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Rotaxanes from Tetralactams

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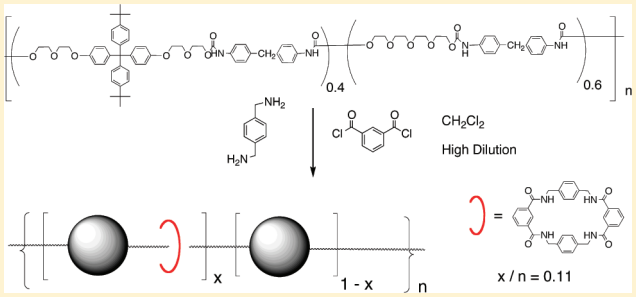
Supporting Information

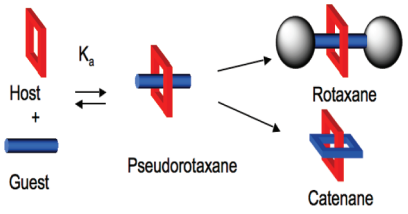
ABSTRACT: Attempts to incorporate a tetralactam (**3a**) into a side-chain polyrotaxane by formation of its complex with *p*-tritylphenolate and reaction with poly(vinybenzyl chloride) failed, probably due to steric hindrance. However, three new small molecule model rotaxanes (acetal **11a** and ethers **14a** and **14b**) were prepared based on this macrocycle, and one (**14b**) was characterized by X-ray crystallography. Attempts to prepare poly(ether rotaxane)s such as **18** and **20b** via polymerizations in the presence of this tetralactam failed because the mild conditions required for complexation (nonpolar solvent, room temperature) are not sufficient for effective step-growth polymerizations, resulting in only oligomer formation. In an alternative approach, clipping of the tetralactam **23** onto a preformed poly(urethane rotaxane) (**27**) in CH_2Cl_2 was successful, and the original biphasic segmented polymer was converted to a single-phase polyrotaxane (**28**) with a significantly lower glass transition temperature.



INTRODUCTION

Pseudorotaxanes, threaded entitities, exist in equilibrium with their linear and cyclic molecular components; attachments of bulky terminal groups on the linear molecules yield mechanically linked rotaxanes, and cyclizations of the linear component form catenanes, interlocked rings (Scheme 1), both

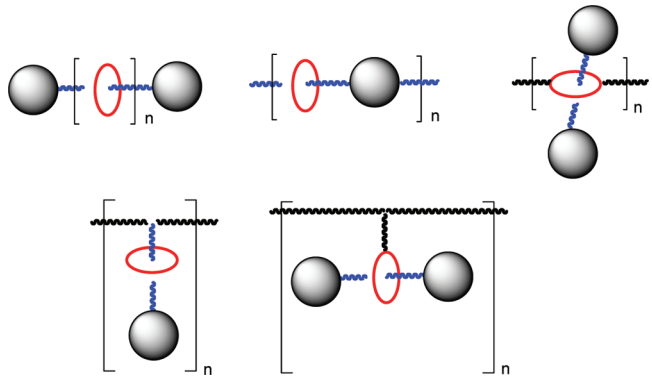
Scheme 1. Pseudorotaxanes: Precursors to Rotaxanes and Catenanes



of which can be converted to the independent species *only* by cleavage of a covalent bond.[1,2] Polyrotaxanes are polymers that include a rotaxane unit; the rotaxane unit may be in the main chain or a side chain (Scheme 2).[3,4]

We have synthesized a variety of main-chain polypseudorotaxanes and polyrotaxanes by carrying out classical step-growth[5] or free radical[6] polymerizations in the presence of cyclic components. Initially, the cyclic species were unfunctionalized aliphatic crown ethers;[7] however, functionalized crown ethers have been used by us as components of a number of types of main-chain polyrotaxanes as well.[8] Other investigators have also prepared such topologically interesting systems.[4]

Scheme 2. Polyrotaxanes: (top) Main-Chain Polyrotaxanes; (bottom) Side-Chain Polyrotaxanes



In the present work our initial aim was to prepare side-chain polyrotaxane (**4a**) from a preformed polymer, poly(vinylbenzyl chloride) (**1**), through reaction with a stopper, *p*-tritylphenol (**2a**), in the presence of tetralactam **3a** (Scheme 3). This method is based on the work of Vögtle et al.,[9] who demonstrated the formation of small molecule-based rotaxanes by initial complexation of phenolate anions with such cyclic amides, originally reported by Hunter et al.,[10] followed by alkylation with bulky stoppers in dichloromethane (Scheme 4).

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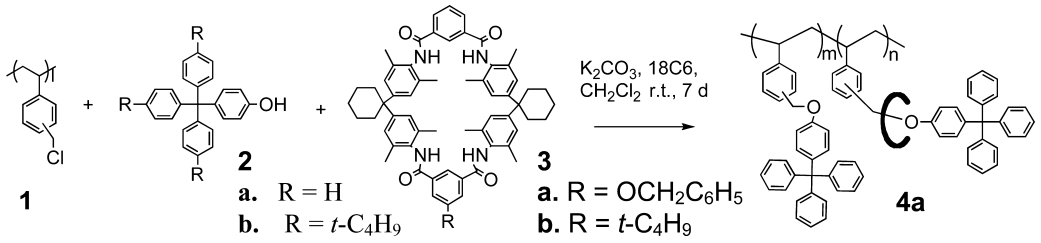
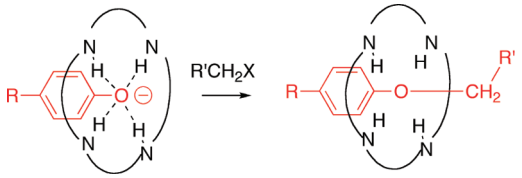
Scheme 3. Attempted Synthesis of Side-Chain Polyrotaxane 4a



Scheme 4. Schematic Illustration of Rotaxane Formation by Interaction of a Bulky Phenolate with a Tetralactam Followed by Williamson Ether Formation with a Bulky Alkyl Halide



RESULTS AND DISCUSSION

Attempted Synthesis of a Side-Chain Polyrotaxane via Threading of a Preformed Macrocycle. We prepared the known[11a] 32-membered, benzyloxy-substituted tetralactam **3a** by a process that paralleled the reported synthesis of **3b** (Scheme 5).[9a] The reported reaction[11a] that produced **3a** also produced two isomeric [2]catenanes that after deprotection were incorporated into polycatenanes.[11b,12] **3a** provides reasonable solubility in low-polarity solvents, like dichloromethane, which are required for the phenolate templation, combined with a protected functional group for later modification. The hydroxy group of dimethyl 5-hydroxyisophthalate (**5**) was protected with a benzyl moiety; **6** was obtained in 98% yield. By hydrolysis of ester **6**, diacid **7** was isolated in 89% yield; after treatment with thionyl chloride the diacid chloride **8** was isolated as a crystalline solid (72%). 1,1-Bis(4′-amino-3′,5′-dimethylphenyl)cyclohexane (**9**) was reacted with half an equivalent of isophthaloyl chloride to form the known[9,10] diamine **10** in 61% yield. Reaction of the diacid chloride **8** with diamine **10** under pseudo-high dilution conditions afforded the tetralactam **3a** in 57% yield. The composition of **3a** was confirmed by mass spectrometry; the lithium adduct was detected at *m/z* 1017.9 (theory 1017.5) in a low-resolution FAB experiment, and the macrocycle itself was detected in a high-resolution experiment at *m/z* 1011.5433 [theory for $(M + H)^+$ 1011.5424] (see Supporting Information). The ^{1}H NMR spectrum of **3a** is analogous to that of **3b**,[9a] with the exception that it lacks the *tert*-butyl methyl signals and has additional signals arising from the benzyloxy moiety. Because of its asymmetry the compound displays separate signals for protons 1 and 9 and 2 and 10 (see labeled structure in Figure 1); the signals for protons 5/5′ and

