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Multicyclic Polyethers of 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-Tetramethyl Spirobisindane and Di- or Triethyleneglycol. Multipotent Kryptands

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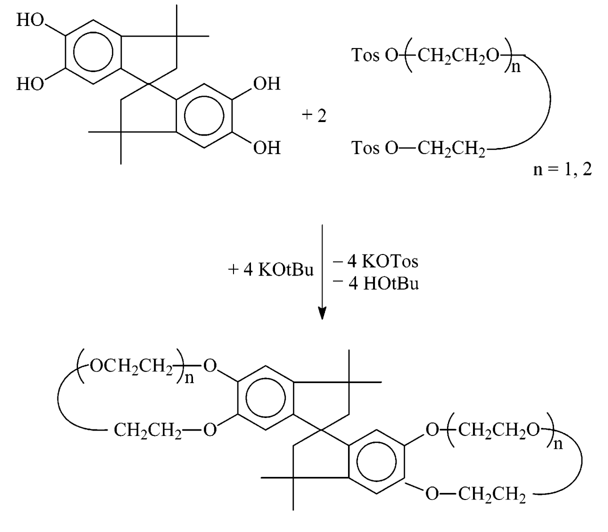
ABSTRACT: 5,5′-Tetrahydroxy-3,3,3′,3′-tetramethyl spirobisindane (TTSBI) was deprotonated with potassium *tert*-butoxide and polycondensed with di(ethylene glycol) tosylate or tri(ethylene glycol) tosylate. Polycondensations in DMSO gave cleaner reaction products than in DMF. At concentrations of 0.1 or 0.2 mol/L no cross-linking was observed and multicyclic polyethers were isolated. The high yields (up to 99%), the ^{1}H NMR and the MALDI−TOF mass spectra proved almost complete conversion. The DSC measurements indicated an amorphous character with two glass-transition temperatures. The SEC measurements showed rather narrow mass distributions with polydispersities below 2. The multicyclic polyethers dissolved lithium, sodium, potassium, and cesium benzoate in tetrahydrofuran at weight ratios around 1/50 (salt/multicycle).

Introduction

Almost all technical polycondensates such as polyesters, polyamides and polyimides are based on polycondensations of two difunctional monomers and are called "$a_2 + b_2$" or "two-dimensional polycondensations".[1] Polycondensations involving a difunctional monomer in combination with a trifunctional one are analogously called "$a_2 + b_3$" polycondensations or "three-dimensional polycondensations".[1] This latter attribute resulted from the fact that in early studies of "$a_2 + b_3$" polycondensations, three-dimensional networks were obtained as endproducts at high conversion.[1−4] Meanwhile "$a_2 + b_3$" polycondensations were studied by numerous research groups in much detail and it was learned how gelation can be avoided. Depending on monomer structure, concentration, feed ratio and conversion, hyperbranched polymers and multicyclic polymers were isolated in high yields. Much less is known about "$a_2 + b_4$" polycondensations.[1,5−12] Part of these polycondensations were reversible (thermodynamically controlled) chain growth polymerizations yielding soluble spirocycles and higher multicyclic oligomers.[5−7] Another part were irreversible (kinetically controlled) polycondensations yielding insoluble networks[8,9] or soluble multicyclic polymers.[10−12] These multicyclic polymers were all prepared from electrophilic "b_4" monomers. In this context, the present work served two purposes. On the one hand, it was meant as a fundamental study attempting the synthesis of soluble multicyclic polyethers (completely avoiding gelation) by an irreversible polycondensation with nearly quantitative conversion from a nucleophilic "b_4" monomer. On the other hand, a combination of monomers was selected which should yield multicyclic polyethers capable of complexing various cations. The structure of the monomers and the reaction pathway are outlined in Scheme 1. The complexity of even the simplest reaction products resulting from a quantitative conversion at a feed ratio of 2:1 (a_2:b_4) is illustrated in Schemes 2 and 3.

