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Synthesis and Characterization of Poly[2]-catenanes Containing Rigid Catenane Segments

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ABSTRACT: The synthesis and the structure elucidation by ^1H NMR and IR spectroscopy, MALDI-TOF mass spectrometry, gel permeation chromatography, and viscometry of two novel poly[2]-catenanes, composed of rigid catenanes connected by semirigid spacers, are reported. The poly[2]-catenanes **4** and **5** differ by the geometry of the catenane units forming kinks between repeat units of angle $\beta \approx 60^\circ$ and 150° , respectively. The geometry of the catenane units governs the shape of the molecular weight distribution, the conformational behavior, and the thermal properties of poly[2]-catenanes **4** and **5**.

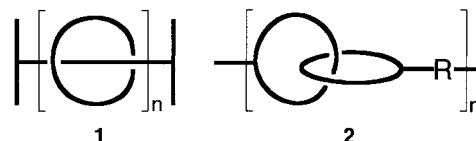
Introduction

Increasing interest has been shown in new types of macromolecular architectures containing topological bonds,¹ such as polyrotaxanes **1**² and poly[2]-catenanes **2**^{3–5} (Scheme 1). A topological bond is a noncovalent bond connecting two chemically independent subunits of a molecule which cannot be separated from each other without breaking a covalent bond; e.g., the two constitutive macrocycles of a catenane are connected by a topological bond.¹ The interest in polyrotaxanes and poly[2]-catenanes can be attributed, in part, to their aesthetic structures but also to the fundamental role played by topological constraints, i.e., entanglements, on polymer rheology,^{6a} mechanical properties of polymers,^{6b} elasticity of elastomeric networks,^{6c} surfaces and interfaces of polymers,^{6d} and interpenetrated polymer networks.^{6e} Although both polyrotaxanes **1** and poly[2]-catenanes **2** contain topological bonds, they differ fundamentally in their structure. Polyrotaxanes consist of linear macromolecules threading macrocycles; i.e., they do not contain topological bonds in the polymer main chain. In particular, the rupture of a single topological bond will not substantially affect the macromolecular structure of the polyrotaxane backbone. Conversely, poly[2]-catenanes are composed of alternating topological and covalent bonds in the polymer main chain; i.e., the repeat units are mechanically held together, and breaking one or several topological bonds will result in the rapid degradation of the polymer. From the structural differences between polyrotaxanes and poly[2]-catenanes, it is anticipated that their conformations, properties, and dynamics will significantly differ.

To date, numerous polyrotaxanes have been reported, whereas only a few examples of poly[2]-catenanes are known in the literature.^{3–5,7} A high molecular weight poly[2]-catenane **3a** and poly[2]-catenane **3b**, based on a highly mobile catenane containing very large macrocycles of 45 atoms, were synthesized by us in collaboration with the group of Sauvage⁴ (Scheme 2).

More recently, we have briefly reported on a poly[2]-catenane **4** composed of rigid catenanes connected by semirigid spacers⁵ (Scheme 3).

Scheme 1. Schematic Drawings of Polyrotaxane 1 and Poly[2]-catenane 2

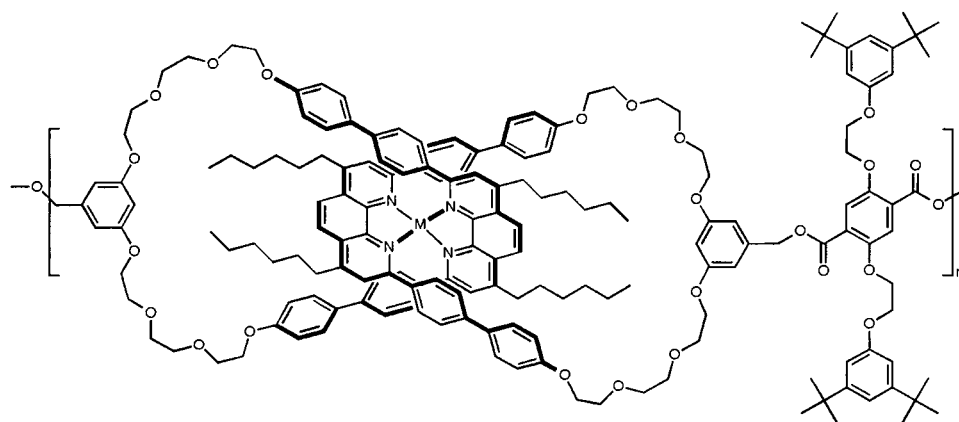


The motivation of this research program aiming at the introduction of catenanes into a polymer main chain is dual. On one hand, the large scale synthesis of poly[2]-catenanes represents a synthetic challenge in its own right and is a prerequisite for any physical property investigations. On the other hand, it is anticipated that poly[2]-catenanes will exhibit unusual viscoelastic properties, e.g. very large loss modulus, low activation energy for viscous flow, and rapid stress relaxation, due to the presence of the mobility elements contained in the catenane units.³ Conceptually, the mobility elements present in a catenane unit can be factored into two rotational mobility elements (β , γ) and an elongational mobility element (a) (Scheme 4).^{4b}

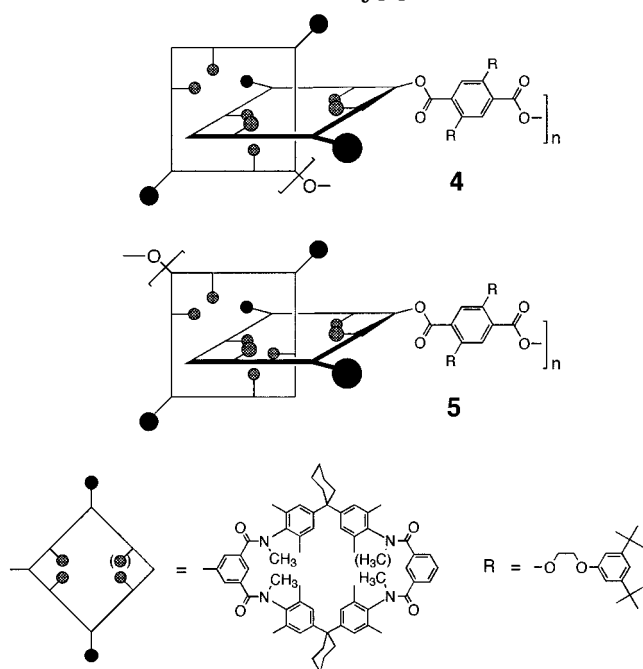
The mobility element γ is defined as the angle between the planes of the catenane macrocycles. This mobility element corresponds to rocking motions and is present in numerous polymers, whereas the angle between the two spacer segments connected to the catenane unit, β , is a mobility element which has not yet been introduced in a polymer main chain, except in poly[2]-catenane **3b**.⁴ Similarly, the elongational mobility element a is also characteristic of the motions of catenane macrocycles. Clearly, only the comparison between poly[2]-catenanes containing catenane segments with very different mobility will shed light on the unusual viscoelastic properties expected from the introduction of topological bonds into a polymer main chain.³ The poly[2]-catenane **3b** presents the particularity that the macrocycles of the catenane are highly mobile. The aim of this paper is to report the converse situation, i.e., poly[2]-catenanes **4** and **5** where the rotational mobility elements β , γ and elongational mobility element a are frozen.⁵ Specifically, the detailed synthesis, comprehensive elucidation of the macromolecular characteristics, macroconformation investigations in solution, and solid-state properties of poly[2]-

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Scheme 2. Previously Reported Poly[2]-catenate 3a and Poly[2]-catenand 3b (Ref 4)

3a : M = Cu⁺, 3b : M absent

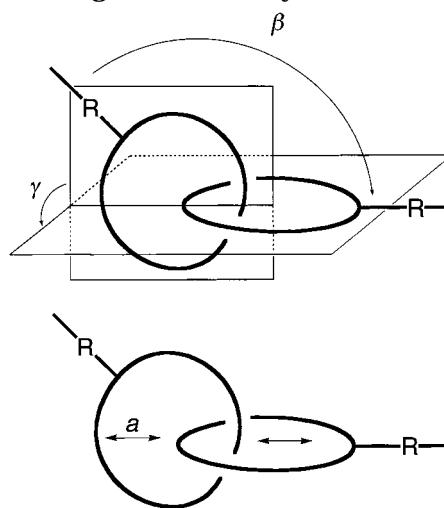
Scheme 3. Structures of Poly[2]-catenanes 4 and 5



catenanes **4** and **5** are presented and discussed in light of their structure.