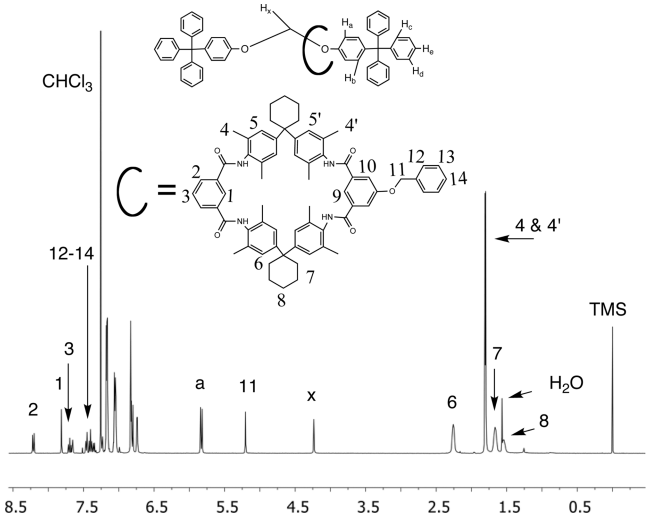
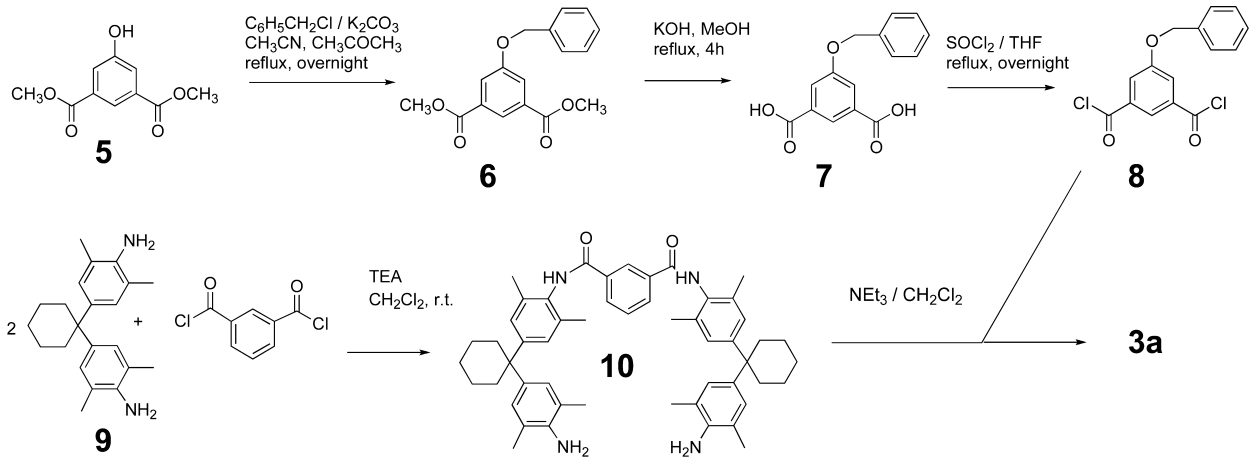


Figure 1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of rotaxane **11a**.

Scheme 5. Synthesis of Tetralactam 3a



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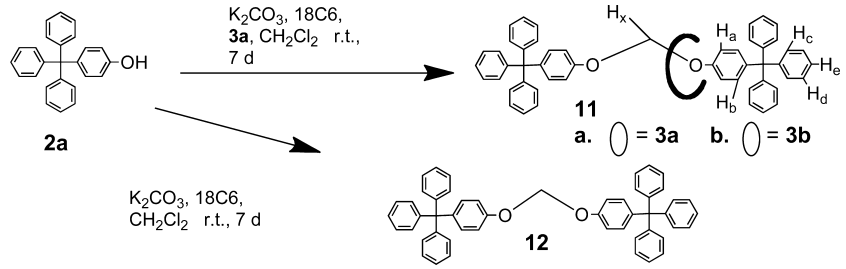
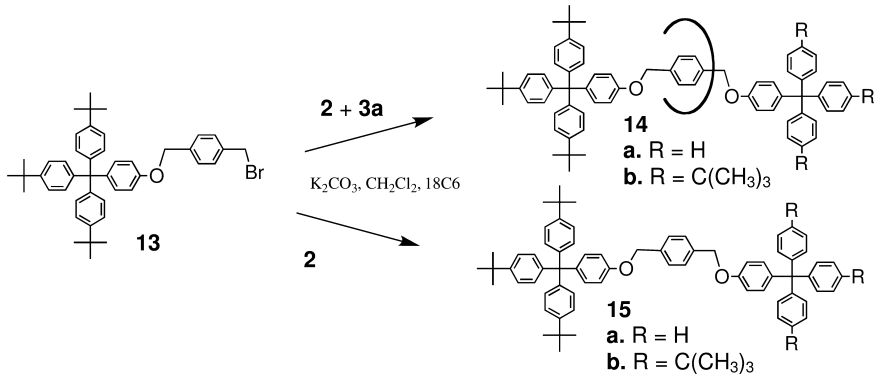
Scheme 6. Synthesis of Model Rotaxanes 11a and 11b and Dumbbell 12



Scheme 7. Synthesis of Model Rotaxanes 14a and 14b and Dumbbells 15a and 15b



4/4′ overlap, yielding broad peaks in $CDCl_3$. We were also able to obtain a crystal structure of the macrocycle, although it was seriously disordered in terms of the position of the benzyloxy group (see Supporting Information); interestingly, two opposing carbonyl groups point inward and the other pair point outward.

In varied attempts to prepare the side-chain polyrotaxane under the conditions analogous to those used by Vögtle et al.,[9] the functionalized polymer **4a** was never isolated. Even an 11:1 styrene:vinylbenzyl choride copolymer, used in an attempt to reduce possible steric problems, did not react under these conditions. However, a nonpolymeric product was isolated in high yields from each of these attempts. The product was identified as the methanol-soluble rotaxane **11a** derived by reaction of the phenolate with the solvent, CH_2Cl_2, via its FAB HR MS, which displayed the $(M + Na)^+$ ion at m/z 1717.8342 (theoretical 1717.8272). This acetal rotaxane was also produced in the absence of the polymer for confirmation of its structure. Rotaxane **11a** yields an ^1H NMR spectrum (Figure 1) and displays properties that are similar to those reported by Vögtle et al. for the analogous acetal rotaxane **11b**.[9d] In particular, the signal for the acetal methylene protons H_x of **11a** appeared at 4.25 ppm in $CDCl_3$ in the present work; the reported postion for H_x of **11b** in DMF-d_7 was 4.08 ppm. Moreover, the signal for the ortho protons H_a shifted upfield from 6.7 ppm in *p*-tritylphenol to 5.85 ppm in rotaxane **11a** in $CDCl_3$, while in **11b** it appears at 6.19 ppm in DMF-d_7. A similar trityl acetal rotaxane was reported to form from a cryptand containing two amide linkages.[13] COSY experiments (see Supporting Information) confirm the assignments shown in Figure 1. ROESY and 1D NOESY experiments (see Supporting Information) indicate correlation of inner macrocyclic proton H_1 with guest proton H_x and macrocyclic methyl protons H_4 and $H_{4'}$ with guest protons H_a, consistent with the rotaxane structure. In the absence of the macrocycle the linear dumbbell molecule **12** was formed; this compound has been reported before as the linear component of rotaxanes,[9a,c−e] but not characterized itself.

Model Small Molecule Rotaxanes. Two small molecule rotaxanes **14** were synthesized from benzylic bromide precursor **13**[5h,14] and *p*-tritylphenols **2a** and **2b** in the presence of macrocycle **3a** (Scheme 7). The two dumbbell guests **15** were synthesized also. Molecular ion peaks were observed in HR MS of rotaxanes **14**: at m/z 1953.09 (theoretical 1953.07) for **14a** and at m/z 2122.25 (theoretical 2121.26) for **14b**, respectively. The ^1H NMR spectra of **14a** and **14b** (Figure 2) display signals for the central protons of the guest that are shifted upfield due to diamagnetic shielding effects of the aromatic nuclei; in rotaxane **14a** the different stoppers and the resultant unsymmetrical structure lead to doubling of some of the signals. The xylyl aromatic protons (g and g′) shift upfield from 7.38 to 5.96 ppm for **15a** vs **14a** and from 7.45 to 5.97 ppm for **15b** vs **14b**. The benzylic protons (f and f′) also shift upfield from 4.52/4.98 to 4.31/4.41 ppm for **15a** vs **14a** and from 5.04 to 4.36 ppm for **15b** vs **14b**. The aromatic protons *ortho* to the phenolic ether (a and a′) also shift upfield: from 6.77/6.79 to 6.35/6.46 ppm for **15a** vs **14a**, and from 6.85 to 6.38 ppm for **15b** vs **14b**. The integrations are all consistent with the corresponding structures.

