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Stepwise Synthesis of "Main-Chain" Liquid-Crystalline Macrocyclics Based on Conformationally Flexible Mesogens

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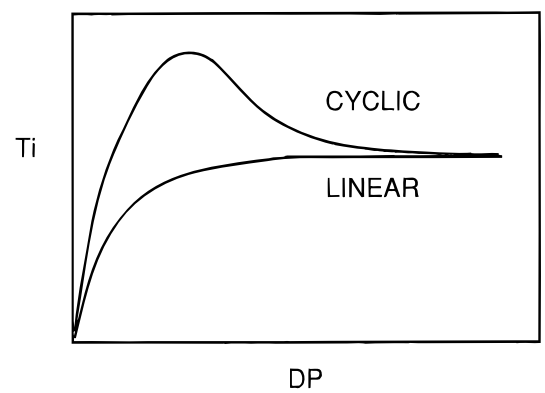
A stepwise synthesis of "main-chain" regioirregular liquid-crystalline macrocyclic oligoethers based on conformationally flexible mesogens and flexible spacers is described. This method was applied to the synthesis of the previously unreported cyclic trimer TPB′-(c)10-(3), tetramer TPB′-(c)10(4), and pentamer TPB′-(c)10(5), based on 1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)butane (TPB′) and 1,10-dibromodecane. The method consists of the stepwise synthesis of the bisphenolic linear trimer of TPB′ (**5**) and its phase-transfer-catalyzed etherification under high dilution with 1,10-dibromodecane to yield the cyclic trimer TPB′-(c)10(3). The biselectrophilic linear monomer **6** and dimer **7** were separated from a one step synthesis at high concentration, and their cyclization with the bisphenolic linear trimer **5** at high dilution yielded the macrocyclic tetramer TPB′-(c)10(4) and respectively pentamer TPB′-(c)10(5). The unoptimized separated yields are up to 45%, making this synthetic method extremely valuable for preparative purposes. The phase behavior of the macrocyclic liquid crystals based on TPB′ (i.e., TPB′-(c)10(z) with $z = 1-5$) was compared with that of the corresponding macrocyclics based on the constitutional isomer 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB) [i.e., TPB-(c)10(z) with $z = 1-5$] which were prepared by a one-step synthesis. Advantages and disadvantages of the stepwise versus one-step methods are discussed.

Introduction

In 1992 we have predicted and demonstrated that main-chain liquid-crystalline (LC) macrocyclics of a certain degree of oligomerization should display a higher ability to generate LC phases than their linear homologues with identical molecular weights and than the corresponding macrocylic and linear polymers with higher molecular weights.[1] This trend is outlined in Scheme 1 and demonstrates that cyclic and not linear is the most suitable architecture that generates liquid crystallinity. In the LC phase a macrocyclic of a suitable size exhibiting a minimum extent of ring strain and a proper combination of mesogenic and spacer lengths generates a collapsed quasi-rigid rod. These collapsed macrocyclics are more rigid than their corresponding linear structures, and, despite this, have a lower difference between their entropy in the LC and isotropic phases.[2] Recently, the higher rigidity of macrocyclic LC was demonstrated experimentally.[3]

The mesogenic unit based on conformational isomerism 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB)[4] was used in all our investigations. The anti conformer of TPB induces the LC phase while the gauche one favors the cyclization and the generation of the LC phase for the odd degrees of oligomerization of the macrocyclic. At the same time the conformational flexibility and the large number of constitutional and stereoisomers of TPB enhance the solubility of the resulting macrocyclics.

Scheme 1. Theoretical and Experimental Dependence of the Isotropization Temperature (T_i) of the Cyclic and Linear "Main Chain" Polymers on Their Degree of Polymerization (DP). Both T_i and DP Are in Arbitrary Units



A one-pot phase-transfer-catalyzed cyclization of TPB with α,ω-dibromoalkanes under high dilution conditions followed by separation by column chromatography yields up to five macrocyclics in quantities sufficient to perform only basic structural and thermal characterization experiments.[1]

Questions such as, what is the shortests spacer length and minimum ring size for which the macrocyclic

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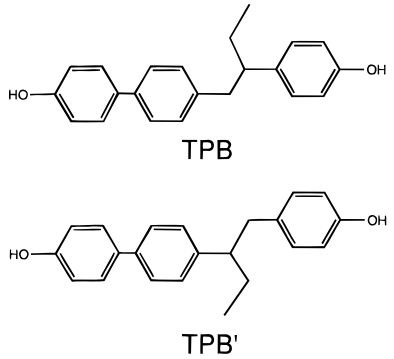
displays a LC phase?[5a] What is the lowest macrocyclic size that exhibits a LC phase with a higher isotropization temperature than that of its high molecular weight linear homologues?[5b,c] What is the probability of transforming virtual (i.e., kinetically prohibited)[5d] and/or kinetically controlled[5e] mesophases of the linear polymer into enantiotropic mesophases via cyclization? What is the ability to generate noncrystallizable macrocyclics with a high glass transition and a broad range of temperature of their mesophase?[5f] What is the difference between chiral and racemic macrocylics?[5g] What is the dependence of the transition temperatures of a certain macrocyclic size on its spacer length (*X*) and how does it compare to that of the corresponding linear polymers?[5h] were adresssed, answered, and explained. Uniaxial nematic,[1,5a−f,h] cholesteric,[5g] and biaxial nematic[6b] phases were observed in these macrocyclic LC. Some of these particularities were briefly reviewed,[7] and recently the investigation of macrocyclic LC received interest in other laboratories.[8,9]

The enhanced rigidity of these quasi-rigid rods accommodates a higher conformational entropy than that of the corresponding linear counterparts. As a consequence, macrocyclic LC generate more stable mesophases based on more soluble building blocks than the corresponding linear homologues. This new concept opens novel capabilities for the molecular design of LC with complex architecture based on extremely rigid-rod-like mesogens that previously were not synthetically accessible.

Elaboration of new molecular, macromolecular, and supramolecular architectures based on macrocyclic LC and a detailed investigation of the dynamics and of the physical properties of this novel class of LC compounds requires a preparative method that generates a higher yield of individual macrocyclics than the one step method.[1,5] The goal of this publication is to describe a stepwise preparative method for the synthesis of regioirregular macrocyclic trimer, tetramer, and pentamer based on 1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)butane (TPB′)[10] which is the constitutional isomer of TPB (Scheme 2) and 1,10-dibromodecane. The synthetic strategy elaborated for this method consists of the stepwise generation of the bisphenolic and biselectrophilic linear oligomers of TPB′ followed by their phase-transfer-catalyzed cyclization under high dilution conditions with a biselectrophilic and respectively bis-

Scheme 2. Structures of the Constitutional Isomeric TPB and TPB′



nucleophilic monomer or linear oligomer. The phase behavior of the two series of regioirregular constitutional isomeric macrocyclics TPB′-(c)X(*z*) and TPB-(c)X-(*z*) (where c stands for cyclic, *X* represents the number of methylenic groups in the spacer, i.e., 10, and *z* is the degree of oligomerization of the macrocyclic) will be discused.