Results and Discussion

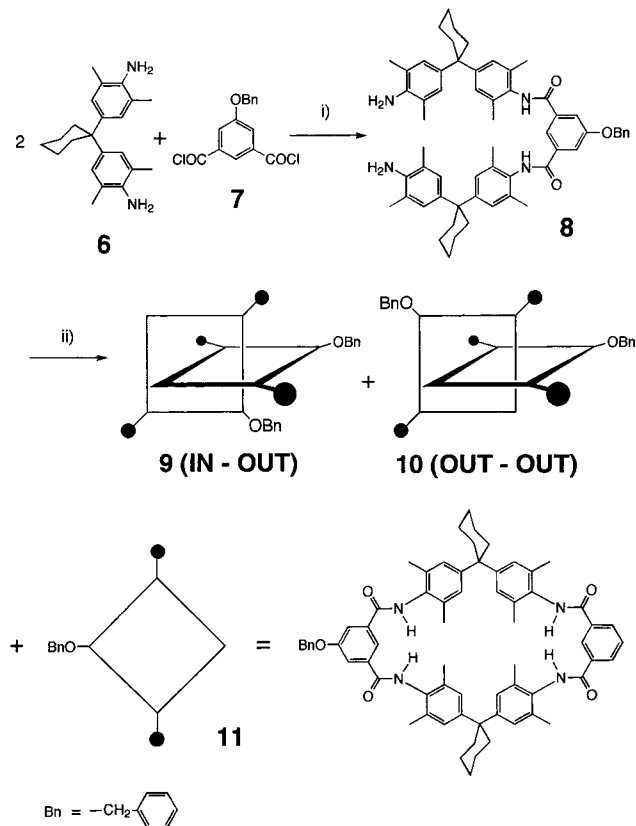
Monomer Syntheses. For this study the aromatic amide type catenanes **9** and **10**, previously reported by Hunter⁸ and Vögtle,^{9,10} have been selected. These catenanes offer several decisive advantages such as a simple two-step synthesis,^{8–10} an easy functionalization, a facile modification,⁵ and a high thermal stability.³ The synthesis of catenanes **9** (IN–OUT) and **10** (OUT–OUT)^{3,10} was performed according to Scheme 5. The macrocycles bearing the benzyloxy substituent out (in) of the catenane structure are referred to as OUT (IN) macrocycle, respectively.^{5,10} The catenane **9**, catenane **10**, and macrocycle **11** were afforded in 10%, 13%, and 25% yields, respectively.⁵ The macrocycle **11** has been found to be a valuable compound to favor the catenane formation. When a 0.44 M amount of macrocycle **11** was introduced with the catenane precursor **8** and isophthaloyl dichloride in the high dilution reaction, the yield of catenanes **9** and **10** reached 26% and 30%, respec-

Scheme 4. Mobility Elements Contained in a Catenane Unit: β , γ Rotational Mobility Elements and Elongational Mobility Element *a*

tively. Thus, starting with 1 g of precursor **8** for each catenane generating reaction, under high dilution, approximately 0.7 g of catenanes was obtained. Interestingly, the initial quantity of macrocycle **11** (0.5 g) was recovered after workup, allowing an easy repetition of this procedure. Therefore, the rapid synthesis of catenanes **9** and **10** on a multigram scale should be possible. This important synthetic improvement, as compared to previously reported catenane synthesis,^{3,5} not only is encouraging but also paves the way toward the preparation of poly[2]-catenanes on amounts sufficient to carry out a full characterization and elucidation of their thermal, macroconformational, and viscoelastic properties.

The amide-type catenanes **9** and **10** are only poorly soluble in common organic solvents, due to their compact structure and intermolecular hydrogen bonding. This prevents their easy incorporation into polymers. To increase the solubility and to restrict the mobility of its interlocked macrocycles, the catenanes **9** and **10** were subjected to methylation⁹ of the amide functions to afford the catenanes **12** and **14**, respectively (Scheme 6). Interestingly enough, the catenane **9** (OUT–IN) and **10** (OUT–OUT) display different reactivities. Although the catenane **9** contains eight amide functions, only seven methyl groups could be introduced, even in the presence of a large excess of methyl iodide (65-fold) and

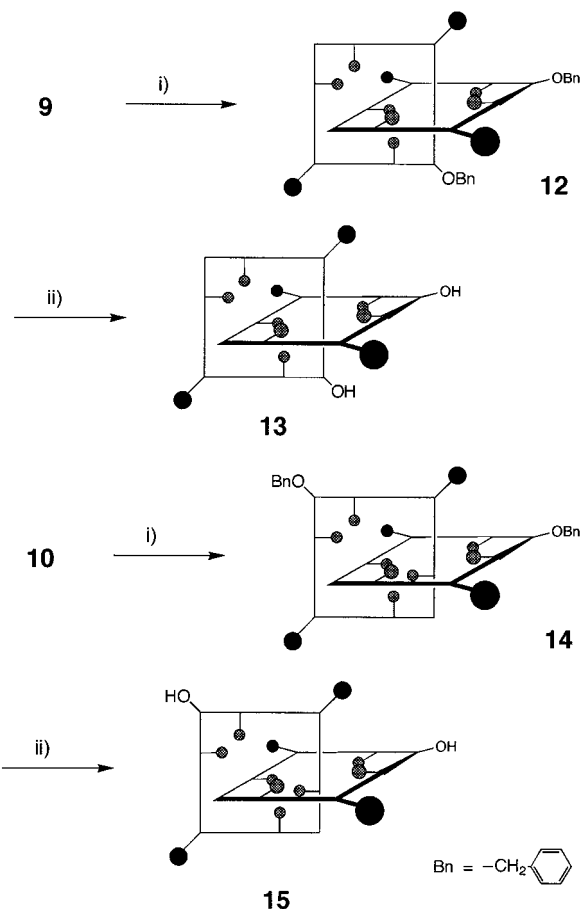
Scheme 5. Synthesis of Catenanes 9 and 10: (i) Et_3N , CH_2Cl_2 , (ii) Isophthaloyl Dichloride, Et_3N , CH_2Cl_2 , High Dilution



sodium hydride (20-fold). A catenane containing only six methyl groups was isolated as side product and was again subjected to the methylation procedure, affording the 7-fold methylated catenane **12**. The total yield calculated from the initial amount of catenane **9** reached 77%. Conversely, the catenane **10** subjected to comparable reaction conditions as **9**, i.e., excess of sodium hydride and methyl iodide, and repeated methylation procedure, afforded the 8-fold methylated catenane **14** in 33% yield. The reactivity difference between the catenane **9** (OUT-IN) and **10** (OUT-OUT) is attributed to the steric hindrance of the IN substituent on the OUT macrocycle of catenanes **9**. However, it has not been possible to identify the exact position of the unmethylated amide function in the catenane **12** because the ^1H NMR is too complicated (see below). Note that the occurrence of several isomers with respect to the position of the unmethylated amide function in the catenane **12** cannot be strictly ruled out although only one component is observed on thin-layer chromatography (TLC) in various solvents. The reactivity difference between the catenanes **9** and **10** documents the unique character of catenane macrocycles where the reactivity of one macrocycle is influenced by the presence of the other.¹¹ In contrast to catenanes **9** and **10**, catenanes **12** and **14** are highly soluble in various chlorinated solvents, tetrahydrofuran and dimethylformamide.

