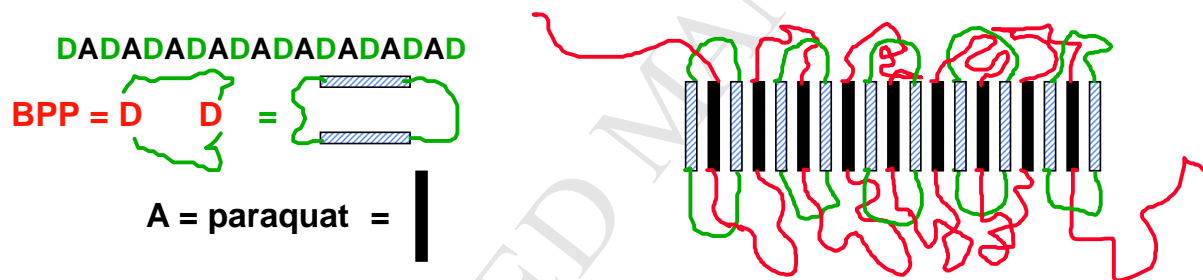


Figure 2. Proposed donor-acceptor alternating stacks formed by chain folding during solution threading of preformed polyurethane **10M4** by crown ether **2**, forming **10P5**.

orange. After purification **10P5**, $a=27.5$, $x/y = 0.45$ was isolated as a red-orange elastomer.

Thus, nearly one half of the bipyridinium sites along the backbone became occupied during the equilibration. This is very interesting in light of results for low molar mass rotaxanes of this type. Previously we [12] and Stoddart and coworkers [13] have reported that low molar mass rotaxanes can be prepared in this way beginning with linear paraquat-containing molecules with end blocking groups smaller than the cavity of BPP34C10. The incomplete occupation of the paraquat sites is attributed to chain folding of the polymer backbone to form DADADA stacks (**Figure 2**), in which the donors are the two hydroquinone units of the BPP34C10 and the acceptors are the paraquat units; since there are two donors per macrocycle, a 1:2 macrocycle:paraquat ratio would represent 100% equivalency of donor and acceptor sites. The

solid state DADA packing motifs of several rotaxanes and catenanes reported by Stoddart et al. [14] support this concept.

IV. Physical Properties

Films of the model polymers ($x=0$) cast from acetone were transparent and light yellow in contrast to the scarlet color of the poly(pseudo)rotaxane ($x>0$) films. Both poly(pseudo)rotaxanes and model polymers displayed room temperature elastomeric behavior. [15]

In acetone, we observed that the reduced viscosity values of all polymer solutions increased drastically at high dilutions, due to the polyelectrolyte effect. However, this effect was suppressed by using 0.06 M LiBr in N-methylpyrrolidone (NMP) as the solvent; linear dependences of reduced viscosity versus concentration were obtained, affording intrinsic viscosity values (**Table 2**); the intrinsic viscosity of polyrotaxane **13R**, $x/y=0.82$ was 0.382 dL/g at 30 °C. Molecular weights of some representative polymers were measured by static light scattering in 60 mM LiBr/NMP (**Table 2**). The molecular weights of polymers **10** generally increase with increasing molecular weight of the PTMO used, nearly linearly in fact for the model systems. Molecular weights of the polypseudorotaxanes **10P** are higher than the corresponding model polymers **10M** partly due to the contribution of BPP34C10, raising the molecular weights of the polyrotaxanes relative to the corresponding model polymers with same number of repeat units. It was expected that BPP34C10 would tend to "stay" on the hard segments due to the strong charge transfer and electrostatic interactions between BPP34C10 and the paraquat dication. Thus, the macrocycles in the hard segment domain were expected to cause physical property differences between polyrotaxanes and the model polymers in the solid state. These structure-property relationships have been reported separately for polymers **10**. [15] Films of **10P1** cast from THF and dried at 90 °C displayed markedly higher tensile moduli and strains at break than the model polymer **10M1**; these results clearly indicate that the threaded crown ether affects the properties. However, on the basis of the observed shuttling in these systems (see below) we anticipate that the locus of the crown ethers and hence physical properties may depend on processing conditions.

V. NMR Spectroscopy: Dynamic Behavior, Shuttling of BPP34C10 Rings

Figure 3 contains spectra for a model prepolymer oligomer made by quenching **9** with methanol, model polyurethane **10M4**, $a = 27.5$, $x = 0$, $y/z = 1.00$ and polypseudorotaxane **10P4**, $a = 27.5$, $x/y/z = 1.00/1.00/1.00$, all taken in acetone- d_6 ; it is interesting to compare the chemical

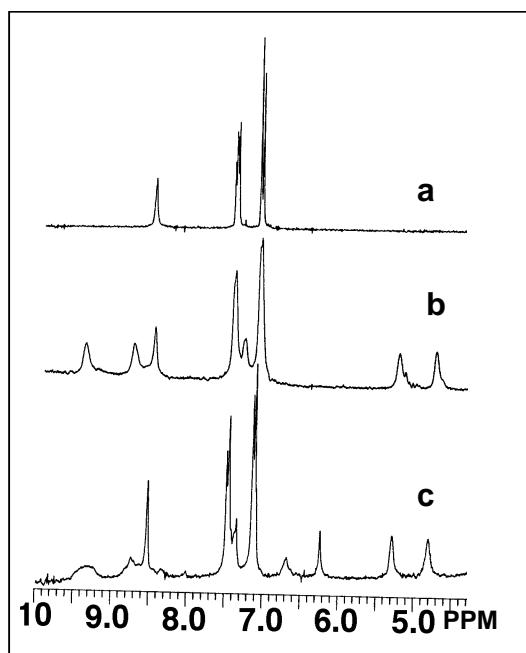


Figure 3. ^1H NMR spectra (270 MHz, acetone- d_6) of **a)** model oligomer from **9**, $a=27.5$ by quenching with methanol, **b)** model polyurethane **10M4** and **c)** polypseudorotaxane **10P4**.