Experimental Section

Materials. Tetrabutylammonium hydrogen sulfate (TBAH, 97%, Aldrich), palladium (5% on carbon, Lancaster), and benzyl bromide (98%, Fluka) were used as received. 1,10-Dibromodecane and *o*-dichlorobenzene (*o*-DCB, both from Aldrich) were purified by vacuum distillation. All other chemicals were commercially available and were used as received.

Techniques. A 200 MHz Varian Gemini 200 spectrometer was used to record the ^{1}H NMR spectra at 20 °C. TMS was used as internal standard. Relative molecular weights and purities were determined on a Perkin-Elmer Series 10LC GPC/HPLC instrument, equipped with a LC-100 column oven, a Nelson Analytical 900 Series data station, and a UV detector. The measurements were done using THF as solvent (1 mL/min, 40 °C) and two PL gel columns of 5×10^2 and 10^4 Å. A calibration plot constructed with polystyrene standards was used for the determination of the relative molecular weights. A Perkin-Elmer PC Series DSC-7 differential scanning calorimeter equipped with a TAC7/DX thermal analysis controller was used to record the first-order thermal transitions which were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transitions were measured at the middle point of the change in heat capacity. The instrument was calibrated with In and Zn standards. Scanning rates were 20 °C/min in all cases. All heating and cooling scans were perfectly reproducible after the first heating scan.The first heating scan could be reobtained after proper annealing. An Olympus BX40 optical polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to analyze the anisotropic textures.

Synthesis of 1-(4-Hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)butane (TPB′) and of 1-(4-Hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB). TPB′[10] (purity >99%, HPLC) and TPB[4] (purity >99%, HPLC) were synthesized as previously described.

Synthesis of a Mixture Containing 75% 1-(4-Hydroxyphenyl)-2-(4-benzyloxy-4′-biphenylyl)butane (2) and 25% 1-(4-Benzyloxyphenyl)-2-(4-hydroxy-4′-biphenylyl)butane (2′). To a refluxing solution of CH_3OH (50 mL), water (10 mL), NaOH (1.25 g, 31 mmol), and TPB′ (10 g, 31 mmol) was added $C_6H_5CH_2Br$ (5.37 g, 31 mmol) dropwise under stirring. After 10 h, CH_3OH was evaporated; the reaction mixture was diluted with NaOH (10%, 200 mL) and extracted with Et_2O (four times, 200 mL). The organic layer which contained a mixture of diprotected and monoprotected TPB′ was washed with water, dilute HCl, and water and dried over $MgSO_4$. The solvent was evaporated and the mixture of **2** and

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2′ was separated by column chromatography (neutral Al_2O_3, $CHCl_3$) from the diprotected TPB′, which eluted first. Recrystallization from hexane/ethyl acetate (5/1 v/v) afforded 3.4 g (25%) of white crystals, mp = 125−129 °C, purity (HPLC) >99%. The ratio **2**/**2′** determined from the integration of the $C_6H_5-CH_2-O-$ singlets was 3/1 (75% protected on the biphenyl side and 25% protected on the monophenyl side). ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 0.8 (t, 3H, CH_2CH_3, J = 7.3 Hz), 1.7 (m, 2H, CH_3CH_2-), 2.7 (m, 1H, $-CH(Et)CH_2-$), 2.84 (d, 2H, $-CH(CH_2CH_3)CH_2$, J = 7.5 Hz), 4.54 (s, 1H, $HO-$ on the monophenyl ring 75%), 4.75 (s, 1H, HO on the biphenyl ring 25%), 5.04 (s, 2H, $C_6H_5CH_2OC_6H_4C_6H_4-$ 25%), 5.13 (s, 2H, $C_6H_5CH_2C_6H_4CH_2-$, 75%), 6.68 (d, 2H, ortho to the OH on the monophenyl ring, J = 8.5 Hz), 6.83 (d, 2H, ortho to the benzyloxy of the monophenyl ring, J = 8.5 Hz), 6.92 (d, 2H, meta to the hydroxy of the monophenyl ring, J = 8.5 Hz), 7.04 (d, 2H, ortho to the benzyloxy of the biphenyl ring, J = 8.6 Hz), 7.14 (d, 2H, ortho to $-CH(Et)CH_2-$ on the biphenyl ring, J = 8.14 Hz), 7.44 (m, 9H; 2H, meta to the benzyloxy on the biphenyl, 2H, meta to $-CH(Et)CH_2-$ on the biphenyl and 5H of the benzyl group).

Synthesis of a Mixture Containing 75% 1-(4-(Bromodecyloxy)phenyl)-2-(4-benzyloxy-4′-biphenylyl)butane (3) and 25% 1-(4-Benzyloxyphenyl)-2-(4-(Bromodecyloxy)-4′-biphenylyl)butane (3′). A mixture of **2** and **2′** (1.93 g, 4.73 mmol), 1,10-dibromodecane (4.25 g, 14 mmol), K_2CO_3 (3.3 g, 24 mmol), and EtOH (20 mL) was stirred at reflux for 4 h, then was poured into water, and washed with dilute HCl and water again. After precipitation from $CHCl_3$ into CH_3OH the solid was recrystallized from hexane/ethyl acetate (8/1 v/v) to yield 2.35 g (80%) of white crystals, mp = 83−86 °C, purity (HPLC) 98.9%. The ratio **3**/**3′** was 3:1 (75% protected on the biphenyl side, 25% protected on the monophenyl side). ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 0.78 (t, 3H, $-CH_3$, J = 7.3 Hz), 1.3 (m, 12 H, $-OCH_2CH_2(CH_2)_6CH_2CH_2Br$), 1.78 (m, 6H; 2H, $-CH(Et)CH_2-$, 2H, $-OCH_2CH_2-$, 2H, $BrCH_2CH_2-$), 2.7 (m, 1H, $-CH(Et)-$), 2.84 (d, 2H, $-CH(Et)CH_2-$, J = 6.96 Hz), 3.41 (t, 2H, $-CH_2Br$, J = 6.76 Hz), 3.89 (t, 2H, $-CH_2C_6H_4-OCH_2(CH_2)_9Br$, J = 6.5 Hz), 3.96 (t, 2H, $-C_6H_4C_6H_4OCH_2(CH_2)_9-Br$, J = 6.2 Hz), 5.01 (s, 2H, $-CH_2C_6H_4OCH_2C_6H_5$, 25%), 5.11 (s, 2H, $-C_6H_4C_6H_4OCH_2C_6H_5$, 75%), 6.74 (d, 2H, ortho to $O(CH_2)_{10}Br$, J = 8.52 Hz), 6.83 (d, 2H, ortho to the benzyloxy on the monophenyl, J = 8.5 Hz), 6.95 (d, 2H, ortho to $-CH(Et)CH_2-$ on the monophenyl, J = 8.5 Hz) 7.04 (d, 2H, ortho to the benzyloxy on the biphenyl J = 8.7 Hz), 7.15 (d, 2H, ortho to $-CH(Et)CH_2-$ on the biphenyl, J = 8.1 Hz), 7.44 (m, 9H; 2H, meta to the benzyloxy on the biphenyl, 2H, meta to $-CH(Et)CH_2-$ on the biphenyl and 5H of the benzyl group).