The evidence for the structure of the catenanes **12** and **14** arises from FAB-MS and by FT-IR spectroscopy. The catenane structure of **12**, i.e., the presence of two interlocked rings, was proven by FAB-MS where the catenane peak of **12** appeared at m/z 2120 as a parent ion, while two other peaks were observed at m/z 1053 and 1067, corresponding to the macrocycles containing

Scheme 6. Synthesis of Catenane Monomers 13 and 15: (i) NaH , MeI , (ii) $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ (3:2:1); the Exact Position of the Unmethylated Amide Function in the Catenanes **12** and **13** Has Not Be Determined Unambiguously (See Text for Details)



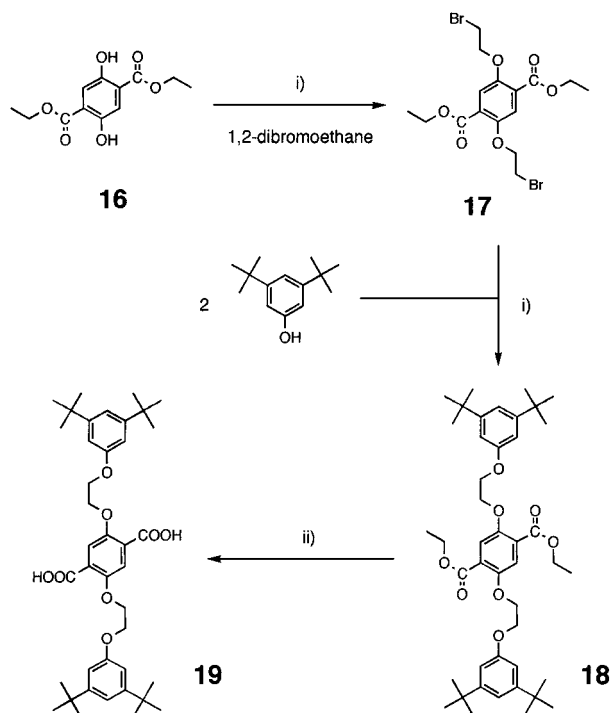
three and four methyl substituents, respectively. This indicates that ring opening occurs and, subsequently, that the fragment becomes unthreaded from the intact remaining ring.¹ Accordingly, in the case of catenane **14**, two peaks were observed at m/z 2135 and 1067, corresponding to the catenane mass and half of the catenane mass.

The intensity of the characteristic N-H stretching band around 3280 cm^{-1} decreases but remains significant for catenane **12** as compared to **9**, whereas the N-H stretching band cannot be observed anymore in the case of the fully methylated catenane **14**. Accordingly, another strong band, corresponding to N-CH₃ stretching, appears for catenanes **12** and **14** around 1367 cm^{-1} . The typical C=O amide band around 1645 cm^{-1} remains similar for **12** and **14** as compared to **9** and **10**, respectively.

The ^1H NMR spectra of **12** and **14** are comparable in that they are too complicated to be fully interpreted. However, some information about the dynamics of catenanes **12** and **14** was obtained from the ^1H NMR spectra at different temperatures (-50 , 0 , 30 , and $50\text{ }^\circ\text{C}$) where the line shape remained nearly unchanged. This observation demonstrates the high structural rigidity of the catenanes **12** and **14** as compared to the unmethylated precursors **9** and **10**, where a dramatic dependence of the ^1H NMR spectra upon temperature was observed.^{3,8,12}

The benzyl substituents of the catenanes **12** and **14** were easily removed under acidic conditions to give the

Scheme 7. Synthesis of Spacer 19: (i) K_2CO_3 , DMF, (ii) KOH, EtOH/H₂O (1:1)



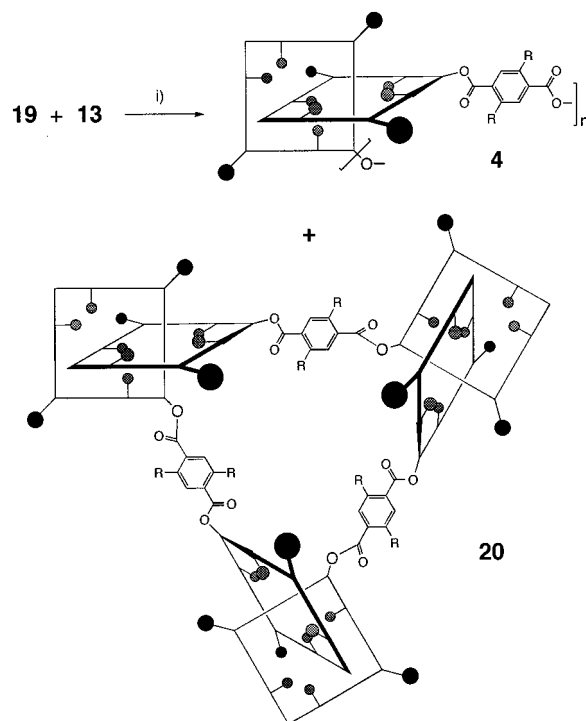
dihydroxy catenanes **13** and **15**. On the basis of the observation of the aforementioned methylation reaction, a difference in reactivity between catenanes **12** and **14** was expected. Surprisingly enough, the kinetics of the deprotection reaction were similar (15–18 min) for catenanes **12** and **14**, and the yields of catenanes **13** and **15** were comparable (82%). Thus, no reactivity difference was observed between 7-fold methylated catenane **12** and 8-fold methylated catenane **14** and between the IN and OUT benzyl substituents of catenane **12**. Both catenanes **13** and **15** were characterized by FAB-MS and by FT-IR and ¹H NMR spectroscopy and were found to be in excellent agreement with the proposed structures.

The conclusions at this stage are (i) the efficient catenane synthesis, methylation, and deprotection procedures allowed the preparation of catenane monomers **13** and **15** in 16% and 8% total yield, respectively, and (ii) the presence of methylated amide functions in **13** and **15** not only dramatically increases their solubility but also induces high structural rigidity.

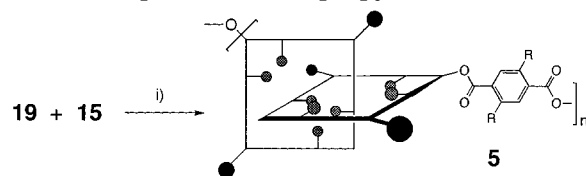
With the aim of introducing the catenanes **12** and **14** into a polymer main chain via the very mild and convenient polyesterification at room temperature developed by Moore and Stupp,¹³ we have designed the decorated terephthalic acid spacer **19** (Scheme 7). The spacer **19** combines several advantages: it is highly soluble in common organic solvents, in particular dichloromethane, and crystalline in the solid state, allowing then an easy purification and handling. An additional advantage is to have a spacer of molecular weight high enough, as compared to the catenanes, to ensure an accurate stoichiometry for AA + BB type polycondensation.

