Hydrocarbon-Based 40- and 44-Membered Macrocycles as Potential Components of Polyrotaxanes

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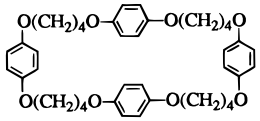
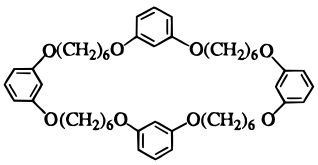
Introduction

Several polyrotaxanes with crown ethers as cyclic species have been synthesized and characterized in our labs.[1] Threading of cyclic components onto polymer backbones allows the modification of properties of the polymers such as solubility and thermal behavior.[1,2] Recently, we synthesized predominantly hydrocarbon-based macrocycles, 40- and 44-membered (**M40** and **M44**, respectively), for the ultimate syntheses of polyrotaxanes. In contrast to crown ethers, which are flexible and hydrophilic, these macrocycles are stiffer and hydrophobic rings. Thus, polyrotaxanes containing these macrocyles are expected to show different property changes as compared to the polyrotaxanes containing crown ethers. Also, due to their symmmetic structures, they were expected to crystallize easily. These particular macrocycles are expected to have no specific attractive forces with polar monomers so that we may be able to isolate the threading effects from other effects due to chain−cyclic interactions such as hydrogen bonding and dipole−dipole forces.

The names **M40** and **M44** for the macrocycles are assigned arbitrarily based on the numbers of atoms in the rings.



M40



M44

Experimental Section

Measurements. Melting points were taken in capillary tubes with a Melt-Temp II melting point apparatus and corrected. IR spectra were obtained on a Nicolet MX-1 or Perkin-Elmer 283B infrared spectrophotometer using KBr pellets unless otherwise noted and reported in cm^{-1}. NMR spectra were obtained on a Varian Unity 400 MHz spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C) at ambient temperature using tetramethylsilane as an internal standard. Elemental analyses were done by Supersun Technology Analytical Laboratory, Stony Brook, NY. FAB mass spectra were obtained from the Washington University Resource for Biomedical and Bioorganic Mass Spectrometry, St. Louis, MO. For the HPLC analyses, an ISCO model 2350 HPLC instrument was used. The column used was a Novapak-C_{18}, and the eluent was a mixture of tetrahydrofuran and water (65:35 by vol). The flow rate was 2 mL/min, and a refractive index detector (Waters, differential refractometer R401) was used. GPC analysis was performed at 20 °C in THF using a Waters system with a refractive index detector calibrated with PS standards.

***p*-Bis[(4-(*p*′-hydroxyphenoxy)butyl)oxy]benzene (2).** A mixture of hydroquinone (86.9 g, 790 mmol), K_2CO_3 (120 g, 870 mmol), and ethanol (350 mL) was refluxed for 1 h. THF (200 mL) was added to the mixture, and *p*-bis[(4-bromobutyl)-oxy]benzene[3] (**1**) (10.0 g, 260 mmol) in THF (80 mL) was added dropwise over 40 min. The mixture was refluxed for 13 h and poured into water (8 L total). The off-white precipitate was filtered and washed with water (1.5 L). The solid was dispersed in a DMAc/DMF (200 mL, 1/1, v/v) mixture, and it was acidified to pH 3−4 by addition of HCl. The suspension was poured into water (900 mL) again, and the precipitate was filtered off, washed with methanol, and dried. The precipitate was dissolved in hot DMF (300 mL) and filtered to remove some insoluble part. The residual solid was recrystallized from xylene to give 9.1 g (79% yield) of off-white powdery crystals. Mp: 208−210.5 °C. IR: 3360, 2901, 2780, 2840, 1488, 1456, 1434, 1358, 1304, 1302, 960, 798, 775, 690. ^1H NMR (DMSO-d_6): 1.81 (s, 8H, $CH_2CH_2CH_2CH_2$), 3.90 (t, J = 5.1 Hz, 4H, OCH_2), 3.94 (t, J = 5.1 Hz, 4H, OCH_2), 6.66 (d, J = 8.8 Hz, 4H, arom), 6.74 (d, J = 8.8 Hz, 4H, arom), 6.84 (s, 4H, arom), 8.89 (s, 2H, OH). ^{13}C NMR (DMSO-d_6): 25.45, 25.48, 67.45, 115.18, 115.26, 115.56, 150.99, 151.30, 152.48, 172.62 (theory 10, found 10). Anal. Calcd for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 70.93; H, 7.04.