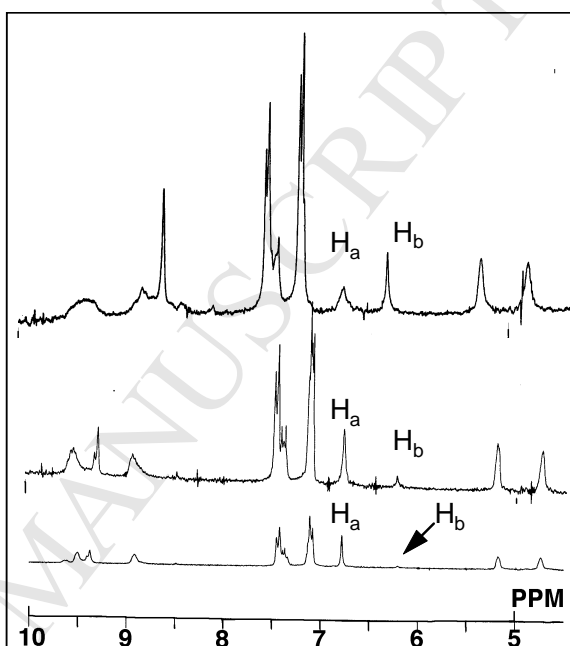


Figure 4. ^1H NMR spectra (270 MHz, acetone- d_6) of **a)** polypseudorotaxane **10P4**, **b)** with one drop of DMSO- d_6 and **c)** with several drops of DMSO- d_6 .

shift differences for the α -protons of the bipyridinium units in the model polymer and the polypseudorotaxane, which shifted upfield from 9.5 (**Figure 3b**) to 9.35 (**Figure 3c**) and broadened. In the polypseudorotaxane, the aromatic protons of BPP34C10 gave rise to two signals, at 6.70 ppm and 6.25 (**Figure 3c**). These and other chemical shift changes, which are generally consistent with the results of Stoddart et al. [8b,13,14] and our own [16], revealed the formation of the polymeric host-guest complex.

The effect of solvent was examined by addition of DMSO- d_6 to an acetone solution of **10P4**, $a = 27.5$, $x/y/z = 1.00/1.00/1.00$ (**Figure 4**). One drop of DMSO initially caused a decrease in the signal H_b at 6.25 ppm and an increase in signal H_a at 6.70 ppm and addition of several drops caused total loss of H_b . Likewise, the broad bipyridinium signal at 9.4 ppm shifted

and split into three distinct signals. As expected,[13a] DMSO disrupted the interaction between the crown ether and paraquat units. Similar changes were observed for polyrotaxane **13R**, $x/y=0.82$ (**Figure 5**); in DMSO H_a dominated H_b , whereas in acetone the two signals were of almost equal intensity.

We then examined the effects of temperature using the signals for H_a and H_b to monitor the changes in structure of both **13R**, $x/y=0.82$ (**Figure 6**) and **10P4**, $a=27.5$, $x/y/z = 1.00/1.00/1.00$ (**Figure 7**). The polypseudorotaxane and the polyrotaxane behave similarly; at -50 to -60 °C there is no signal for H_a , only H_b .

The solvent and temperature effects are interpreted in terms of shuttling of the crown ether between two binding sites-one the bipyridinium units and the other the urethane moieties (**Figure 8**). The upfield signal for H_b is assigned to the aromatic protons of the crown ether bound at the bipyridinium site, based on the shielding effect resulting from π -stacking with the bipyridinium units, and H_a is assigned to the urethane site, with which the crown ether interacts via hydrogen bonds. [6b] It is noted that the H_a signal of **10P4** is time averaged; this indicates that the crown ether is exchanging between threaded and unthreaded (free) states; in other words,

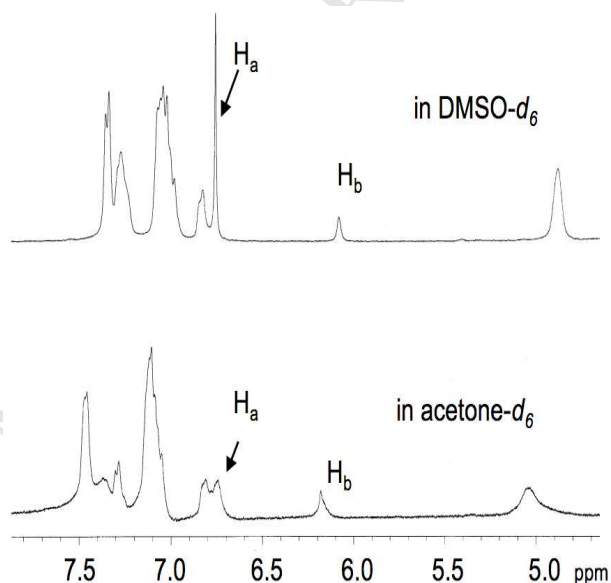


Figure 5. Partial ^1H NMR spectra (400 MHz, 22 °C) of poly(urethane rotaxane) **13R** in a) DMSO- d_6 and b) acetone- d_6 .