A single crystal of rotaxane **14b** suitable for X-ray diffraction was grown from acetone by vapor diffusion of pentane. Its structure (Figure 3)[15] is triclinic with *P*1 symmetry. The tetralactam is symmetrically located between the two stoppers. The two benzylic ether moieties of the guest take on a trans disposition. The benzyloxyphenyl ring of the macrocycle is nearly perpendicular (88°) to the plane of the xylyl ring of the guest, and proton H_9 of the macrocycle is situated over the central xyly ring at a distance of 4.26 Å. Likewise, the opposing *m*-isophthaloyl ring of the host lies at an angle of 84° to the plane of the xylyl ring and H_1 is also 4.26 Å from the central xylyl ring. The phenolic rings of the stoppers are nearly coplanar (3° out) and lie at angles of 58° and 61° with respect

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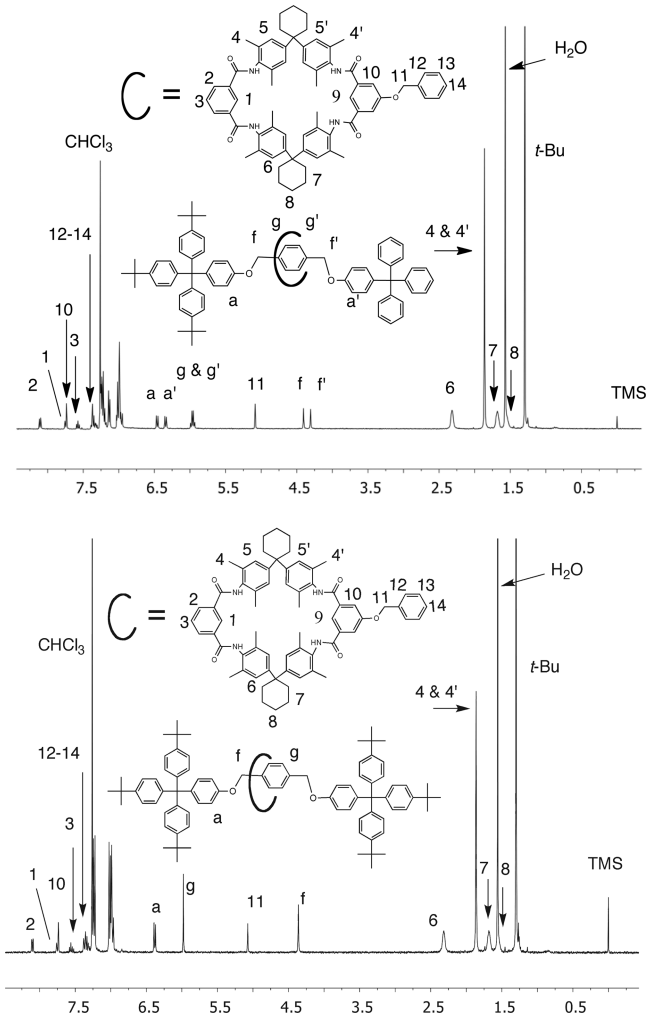

Figure 2. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of rotaxanes **14a** (top) and **14b** (bottom).

to the central xylyl ring of the guest. Unlike the situation in the macrocycle itself, all of the carbonyl moieties point outward. Two of the amide NHs are hydrogen bonded to acetone molecules (O---H distances 2.10 and 2.14 Å, not shown); however, there are no close contacts between the cyclic and linear components.

These rotaxanes, **14a** and **14b**, represent a novel class in which there is little or no interaction between the linear and cyclic components; that is, there is no "memory" of the intermolecular interactions that produced the threaded structures. Such structures in polymeric systems should allow facile movement of the cyclic species along the backbone, an adaptive advantage for some applications, such as surface modification, for example.

Oligomeric Rotaxanes by Threading a Preformed Macrocycle. To take advantage of this translational freedom, the Vögtle tetralactam macrocycles have not been incorporated into analogous polymeric rotaxanes as far as we know. Thus, we thought it was of interest to extend the above small molecule model reactions to the construction of main chain polymeric analogues. We studied the reactions of bisphenol-A with difluorobenzophenone to produce a poly(ether ketone) and with difluorodiphenyl sulfone to produce a poly(ether sulfone) with no success under the mild conditions required for adequate complexation of the bisphenolate anion with the tetralactam. For example, reaction of bisphenol A (**16**) and bis(*p*-bromomethylphenyl) ether (**17**)[16] at room temperature (Scheme 8) in chloroform after precipitation from methanol produced in 71% yield only oligomeric **18**, as determined by its observed low viscosity, GPC (bimodal, M_n 610, PDI 1.3, average of three runs with universal calibration), and ^{1}H NMR spectrum; again, the nonpolar solvent and low temperature limited the molecular weight. Nonetheless, we then carried out the same reaction in the presence of cyclic tetralactam **3a**; after precipitation from methanol, the product's ^{1}H NMR spectrum indicated that it contained no cyclic component, i.e., it was identical to **18**. We concluded that in the absence of any binding interaction between the linear polymer or oligomer and the cyclic compound, the cyclic species in the presumed pseudorotaxane was removed by the precipitation process. Hence, we concluded that stoppers were necessary to form an isolable polyrotaxane.

Therefore, "bis(tritylphenol)" **19**[17] was reacted with bis(*p*-bromomethylphenyl) ether (**17**) under basic conditions in chloroform at room temperature (Scheme 9). In the absence of the cyclic species, model oligomer **20a** was formed; it had M_n 3.15 kDa and polydispersity (PDI) 2.1 by GPC analysis relative

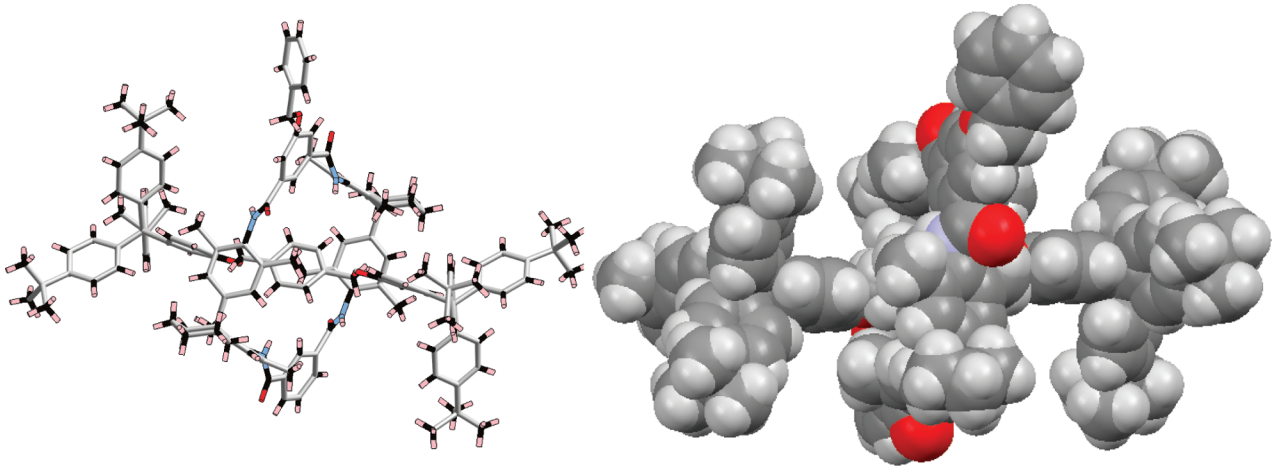

Figure 3. Structure of rotaxane **14b** as deduced from its single-crystal X-ray diffraction pattern. Left: stick figure. Right: space-filling representation. Oxygens are red, nitrogens are blue, carbons are black or dark gray, and hydrogens are white or light gray.