***p*-Bis[(4-(*p*′-(benzyloxy)phenoxy)butyl)oxy]benzene (4).** NaH (0.65 g, 60% oil dispersed, 16 mmol) was washed with hexane (30 mL) and added slowly to a solution of *p*-(benzyloxy)-phenol[4] (**3**) (2.40 g, 12 mmol) in DMF (40 mL). The mixture contained lots of precipitate. After 5 min of stirring, *p*-bis[(4-bromobutyl)oxy]benzene[3] (**1**) (1.52 g, 4.0 mmol) was added all at once. The mixture was stirred at 85 °C for 20 h and poured into water (700 mL). The precipitate was filtered off, washed with water (100 mL), and dried. The precipitate (2.5 g, 100% yield) was dissolved in hot ethyl acetate (75 mL), and the solution was cooled to room temperature. The powdery crystals were filtered off and washed with ethyl acetate. Yield: 2.4 g (97% yield). Mp: 197.4−198.2 °C. IR: 3010, 2919, 2885, 2848, 1485, 1456, 1210, 998, 804, 713, 670. ^1H NMR ($CDCl_3$): 1.96 (s, 8H, $CH_2CH_2CH_2CH_2$), 3.98 (s, 8H, $OCH_2CH_2CH_2CH_2O$), 5.01 (s, 4H, $PhCH_2$), 6.72 (s, 4H, arom), 6.76 (d, J = 9.4 Hz, 4H, arom), 6.82 (d, J = 9.4 Hz, 4H, arom), 7.39 (m, 10H, arom). Anal. Calcd for $C_{40}H_{42}O_6$: C, 77.64; H, 6.84. Found: C, 77.34; H, 6.91.

Cyclotetrakis(oxytetramethyleneoxy-*p*-phenylene) (M40). In a 5-L flask equipped with a mechanical stirrer, a Dean-Stark trap, and a condenser, a mixture of DMAc (2 L), toluene (1.1 L), and K_2CO_3 (5.0 g, 36.2 mmol) was refluxed for 3 days. *p*-Bis[(4-bromobutyl)oxy]benzene[3] (**1**) (1.14 g, 3.00 mmol) and *p*-bis[(4-(*p*′-hydroxyphenoxy)butyl)oxy]benzene (**2**) (1.315 g, 3.00 mmol) were dissolved in hot DMAc (15 mL), and the solution was poured into the reaction mixture. Every 8 h an identical solution was added to the reaction mixture. The total amount of each precursor was 18.0 mmol. The reaction mixture was refluxed further for 5 days. Solvents were evaporated, and the residual solid was Soxhlet extracted with $CHCl_3$. $CHCl_3$ was evaporated, the residual solid (7 g) was dissolved in boiling ethyl acetate (200 mL), and the solution was filtered to remove some insoluble parts. The solution was allowed to stand at room temperature for a couple of days. The white granular crystals were collected and subjected to another recrystallization from ethyl acetate. The crystals were dried under vacuum at 80 °C to give 3.0 g of product (25% yield). Mp: 160.8−162.1 °C. IR: 2880, 2844, 1458, 1280, 1200, 1085, 1028, 1003, 957, 785, 762, 690. ^1H NMR ($CDCl_3$): 1.93 (p, J = 3.6 Hz, 16H, $CH_2CH_2CH_2CH_2$), 3.98 (t, J = 6.4 Hz, 16 H, OCH_2), 6.79 (s, 16H, arom). ^{13}C NMR ($CDCl_3$): 25.60, 67.83, 115.55, 152.95 (theory 4, found 4). High-resolution FAB MS: $[M + Na]^+$, m/z = 679.3274 (calcd m/z = 679.3247, deviation 4.0 ppm). NMR, HPLC, and MS traces are included in Supporting Information.