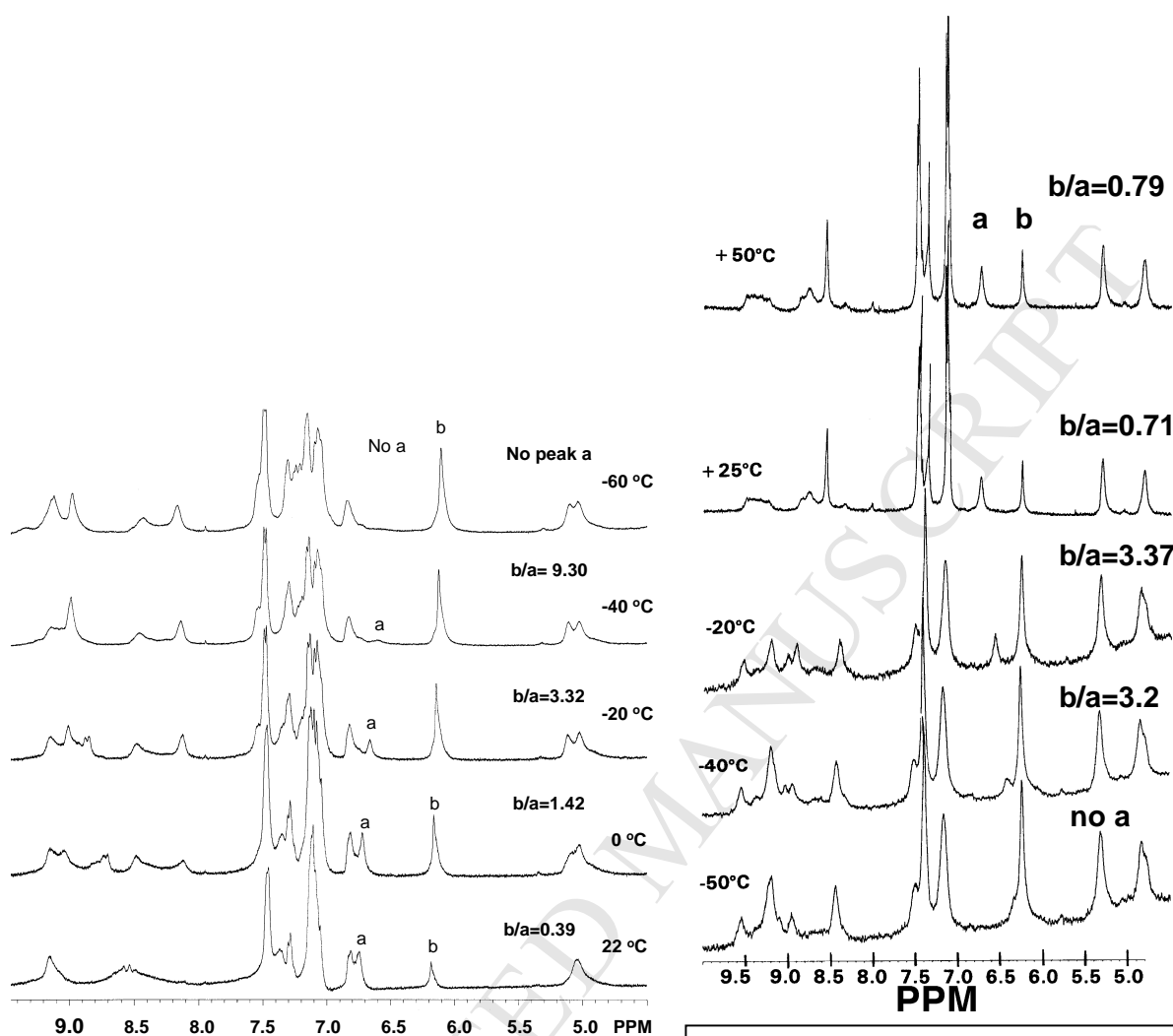


Figure 6. Partial ^1H NMR spectra (400 MHz, acetone- d_6) of poly(urethane rotaxane) **13R** at different temperatures.

Figure 7. Temperature dependence of ^1H NMR spectra (CDCl_3) of polypseudorotaxane **10P4**.