The three-step synthesis of spacer **19** is detailed in Scheme 7. The first step consists of the etherification of the diester hydroquinone **16** by 1,2-dibromoethane in excess. The resulting dibromo compound **17** was reacted with 3,5-di-*tert*-butylphenol to afford the diester

Scheme 8. Synthesis of Poly[2]-catenane 4 and Cyclic Trimer 20: (i) 4-(Dimethylamino)pyridine/*p*-Toluenesulfonic Acid 1:1 Complex, *N,N*-Diisopropylcarbodiimide; the Cyclic Trimer **20** Probably Exists as Several Isomers Due to the Unspecified Position of the Unmethylated Amide Function in Each Catenane Fragment (See also Scheme 6)



Scheme 9. Synthesis of Poly[2]-catenane 5: (i) 4-(Dimethylamino)pyridine/*p*-Toluenesulfonic Acid 1:1 Complex, *N,N*-diisopropylcarbodiimide



18. The highly soluble terephthalic acid **19** was obtained under conventional saponification conditions. The overall yield (66%) allowed **19** to be prepared on a gram scale.

Polymer Synthesis and Characterization. Catenanes **13** and **15** were copolymerized with the highly soluble terephthalic acid **19** to afford poly[2]-catenanes **4** and **5**, respectively (Schemes 8 and 9). The polyesterification proceeded smoothly at low temperature (−20 °C) for 6 days in dichloromethane, using a large excess of *N,N*-diisopropylcarbodiimide as coupling reagent.⁴ The choice of the polymerization conditions has been dictated by the fact that it has been experimentally observed that the polycondensation of bulky monomers such as catenanes **13** and **15** affords higher molecular weight polymers at lower temperature than at room temperature.^{5b} A likely explanation is that the polyesterification is favored at low temperature over side reactions, i.e., the formation of *N*-acylureas, which preclude the formation of high molecular weight products.¹³ Detailed polymerization conditions are collected in Table 1.

The resulting poly[2]-catenanes **4** and **5** were easily soluble in chlorinated solvents, THF and DMF. The

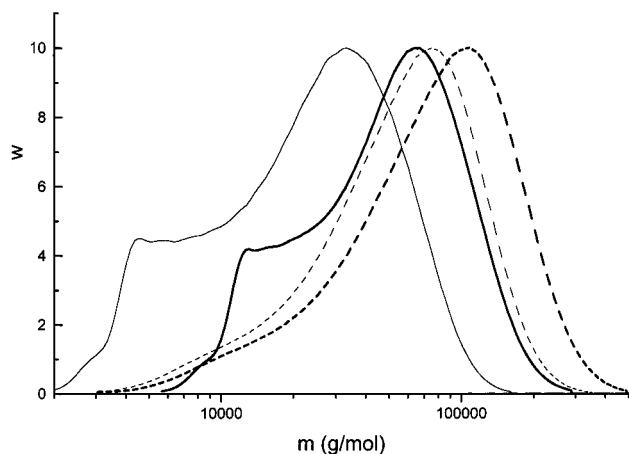


Figure 1. GPC traces in THF of poly[2]-catenane **4** (solid line calibrated with PS standards, bold solid line MALDI-TOF calibrated) and of poly[2]-catenane **5** (dashed line calibrated with PS standards, bold dashed line MALDI-TOF calibrated).

Table 1. Polymerization Conditions

batch	catenane	initial concn (mmol/L)	poly[2]-catenane	yield (%)
1	13	26.0	4	97
2	13	23.2	4	97
3	13	56.0	4	97
4	15	26.5	5	94

purification of polymers was carried out by precipitation in methanol, affording poly[2]-catenanes in yields ranging from 94% to 97%. It can also be seen in Table 1 that the variation of the initial concentration of catenane monomer **13** from 23.2 to 56.0 mmol/L has no influence on the yield of the resulting poly[2]-catenanes **4**.

The ^1H NMR spectra of the poly[2]-catenanes **4** and **5** exhibit a similar pattern and appear broadened in comparison to the spectra of their corresponding catenane monomers **13** and **15**. An additional reason for this broadening can be invoked in the case of poly[2]-catenane **4** where the catenane monomer **13** is probably randomly introduced head-to-head, head-to-tail, or tail-to-tail in the polymer chain. The typical resonances of the *tert*-butyl groups of the spacer at $\delta \approx 1.3$ are present, confirming the incorporation of the spacer into the polymer, in agreement with the proposed poly[2]-catenane structures **4** and **5**. Independent evidence of the poly[2]-catenane structure **4** and **5** is provided by the FT-IR spectra, where the characteristic ester band at 1753 cm^{-1} is clearly visible, whereas no hydroxyl end groups in the range from 3200 to 3500 cm^{-1} and carboxylic end groups in the range from 1700 to 1725 cm^{-1} groups are observed.

Gel permeation chromatography (GPC), viscometry, and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS)¹⁴ have been used to characterize the molecular weight distribution of poly[2]-catenane structures **4** and **5**. The considerable intrinsic viscosity values obtained by viscometry in tetrahydrofuran: $[\eta] = 9.8\text{ mL/g}$ and $[\eta] = 26.1\text{ mL/g}$ of poly[2]-catenanes **4** and **5**, respectively, indicates the presence of high molecular weight poly[2]-catenanes and agrees well with the absence of end groups observed by FT-IR. GPC curves in THF calibrated with polystyrene (PS) standards (Figure 1) afford number-average molecular weight $M_n = 13\,500$ and weight-average molecular weight $M_w = 29\,100$ for poly[2]-catenane **4** and $M_n = 35\,500$ and $M_w = 67\,500$ for poly[2]-catenane **5** (Table 2).

Table 2. Molecular Weight Determination of Poly[2]-catenanes **4 and **5** Obtained by GPC in THF Using PS Standards, Universal Calibration for $\alpha = 0.5$ and $\alpha = 0.8$, and MALDI-TOF Calibration^{14c}**

polymer	PS standards	$\alpha = 0.5$	$\alpha = 0.8$	MALDI-TOF calibration
4	$M_n = 13\,500$ $DP_n = 5$ $M_w = 29\,100$ $M_w/M_n = 2.2$	$M_n = 25\,500$ $DP_n = 10$ $M_w = 60\,900$ $M_w/M_n = 2.3$	$M_n = 31\,800$ $DP_n = 12$ $M_w = 58\,700$ $M_w/M_n = 1.8$	$M_n = 34\,200$ $DP_n = 13$ $M_w = 59\,100$ $M_w/M_n = 1.7$
5	$M_n = 35\,500$ $DP_n = 14$ $M_w = 67\,500$ $M_w/M_n = 1.9$	$M_n = 41\,500$ $DP_n = 16$ $M_w = 96\,800$ $M_w/M_n = 2.3$	$M_n = 52\,600$ $DP_n = 20$ $M_w = 94\,200$ $M_w/M_n = 1.8$	$M_n = 46\,600$ $DP_n = 18$ $M_w = 95\,600$ $M_w/M_n = 2.1$