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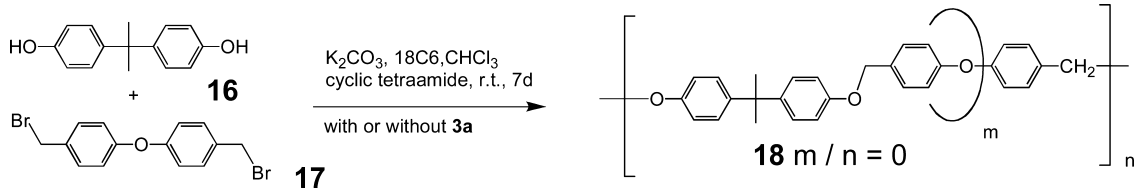
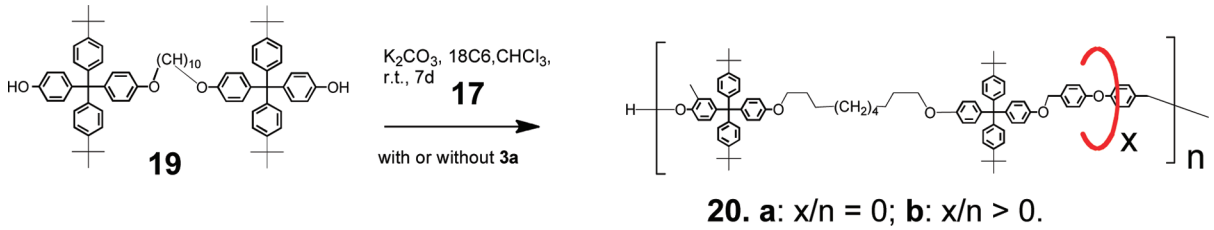
Scheme 8. Attempted Synthesis of Model Polyether 18a and Polyrotaxane 18b



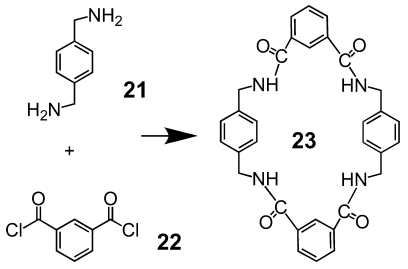
Scheme 9. Attempted Syntheses of Polyether 20a and Poly(ether rotaxane) 20b



to polystyrene standards. This corresponds to a degree of polymerization, n, of ~2.5, since the repeat unit mass is 1260 Da. When 1 equiv of cyclic tetralactam **3a** was used, **20b** resulted; the product was reprecipitated from chloroform into methanol three times before analysis. By GPC it had M_n 4.9 kDa and PDI 2.1. The ^{1}H NMR spectrum of **20b** displayed signals due to the tetralactam and a new signal for complexed benzylic protons. However, passage of this sample through a short silica gel column demonstrated the presence of unthreaded oligomer **20a** (see Supporting Information for details). Because of the low molecular weight and the mixed nature of the product, this approach was abandoned.

Main-Chain Polyrotaxanes by Clipping a Tetralactam around Preformed Polyamides. In order to prepare main-chain polyrotaxanes with tetralactams, we turned to the clipping approach, in which the cyclic component is formed around a preformed linear species.[1,18] For the cyclic species we used the 26-membered tetralactam **23** reported by Leigh et al., who demonstrated that rotaxanes could be formed by clipping its precursors, **21** and **22** (Scheme 10), around preformed small

Scheme 10. Synthesis of Leigh's Tetralactam 23



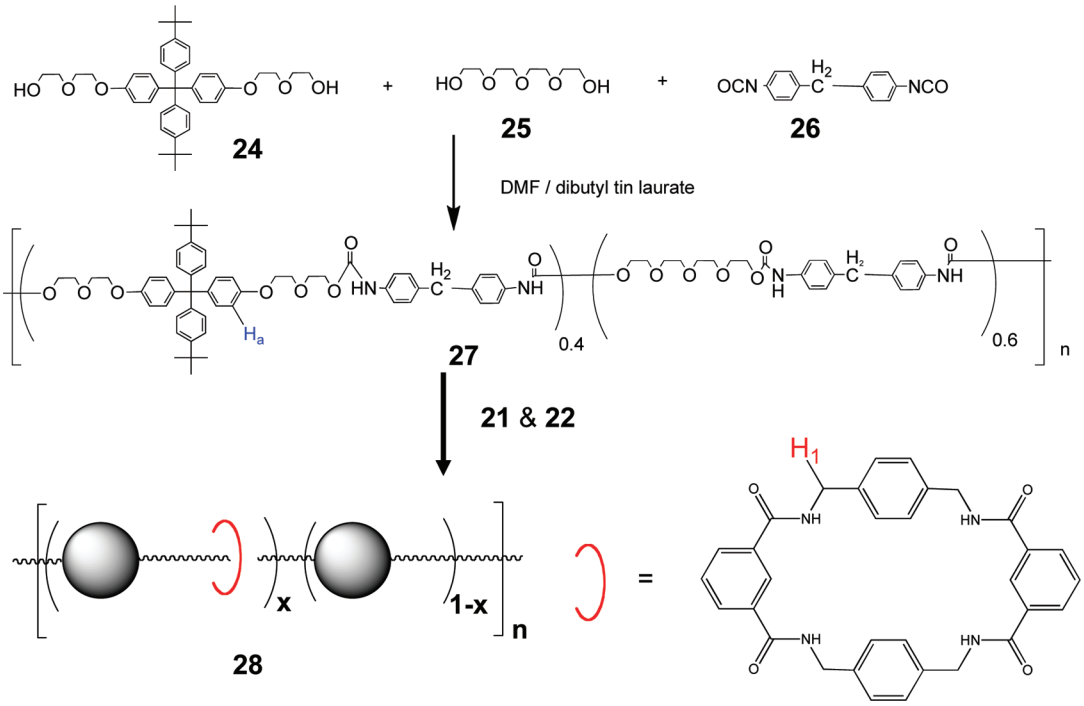
molecule amides.[19] In pursuit of our goal of incorporating Leigh's tetralactam into polyrotaxanes, we prepared a polymer that possessed suitable in-chain stoppers and solubility in nonpolar solvents. In particular, the bulky diol **24**[5i,j] was copolymerized with tetra(ethylene glycol) (**25**) (39.9:60.1 molar ratio) and MDI (**26**) to afford segmented polyurethane **27**, M_n 18.5 kDa, DP_n = 30 (Scheme 11). To bring about clipping[1,18] of the macrocycle around the polyurethane, a dilute solution of **27** in dichloromethane (1.09 g/1.5 L) was treated with diamine **21** and diacid chloride **22** by slow syringe pump addition. The resulting polymer was precipitated from dichloromethane into methanol three times until the signals due to the macrocycle no longer changed in proportion to the backbone signals. As determined by GPC, the polyrotaxane **28** had M_n 19.7 kDa. The clipping efficiency was determined to be 11 ± 1%, i.e., x/n = 0.11 ± 0.01, based on the ratio (0.55 ± 0.03) of integrals of the signals for the eight protons H_1 of the macrocycle and the four (times 0.4) aromatic protons H_a of the polymer in the NMR spectrum (Figure 4). Considering that the concentration of the urethane repeat units from **27** was 1.1 mM and only 0.8 equiv each of the building blocks **21** and **22** was applied, 14% of the theoretical yield of the macrocycle was captured in the polyrotaxane. Thus, the threading yield is impressive, and no doubt x/n could be increased by using an excess of the precursors of macrocycle **23**, analogous to our results with other polyrotaxane systems.[5c,d,h,j,n,6a,c,8e]

As shown in Figure 5, polyurethane **27** displays two glass transitions, one at 71 °C and the other at 150 °C, reflecting its phase-separated hard and soft domains. In contrast, polyrotaxane **28** has a single glass transition at 42 °C. Thus, rotaxanation of the polyurethane affects both the hard and soft phases, compatibilizing them to yield a single amorphous phase, presumably by location of the macrocycle along both segments of the copolymer through hydrogen bonding with the urethane and ether linkages, thereby interfering with interchain hydrogen bonding.

■ CONCLUSIONS

Attempts to incorporate a derivative of a tetralactam reported by Vögtle et al. into a side-chain polyrotaxane by reaction of tritylphenol with poly(vinybenzyl chloride) failed, apparently due to steric hindrance. However, three new small molecule model rotaxanes based on this macrocycle were prepared, and one was characterized by X-ray crystallography. Attempts to prepare poly(ether rotaxane)s based on this tetralactam failed because the conditions for complexation of the phenolate ion with the tetralactam (low temperature, low polarity) are not conducive to efficient step-growth polymerization. However, the first polyrotaxane **28** based on a tetralactam was synthesized by clipping Leigh's tetralactam **23** onto preformed polyurethane **27** in CH_2Cl_2. Incorporation of the macrocycle resulted in converting the two-phase segmented polyurethane **27** into a single-phase system with a significantly lower glass transition temperature in **28**.