***m*-Bis[(6-bromohexyl)oxy]benzene (5).** A mixture of resorcinol (12.5 g, 114 mmol), K_2CO_3 (40.0 g, 290 mol), and ethanol (500 mL) was refluxed for 1 h. 1,6-Dibromohexane (500 g, 2.05 mol) was added to the mixture, and it was refluxed for 1.5 days. The mixture was cooled to room temperature, and the salts were filtered off and washed with diethyl ether (400 mL). After the solvents (ethanol and ether) and unreacted 1,6-dibromohexane were removed, a dark brown oil was obtained. The oil was subjected to column chromatography (silica gel) using ethyl acetate/hexane (1/20, v/v). The crude

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product was further purified by a flash column (silica gel) with hexane to give a colorless oil (24.1 g, 47% yield). IR: 2910, 2840, 1578, 1453, 1270, 1451, 1370, 1348, 1166, 1135, 1030, 815, 742, 668. ^{1}H NMR ($CDCl_3$): 1.50 (t, J = 3.6 Hz, 8H, $O(CH_2)_2CH_2CH_2(CH_2)_2Br$), 1.79 (p, J = 6.8 Hz, 4H, $O(CH_2)_4CH_2$-CH_2Br), 1.89 (p, J = 6.8 Hz, 4H, $OCH_2CH_2(CH_2)_4Br$), 3.42 (t, J = 6.8 Hz, 4H, $O(CH_2)_5CH_2Br$), 3.94 (t, J = 6.8 Hz, 4H, $OCH_2(CH_2)_5Br$), 6.47 (m, 3H, arom), 7.15 (t, J = 8.0 Hz, 1H, arom). ^{13}C NMR ($CDCl_3$): 25.32, 27.93, 29.09, 32.70, 33.80, 67.70, 101.47, 106.69, 129.81, 160.29 (theory 10, found 10). Anal. Calcd for $C_{18}H_{28}O_2Br_2$: C, 49.56; H, 6.47. Found: C, 49.54; H, 6.47.

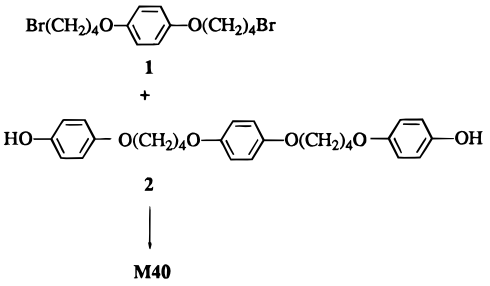
***m*-Bis[(6-(*m*-hydroxyphenoxy)hexyl)oxy]benzene (6).** A mixture of resorcinol (130 g, 1.18 mol), K_2CO_3 (163 g, 1.18 mol), and ethanol (350 mL) was refluxed for 30 min and cooled to room temperature. *m*-Bis[(6-bromohexyl)oxy]benzene (**5**) (15.0 g, 34 mmol) in THF (100 mL) was added dropwise over 50 min, and the solution was the heated at reflux for 28 h. The reaction mixture was poured into excess water (8 L total). The suspension containing precipitate was neutralized by addition of HCl. The precipitate was filtered off, washed with water to remove remaining resorcinol, and subjected to column chromatography (silica gel) with ethyl acetate/hexane (1/3, v/v), followed by recrystallizations from acetone and from acetone/ethyl acetate (1/2, vol). White clear crystals (13.5 g, 79%) were obtained. Mp: 103.4−105.9 °C. IR: 3432, 3332, 2899, 2825, 1570, 1447, 1270, 1135, 1034, 998, 827, 740, 663. ^{1}H NMR (DMSO-d_6): 1.43 (p, J = 3.6 Hz, 8H, $OCH_2CH_2CH_2CH_2CH_2$-CH_2O), 1.68 (broad p, J = 3.6 Hz, 8H, $OCH_2CH_2CH_2CH_2CH_2$-CH_2O), 3.86 (t, J = 6.4 Hz, 4H, OCH_2), 3.91 (t, J = 6.4 Hz, 4H, OCH_2), 6.3 (m, 6H, arom), 6.45 (m, 3H, arom), 7.00 (t, J = 8.0 Hz, 2H, arom), 7.11 (t, J = 8.0 Hz, 1H, arom), 9.31 (s, 2H, OH). ^{13}C NMR (DMSO-d_6): 25.78, 29.11, 67.54, 67.74, 101.47, 102.10, 105.54, 107.02, 108.09, 130.21, 130.29, 158.96, 160.33, 160.34 (theory 16, found 14). Anal. Calcd for $C_{30}H_{38}O_6$: C, 72.85; H, 7.74. Found: C, 72.66; H, 7.84.