Synthesis of 1-[4-(Oxadecamethyleneoxy)(4-(2-ethyl-2-(benzyloxybiphenyl)ethyl)phenyl)phenyl]-2-[4′-(oxadecamethyleneoxy)(2-ethyl-2-benzyloxybiphenyl)ethyl)-biphenylyl]butane (4). A mixture of **3** and **3′** (2.3 g, 3.66 mmol), **1** (0.58 g, 1.83 mmol), *o*-DCB (5 mL), NaOH (10 N, 5 mL) and TBAH (0.25 g, 0.73 mmol) was stirred under Ar at 80 °C for 2 h, then was acidified with dilute HCl, and washed with water. After precipitation from $CHCl_3$ into CH_3OH, the solid was recrystallized from toluene to yield 2.5 g (93%) of white crystals, purity (HPLC) 99%. Thermal transitions (DSC): first heating k 98 k 105 i, cooling i 75 n 22 g, second heating g 28 n 85 i. ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 0.78 (t, 9H, CH_3-, J = 7.3 Hz), 1.32 (m, 24H, $-O(CH_2)_2(CH_2)_6(CH_2)_2O-$), 1.74 (m, 14H; 6H, $-CH_2CH_3$, 8H, $-OCH_2CH_2(CH_2)_6CH_2-CH_2O-$), 2.7 (m, 3H, $-CH(Et)-$), 2.83 (d, 6H, $-CH(Et)CH_2-$, J = 6.9 Hz), 3.89 (t, 8H, $-CH_2C_6H_4OCH_2(CH_2)_8CH_2OC_6H_4-CH_2-$, J = 6.5 Hz), 3.98 (t, 8H, $-C_6H_4C_6H_4OCH_2(CH_2)_8CH_2-OC_6H_4C_6H_4-$, J = 6.4 Hz), 5.01 (s, 4H, $C_6H_5CH_2OC_6H_4CH_2-$), 5.10 (s, 4H, $C_6H_5CH_2OC_6H_4C_6H_4-$), 6.75 (d, 6H, ortho to $-O(CH_2)_{10}-$ on the monophenyl ring, J = 8.5 Hz), 6.83 (d, 6H, ortho to the benzyloxy on the monophenyl ring J = 8 Hz), 6.95 (d, 6H, meta to $-O(CH_2)_{10}O-$ on the monophenyl ring, J = 8.3 Hz), 7.03 (d, 6H, ortho to the benzyloxy on the biphenyl, J = 8.7 Hz), 7.14 (d, 6H, ortho to $-CH(Et)-$ on the biphenyl, J = 8.14 Hz), 7.4 (m, 22H; 6H, meta to the benzyloxy on the biphenyl, 6H, meta to $-CH(Et)-$ on the biphenyl and 10H of the two benzyl groups).

Synthesis of 1-[4-(Oxadecamethyleneoxy)(4-(2-ethyl-2-(4′-hydroxybiphenyl)ethyl)phenyl)phenyl]-2-[4′-(oxadecamethyleneoxy)(2-ethyl-2-(4′-hydroxybiphenyl)ethyl)-biphenylyl]butane (5). A mixture of **4** (2.5 g, 1.84 mmol), Pd/C (0.25 g), and CH_3COOH (25 mL) was repeatedly vacuumed and flushed with H_2 then was stirred under a H_2 atmosphere at 60 °C for 10 h. The solution was filtered and the solvent was evaporated to yield an oil which crystallized on standing. The solid was washed with MeOH to afford 1.78 g (84%) of white crystals. Purity (HPLC) >99%. Thermal transitions (DSC): first heating k 54 k 132 i, cooling i 42 n 36 g, second heating g 43 n 57 i. ^{1}H NMR ($CDCL_3$, TMS, δ, ppm) 0.78 (t, 9H, $-CH_3$, J = 6.96 Hz), 1.32 (m, 24H, $-O(CH_2)_2(CH_2)_6(CH_2)_2O-$), 1.74 (m, 14H; 6H, $-CH_2CH_3$, 8H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 2.7 (m, 3H, $-CH(Et)-$), 2.84 (d, 6H, $-CH_2CH_3$, J = 6.9 Hz), 3.89 (t, 8H, $-CH_2C_6H_4OCH_2(CH_2)_8CH_2OC_6H_4CH_2-$, J = 6.4 Hz, 80%), 3.98 (t, 8H, $-C_6H_4C_6H_4-OCH_2(CH_2)_8CH_2OC_6H_4C_6H_4-$, J = 6.4 Hz, 20%), 4.54 (s, 1H, $CH_2C_6H_4OH$, 20%), 4.76 (s, 1H, $-C_6H_4C_6H_4OH$ 80%), 6.68 (d, 4H, ortho to the OH on the monophenyl ring, J = 8 Hz), 6.74 (d, 6H, ortho to $-O(CH_2)_{10}O-$ on the monophenyl ring, J = 8.06 Hz), 6.88 (d, 4H, ortho to the OH on the biphenyl, J = 8.42 Hz), 6.95 (d, 6H, ortho to $-CH(Et)-$ on the biphenyl, J = 7.8 Hz), 7.44 (d, 6H, meta to $-CH(Et)-$ on the biphenyl, J = 8 Hz), 7.5 (d, 6H, meta to $-OH$ on the biphenyl, J = 8.3 Hz).

Synthesis of 1-(4-Bromodecanoxyphenyl)-2-(4-bromodecanoxy-4′-biphenylyl)butane (6). A mixture of **1** (3.18 g, 10 mmol), 1,10-dibromodecane (12 g, 40 mmol), TBAH (0.5 g, 1.5 mmol), NaOH (80 mL, 10 N), and *o*-DCB (80 mL) was stirred at 80 °C under Ar for 12 h. The organic layer was washed with water, dilute HCl, and water. *o*-DCB was distilled, and the product was precipitated from $CHCl_3$ into CH_3OH to give a white solid that consisted of **6** (57%), **7** (30%), **8** (9%), and higher oligomers (4%). Separation by column chromatography (SiO_2, acetone/hexane = 1/15) afforded 3.2 g (42%) of **6** as the first fraction, purity (HPLC) >99%, mp = 57−60 °C. ^{1}H NMR (δ, ppm, $CDCl_3$, TMS) 0.79 (t, 3H, CH_2CH_3, J = 7.3 Hz), 1.32 (m, 24H, $-O(CH_2)_2(CH_2)_6(CH_2)_2-Br$), 1.82 (m, 10H, 2H, $-CH(CH_2CH_3)-$, 4H, $-OCH_2CH_2-$, 4H, $BrCH_2CH_2-$), 2.69 (m, 1H, $-CH(Et)-$), 2.84 (d, 2H, $-CH(Et)-CH_2-$, J = 6.9 Hz), 3.41 (t, 4H, $-CH_2Br$, J = 6.6 Hz), 3.9 (t, 2H, $-OCH_2-$ on the monophenyl side, J = 6.3 Hz), 3.99 (t, 2H, $-OCH_2-$ on the biphenyl side, J = 6.3 Hz), 6.74 (d, 2H, ortho to $-OCH_2-$ on the monophenyl ring, J = 8.4 Hz), 6.94 (d, 2H meta to $-OCH_2-$ on the monophenyl ring, J = 8.7 Hz), 6.96 (d, 2H, ortho to $-OCH_2-$ on the biphenyl ring, J = 8.6 Hz), 7.14 (d, 2H, ortho to $-CH(Et)-$ on the biphenyl, J = 8.1 Hz), 7.45 (d, 2H, meta to $-CH(Et)-$ on the biphenyl, J = 8.1 Hz), 7.51 (d, 2H, meta to $-OCH_2-$ on the biphenyl, J = 8.66 Hz).