Scheme 11. Synthesis of Segmented Polyurethane 27 and Its Conversion to Polyrotaxane 28 via Clipping of Tetralactam 23



EXPERIMENTAL SECTION

Materials. 1,4-Dioxane was freshly distilled over CaH_2; pyridine, distilled over CaH and stored over 3 Å molecular sieves; poly(vinylbenzyl chloride), Aldrich, 60/40 mixture of 3- and 4-isomers, typical M_n 55 kDa, typical M_w 100 kDa; *p*-tritylphenol, Aldrich, recrystallized from ethanol; 18C6, Aldrich, 99%; *N*,*N*-dimethylformamide (DMF), acetone, and triethylamine (TEA) were dried over 3 Å molecular sieves. K_2CO_3, tetrabutylammonium iodide (TBAI), NaOH, THF, CH_3Cl, CH_2Cl_2, toluene, HCl (36%), 1,1-bis(4′-amino-3′,5′-dimethylphenyl)cyclohexane (**9**, Aldrich), *p*-xylylenediamine (**21**, Aldrich), and isophthaloyl chloride (**22**, Aldrich) were used as received. Dimethyl 5-hydroxyisophthalate (Aldrich) was recrystallized from toluene/methanol. Compounds **13**[14a] and bis(*p*-hydroxymethylphenyl) ether[16] were prepared as previously reported.

Methods. Thin layer chromatography (TLC) utilized Whatman PE SIL G/UV254 plates. Flash column chromatography and column chromatography were carried out on silica gel. ^1H and ^{13}C NMR spectra were obtained on Varian Unity (or Inova) 400/100 MHz or JEOL Eclipse 500/125 MHz instruments instruments at ambient temperature; the usual designations of multiplicity are employed, and coupling constants (*J*) are reported in Hertz. Mass spectra (HR FAB) were obtained on a VG Quattro Fisons Instrument in positive ion mode; 3-nitrobenzyl alcohol (NBA) and poly(ethylene glycol) (PEG) matrices were employed, sometimes with other additives such as LiBr and CsI. DSC results were obtained on a TA Instruments Q2000 differential scanning calorimeter at a scan rate of 5 or 10 °C/min under a N_2 purge. Melting points (uncorrected) were observed on a Büchi B-540 apparatus at a 2 °C/min heating rate. Gel permeation chromatography (GPC) was conducted in $CHCl_3$ at 30 °C on an Alliance Waters 2690 separations module with a Viscotek T60A dual viscosity detector and laser refractometer equipped with a Waters HR 0.5 + HR 2 + HR 3 + HR 4 styragel column set and data analysis by universal calibration to obtain absolute or polystyrene equivalent molecular weights.

Dimethyl 5-Benzyloxyisophthalate (6). A mixture of 12.20 g (58.05 mmol) of dimethyl 5-hydroxyisophthalate and 9.23 g (66.8 mmol) of K_2CO_3 in CH_3CN/acetone (120 mL/100 mL) was refluxed 0.5 h to give a light yellow suspension. To this mixture was added 7.35 g (58.1 mmol) of benzyl chloride dropwise. After reaction overnight at reflux, the resulting light yellow suspension was concentrated by rotoevaporation. Water and EtOAc were added, and the water layer was extracted with EtOAc three times. The combined organic solution was washed with water to pH 7.00 and then washed with saturated NaCl solution. After drying over anhydrous Na_2SO_4, the clear solution was concentrated by rotoevaporation to give an oil, which solidified. The off-white solid was dried in vacuum (17.06 g, 98%) and recrystallized from toluene as needlelike crystals; mp 87.5–90.0 °C, lit.[20] mp 94–95 °C. ^1H NMR (400 MHz, acetone-d_6): δ 3.94 (s, 6H), 5.32 (s, 2H), 7.39 (t, J = 8 Hz, 1H), 7.44 (t, J = 8 Hz, 2H), 7.56 (d, J = 8 Hz, 2H), 7.83 (s, 2H), 8.22 ppm (s, 1H).

5-Benzyloxyisophthalic Acid (7). A solution of 3.94 g (13.1 mmol) of dimethyl 5-benzyloxyisophthalate and KOH (30.0 g, 535 mmol) in 300 mL of CH_3OH was stirred at reflux 2 h, cooled to rt, and acidified with 2 N HCl. The white precipitate was collected by filtration and dried in vacuum, 3.16 g (88%); mp 268–271 °C, lit. mp 252 °C.[21] ^1H NMR (400 MHz, acetone-d_6): δ 5.33 (s, 2H), 7.33 (t, J = 8 Hz, 1H), 7.42 (t, J = 8 Hz, 2H), 7.58 (d, J = 8 Hz, 2H), 7.92 (s, 2H), 8.33 (s, 1H), 11.6 ppm (bs, 2H).

5-Benzyloxyisophthaloyl Chloride (8). A mixture of $SOCl_2$ (55 mL, 0.75 mol), 5-benzyloxyisophthalic acid (**7**, 5.0 g, 18 mmol), and 5 drops of DMF was refluxed under N_2 protection; after 1 h a clear yellow solution formed. After 5 h of reflux, the excess $SOCl_2$ was removed by rotoevaporation. The residue was boiled with hexane, and the insoluble solid was removed by hot filtration. White crystals formed in the hexane solution as it cooled; filtration and vacuum drying afforded 4.10 g (72%) of **8**; mp 61.5–62.8 °C, lit.[10a] mp 66 °C. ^1H NMR (400 MHz, acetone-d_6): δ 5.46 (s, 2H), 7.39 (t, J = 8 Hz, 1H), 7.50 (t, J = 8 Hz, 2H), 7.57 (d, J = 8 Hz, 2H), 8.07 (s, 2H), 8.41 ppm (s, 1H).

Diamine 10. To a vigorously stirred yellow solution of 1,1-bis(4′-amino-3′,5′-dimethylphenyl)cyclohexane (**9**, 45.32 g, 139.7 mmol) in 300 mL of CH_2Cl_2 and 9.8 mL (70 mmol) of anhydrous TEA was added isophthaloyl chloride (4.53 g, 22.3 mmol) in CH_2Cl_2 (500 mL) slowly under N_2 protection. After the addition, the solution was stirred 2 days at rt. It was filtered and concentrated by rotoevaporation. The off-white solid obtained was dissolved in 200 mL of CH_2Cl_2 and added dropwise to 1.8 L of hexane. The precipitate was collected by filtration. The hexane solution was concentrated to give 7.56 g of starting diamine. The crude solid product was subjected to flash column chromatography; the eluent was changed from 1/10 v/v EtOAc/

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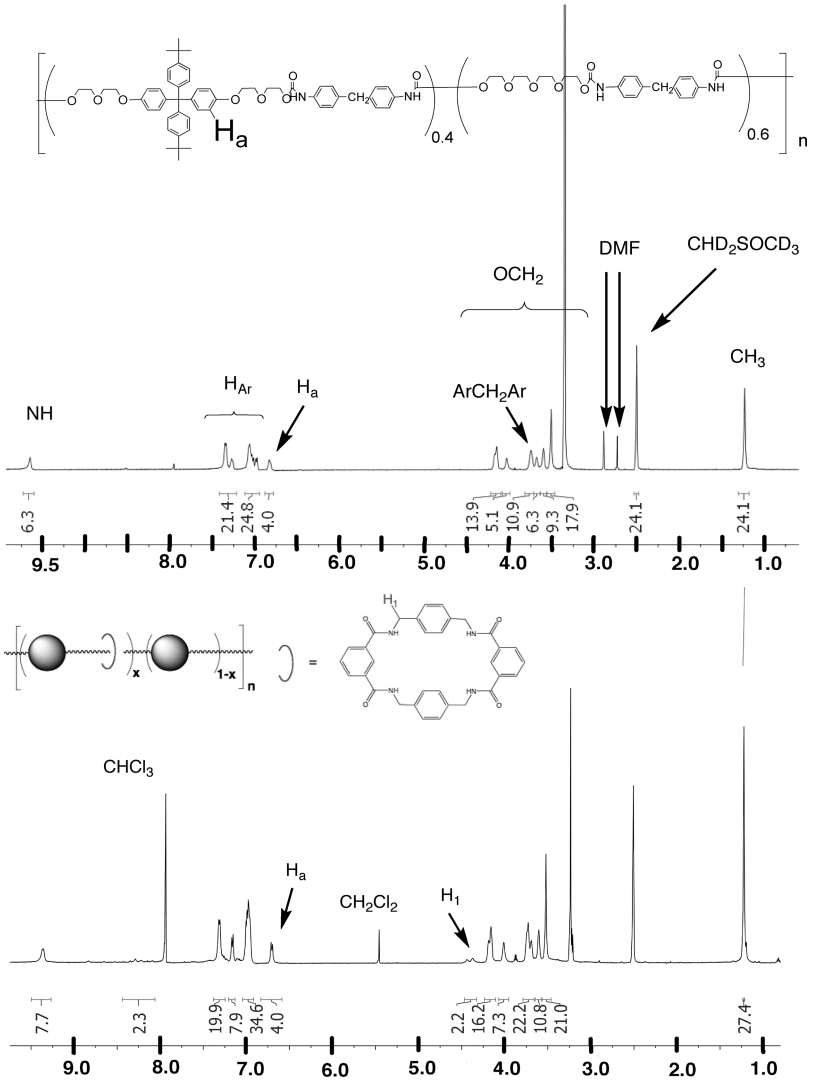