The molecular weight distribution obtained by GPC probably underestimates the true molecular weight distribution, because the PS calibration does not take into account the very compact molecular structures of poly[2]-catenanes **4** and **5**. To circumvent this problem, a universal calibration has been employed.¹⁵ The Mark–Houwink–Sakurada equation¹⁶

$$[\eta] = KM^\alpha \quad (1)$$

relates the intrinsic viscosity $[\eta]$ to the molecular weight M . Since there are two unknowns in eq 1, namely K and α , and only one independently measured property of the polymer under investigation, the intrinsic viscosity $[\eta]$, the problem is unsolved.¹⁷ It is, however, well-established that for random coil polymer $0.5 \leq \alpha \leq 0.8$, depending on the solvent quality. Hence, while no unique solution can be obtained, reasonable estimates are possible by employing the two limiting values of α . Notably, $\alpha = 0.5$ corresponds to θ conditions and $\alpha = 0.8$ to a random coil in a good solvent. Using $\alpha = 0.5$, one finds for poly[2]-catenanes **4** and **5** $M_n = 22\,500$ and $M_n = 41\,500$, corresponding to a $DP_n = 10$ and 16 , respectively (Table 2). These values are even higher when using $\alpha = 0.8$: $M_n = 31\,800$ and $M_n = 58\,700$, corresponding to a $DP_n = 12$ and 20 for **4** and **5**, respectively. The molecular weight averages calculated using universal calibration are recognizably higher than values obtained by comparison with polystyrene standards, corroborating the view of a compact structure of the poly[2]-catenanes **4** and **5**. The polydispersity index (M_w/M_n) of both poly[2]-catenanes varies from 1.8 to 2.3 for $\alpha = 0.8$ and 0.5 , respectively. However, as a first approximation, M_w/M_n remains close to 2.0 , which is the generally observed value for polycondensation products.¹⁸

Interestingly enough, the shapes of the GPC traces of poly[2]-catenanes **4** and **5** (Figure 2) are not comparable: an important shoulder appears on the oligomeric tail in the case of **4** whereas the GPC trace of **5** is strictly monomodal. The species corresponding to the shoulder in the GPC trace of **4** was separated by preparative GPC using chloroform as eluent. MALDI-TOF MS indicates that the separated fraction is composed nearly exclusively of the cyclic trimer **20**. Further structural evidence of the cyclic trimer **20** arises from its ^1H NMR spectrum where the characteristic resonances of the catenane and of the spacer moieties are present. The ^1H NMR spectrum of **20** is also comparable to those of catenane precursors **12** and **13** in that it is too complicated to allow a complete assignment of the peaks. Clearly, the occurrence of cyclic trimer **20**¹⁹ in the molecular weight distribution of **4** results from the geometry of the catenane monomer **13** where the

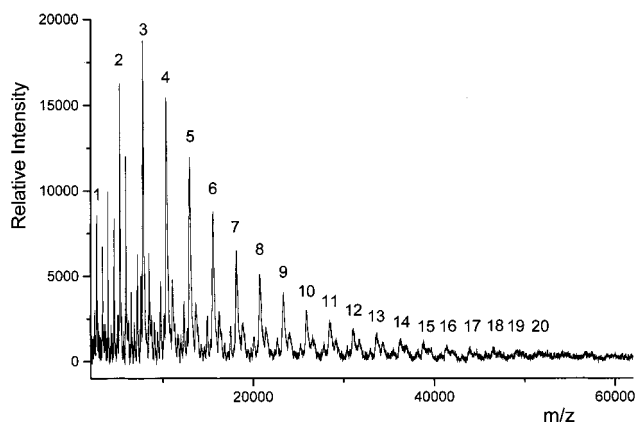


Figure 2. MALDI-TOF mass spectrum of poly[2]-catenane **4**.

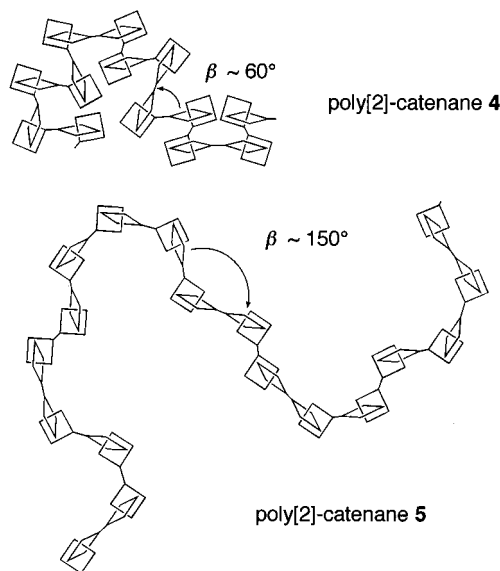
functional groups are oriented one to the other by an angle of roughly 60° .

The MALDI-TOF MS spectra of poly[2]-catenane **4** (Figure 2) and **5** (not shown) are comparable and typify the highly asymmetric and dispersed molecular peaks distribution as expected for polycondensates.²⁰ Remarkably enough, signals up to 52 000 ($n = 20$) and to 62 000 ($n = 23$) were observed for poly[2]-catenanes of **4** and **5**, respectively. This is attributed to the high molecular weight of polycatenane repeat units, i.e., 2567 (sample **4**) and 2580 (sample **5**), allowing distinct signals to be acquired even in the high mass region of the polymer distribution. The most intense signals in Figure 2 are labeled with the number of repeating units and show the expected mass difference of approximately 2750 g/mol for sample **4**. The absolute masses of these peaks can be attributed to polymers bearing a catenane and a spacer as end monomers. The satellite peaks, which appear with a mass difference of approximately 660 g/mol at the upper and lower mass side, of the most intense signals belong to polymers with two catenanes or two spacers as end monomers. The average molecular weight values determined from the mass spectrum in Figure 2 are $M_n = 18\,700$ and $M_w = 27\,600$. It is known, however, that MALDI-TOF-MS does not yield reliable average molecular weight values by direct measurement of broad molecular weight distribution like in the case of polycondensates.^{14d-f} To obtain absolute values of such polydisperse samples, one had to combine GPC and MALDI-TOF-MS to take advantage and benefits of both methods.^{14c} Fractionation of the poly[2]-catenanes by GPC leads to a series of narrow polydisperse cuts of the complete polymer distribution, which can then be measured by MALDI-TOF-MS with high accuracy. The so-obtained reliable mass values of the separated fractions are used to calibrate the GPC curve to get absolute average molecular weight values of $M_n = 34\,000$ and $M_w = 59\,100$ for poly[2]-catenane **4** and $M_n = 46\,600$ and $M_w = 95\,600$ for poly[2]-catenane **5**. Clearly, the M_n and M_w values of both polymers agree very well with those obtained using GPC with a universal calibration for a good solvent ($\alpha = 0.8$).

In addition to the previously used techniques, several attempts to characterize the molecular weight distribution of poly[2]-catenanes **4** and **5** by dynamic light scattering in THF have been unsuccessful probably due to the formation of aggregates in solution.

Solution Properties. The overall shape of poly[2]-catenanes **4** and **5** is related to the geometrical structure of the catenane segments, i.e., OUT-IN and OUT-OUT

Scheme 10. Schematic Illustration of the Macroconformation of Poly[2]-catenanes **4** ($DP_n = 13$) and **5** ($DP_n = 18$)



isomers, respectively. A schematic drawing illustrating the conformation of **4** and **5** is given in Scheme 10.