Synthesis of 1,10-Bis(4-(2-ethyl-2-(4-(bromodecyloxy)-4′-biphenylyl)ethyl)phenyl)decane (7). Under the same conditions as in the synthesis of **6**, 1.5 g (12%) of **7** was obtained as the second fraction, purity (HPLC) >99%. Thermal transitions (DSC): first heating: k 72 i, cooling 46 n −14 g, second heating g −8 k 39 k 63 k 75 i. ^{1}H NMR (δ, ppm, $CDCl_3$, TMS) 0.79 (t, 3H, $-CH_3$), 1.32 (m, 36H; 24H, $BrCH_2-CH_2(CH_2)_6CH_2CH_2O-$, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 1.81 (m, 16H; 4H, $-CH(CH_2CH_3)-$, 8H, $BrCH_2CH_2(CH_2)_6CH_2CH_2O-$, 4H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 2.7 (m, 2H, $-CH(Et)-$), 2.87 (d, 4H, $-CH(Et)CH_2-$, J = 6.96 Hz), 3.41 (t, 4H, $-CH_2Br$, J = 6.6 Hz), 3.9 (t, 4H, $-CH_2C_6H_4OCH_2-$, J = 6.32 Hz), 3.99 (t, 4H, $-C_6H_4C_6H_4OCH_2-$, J = 6.32 Hz), 6.75 (d, 4H, ortho to $-OCH_2-$ on the monophenyl ring, J = 8.5 Hz), 6.94 (d, 4H, meta to $-OCH_2-$ on the monophenyl ring, J = 8.6 Hz), 6.96 (d, 4H, ortho to $-OCH_2-$ on the biphenyl, J = 8.6 Hz), 7.14 (d, 4H, ortho to $-CH(Et)-$ on the biphenyl, J = 8.05 Hz), 7.45 (d, 4H, meta to $-CH(Et)-$ on the biphenyl, J = 8.06 Hz), 7.51 (d, 4H, meta to $-OCH_2-$ on the biphenyl, J = 8.6 Hz).

Synthesis of 1-[4-(Oxadecamethyleneoxy)(4-(2-ethyl-2-(4′-(bromodecyloxyoxy)biphenyl)ethyl)phenyl)phenyl]-2-[4′-(oxadecamethyleneoxy)(2-ethyl-2-(4′-(bromodecyloxy)biphenyl)ethyl)biphenylyl]butane (8). Under the same conditions as in the synthesis of **6**, 0.5 g (3%) of **8** was obtained as the third fraction, purity (HPLC) >99%. Thermal

Table 1. Characterization of TPB-(c)10(*z*) and TPB′-(c)10(*z*) Synthesized by One-Step and Respectively Stepwise Methods (Data for the Corresponding TPB-(l)10 and TPB′-(l)10 Also Included)

macrocycle	separated yield (%)	purity (HPLC) (%)	mol wt (GPC) measd	mol wt (GPC) calcd	thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses: second heating	first cooling
TPB′-(c)10(1)[a]	7.80	98	550	456	i	i
TPB -(c)10(1)[a]	6.40	98	565	456	i	i
TPB′-(c)10(2)[a]	4.50	98.8	1116	912	g 18 k 64 (-3.67) k 113 (3.94) i	i 12 g
TPB -(c)10(2)[a]	4.10	99	1110	912	k 132 (2.5) k 140 (0.7) i	i 84 (1.41) k
TPB′-(c)10(3)[b]	45.5	99	1928	1368	g 33 s_A 64 (0.12) n 80 (0.28) i	i 75 (0.28) n 57 (0.12) s_A 27 g
TPB -(c)10(3)[a]	2.90	97.2	1890	1368	g 30 s_A 56 (0.09) n 93 (0.28) i	i 87 (0.28) n 52 (0.08) s_A 23 g
TPB′-(c)10(4)[b]	10.8	98.7	2692	1824	g 31 n 123 (1.28) i	i 117 (1.25) n 23 g
TPB -(c)10(4)[a]	1.70	97.3	2560	1824	g 30 n 129 (1.25) i	i 122 (1.21) n 23 g
TPB'-(c)10(5)[b]	5.10	98.5	3450	2280	g 31 n 122 (1.27) i	i 113 (1.23) n 25 g
TPB -(c)10(5)[a]	0.90	95.8	3410	2280	g 31 n 120 (1.26) i	i 114 (1.23) n 25 g
TPB′-(l)10	93.8		4.8×10^4		g 42 n 118 (3.48) i	i 101 (3.24) n 33 g
TPB -(l)10	97.5		3.7×10^4		g 44 n 112 (2.72) i	i 93 (2.65) n 33 g

[a] Synthesized by the one step method. [b] Synthesized by the stepwise method.

transitions (DSC) first heating: g 6 k 37 n 68 i, cooling: i 59 n −5 g, second heating: g 5 n 68 i. ^{1}H NMR (δ, ppm, $CDCl_3$, TMS) 0.79 (t, 9H, $-CH_3$, J = 7.12 Hz), 1.33 (m, 48H; 24H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$, 24H, $BrCH_2CH_2(CH_2)_6CH_2CH_2O-$), 1.77 (m, 22H; 6H, $-CH(CH_2CH_3)-$, 4H, $BrCH_2CH_2-$, 12H, $-OCH_2CH_2-$), 2.7 (m, 3H, $-CH(Et)-$), 2.84 (d, 6H, $-CH(Et)CH_2-$, J = 6.96 Hz), 3.41 (t, 4H, $BrCH_2-$, J = 6.88 Hz), 3.9 (t, 6H, $-CH_2C_6H_4OCH_2-$, J = 6.52 Hz), 3.99 (t, 6H, $-C_6H_4C_6H_4OCH_2-$, J = 6.58 Hz), 6.75 (d, 6H, ortho to $-OCH_2-$ on the monophenyl, J = 8.42 Hz), 6.94 (d, 6H, meta to $-OCH_2-$ on the monophenyl, J = 8.6 Hz), 6.97 (d, 6H, ortho to $-OCH_2-$ on the biphenyl, J = 8.6 Hz), 7.15 (d, 6H, ortho to $-CH(Et)-$ on the biphenyl, J = 8.14 Hz), 7.46 (d, 6H, meta to $-CH(Et)-$ on the biphenyl, J = 8.14 Hz), 7.52 (d, 6H, meta to $-OCH_2-$ on the biphenyl, J = 8.7 Hz).