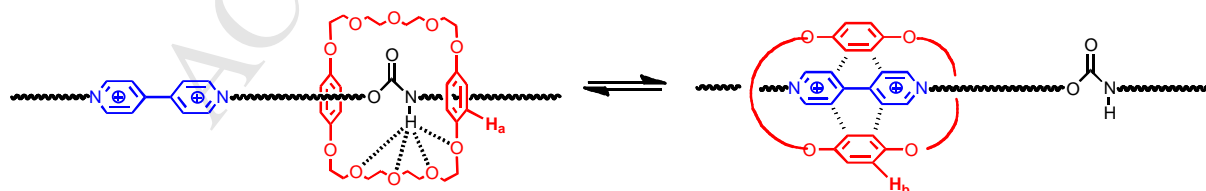
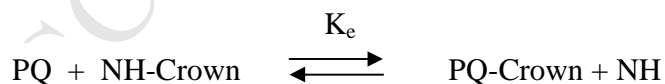


Figure 8. Shuttling equilibrium of crown ether **2** in poly[urethane (pseudo)rotaxane]s between urethane moieties (left) and paraquat units (right).

some of the crown ether molecules are escaping into solution and exchanging with those on the paraquat ends of the polyurethane; a similar situation was observed in “inverse” poly(urethane pseudorotaxane)s in which cyclobis(paraquat) was the cyclic component. [17] This and the resulting partial overlap of signals renders the values for polypseudorotaxane **10P4** less reliable and their interpretation more difficult. Although the mole fraction of paraquat repeat units in the two polymers was the same, 50%, in **13R** the bulky blocking groups at the ends of the paraquat-containing segments prevented loss of the threaded crown ether to solution, while in **10P4** some the paraquat-containing moieties were located at the chain ends and there was no bulky stopper to prevent exchange of the threaded crown ether with free crown ether in solution. That is, motion of the crown ether along the backbone in **13R** was limited to the segments between stoppers, in effect forming a molecular abacus.

In **13R** on average there were 2.5 paraquat units and 1.5 PTMO units between the bulky blocking groups. In total then this amounts to 2.5 paraquat units and 8 urethane moieties. The equilibrium process is as follows:



and the approximate average equilibrium constant is therefore:

$$K_e = [\text{PQ-Crown}] [\text{NH}] / [\text{NH-Crown}][\text{PQ}] = (8/2.5) (b/a) = 3.2 (b/a)$$

Thus, using the results from polymer **13R** K_e values were calculated and a van't Hoff plot allowed estimates of the ΔH and ΔS values for the equilibrium of **Figure 8** as noted in **Figure 9**. These thermodynamic quantities represent the difference in binding enthalpies and binding entropies between the two sites, the paraquat site and the urethane site.

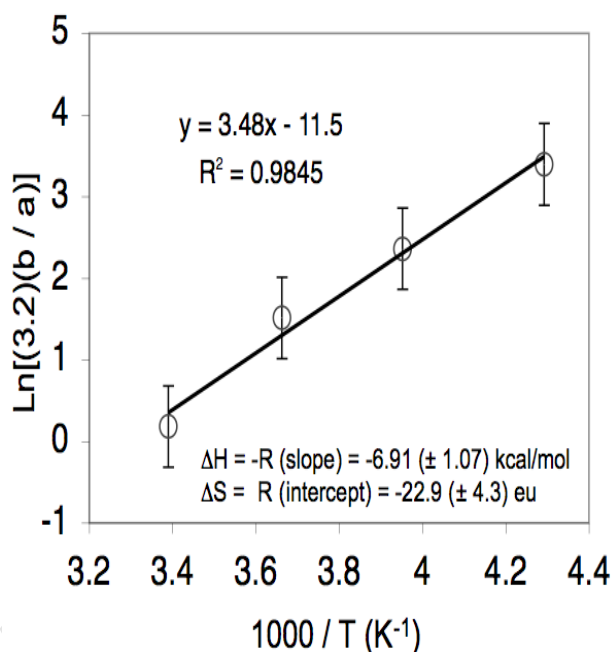


Figure 9. Van't Hoff plot for shuttling of poly(urethane rotaxane) **13R** in acetone- d_6 . The error bars represent ± 20 % variation in the b/a ratios.

CONCLUSIONS

We have successfully synthesized a series of poly[urethane (pseudo)rotaxane]s via host-guest complexation of paraquat diols and BPP34C10 and reaction of the *in situ* generated pseudorotaxane with other diols and a diisocyanate. The threading efficiency is nearly quantitative with this complexation as a driving force. Extensions of this methodology will allow precise stoichiometric control of the macrocycle content of a variety of polyrotaxane architectures.

Molecular shuttles form the basis of many types of proposed molecular switches and machines,[18] sensors [19] and nanoelectronic devices. [20] And polyurethanes continue to be commercially important in a number of fields. [21] The methods described here enable synthesis of polyurethane rotaxanes that could be tailored for these applications.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Chemicals and Instruments: N,N'-Bis(2-hydroxyethyl)-4,4'-bipyridinium hexafluorophosphate was prepared by the Menshutkin reaction of 4,4'-dipyridyl with 2-iodoethanol and then anion exchange with NH₄PF₆ in water. [9] 4,4-Bis(*p*-t-butylphenyl)-4-phenylbutanol (**6**) was prepared as previously reported. [10] MDI (**4**) was purchased from Eastman Kodak Co. and purified by two vacuum distillations. PTMOs (**8**) were purchased from Polyscience Inc. or Aldrich and used without purification. Bis(*p*-t-butylphenyl)bis[*p*-2-(2'-hydroxyethoxy)ethoxyphenyl]methane (**12**) was prepared by the reported method. [5c] The FT-NMR (proton) spectra were recorded on Bruker WP270 MHz or Varian Unity 400 Mhz instruments using tetramethylsilane as the internal standard. The instruments used for measuring molecular weights were a Chromatrix KMX-6 LALLS and a Chromatrix KMX-16 differential refractometer. The viscosity measurements were carried out at 30 or 31 (±0.3) °C with a Canon-Ubbelohde micro dilution solution capillary viscometer with a diameter of 100 centipoise using 60 mM LiBr in N-methylpyrrolidinone as solvent.