Figure 4. NMR spectra (500 MHz, 1:1 $CDCl_3$:DMSO-d_6) of polyurethane **27** (top) and polyrotaxane **28** (bottom).

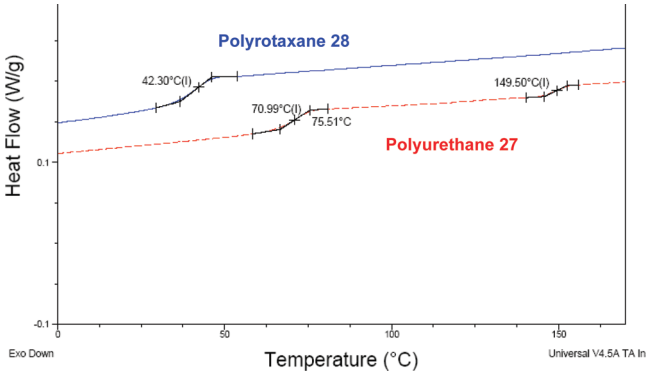

Figure 5. DSC traces of polyurethane **27** and polyrotaxane **28** (5 °C/min).

hexane to 1/3. Altogether 22.48 g of starting diamine was recovered, and 10.5 g (61%) of product **10** (mp 174–184 °C (lit.[9c] mp 179–180 °C)) was obtained. HR FAB MS (NBA PEG): m/z 775.4912 $(M + H)^+$; calcd for $C_{52}H_{63}N_4O_2$ m/z 775.4873 (error 5.0 ppm). ^{1}H NMR (400 MHz, $CDCl_3$): 1.4–1.6 (m, 12H), 2.1–2.22 (m, 8H), 2.15 (s, 12H), 2.21 (s, 12H), 3.44 (s, 4H), 6.58 (s, 4H), 7.01 (s, 4H), 7.45, (s, 2H), 7.52 (t, 1H, J = 8 Hz), 8.03 (d, 2H, J = 8 Hz), 8.44 ppm (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.12, 148.69, 140.03, 137.63, 134.82, 134.70, 130.65, 130.23, 129.11, 127.03, 126.91, 125.93, 121.49, 44.87, 37.14, 26.43, 22.95, 18.78, 18.04 ppm.

Tetralactam 3a. A solution of diamine **10** (1.0000 g, 1.2902 mmol) and anhydrous TEA (0.4 mL, 3 mmol) in 10 mL of CH_2Cl_2 was prepared. A separate solution of 5-benzyloxyisophthaloyl chloride (**8**, 0.3986 g, 1.289 mmol) in 10 mL of CH_2Cl_2 was prepared These two separate solutions were simultaneously added via a syringe pump over 4 h to a vigorously stirred flask containing 1.5 L of CH_2Cl_2. After the addition, the solution was stirred 2 days at rt under N_2 protection. The mixture was filtered and concentrated to give 1.6 g of off-white solid. It was combined with the crude product of two separate reactions (starting with 1.7 and 1.4 g of **10**) and subjected to flash chromatography (silica gel, v/v 99/1 $CHCl_3$/CH_3OH to 98/2). An off-white solid was obtained, 0.75 g (57%); mp 310 °C (dec), lit.[10a] mp 297 °C . LR FAB MS (NBA): m/z 1010 $(M)^+$. LR FAB MS (NBA-LiBr): m/z 1033.5 $(M + Na)^+$; 1017.9 $(M + Li)^+$; 781.7 $(M - C_{15}H_{19}NO)^+$. HR FAB MS (NBA-PEG): m/z 1011.5433 $(M + H)^+$; calcd for $C_{67}H_{71}N_4O_5$ 1011.5424 (error 0.8 ppm). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56 (bs, 4H), 1.64 (bs + HOD, 8(?)H), 2.20 (bs, 24H), 2.33 (bs, 8H), 5.20 (s, 2H), 6.78 (s, 1H), 7.00 (s, 4H), 7.03 (s, 4H), 7.3–7.7 (m, 7H), 7.78 (bs, 1H), 7.81 (bs, 1H), 8.08 (d, J = 8, 2H), 8.14 (d, J = 8; 2H), 8.25 (s, 1H), 8.47 ppm (s, 1H).

Typical Attempted Synthesis of Polyrotaxane 4a, Producing Rotaxane 11a. A mixture of poly(vinylbenzyl chloride) (**1**, 8.23 mg, 0.064 mmol repeat units), *p*-tritylphenol (**2a**, 21.48 mg, 0.064 mmol), 18C6 (23.89 mg, 0.090 mmol), tetralactam **3a** (79.04 mg, 0.078

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mmol), and K_2CO_3 (19.68 mg, 0.142 mmol) in CH_2Cl_2 (20 mL) was stirred at rt under N_2 protection for 7 days. The solid was removed by filtration. The filtrate was evaporated, and the residue was treated with a small amount of $CHCl_3$. The insoluble solid (40.5 mg) was removed by filtration, and the filtrate was precipitated into a large amount of CH_3OH. The white precipitate was collected by filtration and dried in a vacuum: 8.28 mg, identified as unreacted **1**. The filtrate was concentrated to give a white solid, which was dissolved in $CHCl_3$ and precipitated into hexane, yielding 53.2 mg (98% based on limiting tritylphenol) of an off-white solid (crude **11a**). Flash column chromatography with $CHCl_3$ as eluent afforded 22.0 mg of purified rotaxane **11a**; mp 315 °C (color change to light brown at 245 °C, then to dark brown at 290 °C). HR FAB MS (NBA-PEGNa): *m/z* 1717.8342 $(M + Na)^+$; calcd for $C_{118}H_{110}N_4O_7Na$ 1717.8273 (error 4 ppm). ^1H NMR (400 MHz, $CDCl_3$, Figure 1): δ 1.54 (bs, 4H), 1.67 (bs, 8H), 1.79 (s, 12H), 1.83 (s, 12H), 2.26 (bs, 8H), 4.22 (s, 2H), 5.19 (s, 2H), 5.83 (d, J = 8, 4H), 6.77 (bs, 4H), 6.81 (d, J = 8, 4H), 6.82 (s, 8H), 7.05 (m, 12H), 7.16 (m, 18H), 7.24 (s, 1H), 7.36 (m, J = 8, 1H), 7.40 (t, J = 8, 2H), 7.46 (bd, J = 8, 2H), 7.65 (bs, 1H), 7.70 (t, J = 8, 1H), 7.81 (d, J = 2, 2H), 8.21 ppm (dd, J = 2, 8; 2H).

Reaction of Dichloromethane with *p*-Tritylphenol in the Presence of Tetralactam (11a). To a solution of tritylphenol (**2a**, 13.25 mg, 0.0394 mmol), tetralactam **3a** (19.54 mg, 0.0193 mmol), and 18C6 (5.21 mg, 0.0197 mmol) in CH_2Cl_2 (20 mL) was added K_2CO_3 (4.6 mg, 0.033 mmol). The mixture was stirred at rt under N_2 for 7 days. The precipitate was removed by filtration. The solution was treated as outlined above to yield a white solid identical in all respects to **11a** obtained earlier.