Poly[2]-catenane **4**, composed of OUT-IN rigid catenane segments connected by semirigid aromatic ester bridges, can only adopt a coil shape since each catenane constitutes a kink of angle β of approximately 60° . Conversely, the angle between monomer units is much more open, approximately $\beta = 150^\circ$, for poly[2]-catenane **5**. As a result, the presence of OUT-OUT rigid catenane segments in poly[2]-catenane **5** leads to a more extended polymer. It should then be informative to measure the Kuhn segment length, which is a measure of the degree of coiling of polymers.^{18,21} Assuming that the poly[2]-catenanes **4** and **5** can be adequately represented by the freely jointed chain model,²¹ the length of the Kuhn segment was estimated from GPC and viscometry results in THF. For flexible coils under θ conditions the Kuhn length l_k is defined as

$$l_k = 6R_g^2/Nl \quad (2)$$

l is the length of the repeat unit, N the number of repeat units, and R_g the radius of gyration. The Fox-Flory equation¹⁶ relates the intrinsic viscosity to R_g :

$$[\eta] = \phi(6R_g^2)^{3/2}/M \quad (3)$$

ϕ is the Flory viscosity constant. Combining eqs 2 and 3 with the Mark-Houwink-Sakurada equation (eq 1), l_k can be calculated as

$$l_k = K_\theta^{2/3} \phi^{-2/3} M_0/l \quad (4)$$

K_θ is the viscosity constant for $\alpha = 0.5$ and M_0/l the molar mass per unit length. The values of K_θ , ϕ , M_0 , l , and l_k are given in Table 3.²²

Kuhn lengths of $l_k = 27$ and 44 \AA are obtained as a crude estimation for poly[2]-catenanes **4** and **5**, respectively. These values must be reported as upper limits, since swelling of the polymer coil in a good solvent has not been taken into account and would result in a further decrease of l_k .²³ Clearly, poly[2]-catenane **4** forms a more compact coil in solution in comparison to

Table 3. Value of the Flory Viscosity Constant (ϕ) and Experimental Data Used for the Estimation of the Kuhn Segment Length of Poly[2]-catenanes 4 and 5 in THF

polymer	K_θ (mL/g)	ϕ (mol ⁻¹)	M_0 (g/mol)	l (Å)	l_k (Å)
4	4.34×10^{-2}	2.7×10^{23} ^a	2567	28	27
5	9.02×10^{-2}	2.7×10^{23} ^a	2580	28	44

^a From ref 22.

poly[2]-catenane **5** (Scheme 10). Interestingly enough, the difference of the catenane mobility between the poly[2]-catenane **3b** containing highly mobile catenane units and poly[2]-catenanes **4** and **5** made of highly rigid catenane units is illustrated by the comparison of their estimated Kuhn segment length. Specifically, $l_k = 27$ Å for poly[2]-catenane **3b**, i.e., smaller than the length of a repeat unit $l = 32$ Å,^{4b} whereas $l_k = 27$ Å of poly[2]-catenane **4**, matching the length of a repeat unit, 28 Å. The Kuhn segment length of poly[2]-catenane **5**, $l_k = 44$ Å, is higher and corresponds to the length of a repeat unit multiplied by a factor ± 1.6 . Obviously, the nature of the catenane unit, i.e., highly mobile versus highly rigid, and of the catenane geometry, i.e., OUT-IN isomer versus OUT-OUT isomer, has an important role in the macroconformation of poly[2]-catenanes.

Solid-State Properties. The thermal stability of poly[2]catenanes **4** and **5** was expected to be rather high due to the polyaromatic amide-ester structure of the polymer backbone. This feature has been investigated by thermogravimetric analysis (TGA), and no weight loss was observed for both polymers until 380 °C, under nitrogen, confirming their good thermal stability. This finding is important for two reasons: first, it indicates that the presence of either seven or eight methyl substituents on the catenane units of **4** and **5**, respectively, while causing a severe steric hindrance as shown by temperature-dependent ¹H NMR spectroscopy studies (see above), does not dramatically decrease the thermal stability. Second, a high thermal stability is a prerequisite if one wishes to investigate expected high glass transition temperatures of poly[2]-catenanes, resulting from the presence of rigid catenanes connected by semirigid segments.

Differential scanning calorimetry (DSC) has been used to determine the presence of first- or second-order transitions in the 30–380 °C temperature range. No first-order transition was observed for poly[2]-catenanes **4** and **5** whereas second-order transitions at 277 and 207 °C, corresponding presumably to glass transitions, were recorded for **4** and **5**, respectively. These values have been determined from the second heating curve and were taken at the midpoint of the heat capacity change. The comparison of the glass transition temperatures of poly[2]-catenane **3b** made of highly mobile catenane units and poly[2]-catenane **3a** containing fixed catenane units, 75 and 80 °C, respectively,⁴ with that of poly[2]-catenanes **4** and **5** which occur at much higher temperature stresses the importance of the catenane units on the glass transition temperature of poly[2]-catenanes.

Wide-angle X-ray scattering analysis has been carried out on poly[2]-catenanes **4** and **5**. Clearly, the diffraction patterns of both poly[2]-catenanes (not shown) are comparable and indicate that these polymers are amorphous, as expected from their structure and from the absence of first-order transitions in the DSC traces.

Attempts were made to investigate the viscoelastic properties of poly[2]-catenanes by dynamic mechanical

thermal analysis (DMTA). Unfortunately, thick films of poly[2]-catenanes **4** and **5**, cast from solution, are extremely brittle, hampering any investigations of Young's modulus and breakpoint by stress-strain measurements. Another attempt was made to examine the mechanical properties of poly[2]-catenanes **4** and **5** under shear strain using parallel plate geometry. This experiment requires samples to be melted to create the contact between the oscillating plates and the materials in order to be able to pick up different transitions due to segmental and chain relaxation. Unfortunately, neither poly[2]-catenanes **4** nor poly[2]-catenane **5** melted before decomposition indicated by foaming and blackening of the sample and a sudden dramatic decrease in viscosity. GPC analysis of poly[2]-catenanes **4** and **5** later showed a decrease in M_n and M_w . Therefore, no measurement of viscoelastic properties in the solid state were possible.

Conclusions

The synthesis of amide-type difunctionalized catenanes (OUT-OUT and OUT-IN isomers) have been achieved, and their chemical modification by the methylation of their amide functions has been demonstrated. The copolycondensation of modified catenane monomers with a spacer afforded poly[2]-catenanes on a gram scale. The molecular weight distribution of these polymers has been comprehensively characterized by GPC, viscometry, and MALDI-TOF mass spectrometry. An upper value of the Kuhn segment length has been derived and indicates that poly[2]-catenane **4** presents a more compact coil than poly[2]-catenane **5**. This macroconformational difference between the two poly[2]-catenanes emanates directly from the geometry of the constitutive catenane isomers **4** and **5**. The thermal properties of the poly[2]-catenanes in the solid state have been investigated and correlated with their structure. Unfortunately, the investigation of the dynamic mechanical behavior of poly[2]-catenanes has been precluded due to their high brittleness and poor flow properties. Experiments aiming at the accurate determination of the Kuhn segment length of poly[2]-catenanes **4** and **5** by viscometry and by scattering techniques are underway and will be the subject of a forthcoming publication.

Experimental Section

Measurements. ¹H and ¹³C NMR spectroscopy: Varian Gemini 200 MHz, Bruker AC 300 MHz, and Bruker AMX 500 MHz. Mass spectroscopy: VG analytical ZAB2-SE-FPD: FD (8 kV), FAB matrix 3-nitrobenzyl alcohol (acceleration voltage 8 kV). MALDI-TOF: Bruker Reflex (LSI N₂ laser, 3 ns laser pulses at 337 nm, intensity = 10⁷ W/cm², matrix = 1,8,9-trihydroxyanthracene, 100 μm diameter spot). Infrared spectroscopy: Nicolet FT-IR 320. Melting points (uncorrected): Büchi melting point apparatus. Gel permeation chromatography (GPC) analysis: THF, PL gel columns (three columns, 10 mm, pore widths 10³, 10⁵, 10⁶ Å), UV-visible detector. Separation on preparative GPC: chloroform, PL gel columns (10 mm, pore width 500 Å). Thermal analysis: Mettler DSC 30 differential scanning calorimeter (heating rate 20 K/min). X-ray diffraction measurements: Siemens θ - θ -diffractometer D5000 equipped with a scintillation counter (Ni-filtered Cu K α radiation, $\lambda = 1.54$ Å) (1-D WAXS, temperature corrected). Viscometry: Ubbelohde capillary viscometer. Differential thermal analysis: Rheometrics RMS 5800. Dynamic light scattering experiment: ALV 3000, krypton ion laser at 647 nm.