N,N'-Bis[2-hydroxyethoxy(ethoxy)]-4,4'-bipyridinium Di(hexafluorophosphate (1e): To a

solution of 2-(hydroxyethoxy)ethyl chloride (30.0 g, 241 mmol) in acetone (300 mL) was added NaI (38.0 g, 254 mmol). The solution was refluxed for 10 h and stirred for 24 h at room temperature. The salt was removed by filtration and the solvent by evaporation to give 40 g (77 %) of liquid. Proton NMR showed that the product contained 25 % unreacted chloride, but since the impurity does not affect the next reaction, no further purification was done. ^1H NMR in CDCl_3 : δ 2.19 (s, 1H); 3.29 (t, $J = 7$, 2H); 3.62 (t, $J = 7$, 2H); 3.75-3.78 (m, 4H). 4,4'-Dipyridine (5.00 g, 32.0 mmol) and the iodide (28.0 g, 129 mmol) were dissolved in CH_3CN (150 mL) and the solution was refluxed for two days. The red precipitate was filtered and redissolved in water (100 ml). Ammonium hexafluorophosphate (30 g, 184 mmol) was added to the aqueous solution to precipitate the PF_6^- salt. The crude product was recrystallized from water to give colorless crystals, 15.3 g (81%), mp: 154.2-155.7 °C, lit. mp 240 (dec), [22] 167 °C (dec). [23] ^1H NMR in $\text{DMSO}-d_6$: δ 2.1 (s, 2H); 3.27 (m, 8H); 3.98 (t, $J = 5$, 4H); 4.88 (t, $J = 5$, 4H); 6.78 (d, $J = 7$, 4H); 9.32 (d, $J = 7$, 4H). ^{13}C NMR in $\text{DMSO}-d_6$: 60.48; 61.05; 68.98; 72.63; 126.72; 146.65; 149.35 (7 peaks as required).

Bis(*p*-phenylene)-34-crown-10 (2): A solution of hydroquinone (11.1 g, 100 mmol), NaOH (9.10 g, 228 mmol), water (10 mL) and *n*-butanol (450 mL) was stirred at reflux for 30 min under N_2 . Tetra(ethylene glycol) ditosylate (50.2 g, 100 mmol) and Cs_2CO_3 (32.6 g, 100 mmol) in 500 mL of a 3:2 (v:v) mixture of 1,4-dioxane:*n*-butanol were added. The mixture was refluxed with stirring for 20 h. The cooled mixture was filtered and the filtrate was evaporated to afford a dark solid, which was dissolved in CH_2Cl_2 (100 mL) and passed through a short silica gel column with ethyl acetate. The eluent solution was evaporated to dryness and subjected to column chromatography on alumina using diethyl ether as eluent; a colored oil eluted first and then the desired product, which was recrystallized from 3:2 (v:v) toluene:*n*-hexane as clear, colorless crystals that were dried overnight *in vacuo*, 3.35 g (12.5%, lit. yield 8% [24] by a similar one-step process), mp 95.0-96.8 °C (lit. mp 93.5-94.0 °C [24], 87-88 °C [25]).

Typical Procedure for Preparation of Statistical Copolymeric Urethanes 7 According to Scheme 3: A solution of 292.7 mg (1.949 mmol) of tri(ethylene glycol) (**5a**), 809.9 mg (1.51 mmol) of paraquat diol **1b**, 1.00 g (1.86 mmol) of BPP34C10 (**2**) and 29.16 mg (6.92×10^{-5} mol) of 4,4-bis(*p*-*t*-butylphenyl)-4-phenylbutanol (**6**) in 5 mL of acetonitrile in a dry 15 mL 1-necked flask equipped with a condenser was stirred for 10 min. under a positive pressure of nitrogen

Then 874.3 mg (3.494 mmol) of MDI (**4**) were added and the flask was placed in an oil bath maintained at ca. 100 °C for 96 h.

Typical Procedure for Segmented Model Polyurethanes 10 Prepared According to Scheme

4: To an oven-dried 15 mL 1-necked flask, MDI (**4**, 813.70 mg, 3.2514 mmol) was added with 5 mL of dry acetonitrile and 2 mL of dry diglyme. The flask was immersed in an oil bath at 90 °C and magnetically stirred under nitrogen until the MDI had dissolved and then PTMO-650 (**8**, a=8.76, 1.0692 g, 1.6449 mmol) was added and the mixture was stirred for 1.5 h at reflux under nitrogen. Paraquat diol **1b** (861.48 mg, 1.6065 mmol) was added and the reaction solution turned yellow in 10 min. The reaction was continued for 3 days under the same conditions.

Typical Procedure for Segmented Polypseudorotaxanes 10P Prepared According to Scheme

4: To an oven-dried 15 mL 1-necked flask, MDI (827.90 mg, 3.3082 mmol) was added with 5 mL of dry acetonitrile and 1 mL of dry diglyme. The flask was immersed in an oil bath at 90 °C and magnetically stirred under nitrogen until the MDI was dissolved and then PTMO-650 (**8**, a=8.76, 1.0794 g, 1.6606 mmol) was added and the mixture was stirred for 1.5 h at reflux under nitrogen. Paraquat diol **1b** (883.52 mg, 1.6476 mmol) was added 10 min. after BPP34C10 (**2**, 1.0200 g, 1.9050 mol) was added. A deep red color developed immediately upon the addition of **1b**. The reaction was continued for 3 days under the same conditions.