Synthesis of 1,12,33,44,65,76-Hexaoxa(25,57,84-triethyl)-[12.0.2.12.0.2.12.2.0.]paracyclophane (9) and 1,12,32,44,-65,76-Hexaoxa(25,57,89-triethyl)[12.0.2.12.0.2.12.0.2]-paracyclophane (9′). To a 5 L three-neck flask equipped with mechanical stirrer, reflux condenser, and Ar inlet−outlet were successively added **5** (0.8 g, 0.65 mmol), 1,10-dibromodecane (0.165 g, 0.65 mmol), TBAH (0.1 g, 0.3 mmol), *o*-DCB (3 L), and NaOH (10 N, 500 mL). The reaction mixture was stirred vigorously at 80 °C and monitored by HPLC. After 4 days the reaction mixture contained 75% trimer and 25% of larger cyclics. The organic phase was washed with water, dilute HCl, and then water and was dried over $MgSO_4$. The solvent was distilled, and the resulting solid was charged on a column packed with SiO_2 and was eluted as the first fraction with a 1/30 ethyl acetate/hexane mixture to afford 400 mg (45%) of white solid, purity (HPLC) >99%. Thermal transitions are reported in Table 1. ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 0.81 (t, 9H, $-CH_3$, J = 7.04 Hz), 1.32 (m, 36H, $-O(CH_2)_2(CH_2)_6(CH_2)_2O-$), 1.74 (m, 18H; 6H, $-CH_2CH_3$, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 2.68 (m, 3H, $-CH(Et)-$), 2.84 (m, 6H, $-CH(Et)CH_2-$), 3.88 (t, 6H, $-CH_2C_6H_4OCH_2-$, J = 6.2 Hz), 3.98 (t, 6H, $-C_6H_4C_6H_4OCH_2-$, J = 6.2 Hz), 6.7 (d, 6H, ortho to $-OCH_2-$ on the monophenyl ring, J = 8 Hz), 6.87 (d, 6H, meta to $-OCH_2-$ on the monophenyl ring, J = 8 Hz), 6.94 (d, 6H, ortho to $-OCH_2-$ on the biphenyl, J = 8.7 Hz), 7.09 (d, 6H, ortho to $-CH(Et)-$ on the biphenyl, J = 8 Hz), 7.42 (d, 6H, meta to $-CH(Et)-$ on the biphenyl, J = 8 Hz), 7.5 (d, 6H, meta to $-OCH_2-$ on the biphenyl, J = 8.5 Hz).

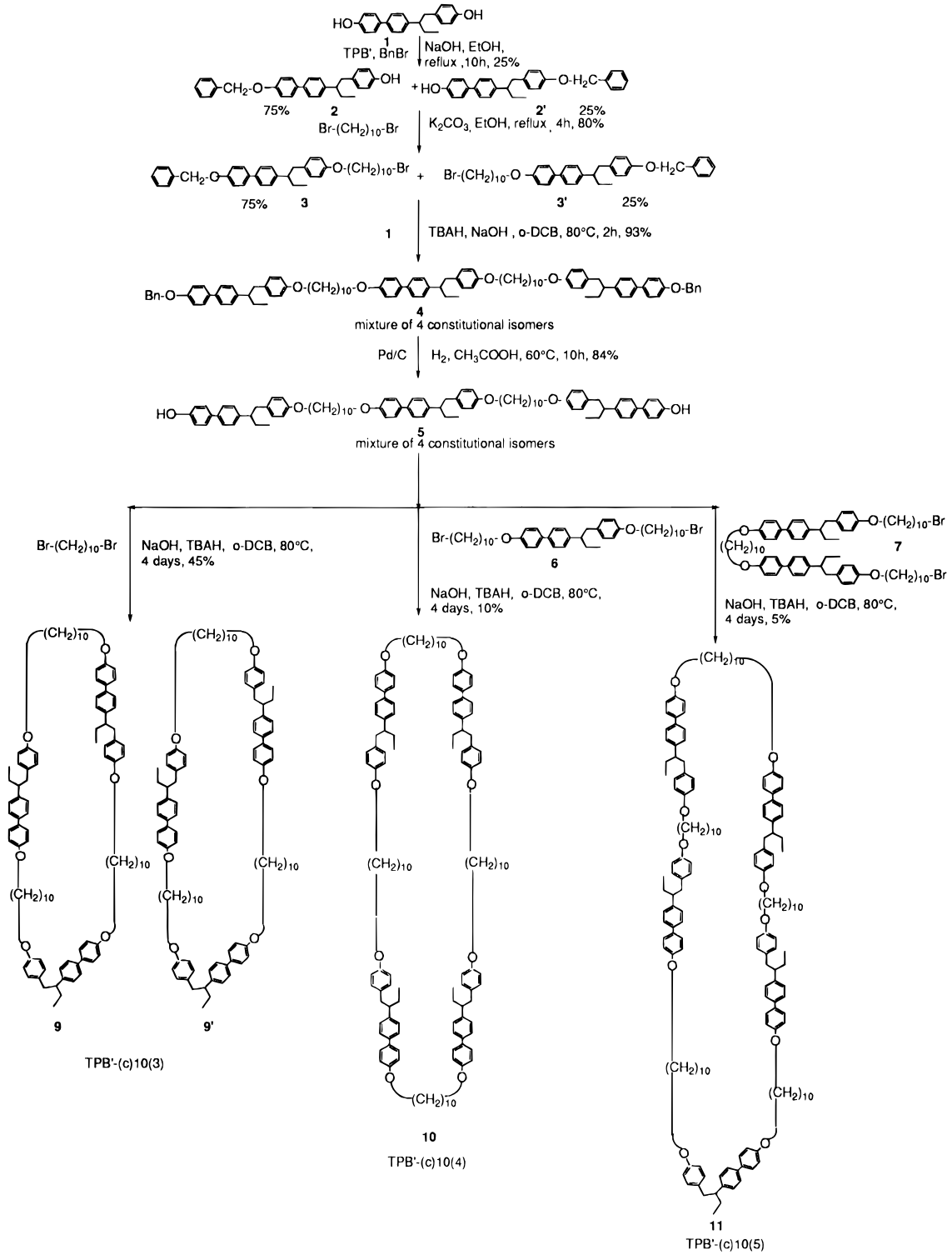
Synthesis of 1,12,33,44,65,76,97,108-Octaoxa(25,57,89,-121-tetraethyl)[12.0.2.12.0.2.12.0.2.12.0.2]paracyclophane (10) and of Its Constitutional Isomers. To a 5 L three-neck flask equipped with a mechanical stirrer were added **5** (0.2 g, 0.16 mmol), **6** (0.126 g, 0.16 mmol) TBAH (0.55 g, 0.16 mmol), *o*-DCB (3 L), and NaOH (10 N, 1.5 L), and the mixture was stirred vigorously at 80 °C. After 4 days the GPC conversion of the tetramer was 65%. The organic phase was washed with water, dilute HCl, and then water and was dried over $MgSO_4$. The solvent was distilled, and the product was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/20) to afford 32 mg (10.8%) of a white solid as the first fraction, purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 0.81 (t, 12, $-CH_3$, J = 7.24 Hz), 1.33 (m, 48H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 1.76 (m, 24H; 8H, $-CH(CH_2CH_3)-$, 16H, $-OCH_2CH_2-$), 2.72 (m, 4H, $-CH(Et)-$), 2.83 (m, 8H, $-CH(Et)CH_2-$), 3.89 (t, 8H, $-CH_2C_6H_4OCH_2-$, J = 6.4 Hz), 3.99 (t, 8H, $-C_6H_4C_6H_4OCH_2-$, J = 6.3 Hz), 6.73 (d, 8H, ortho to $-OCH_2-$ on the monophenyl, J = 8.3 Hz), 6.92 (d, 8H, meta to $-OCH_2-$ on the monophenyl, J = 8 Hz), 6.95 (d, 8H, ortho to $-OCH_2-$ on the biphenyl, J = 8.5 Hz), 7.12 (d, 8H, ortho to $-CH(Et)-$ on the biphenyl, J = 8.06 Hz), 7.44 (d, 8H, meta to $-CH(Et)-$ on the biphenyl, J = 8.06 Hz), 7.51 (d, 8H, meta to $-OCH_2-$ on the biphenyl, J = 8.7 Hz).