Cyclotetrakis(oxyhexamethyleneoxy-*m*-phenylene) (M44). In a 5-L three-neck round-bottomed flask equipped with a mechanical stirrer and a condenser with a Dean-Stark trap and a N_2 bubbler, a mixture of DMAc (2 L) and toluene (1 L) was refluxed to remove water. K_2CO_3 (6 g, 43.4 mmol) was added, and the mixture was refluxed for several hours further. *m*-Bis[(6-bromohexyl)oxy]benzene (**5**) (7.40 g, 17 mmol) and *m*-bis[(6-(*m*-hydroxyphenoxy)hexyl)oxy]benzene (**6**) (8.40 mmol, 17 mmol) were dissolved in DMAc (75 mL). An aliquot (15 mL) of the solution was charged to the reaction mixture every 8 h (total addition was done over 32 h). After the reaction mixture had refluxed for 5 days, the salt was filtered off and the solvents were rotary evaporated. The residual solid was subjected to two recrystallizations from ethyl acetate, followed by column chromatography (silica gel, CH_2Cl_2) and recrystallization from ethyl acetate. A total of 4.8 g (37% yield) of white crystals was obtained. Mp: 118.0−120.0 °C. IR: 2898, 2827, 1567, 1436, 1366, 1270, 1244, 1154, 1120, 995, 803, 739, 662. ^{1}H NMR ($CDCl_3$): 1.53 (p, J = 3.6 Hz, 16H, $OCH_2CH_2CH_2CH_2CH_2CH_2O$), 1.80 (p, J = 6.4 Hz, 16H, $OCH_2CH_2CH_2CH_2CH_2CH_2O$], 3.94 (t, J = 6.4 Hz, 16H, $OCH_2CH_2CH_2CH_2CH_2CH_2O$], 6.45 (m, 12H, arom), 7.14 (t, J = 8.0 Hz, 4H, arom). ^{13}C NMR ($CDCl_3$): 25.76, 29.12, 67.71, 101.42, 106.73, 129.77, 160.30 (theory 7, found 7). High-resolution FAB MS: $[M + Na]^+$; m/z = 791.4504 (Calcd m/z = 791.4499, deviation 0.6 ppm). NMR, HPLC, and MS traces are included in Supporting Information.

Attempted Synthesis of Poly(styrene−rotaxa-M44). Into a 50-mL flask equipped with a Teflon valve and a magnetic stirring bar was placed styrene (0.25 g, 2.4 mmol), **M44** (1.0 g, 1.3 mmol), BG/init (**7**) (30 mg, 0.024 mmol), and toluene (1.0 g). The mixture was treated with two cycles of freeze−pump−thaw processes. The mixture was placed in a preheated oil bath and allowed to react for 3 days at 95 °C. The mixture was Soxhlet extracted with ethanol for 2 weeks. The remaining solid was dissolved in toluene (5 mL) and the solution poured into ethanol (100 mL) to form a suspension. The suspension was stirred for 2 h at 50−60 °C. During stirring the fine particles coagulated; the precipitate was filtered off. Another precipitation process was done, and the precipitate was dried under vacuum at room temperature. A total of 1.2 g (48% yield) of solid was obtained. According to the GPC, the number average molecular weight of the polymer was 18.3K and the polydispersity index was 2.26.