Threading of Preformed Polyurethane 10M4 with Bis(*p*-phenylene)-34-crown-10 (2**) to**

Form 10P5: A solution of 1.2 g of **10M4** (0.395 mmol of paraquat units) and 2.12 g (3.95 mmol) of **2** in 30 mL of acetone and 10 mL of dichloromethane for 5 days. Most of the solvent was removed and 25 mL of hexane were added; the mixture was stirred 30 min and the colorless but cloudy solvent was decanted from the red polymer. The washing procedure was repeated 15 times with 25-40 mL of 5:95 (v:v) dichloromethane:hexanes until no more **2** could be extracted (TLC). The polymer was soaked in 40 mL of dichloromethane for 24 h, filtered and washed with dichloromethane (5 x 25 mL) and dried. The red-orange polymer weighed 1.3 g (100% based on x/y = 0.45). By integration of the aromatic signals of **2** vs. the aromatic signals of the bipyridinium units in the ¹H NMR spectrum, x/y was determined to be 0.45.

Model Segmented Copolyurethane 13M, x = 0 (Scheme 5): PTMO-1000 (**8**, a=13.6, 195 mg, 0.195 mmol) was added to a solution of MDI (**4**, 162.7 mg, 0.6501 mmol) in 1 mL of DMF. After the solution had stirred for 1.5 h at 90-100 °C, paraquat diol (**1e**, 181.5 mg, 0.3251 mmol) in 1 mL of acetonitrile was added and polymerization was allowed to proceed for 2 h. Then diol

BG **12** (83.1 mg, 0.130 mmol) was added and reaction was continued for 5 h at the same temperature.

Segmented Copolyurethane 13R, x/y=0.82 (Scheme 5): PTMO-1000 (**8**, $a=13.6$, 183 mg, 0.183 mmol) was added to a solution of MDI (**4**, 152.2 mg, 0.6082 mmol) in a mixture of diglyme (0.6 mL) and acetonitrile (1.5 mL). After the solution had stirred for 1.5 h at 90-100 °C, a solution of paraquat diol **1e** (169.8 mg, 0.3041 mmol) in 2 mL of acetonitrile, which had previously been stirred at room temperature for 0.5 h, was added and polymerization was carried out for 2 h under reflux. Then diol BG **12** (83.1 mg, 0.130 mmol) was added and reaction was continued for 20 h. $[\eta] = 0.382$ dL/g (60 mM LiBr/NMP, 30 °C)

Isolation and Purification (General Procedure): When the system had cooled to room temperature, the solution was added dropwise to 400 ml of methanol with stirring and the precipitated polymer was collected by filtration. The polymer was dissolved in 10-15 mL of acetone or acetonitrile and added dropwise to 400 mL of methanol with stirring and the precipitated polymer was filtered. The procedure was repeated three times. ¹H-NMR analysis was done on the dried polyrotaxane sample after each reprecipitation. The x/y values were constant after the second precipitation, e. g., for **10P1**: 1.04, 0.98, 0.95, 0.98; for **10P4**: 1.04, 0.99, 0.99, 1.00.

REFERENCES

1. a) Schill, G.; Zuercher, C. *Naturwissensch.* **1971**, *58*, 40–45.
- b) Schill, G. *Catenanes, Rotaxanes and Knots*, Academic Press, New York, 1971.
- c) Sauvage, J.-P. *Acc. Chem. Res.* **1990**, *23*, 319-27.
- d) Seeman, N. C.; Chen, J.; Du, S. M.; Mueller, J. E.; Zhang, Y.; Fu, T. J.; Wang, Y.; Wang, H.; Zhang, S. *New J. Chem.* **1993**, *17*, 739-55.
- e) *Molecular Catenanes, Rotaxanes and Knots*, Sauvage, J.-P., Dietrich-Buchecker, C. O., eds., Wiley-VCH, Weinheim, 1999.
- f) Mahan, E.; Gibson, H. W. in *Cyclic Polymers*, 2nd ed.; Semlyen, J. A., ed.; Kluwer Publishers, Dordrecht, 2000, pp 415–560.
- g) Leigh, D. A.; Smith, R. A. in *Cyclic Polymers*, 2nd ed., Semlyen, A. J., ed., Kluwer Publishers, Dordrecht, 2000, pp 561-600.
- h) Hubin, T. J.; Busch, D. H. *Coord. Chem. Rev.* **2000**, *200–202*, 5–52.