Synthesis of 1,12,33,44,65,76,97,108,129,140-Decaoxa-25,57,89,121,153-pentaethyl[12.0.2.12.0.2.12.0.2.12.0.2.12.0.2.]-paracyclophane (11) and of Its Constitutional Isomers. To a 5 L one-neck flask equipped with a mechanical stirrer were added **5** (0.2 g, 0.162 mmol), **7** (0.19 g, 0.162 mmol), TBAH (0.55 g, 0.16 mmol), *o*-DCB (3 L), NaOH (10 N, 1.5 L), and the reaction mixture was stirred vigorously at 80 °C under argon. After 4 days the GPC conversion of the pentamer was 35%. The organic layer was washed with water, dilute HCl, and then water and dried over $MgSO_4$, and the product was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/20) to afford 15 mg (5%) of a white solid as the first eluted fraction, purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H NMR (δ, ppm, $CDCl_3$, TMS) 0.81 (t, 15H, $-CH_3$, J = 7.06 Hz), 1.34 (m, 60H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 1.76 (m, 30H; 10H, $-CH_2CH_3$, 20H, $-OCH_2CH_2-$), 2.72 (m, 5H, $-CH(Et)-$), 2.84 (d, 10H, $-CH(Et)CH_2-$, J = 5.94 Hz), 3.89 (t, 10H, $-CH_2C_6H_4OCH_2-$, J = 6.3 Hz), 3.99 (t, 10H, $-C_6H_4C_6H_4OCH_2-$, J = 6.2 Hz), 6.73 (d, 10H, ortho to $-OCH_2-$ on the monophenyl, J = 8.06 Hz), 6.93 (d, 10H, meta to $-OCH_2-$ on the monophenyl, J = 8.02 Hz), 6.95 (d, 10H, ortho to $-OCH_2-$ on the biphenyl, J = 8.4 Hz), 7.12 (d, 10H, ortho to $-CH(Et)-$ on the biphenyl, J = 7.9 Hz), 7.44 (d, 10H, meta to $-CH(Et)-$ on the biphenyl, J = 7.9 Hz), 7.51 (d, 10H, meta to $-OCH_2-$ on the biphenyl, J = 8.5 Hz).

Results and Discussion

The synthetic strategy elaborated for the stepwise preparation of cyclic compounds was described briefly in the introduction. Scheme 3 outlines the synthetic procedure elaborated for the stepwise synthesis of TPB′-(c)10(3), TPB′-(c)10(4), and TPB′-(c)10(5). The synthesis of linear bisnucleophilic oligomers was carried out by a combination of protection of one nucleophile of TPB′ followed by a series of etherifications and deprotection reactions. In the first step TPB′ is monoalkylated with benzyl bromide to yield a mixture of the dibenzyl ether of TPB′ and the monobenzyl ethers **2** and **2′**. The dibenzyl ether of **1** was separated from the mixture of **2** and **2′** by column chromatography (Al_2O_3, $CHCl_3$).

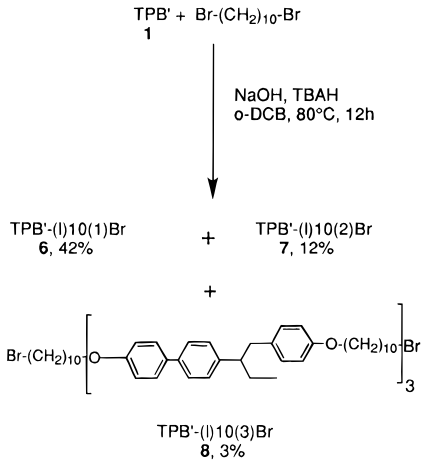
Scheme 3. Stepwise Synthesis of the Cyclic Trimer TPB′-(c)10(3), Tetramer TPB′-(c)10(4), and Pentamer TPB′-(c)10(c)



After recrystallization from hexane/ethyl acetate = 5/1 a mixture containing a 75/25 mole ratio of **2** and **2′** was obtained in 25% yield. Although pure **2** and **2′** could be separated by successive recrystallizations, their mixture was used in the next reaction step. Alkylation of the **2**/**2′** mixture with a three times excess of 1,10-dibromodecane yielded the mixture of **3** and **3′** in 80% yield after recrystallization from hexane/ethyl acetate (8/1 v/v). Phase-transfer-catalyzed etherification of TPB′ with 2 mol of the mixture **3**/**3′** produced **4** in 93% yield after recrystallization from toluene. **4** consists of a mixture of four constitutional isomers. The cleavage of the benzyl ether groups of **4** by hydrogenolysis with Pd/C in CH_3COOH (60 °C, 10 h) yielded **5** in 84% yield after recrystallization from methanol. **5** consists also of a mixture of four constitutional isomers.

The synthesis of the biselectrophilic linear oligomers was accomplished by a one-step phase-transfer-catalyzed reaction of TPB′ with 1,10-dibromoalkane followed by separation (Scheme 4). A mixture of compounds **6** (57%), **7** (30%), **8** (9%), and higher oligomers (4%, Scheme 4) was obtained by the phase-transfer-catalyzed

Scheme 4. One-Step Synthesis of the Linear Bromine Terminated Monomer [TPB′-(l)10(1)Br], Dimer [TPB′-(l)10(2)Br], and Trimer [TPB′-(l)10(3)Br]



eterification of TPB′ with 1,10-dibromodecane at a high total monomer concentration. Chromatographic separation (SiO_2, acetone/hexane = 1/15) afforded **6** in 42% yield, **7** in 12% yield, and **8** in 3% yield.

Phase-transfer-catalyzed etherification of **5** with 1,-10-dibromodecane performed under high dilution conditions yielded after 4 days a mixture containing 75% of TPB′-(c)10(3) (i.e., **9** and **9′**) and 25% of larger cyclics. To facilitate the separation of the cyclic trimer from the larger cyclics, the reaction should be carried out until the starting compound **5** is completely consumed. Separation by column chromatography (SiO_2, ethyl acetate/hexane = 1/30) yielded TPB′-(c)10(3) in 45% yield. Cyclization of **5** with **6** under identical reaction conditions with those used in the synthesis of TPB′-(c)10(3) yielded the cyclic tetramer TPB′-(c)10(4) (i.e., **10**) in 65% conversion. After separation by column chromatography (SiO_2, ethyl acetate = 1/20) 10.8% of pure tetramer **10** was obtained. The cyclic pentamer TPB′-(c)10(5) (**11**) was synthesized from **5** and **7** in 32% yield (5% separated yield). No attempts to optimize the isolated yields were made.