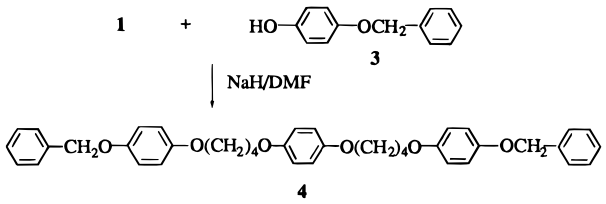
Results and Discussion

Cyclotetrakis(oxytetramethyleneoxy-*p*-phenylene) (M40). M40 was synthesized by a combination of the two precursors, *p*-bis[(4-bromobutyl)oxy]benzene (**1**) and *p*-bis[(4-(*p*-hydroxyphenoxy)butyl)oxy]benzene (**2**).



p-Bis[(4-bromobutyl)oxy]benzene (**1**) was synthesized (70%) by the reaction of hydroquinone and excess 1,4-dibromobutane in DMF with NaH as base.[3] Aternatively, compound **1** may be prepared using mild bases in alcoholic or mixtures of alcohols and THF or acetone solutions.[3,5]

p-Bis[(4-(*p*-hydroxyphenoxy)butyl)oxy]benzene (**2**), at first, was approached *via* protected precursor **4**, which was prepared by the reaction of **1** and *p*-(benzyloxy)-phenol (**3**). However, *p*-bis[(4-(*p*-(benzyloxy)phenoxy)-



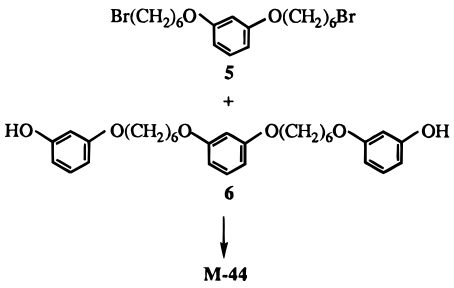
butyl)oxy]benzene (**4**) could not be deprotected with H_2/Pd/C due to its limited solubilities in most common solvents.

Therefore, the synthesis of **2** was achieved directly in 79% yield from the reaction of **1** and excess hydroquinone in K_2CO_3/ethanol/THF. It was only slightly soluble in toluene, THF, and chloroform even at elevated temperature.

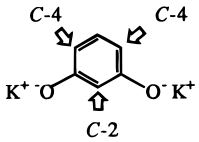
The synthesis of macrocycle **M40**, mp 160.8−162.1 °C, was accomplished by the reaction of precursors **1** and **2** in DMAc/toluene solution using K_2CO_3 as base under a high dilution condition in 25% yield. HPLC indicated that the sample contained some impurities (8%), probably linear oligomers. The structure of the macrocycle was confirmed by IR, NMR, and mass spectroscopies.

It was unexpected that **M40** showed very low solubilities in aromatic hydrocarbons (toluene, and benzene) or moderately polar solvents (THF and ethyl acetate). The best solvents were chlorinated hydrocarbons such as chloroform and methylene chloride, but they are not very good solvents either. The low solubility is probably due to the rigidity and the lack of polar functionalities; this is a major drawback for utilization as a cyclic component of polyrotaxanes. Therefore, in order to prepare a highly soluble macrocycle, we prepared **M44**, which contains resorcinol and hexamethylene units instead of hydroquinone and tetramethylene units, respectively.

Cyclotetrakis(oxyhexamethyleneoxy-*m*-phenylene) (M44). The desired macrocycle **M44** was synthesized by cyclization of precursors **5** and **6**.