- i) Godt, A. *Eur. J. Org. Chem.* **2004**, 1639-1654.
- j) Menon, S. K.; Guha, T. B.; Agrawal, Y. K. *Rev. Inorg. Chem.* **2004**, *24*, 97-133.
- k) Lankshear, M. D.; Beer, P. D. *Acc. Chem. Res.* **2007**, *40*, 657-668.
- l) Gassensmith, J. J.; Baumes, J. M.; Smith, B. D. *Chem. Commun.* **2009**, 6329-6338.
- m) Stoddart, J. F. *Chem. Soc. Rev.* **2009**, *38*, 1802-1820.
- n) Amabilino, D. B.; Perez-Garcia, L. *Chem. Soc. Rev.* **2009**, *38*, 1562-1571.
- o) Niu, Z.; Gibson, H. W. *Chem. Rev.* **2009**, *109*, 6024-6046.
- p) Thibeault, D.; Morin, J.-F. *Molecules* **2010**, *15*, 3709-3730.
- q) Zhang, M.; Zhu, K.; Huang, F. *Chem. Commun.* **2010**, *46*, 8131-8141.
- r) Terao, J. *Chem. Rec.* **2011**, *11*, 269-283.
- s) Beves, J. E.; Blight, B. A.; Campbell, C. J.; Leigh, D. A.; McBurney, R. T. *Angew. Chem. Int. Ed.* **2011**, *50*, 9260-9327.
- t) Xue, M.; Yang, Y.; Chi, X.; Zhang, Z.; Huang, F. *Acc. Chem. Res.* **2012**, *45*, 1294-1308.
- u) Barin, G.; Forgan, R. S.; Stoddart, J. F. *Proc. Royal Soc. A: Math., Phys. Eng. Sci.* **2012**, *468*, 2849-2880.
2. a) Lipatov, Y. S.; Lipatova, T. E.; Kosyanchuk, L. F. *Adv. Polym. Sci.* **1989**, *88*, 49-76.
- b) Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11-21.
- c) Gibson, H. W. in *Large Ring Molecules*, Semlyen, J. A., ed., John Wiley & Sons, New York, 1996, pp 191-262.
- d) Ambalino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725-2828.
- e) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843-945.
- f) Gong, C.; Gibson, H. W. in *Molecular Catenanes, Rotaxanes and Knots*, Sauvage, J.-P.; Dietrich-Buchecker, C. O., eds., Wiley-VCH, Weinheim, 1999, pp 277-321.
- g) Raymo, F. M.; Stoddart, J. F. *Supramol. Polym.* **2000**, 323-357.
- h) Panova, I. G.; Topchieva, I. N. *Russ. Chem. Rev.* **2001**, *70*, 23-44.
- i) Takata, T.; Kihara, N.; Furusho, Y. *Adv. Polym. Sci.* **2004**, *171*, 1-75.
- j) Huang, F.; Gibson, H. W. *Prog. Polym. Sci.* **2005**, *30*, 982-1018.

- k) Wenz, G.; Han, B.-H.; Mueller, A. *Chem. Rev.* **2006**, *106*, 782-817.
- l) Yui, N.; Katoono, R.; Yamashita, A. *Adv. Polym. Sci.* **2009**, *222*, 55-77.
- m) Harada, A.; Hashidzume, A.; Yamaguchi, H.; Takashima, Y. *Chem. Rev.* **2009**, *109*, 5974-6023.
- n) Fang, L.; Olson, M. A.; Benitez, D.; Tkatchouk, E.; Goddard, W. A., III; Stoddart, J. F. *Chem. Soc. Rev.* **2010**, *39*, 17-29.
- o) Mayumi, K.; Ito, K. *Polymer* **2010**, *51*, 959-967.
- p) Yuen, F.; Tam, K. C. *Soft Matter* **2010**, *6*, 4613-4630.
- q) Li, J. J.; Zhao, F.; Li, J. *Appl. Microbiol. Biotechnol.* **2011**, *90*, 427-443.
- r) Price, T. L., Jr.; Gibson, H. W. in *Supramolecular Polymers-Bridging Worlds*, Harada, A., ed.; Wiley-VCH, 2012, ch. 7, pp. 151-182.
- s) Kato, K.; Ito, K. *Supramol. Polym. Chem.* **2012**, 205-229.
- t) Takata, T.; Arai, T.; Kohsaka, Y.; Shioya, M.; Koyama, Y. *Supramol. Polym. Chem.* **2012**, 331-346.
- u) Murugan, A.; Gibson, H. W. *Prog. Polym. Sci.* **2014**, *38*, in press.
3. Gibson, H. W.; Liu, S.; Gong, C.; Joseph, E. *Macromolecules* **1997**, *30*, 3711-3727.
4. Wu, C.; Lecavalier, P. R.; Shen, Y. X.; Gibson, H. W. *Chem. Mater.* **1991**, *3*, 569-572.
5. (a) Wu, C.; Bheda, M.; Lim, C.; Shen, Y. X.; Sze, J.; Gibson, H. W. *Polymer Commun.* **1991**, *32*, 204-207.
- b) Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.* **1995**, *117*, 852-874.
- c) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029-7033.
- d) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1997**, *198*, 2331-2342.
- e) Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. W. *Macromolecules* **1997**, *30*, 4807-4813.
- f) Gibson, H. W.; Nagvekar, D.; Powell, J.; Gong, C.; Bryant, W. *Tetrahedron* **1997**, *53*, 15197-15207.
- g) Gong, C.; Gibson, H. W. *Macromolecules* **1997**, *30*, 8524-8525.
6. a) Shen, Y. X.; Gibson, H. W. *Macromolecules* **1992**, *25*, 2058-2059.