Solvents and Reagents. The solvents were used as commercial p.a. quality, except THF which was refluxed over

sodium and distilled under argon. Dichloromethane was purchased from Aldrich as grade 99%+, water-free. The following compounds were previously described in the literature: 1,1-bis(amino-3,5-dimethylphenyl)cyclohexane (**6**),⁸ 5-benzoyloxyisophthaloyl dichloride (**7**),⁵ *N,N*-bis{4-[1-(4-amino-3,5-dimethylphenyl)cyclohexyl]-2,6-dimethylphenyl}-5-benzoyloxyisophthalamide (**8**),^{5a} macrocycle **11**,⁵ catenane **9**,⁵ catenane **10**,⁵ catenane **12**,⁵ dihydroxy catenane **13**,⁵ and poly-[2]-catenane **4**.⁵ All other chemicals were purchased from Aldrich and used as received.

Synthesis. Improved Synthesis of Catenanes 9 and 10.⁵ The diamine **8** (1.0 g, 1.14 mmol) and 0.4 mL of triethylamine were dissolved in 500 mL of dry dichloromethane under argon. Isophthaloyl dichloride (230.4 mg, 1.14 mmol) was similarly dissolved in 500 mL of dry dichloromethane under argon. These two solutions were added dropwise and at the same rate to a solution of macrocycle **11** (500 mg, 4.94 mmol) in 1000 mL of dry dichloromethane over a period of 2 days with stirring under argon. The precipitate was filtered off and the solvent removed under vacuum. The residue was chromatographed on silica with CH₂Cl₂/ethyl acetate (9/1) as eluent. In each case, precipitation in a 10-fold volume of pentane, followed by filtration, afforded 338 mg of **9** in 26% yield, 369 mg of **10** in 30% yield, and 500 mg of **11**, corresponding to the initial amount introduced. All products appeared as white powders. The mp, NMR, IR, and MS data of the catenanes **9** and **10** and of macrocycle **11** have already been reported in ref 5a.

Improved Synthesis of Catenane 12.⁵ To a solution of dibenzoyloxy-functionalized [2]-catenane **9** (200 mg 0.989 mmol) in 30 mL of dry tetrahydrofuran under argon were added large excesses of sodium hydride (95% in paraffin) (500 mg, 19.8 mmol) and methyl iodide (4 mL, 64.3 mmol). The reaction mixture was stirred at room temperature for 7 days and then poured into 100 mL of 2-propanol. The solvent was removed by vacuum, and 100 mL of water was added to the crude mixture. The solution was neutralized with HCl and finally extracted with dichloromethane. The organic phase was separated and dried over magnesium sulfate, and the solvent was evaporated under vacuum. The crude product was chromatographed on silica gel with a mixture of dichloromethane/ethyl acetate (5/2) as eluent. Precipitation in pentane followed by filtration afforded 58 mg of a 6-fold methylated catenane (FD-MS: *m/z* 2106.4 (M⁺, 100%) and 126 mg of the title compound **12**. The intermediate 6-fold methylated catenane was dissolved in 20 mL of dry tetrahydrofuran under argon. Large excesses of sodium hydride (125 mg, 5 mmol) and of methyl iodide (1 mL, 16 mmol) were added to this solution. The reaction mixture was stirred at room temperature for 7 days and then poured into 25 mL of 2-propanol. The work-up was identical to the aforementioned, affording 36 mg of the title compound **12** as a white powder. The total yield, calculated from the initial amount of catenane **9**, reached 77%. The mp, NMR, IR, and MS data of the title compound have already been reported in ref 5a.

Catenane 14. To a solution of dibenzoyloxy-functionalized [2]-catenane **10** (200 mg, 0.989 mmol) in 30 mL of dry tetrahydrofuran under argon were added large excesses of sodium hydride (95% in paraffin) (1000 mg, 39.5 mmol) and of methyl iodide (5 mL, 80.4 mmol). The reaction mixture was stirred at room temperature for 7 days and then poured into 100 mL of 2-propanol. The solvent and excess of methyl iodide were removed by vacuum, and 50 mL of water was added to the crude mixture. The solution was neutralized with HCl and finally extracted with dichloromethane. The organic phase was separated and dried over magnesium sulfate, and the solvent was evaporated under vacuum. The crude product was chromatographed on silica gel with a mixture of dichloromethane/ethyl acetate (2/1) as eluent. Precipitation in pentane, followed by filtration, afforded 20 mg of 6-fold methylated catenane (FD-MS: *m/z* 2106.5 (M⁺, 100%) and 54 mg of 7-fold methylated catenane (FD-MS: *m/z* 2120.5 (M⁺, 100%). These intermediate products were collected and dissolved in 30 mL of dry tetrahydrofuran under argon. Large excesses of sodium hydride (400 mg, 15.8 mmol) and of methyl iodide (2 mL, 32.2 mmol) were added to this solution. The reaction mixture was stirred at

room temperature for 7 days and then poured into 40 mL of 2-propanol. The solution was neutralized with HCl and finally extracted with dichloromethane. The organic phase was separated and dried over magnesium sulfate, and the solvent was evaporated under vacuum. The crude product was chromatographed on silica gel with a mixture of dichloromethane/tetrahydrofuran (10/1) as eluent. Precipitation in a 10-fold volume of pentane followed by filtration afforded 72 mg of the title compound **14**, as a white powder in 33% yield.

mp: 293 °C. ¹H NMR (500 MHz, CDCl₃, 30 °C): δ = 8.58 (s, arom), 7.9–6.0 (b, arom), 5.6–5.0 (b, aliph), 3.63 (s, aliph), 3.42 (s, aliph), 3.3–0.6 (b, aliph), 0.4–(–0.1) (b, aliph). FT-IR (KBr) ν = 3061, 3033, 2934, 2859, 1645 (C=O), 1589, 1486, 1452, 1429, 1365 (N–CH₃), 1319, 1284, 1241, 1163, 1095, 1048, 1027, 995, 908, 858, 806, 744, 732, 698, 672, 642 cm^{–1}. FD-MS: *m/z* 2135.1 (M⁺, 100%) C₁₄₂H₁₅₆N₈O₁₀ required M⁺ = 2134.9.