Formaldehyde *p*-Tritylphenyl Acetal, Dumbbell 12. To a solution of tritylphenol (**2a**, 26.68 mg, 0.0794 mmol) and 18C6 (9.64 mg, 0.0365 mmol) in CH_2Cl_2 (40 mL) was added K_2CO_3 (10.04 mg, 0.0726 mmol). It was stirred at rt under N_2 for 7 days. The solid was removed by filtration. The solution was concentrated to give a white solid (25 mg, 93%), which was subjected to column chromatography on silica, eluting with $CHCl_3$, yielding a colorless solid; mp 246.4–247.3 °C. HR ESI-MS: *m/z* 684.2991 $(M + H)^+$, 702.3318 $(M + NH_4)^+$; calcd for $C_{51}H_{40}O_2$ + H: 684.3028 (error −5.5 ppm), calcd for $C_{51}H_{40}O_2$ + NH_4: 702.3374 (error −7.9 ppm). ^1H NMR (400 MHz, $CDCl_3$): 5.69 (s, 2H), 6.97 (d, J = 8, 4H), 7.1–7.3 ppm (m, 34H).

Rotaxane 14a. To a solution of tritylphenol (**2a**, 6.62 mg, 0.0197 mmol), bromide **13** (13.65 mg, 0.0198 mmol), tetralactam **3a** (20.02 mg, 0.0198 mmol), and 18C6 (5.15 mg, 0.0195 mmol) in CH_2Cl_2 (20 mL) was added K_2CO_3 (5.02 mg, 0.0363 mmol). The suspension was stirred at rt for 7 days. Solid was removed by filtration. The filtrate was concentrated and subjected to column chromatography with $CHCl_3$ as eluent. The fractions collected from the column were: F1, 9.34 mg (bromide **13**); F2, 12.83 mg; F3, 7.20 mg; F5–F7, 7.59 mg (tetralactam **3a**); F8–F13, 8.10 mg (mainly 18C6). F2 + F3 = 20.03 mg (52%) of **14a**. Two more column chromatographic separations afforded pure **14a**; mp 291.0–292.0 °C. HR FAB MS (NBA/CsI): *m/z* 1953.20 $(M)^+$; calcd for $C_{137}H_{140}N_4O_7$ *m/z* 1953.07 (error +6.6 ppm). ^1H NMR (400 MHz, $CDCl_3$, Figure 2): δ 1.30 (s, 27H), 1.55 (bs + HOD, 4(?)H), 1.68 (bs, 8H), 1.87 (s, 24H), 2.32 (bs, 8H), 4.31 (s, 2H), 4.41 (s, 2H), 5.09 (s, 2H), 5.96 (AB q, J = 8, 4H), 6.35 (d, J = 8, 2H), 6.46 (d, J = 8, 2H), 6.90–7.30 (m, 44H), 7.30–7.35 (m, 5H), 7.58 (t, J = 8, 1H), 7.78 (m, 3H), 8.10 ppm (dd, J = 2, 8; 2H).

Rotaxane 14b. To a solution of tris(*p-tert*-butylphenyl)-4-hydroxyphenylmethane (**2b**, 10.05 mg, 0.0199 mmol), bromide **13** (13.62 mg, 0.0198 mmol), tetralactam **3a** (19.98 mg, 0.0197 mmol), and 18C6 (5.26 mg, 0.0199 mmol) in CH_2Cl_2 (20 mL) was added K_2CO_3 (5.58 mg, 0.0404 mmol). The suspension was stirred at rt for 7 days. Solid was removed by filtration. The filtrate was concentrated and subjected to column chromatography with $CHCl_3$ as eluent. The fractions collected from the column were: F1, 8.00 mg (bromide **13**); F2, 17.07 mg, F3, 7.47 mg, F5–F8, 6.68 mg (cyclic tetralactam **3a**); F8–F13, 8.03 mg (mainly 18C6). F2 + F3 = 24.54 mg (58%) of **14b**. Two more column chromatographic separations afforded pure **14b**; mp 309.5–310.6 °C. HR FAB MS (NBA): *m/z* 2122.25 $(M + H)^+$; calcd for $C_{149}H_{165}N_4O_7$ *m/z* 2122.26 (error −5 ppm). ^1H NMR (400 MHz, $CDCl_3$, Figure 2): δ 1.30 (s, 54H), 1.55 (bs + HOD, 4(?)H), 1.68 (bs, 8H), 1.86 (s, 24H), 2.32 (bs, 8H), 4.36 (s, 4H), 5.08 (s, 2H), 5.97 (s, 4H), 6.38 (d, J = 8, 4H), 6.9–7.4 (m, 47H), 7.58 (t, J = 8, 1H), 7.74 (s, 2H), 7.75 (s, 1H), 8.11 ppm (d, J = 8, 2H).

Unsymmetrical Dumbbell 15a. To a solution of *p*-tritylphenol (**2a**, 6.80 mg, 0.0202 mmol), bromide **13** (13.63 mg, 0.0198 mmol), and 18C6 (5.37 mg, 0.0230 mmol) in CH_2Cl_2 (20 mL) was added K_2CO_3 (5.05 mg, 0.0365 mmol). It was stirred at rt for 7 days. Solid in the reaction mixture was removed by filtration. The filtrate was concentrated and separated by column chromatography with a mixture of hexane and $CHCl_3$ (from 7/1 to 5/1 v/v ratio) as eluent. The expected product was a solid collected as the second fraction after the bromide starting material: 14.3 mg (76%); mp 218.6–219.3 °C. HR FAB MS (NBA-PEG): *m/z* 942.5392 $(M)^+$; calcd for $C_{70}H_{70}O_2$ *m/z* 942.5376 (error +1.6 ppm). ^1H NMR ($CDCl_3$): δ 1.30 (s, 27H), 4.55 (s, 2H), 4.96 (s, 2H), 6.76 (d, J = 8, 2H), 6.9–7.4 ppm (m, 37H).

Symmetrical Dumbbell 15b. To a solution of bromide **13** (27.84 mg, 0.0405 mmol), tris(*p-tert*-butylphenyl)-4-hydroxyphenylmethane (**2b**, 20.14, 0.0399 mmol), and 18C6 (8.33 mg, 0.032 mmol) in CH_3CN (20 mL) was added K_2CO_3 (11.2 mg, 0.0810 mmol). The suspension was stirred 7 days at rt under N_2. After reaction, the precipitate was removed by filtration. The filtrate was concentrated to give an off-white solid, which was subjected to column chromatography with a mixture of hexane and $CHCl_3$ (from 7/1 to 5/1 v/v ratio) as eluent. The expected product was a solid collected as the second fraction after the bromide starting material: 9.5 mg (40%), mp 270 °C (dec). When the reaction was carried out at 85 °C for 18 h, only 6.5% of the product was isolated. HR FAB MS (NBA-PEG): *m/z* 1110.7214 $(M)^+$; calcd for $C_{82}H_{94}O_2$ *m/z* 1110.7254 (error −3.6 ppm). ^1H NMR ($CDCl_3$): δ 1.30 (s, 54H), 5.04 (s, 4H), 6.82 (d, J = 8, 4H), 7.07–7.12 (m, 16H), 7.22 (d, J = 8, 12H), 7.45 ppm (s, 4H).

Bis(*p*-bromomethylphenyl) Ether (17). To a solution of 4.19 g (18.2 mmol) of bis(*p*-hydroxymethylphenyl) ether[16] in a mixture of THF and toluene (390 mL/775 mL) was added 6.40 mL (67.4 mmol) of PBr_3 dropwise. After the mixture had stirred overnight at rt, it was concentrated by rotoevaporation. $CHCl_3$ was added, and the resulting suspension was cooled in an ice–water bath and stirred vigorously. Water was added slowly to quench the excess PBr_3. After the organic layer was separated, the water layer was washed three times with $CHCl_3$. The combined organic layer was dried over anhydrous Na_2SO_4. After concentration, a yellow oil was obtained, which solidified upon standing. It was subjected to flash column chromatography (silica gel, 10/1 v/v hexane/ethyl acetate mixture). Three fractions were obtained. The first fraction, a white solid, 5.83 g (90%), was the expected product. It was recrystallized three times from hexanes and dried *in vacuo*; mp 84–85 °C (lit. mp 93–95,[22] 98 °C[23]). ^1H NMR ($CDCl_3$): δ 4.51 (s, 4H), 6.99 (d, J = 7, 4H), 7.38 ppm (d, J = 7, 4H).