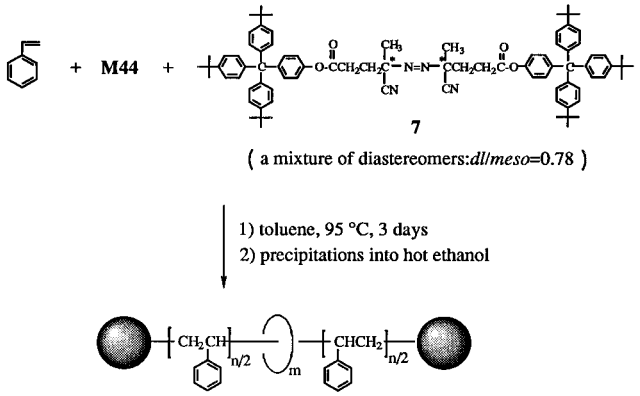
m-Bis[(6-bromohexyl)oxy]benzene (**5**) was obtained by the reaction of resorcinol with excess 1,6-dibromohexane in ethanol using NaOH or KOH as base. Compared to *p*-bis[(4-bromobutyl)oxy]benzene (**1**) the yield of **5** was lower (47% *vs* 70%) even though the reaction conditions were similar. One of the reasons is the great tendency of the resorcinol dianion for *C*-alkylation because two oxy anions are located *meta* to each other so that nucleophilic aromatic substitution reactions at the *C*-2 and *C*-4 positions take place easily.[6] Thus, the extent of the *O*-alkylation reaction which yields the desired product **5** decreases.



The second precursor, *m*-bis[(6-(*m*-hydroxyphenoxy)-hexyl)oxy]benzene (**6**), was prepared in 79% yield by the reaction of **5** with excess resorcinol in a mixture of THF and ethanol.

The synthesis of **M44** was carried out in DMAc/toluene (2/1, v/v) at reflux under high dilution conditions to afford a 37% yield of white crystals with a mp of 118.0−120.0 °C, which was 42 deg lower than that of **M40**, owing to the more flexible structure and the longer aliphatic segment. The purity and structure of the compound were proved by HPLC, IR, NMR, and mass spectroscopies. The macrocycle was very soluble in toluene, THF, and $CHCl_3$ and showed good solubility in acetone and ethyl acetate. Furthermore, it was found that **M44** formed good single crystals. Therefore, the properties of **M44** such as low melting point, good solubility, and well-defined crystal structure make the macrocycle a good candidate for a study on the properties of polyrotaxanes.

Attempted Synthesis of Poly(styrene−rotaxa-M44). The synthesis of poly(styrene−rotaxa-**M44**) was attempted by free radical polymerization of styrene in the presence of **M44**. The free radical initiator used was the blocking group/initiator (BG/init)[7] **7**, which can initiate polymerization of styrene as well as achieve blocking of the resultant polystyrene chain ends. Toluene was used as cosolvent to maintain a homogeneous reaction mixture. The ^1H NMR spectrum of the polymer in $CDCl_3$, however, indicated that there was no **M44** in the final product, i.e., $m/n = 0$. This result was suprising because, due to the relatively high compatibility between **M44** and polystyrene, it was anticipated that the reaction would afford a polyrotaxane. There might be a couple of reasons for the lack of threading. The cavity of the **M44** molecule was probably not open in the reaction mixture; instead, the molecule collapsed on itself to result in a closed cavity, which prevented the threading. Another reason would be the loss of the threaded macrocycles during the extraction and reprecipitation steps. The tris(*p*-*tert*-butylphenyl)methyl unit is known to constrain up to 42-membered rings[8] so that **M44** might slip over the blocking group to dethread. Indeed, a CPK model study indicated the macrocycle could slip over the blocking group. With **M44**, syntheses of polyrotaxanes using methacrylates and acrylates are in progess and will be reported in the near future.



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Supporting Information Available: Figures of NMR, HPLC, and MS (10 pages total). Ordering information is given on any current masthead page.

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