The macrocylics TPB-(c)10(*z*) with *z* = 1−5 were resynthesized as reported in a previous publication from our laboratory.[1] Their separated yields, purities, molecular weights, and phase transition temperatures are reported in Table 1 together with the corresponding data of TPB′-(c)10(*z*) prepared by the stepwise method. TPB′-(c)10(1) and TPB′-(c)10(2) reported in Table 1 were separated from the one-step cyclization of TPB′ with 1,-10-dibromodecane following the same procedure as that used for the synthesis and separation of TPB-(c)10(c).[1] TPB′-(c)10(3) could also be separated from the same synthesis using a combination of column and preparative thin layer chromatography, but in insufficient amount for quantitative characterization. However, TPB′-(c)10(4) could not be isolated from TPB′-(c)10(5). The first remarkable observation which comes from Table 1 is that the separated yields of the products prepared by the stepwise method are between 5 and 16 times higher than the yields of the compounds separated from the one step synthesis. This is despite the fact that the separated yields of stepwise procedure were not optimized. Therefore, the stepwise synthesis of these macrocyclics is of extreme preparative utility.

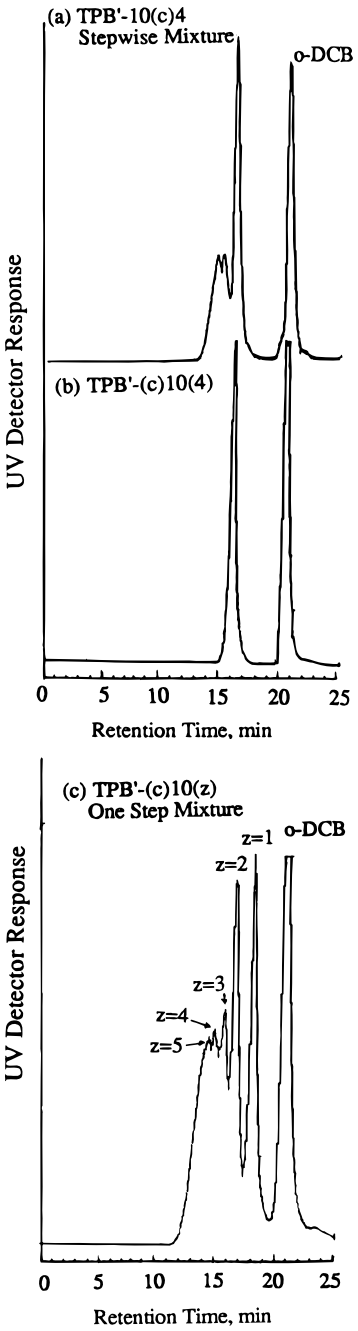


Figure 1. GPC chromatograms of the reaction mixture of the stepwise synthesis of TPB′-(c)10(4) (a), of the separated TPB′-(c)10(4) (b) and of the reaction mixture of the one step synthesis of TPB′-(c)10(*z*) (c).

Figure 1 presents the GPC traces of the reaction mixture of the stepwise synthesis of TPB′-(c)10(4), of the macrocyclic TPB′-(c)10(4) separated from the stepwise experiment and of the reaction mixture of the one pot synthesis of TPB′-(c)10(*z*). The comparison of the chromatograms of the reaction mixtures can easily explain the difficulties encountered in the separation process of the one step reaction mixture. Figure 2 plots the dependence of the theoretical and experimental molecular weights of TPB′-(c)10(*z*) and TPB-(c)10(*z*) as a function of the ring size, *z*. The experimental molecular weights of the two series of cyclics are identical (Table 1) and follow a linear dependence on *z*. This dependence, as expected, is different from the same dependence of their theoretical molecular weights. This effect is due to the different hydrodynamic volume of

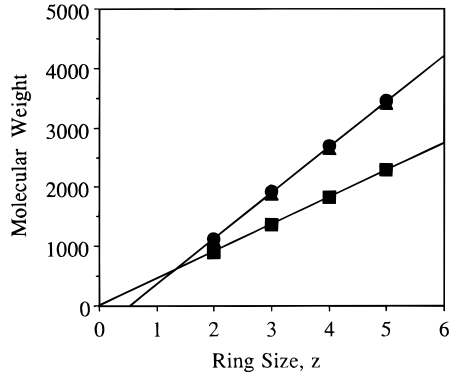


Figure 2. Dependence of the theoretical (Mn_{th}, ■) and experimental molecular weight determined by GPC (Mn_{exp}) for TPB-(c)10(z) (▲) and TPB′-(c)10(z) (●) versus ring size, z.

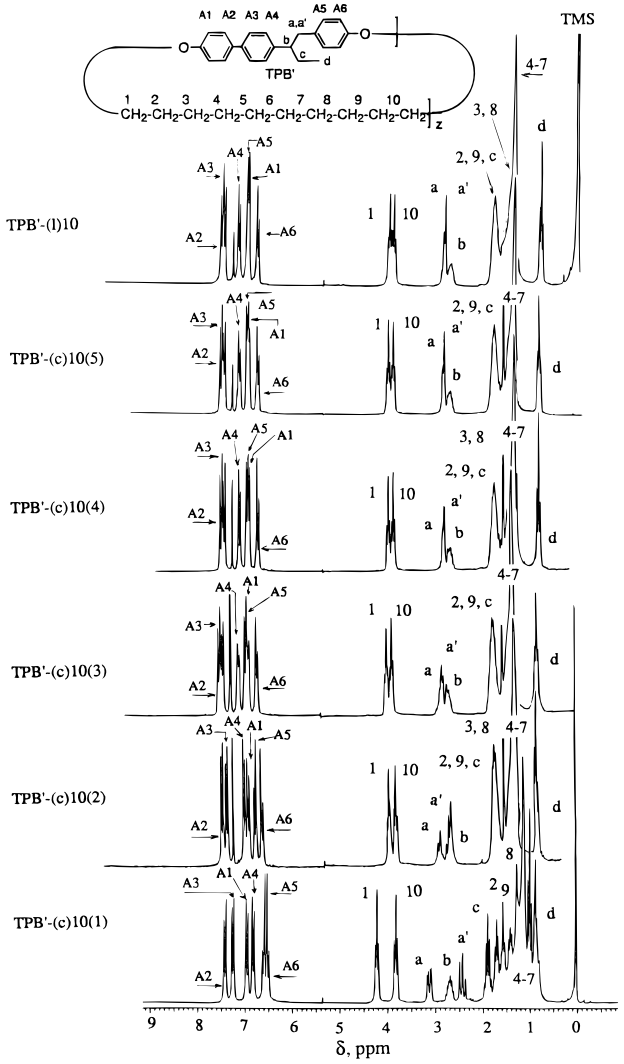


Figure 3. The 200 MHz ^{1}H NMR spectra ($CDCl_3$, TMS) of TPB′-(c)10(z) and TPB′-(l)10.

the macrocyclics and of the linear polystyrene standards. The experimental molecular weights of the macrocyclics are higher than the theoretical ones since the hydrodynamic volume of the cyclics is, as expected, smaller than that of the linear polystyrene. Nevertheless, the linear dependence from Figure 2 demonstrates the corect size (i.e., z values) of these cyclics compounds and can be used for an absolute calibration of the GPC.