Catenane 15. The methylated catenane **14** (200 mg, 0.094 mmol) was dissolved in 20 mL of H₂SO₄ (96%), acetic acid, and water in 3/2/1 volume ratio. The reaction mixture was stirred at 120 °C for 15 min and directly poured onto 100 g of ice, then neutralized, and extracted with dichloromethane. The organic phase was separated and dried over magnesium sulfate, and the solvent was evaporated under vacuum. The crude product was chromatographed on silica gel with a mixture of dichloromethane/ethyl acetate (1/2) as eluent. Precipitation in a 10-fold volume of pentane followed by filtration afforded 150 mg of the title compound **15** with a yield of 82%.

mp > 300 °C. ¹H NMR (500 MHz, CDCl₃, 30 °C): δ = 8.92 (s, arom), 8.53 (s, arom), 8.47 (s, arom), 8.41 (s, arom), 8.33 (s, arom), 7.94 (s, arom), 7.75–6.85 (b, arom), 6.70–6.20 (b, arom), 5.86 (s), 5.57 (s), 5.46 (s), 5.27 (s), 5.20–5.10 (b), 3.56 (s, aliph), 3.42 (s, aliph), 3.20–2.85 (b, aliph), 2.45–1.00 (b, aliph), 0.31 (s, aliph), 0.23 (s, aliph), 0.03 (s, aliph). FT-IR (KBr) ν = 3500–3200 (O–H), 3058, 3047, 2934, 2859, 1737, 1645 (C=O), 1590, 1487, 1451, 1369 (N–CH₃), 1291, 1266, 1217, 1177, 1162, 1095, 1052, 1031, 998, 950, 875, 858, 806, 748, 731, 672, 642 cm^{–1}. FD-MS: *m/z* 1952.8 (M⁺, 60%) C₁₂₈H₁₄₄N₈O₁₀ required M⁺ = 1953.1.

2,5-Bis[2-bromoethoxy]terephthalic Diethylester (17). 2,5-Dihydroxyterephthaloyl diethylester **16** (1.00 g, 3.9 mmol) and 1,2-dibromoethane (2.00 g, 10.65 mmol) were dissolved in 20 mL of DMF, and potassium carbonate (2.00 g, 1.45 mmol) was added. The reaction mixture was stirred overnight at 100 °C and then poured into 100 mL of water at room temperature. The resulting solution was acidified with HCl to pH ~3 and extracted with 15 mL of dichloromethane. The organic phase was separated from the aqueous phase and dried over MgSO₄, and the solvent was removed in vacuo affording 1.60 g of the title compound in 87% yield.

¹H NMR (300 MHz, CDCl₃, 30 °C): δ 7.36 (2H, s), 4.37–4.29 (8H, m), 3.63 (4H, t, *J* = 6.2 Hz), 1.38 (6H, t, *J* = 1.38 Hz). ¹³C NMR (75.45 MHz, CDCl₃, 30 °C): δ 165.4, 151.6, 125.7, 118.0, 70.2, 61.6, 28.9, 14.3. FD-MS: *m/z* 466 (M⁺), C₁₆H₂₀Br₂O₆ required M⁺ = 466. mp = 99 °C.

2,5-Bis[2-(3,5-(di-*tert*-butylphenoxy)ethoxy]terephthalic Diethylester (18). To a solution of **17** (1.60 g, 3.42 mmol) in 20 mL of DMF were added 3,5-di-*tert*-butylphenol (3.00 g, 14.54 mmol) and potassium carbonate (2.00 g, 1.45 mmol). The reaction mixture was stirred overnight at 100 °C and then poured into 100 mL of water at room temperature. The resulting solution was acidified with HCl to pH ~3 and extracted with 15 mL of dichloromethane. The organic phase was separated from the aqueous phase and dried on MgSO₄, and solvent was removed in vacuo. The purification was carried out by chromatography (aluminum oxide mesh 0.05–0.20 nm (Merck), toluene/dichloromethane 1:1), affording 2.01 g of the title compound as a white product in 82% yield.

¹H NMR (300 MHz, CDCl₃, 30 °C): δ 7.48 (2H, s), 7.02 (2H, s), 6.79 (4H, s), 4.39–4.29 (12H, m), 1.33–1.28 (42H, m). ¹³C NMR (75.45 MHz, CDCl₃, 30 °C): δ 165.5, 158.2, 152.3, 152.1, 125.5, 118.0, 115.3, 109.0, 69.1, 66.4, 61.4, 35.0, 31.4, 14.2. FD-MS: *m/z* 718 (M⁺), C₄₄H₆₂O₈ required M⁺ = 718. mp = 152 °C.

2,5-Bis[2-(3,5-(di-tert-butylphenoxy)ethoxy]terephthalic Acid (19). To a suspension of **18** (2.00 g, 2.80 mmol) in 20 mL of a water/ethanol 1:1 solution was added 2.0 g of potassium hydroxide. The reaction mixture was stirred vigorously at 80 °C until a clear solution was obtained. The resulting solution was cooled to room temperature and neutralized with HCl. The resulting precipitate was filtered, washed with 100 mL of water, and dried under vacuum. Recrystallization of the crude precipitate in *n*-heptane afforded 1.71 g of a cottonlike product in 92% yield.

¹H NMR (300 MHz, CDCl₃, 30 °C): δ 11.1 (2H, b), 7.96 (2H, s), 7.07 (2H, s), 6.78 (4H, s), 4.63 (4H, dd, *J* = 8.9 Hz, *J* = 2.6 Hz), 4.40 (4H, dd, *J* = 8.9 Hz, *J* = 2.6 Hz), 1.3 (36H, s). ¹³C NMR (75.45 MHz, CDCl₃, 30 °C): δ 163.8, 157.4, 152.6, 151.7, 123.6, 118.5, 116.2, 109.0, 69.5, 65.2, 35.0, 31.4. FD-MS: *m/z* 662 (*M*⁺), C₄₀H₅₄O₈ required *M*⁺ = 662. mp = 264 °C.

Cyclic Trimer 20. The relative abundance of cyclic trimer **20** in the molecular weight distribution of poly[2]-catenane **4** depended on the initial concentration of monomers (discussed in text). Separation of cyclic trimer **20** from linear high molecular weight poly[2]-catenanes **4** was achieved by preparative size exclusion chromatography in chloroform as eluent affording 14 mg of a white powder.

¹H NMR (500 MHz, CD₂Cl₂, 30 °C): δ 8.98 (s, arom), 8.40–5.65 (b, arom), 5.28 (s), 4.86 (s), 4.70–4.10 (b, aliph), 3.70 – (–0.40) (b, aliph), –0.97 (s, aliph). MALDI-TOF-MS: *m/z* 7736.2 (*M* + *K*⁺) C₅₀₁H₅₇₆N₂₄O₄₈ + *K*⁺, required *M*⁺ = 7735.3.

Poly[2]-catenane 5. Dihydroxycatenane **15** (155.5 mg, 0.0795 mmol), terephthalic acid **19** (52.7 mg, 0.0795 mmol), 4-(*N,N*-dimethylamino)pyridine–toluene-*p*-sulfonic acid 1:1 complex as catalyst (85 mg, 0.289 mmol), and diisopropylcarbodiimide (0.4 mL, 2.55 mmol) were dissolved in 3 mL of dichloromethane at –20 °C under argon. The reaction mixture was stirred at this temperature for 6 days and added dropwise in methanol. Filtration of the precipitate afforded 192 mg of poly[2]-catenane **5** in 94% yield. Variations of reaction conditions are discussed in the text.

¹H NMR (500 MHz, C₂D₂Cl₄, 75 °C): δ 8.94 (m, arom), 7.85–6.10 (b, arom), 5.42 (s), 5.28 (s), 4.7–4.3 (b, aliph), 3.6–0.4 (b, aliph), –0.82 (s, aliph). FT-IR (KBr) *ν* = 3047, 2935, 2861, 1753 (C=O, ester), 1647 (C=O, amide), 1592, 1487, 1452, 1429, 1410, 1363 (N–CH₃), 1299, 1217, 1185, 1092, 1052, 996, 902, 860, 806, 744, 730, 707, 669 cm^{–1}.

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