- b) Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.* **1994**, *116*, 537-548.
- c) Marand, E.; Hu, Q.; Gibson, H. W.; Veytsman, B. *Macromolecules* **1996**, *29*, 2555-2562.
- d) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 8585-8591.
- e) Gong, C.; Gibson, H. W. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2331-2333.
- f) Gong, C.; Gibson, H. W. *Macromolecules* **1998**, *31*, 308-313.
- g) Gong, C.; Subramanian, C.; Ji, Q.; Gibson, H. W. *Macromolecules* **1998**, *31*, 1814-1818.
- h) Gibson, H. W.; Wang, H.; Niu, Z.; Slebodnick, C.; Zakharov, L. N.; Rheingold, A. L. *Macromolecules* **2012**, *45*, 1270-1280.
7. Gibson, H. W.; Engen, P. T. *New J. Chem.* **1993**, *17*, 723-727.
8. a) Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1064-1066.
b) Ashton, P. R.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1066-1069.
9. Shen, Y. X.; Engen, P. T.; Berg, M. A. G.; Merola, J. S.; Gibson, H. W. *Macromolecules* **1992**, *25*, 2786-2788.
10. Gibson, H. W., Lee, S. H., Engen, P. T., Lecavalier, P., Sze, J., Shen, Y. X., Bheda, M. J. *Org. Chem.* **1993**, *58*, 3748-3756.
11. Owen, G. J.; Hodge, P. *J. Chem. Soc., Chem. Commun.* **1997**, 11-12.
12. Shen, Y. X.; Engen, P. T.; Gibson, H. W.; Merola, J. S. *Abstracts, National Meeting Am. Chem. Soc.*, Atlanta, GA, April 1991, ORGN 325; Shen, Y. X., *Ph.D. Dissertation*, Virginia Polytechnic Institute and State University (1992).
13. a) Ashton, P. R.; Belohradsky, M.; Philp, D.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.*, **1993**, 1269-1274.
b) Ashton, P. R.; Belohradsky, M.; Philp, D.; Spencer, N.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1993**, 1274-1277.
14. a) Ortholand, J.-Y.; Slawin, A. M. Z.; Spencer, W.; Stoddart, J. F.; Williams, D. J. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1394-1395.

- b) Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vincent, C.; Williams, D. J. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1396-1399.
- c) Zhang, W.; Dichtel, W. R.; Stieg, A. Z.; Benitez, D.; Gimzewski, J. K.; Heath, J. R.; Stoddart, J. F. *Proc. Nat. Acad. Sci. USA* **2008**, *105*, 6514-6519.
15. Loveday, D.; Wilkes, G. L.; Shen, Y. X.; Bheda, M. C.; Gibson, H. W. *J. Macromol. Sci. Chem.* **1995**, *A32*, 1-27.
16. a) Jones, J. W.; Zakharov, L. N.; Rheingold, A. L.; Gibson, H. W. *J. Am. Chem. Soc.* **2002**, *124*, 13378-13379.
- b) Huang, F.; Fronczek, F. R. Gibson, H. W. *J. Chem. Soc., Chem. Commun.* **2003**, 1480-1481.
- c) Huang, F.; Switek, K. A.; Gibson, H. W. *Chem. Commun.* **2005**, 3655-3657.
- d) Niu, Z.; Slobodnick, C.; Bonrad, K.; Huang, F.; Gibson, H. W. *Org. Lett.* **2011**, *13*, 2872-2875.
- e) Niu, Z.; Slobodnick, C.; Schoonover, D. V.; Azurmendi, H.; Harich, K.; Gibson, H. W. *Org. Lett.* **2011**, *13*, 3992-3995.
17. Mason, P. E.; Bryant, W. S.; Gibson, H. W. *Macromolecules* **1999**, *32*, 1559-1569.
18. a) Berna, J.; Borrari, G.; Leigh, D. A.; Perez, E. M. *Pure Appl. Chem.* **2007**, *79*, 39-54.
- b) Silvi, S.; Venturi, M.; Credi, A. *Chem. Comm.* **2011**, *47*, 2483-2489.
- c) Yang, W.; Li, Y.; Liu, H.; Chi, L.; Li, Y. *Small* **2012**, *8*, 504-516.
19. Langton, M. J.; Beer, P. D. *Acc. Chem. Res.* **2014**, Ahead of Print.
20. a) Coskun, A.; Spruell, J. M.; Barin, G.; Dichtel, W. R.; Flood, A. H.; Botros, Y. Y.; Stoddart, J. F. *Chem. Soc. Rev.* **2012**, *41*, 4827-4859.
- b) Jia, C.; Li, H.; Jiang, J.; Wang, J.; Chen, H.; Cao, D.; Stoddart, J. F.; Guo, X. *Adv. Mater.* **2013**, *25*, 6752-6759.
21. a) Berezkin, Y.; Urick, M. *ACS Symp. Series* **2013**, *1148*, 65-81.
- b) Haettig, J.; Huertgen, D.; Mathias, L. *Kunststoffe* **2013**, *103*, 113-117.
22. Ashton, P. R.; Philp, D.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc. Chem. Comm.* **1991**, 1680-1683.

23. Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradsky, M.; Gandolfi, M. T.; Philp, D.; Prodi, L.; Raymo, F. M.; Reddington, M. V.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 4931-4951.
24. Helgeson, R. C.; Timko, J. M.; Cram, D. J. *J. Amer. Chem. Soc.* **1973**, *96*, 7380-7382; Helgeson, R. C.; Tarnowski, T. L.; Timko, J. M.; Cram, D. J. *J. Amer. Chem. Soc.* **1977**, *99*, 6411-6418.
25. Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. M.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193-218.