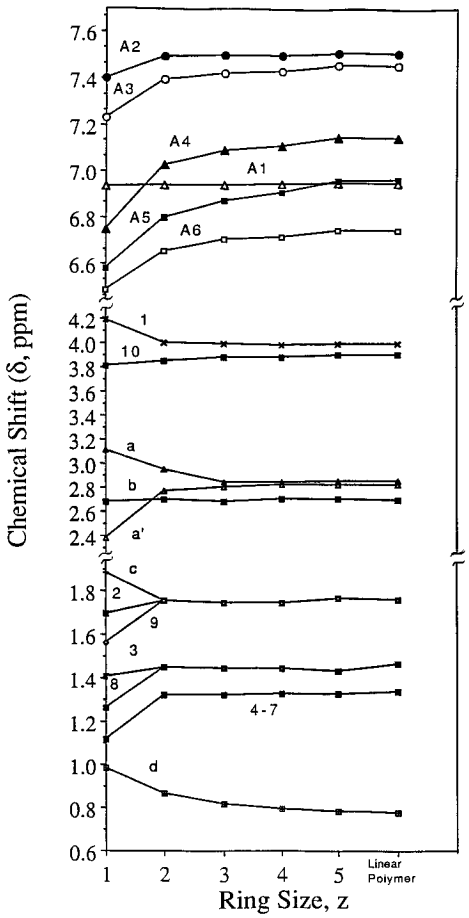


Figure 4. Dependence of the chemical shifts of the protonic resonances of TPB′-(c)10(z) on the ring size and their comparison with those of the linear polymer.

Figure 3 plots the 200 MHz ^{1}H NMR spectra of TPB′-(c)10(z) together with that of the corresponding linear polymer, TPB′-(l)10. The assignment of these spectra was made in an analogous way with that of the spectra of TPB-(c)10(z)[1] and confirms the cyclic structure of the TPB′-based cyclics. Two significant features of these spectra are used to ascertain the cyclic structure of TPB′-(c)10(z). First, the resonances of possible chain ends such as PhOH, $-CH_2OH$, $-CH_2Br$ or $-CH{=}CH_2$ are absent. Second, as shown in Figure 4, the ^{1}H NMR patterns are strongly dependent on the ring size, especially for small values of z. This behavior is not observed for linear oligomers and is due to the dependence of the conformation of the mesogen and of the spacer on ring size, which translates into shielding and deshielding effects. The ring strain of the cyclic monomer (TPB′-(c)10(1)) forces the mesogen into its gauche conformation and causes an upfield shift of the aromatic resonances. A similar effect was observed for the aliphatic resonances. With increasing ring size, as the ring strain alleviates, the population of the anti conformers increases at the expense of the gauche ones, so that the resonances of the cyclic pentamer (TPB′-(c)10(5)) closely resemble those of the linear polymer (TPB′-(l)10).

Figure 5 plots the heating and cooling DSC traces of TPB′-(c)10(z) and of TPB-(c)10(z) with z = 3, 4, and 5. TPB′-(c)10(2) and TPB-(c)10(2) only are crystalline, and their thermal transitions are reported in Table 1. As one can see from Figure 5, TPB-(c)10(4), TPB′-(c)10(4), TPB-(c)10(5), and TPB′-(c)10(5) exhibit an enantiotropic

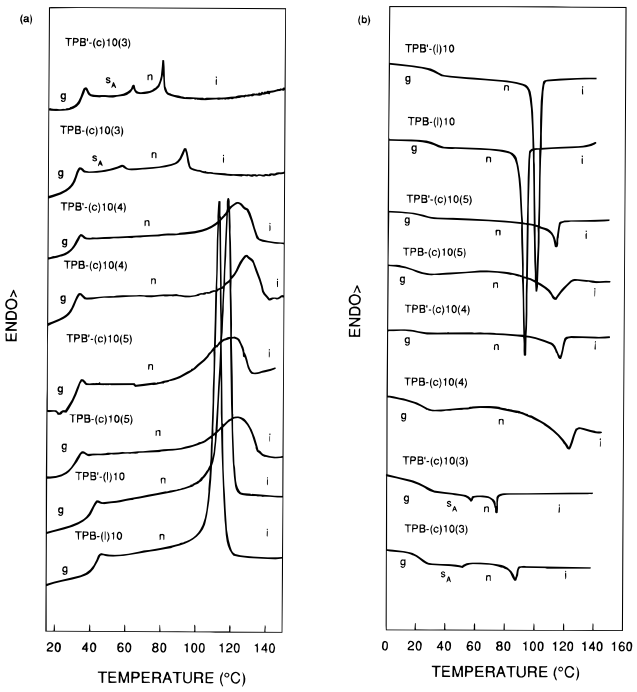


Figure 5. DSC traces of TPB′-(c)10(*z*), TPB-(c)10(*z*), TPB′-(l)10, and TPB-(l)10: (a) second heating scan, (b) first cooling scan.

nematic mesophase while TPB-(c)10(3) and TPB′-(c)10-(3) dispay both smectic A and nematic enantiotropic phases. Therefore, the phase behavior of both sets of macrocyclics is almost identical. The main difference is that the isotropization temperatures of the TPB-(c)-10(*z*) are higher than those of the TPB′-(c)10(*z*) series, regardless of the value of *z*. We have no explanation for this difference at the present time. The other interesting observation is that the isotropization peaks of the cyclic tetramer and pentamer are much broader than those of the corresponding linear polymers (Figure 5). This is due to the large number of constitutional isomeric cyclic compounds, which may have quite different isotropization temperatures, especially at small values of *z*. However, when *z* (i.e., the degree of polymerization) increases, all these constitutional isomers are part of the same cyclic and/or linear chain, and

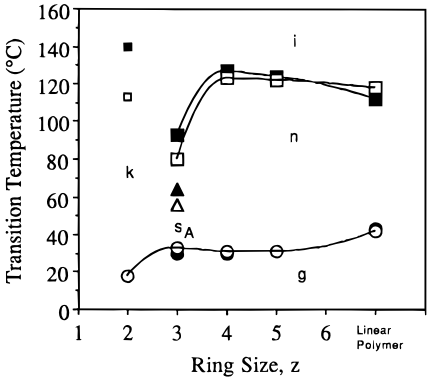


Figure 6. Dependence of the transition temperatures of TPB′-(c)10(*z*), TPB′-(l)10 (open symbols) and of TPB-(c)10(*z*), TPB-(l)10 (closed symbols) on ring size, (X). T_g, ○, ●; T_{s-n}, Δ, ▲; T_{n-i}, □, ■; T_{k-i}, □, ■.

therefore, on their DSC traces, the linear high molecular weight polymers exhibit very sharp transition peaks.

Finally, Figure 6 plots the transition temperatures of the cyclic and linear polymers based on TPB′ and TPB. In both cases, the cyclic tetramer and pentamer display a higher isotropization temperature than the corresponding linear polymer.

This new stepwise procedure is extremely inexpensive and does not require any difficult synthetic steps. Therefore, it is suitable for the preparation of conventional individual macrocyclics when they are required in large quantities. At the same time this method can be adapted to the synthesis of functional macrocyclics that are necessary for the preparation of more complex architectures based on macrocyclic LC building blocks. However, when separation is not generating special difficulties, the one-step method remains the method of choice for the fast synthesis of up to five separable macrocyclics. This is the case when the survey of a large variety of macrocyclic structures is required and only very small quantities of material are sufficient.

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