Model Polyether 18a. To a solution of bisphenol-A (91.22 mg, 0.400 mmol), bromide **17** (142.28 mg, 0.400 mmol), and 18-crown-6 (203.30 mg, 0.769 mmol) in chloroform (10 mL) was added K_2CO_3 (106.20 mg, 0.768 mmol). The suspension was stirred at rt for 7 days. The solid was removed by filtration. The solution was precipitated into methanol to give 0.12 g (71%) of white solid. GPC (universal calibration): bimodal, M_n 610, PDI 1.3, average of three runs; see Supporting Information).

Attempted Synthesis of Polyether Pseudorotaxane 18b. To a solution of bisphenol-A (91.18 mg, 0.399 mmol), bromide **17** (142.28 mg, 0.400 mmol), tetralactam **3a** (50.85 mg, 0.05028 mmol), and 18-crown-6 (203.60 mg, 0.770 mmol) in chloroform (10 mL) was added K_2CO_3 (110.5 mg, 0.800 mmol). The suspension was stirred at rt for 7 days. After reaction, the solid was removed by filtration. The solution was precipitated into methanol to give 0.12 g of white solid. The ^1H NMR spectrum indicated that the sample was similar to model system **18a** and contained no tetralactam.

Polyether 20a. A mixture of 42.66 mg (0.0400 mmol) of diphenol **19**, 14.23 mg (0.0400 mmol) of dibromide **17**, 10.62 mg (0.077 mmol) of K_2CO_3, and 20.43 mg (0.077 mmol) of 18C6 in 10 mL of $CHCl_3$ was stirred 7 days at rt. The solid was removed by filtration. The filtrate was precipitated in CH_3OH. The off-white solid (57 mg,

~100%) was collected by filtration and reprecipitated in CH_3OH twice. A white solid was obtained, T_g 142 °C. GPC (polystyrene equivalents): M_n = 3.15 kDa, M_w = 6.54 kDa, PDI = 2.1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 44H), 1.43 (bs, 4H), 1.75 (bs, 4H), 3.91 (t, J = 7, 4H), 4.96 (bs, 2.2H), 5.07 (bs, 1.2H), 6.75 (d, J = 8, 4H), 6.77−6.86 (m, 4H), 6.98−7.12 (m, 20H), 7.19−7.25 (m, 8H), 7.37 ppm (m, 4H).

Polyether Rotaxane 20b. The same procedure was applied using 40.62 mg (0.0402 mmol) of tetralactam **3a**. A white solid was obtained [70 mg (77% assuming m/n = 1, 100% for m/n = 0.49) initially and 11 mg after 3 precipitations from $CHCl_3$ into CH_3OH]. GPC (polystyrene equivalents): M_n = 4.9 kDa, M_w = 11 kDa, PDI = 2.1. ^{1}H NMR ($CDCl_3$): δ 1.30 (s), 1.35−2.00 (m), 2.30 (bs), 3.91 (bs), 4.64 (bs), 5.00 (bs), 5.07 (bs), 5.14 (bs), 6.10 (d, J = 8), 6.56 (bm); 6.6−6.8 (m), 6.9−8.25 ppm (m). See Supporting Information for further analysis.

Polyurethane 27. A solution of the bulky diol **24** (1.65 g, 2.57 mmol), 0.752 g (3.87 mmol) of tetra(ethylene glycol) (**25**), and 1.69 g (6.76 mmol) of MDI (**26**) and 2 drops of dibutyltin laurate in 20 mL of DMF was stirred at 90 °C for 24 h and precipitated into 300 mL of methanol. The pale yellow solid was filtered and dried in a vacuum oven: 4.04 g (98%). The polymer was reprecipitated twice more from the minimum amount of DMF into >10-fold excess methanol and dried in a vacuum oven: M_n 18.5 kDa (universal calibration, $CHCl_3$), PDI 8.1 (presumed to be due to aggregation). DSC: T_gs at 71 and 150 °C (Figure 5). ^{1}H NMR (400 MHz, DMSO-d_6/$CDCl_3$ = 1/1 v/v, Figure 4): δ 1.23 (s, 24 H), 3.51 (s, 18 H), 3.60 (s, 9 H), 3.68 (s, 6 H), 3.75 (s, 11 H), 4.03 (s, 5 H), 4.15 (s, 14 H), 6.83 (bs, 4 H), 6.97−7.06 (m, 25 H), 7.27−7.35 (m, 21 H), 9.25 (s, 6 H) [7.95, 2.89, 2.73 ppm (DMF)].

Polyrotaxane 28. To a solution of 1.09 g (1.76 mol of urethane moieties) of polymer **27** and 0.486 mL (3.5 mmol) of anhydrous triethylamine in 1500 mL of dichloromethane were added separately 0.190 g (1.4 mmol) of *p*-xylylenediamine (**21**) in 25 mL of dichloromethane and 0.284 g (1.4 mmol) of isophthaloyl chloride (**22**) in 25 mL of dichloromethane via two syringes at 1 mL/h. The solution was stirred for 96 h after addition, filtered, and reduced in volume to 50 mL and precipitated into 500 mL of methanol. The polymer was filtered and dried *in vacuo* (1.58 g, 78% assuming one ring per repeat unit, x/n = 1.0; theoretical yield 2.03 g) before analysis by ^{1}H NMR to determine the ratio of macrocycle (via the signal for proton H_1) to polymer repeat unit (via the signal for proton H_b). The polymer was then dissolved in the minimum amount of DMF and reprecipitated into >10-fold volume of methanol, and the filtration, drying, and analysis were repeated. The result for the third precipitation was the same as that for the second precipitation, indicating x/n = 0.11. GPC (universal calibration, $CHCl_3$): M_n 19.7 kDa, PDI 8.0 (again presumed to be due to aggregation). DSC: T_g at 42 °C (Figure 5). ^{1}H NMR (400 MHz, DMSO-d_6/$CDCl_3$ = 1/1 v/v, Figure 4): δ 1.22 (s, 27 H), 3.52 (s, 21H), 3.61 (s, 11 H), 3.73 (m, 22 H), 3.75 (s, 11.0H), 4.01 (s, 7 H), 4.15 (m, 16 H), 4.44 (m, 2.2 H), 6.71 (m, 4 H), 6.97−7.06 (m, 34 H), 7.17 (m, 8 H), 7.32 (m, 20 H), 8.09−8.35 (m, 2 H), 9.25 (s, 7 H) [plus 5.46 ppm (CH_2Cl_2)].

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra and mass spectrometric traces for various intermediates and products; disordered X-ray structure of tetralactam **3a**; GPC traces for polyurethane **27** and polyrotaxane **28**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystals were grown from acetone/pentane. A colorless prism (0.08 × 0.09 × 0.11 mm^3) was centered on the goniometer of an Oxford Diffraction SuperNova diffractometer operating with Cu Kα radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro (CrysAlisPro v171.33.31, Oxford Diffraction: Wroclaw, Poland, 2009). The Laue symmetry was consistent with the triclinic space groups *P*1 and *P*-1. The structure was solved in both *P*-1 and *P*1 using SIR92 (Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350) (via WinGX: Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837838) and the unit cell contents identified as one rotaxane complex, two acetone molecules, and additional unidentifiable and disordered solvent. The *P*-1 solution, with $Z' = 0.5$, forces apparent 50% disorder of the benzyloxy functional group. The *P*1 solution showed no disorder in the benzyloxy group, indicating the true space group is *P*1 with pseudo-*P*-1 symmetry. The structure was refined in *P*1 using SHELXL-NT (Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122). Because of poor data quality (e.g., mean $I/\sigma(I) = 0.93$ for 0.98−0.94 Å; $I > 2\sigma(I)$ for 34% reflections to 0.84 Å) and the absence of any heavy atoms, the absolute configuration could not be determined from the Friedel pairs; the Friedel opposites were therefore merged. All atoms were refined isotropically, and a riding model was used for all hydrogen atoms. Atoms related by pseudoinversion were restrained to have similar 1,2 and 1,3 distances (SAME) and constrained to have identical U_{iso} values (EADP) to reduce correlation instability during refinement. The residual electron density from the unidentifiable disordered solvent was subtracted out using the SQUEEZE program in PLATON (Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13). A total of 109e^- was subtracted from a total void volume of 540 $Å^3$

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