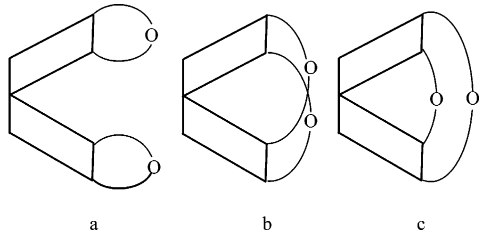
Scheme 1. Syntheses of Multicyclic Polyethers from TTSBI and Oligo(ethylene glycol) Tosylates



1 a, b (+ multicyclic oligomers and polymers)

a: n = 1 b: n = 2

Scheme 2. Isomers of the Monomer 1



Experimental Section

Materials. 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl spirobisindane (TTSBI) was purchased from ABCR Chemicals (Karlsruhe, Germany) and used as received. Di(ethylene glycol), tri(ethylene glycol), 4-toluene sulfonyl chloride, and potassium *tert*-butoxide were purchased from ACROS Chemicals (Geel, Belgium) and used as received. Di(ethylene glycol)tosylate, DEGT (mp = 88−89 °C), and tri(ethylene glycol)tosylate, TrEGT (mp = 80−81 °C), were prepared according to the literature[13] and twice recrystallized. DMF was distilled over P_4O_{10} in vacuo. DMSO was purified by azeotropic distillation with toluene followed by distillation in vacuo.

Polycondensations (Exemplary Procedures). A. With DEGT in DMF (No. 1, Table 2). TTSBI (10.0 mmol) was dissolved in dry DMF (90 mL) and potassium *tert*-butoxide (40.0 mmol or 41.0 mmol) was added. After 5 min, DEGT (20.0 mmol) was added. The reaction mixture was stirred for 1 h at 20 °C and for 5 h at

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Scheme 3. Isomeric Dimers of 1

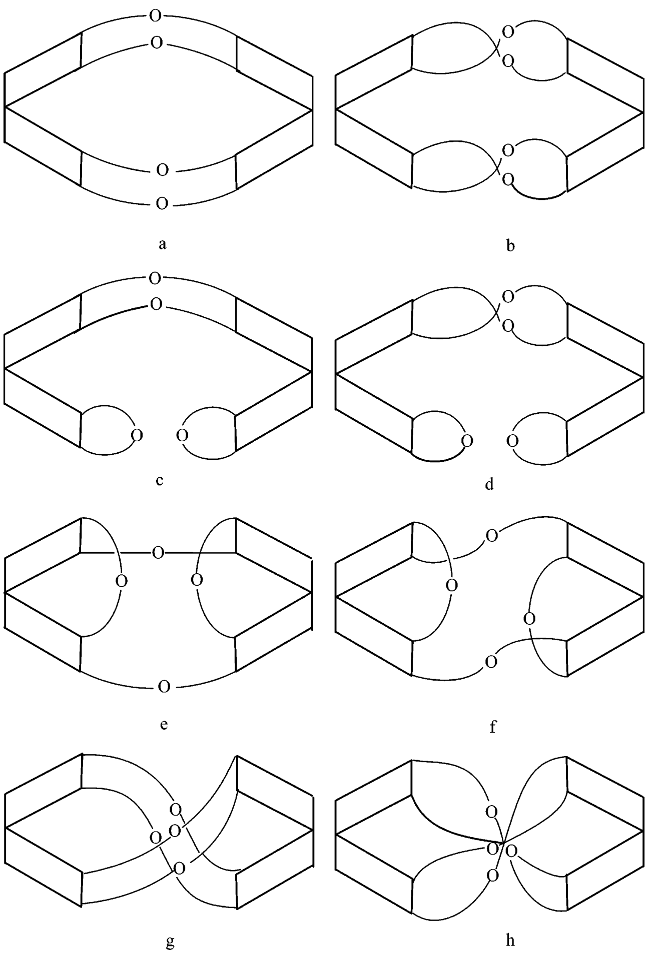


Table 1. Calculated Masses of the Multicyclic Polyethers (and their K-Doped Versions) Derived from TTSBI and Oligo(ethylene Glycol)s

	di(ethylene glycol)		tri(ethylene glycol)	
N	$\mathbf{B}_N\mathbf{C}N$	$\mathbf{B}_N\mathbf{C}N + \mathbf{K}$	$\mathbf{B}_N\mathbf{C}N$	$\mathbf{B}_N\mathbf{C}N + \mathbf{K}$
1	480.61	519.71	568.71	607.81
2	961.22	1000.32	1137.42	1176.52
3	1441.83	1480.93	1706.13	1745.23
4	1922.44	1961.54	2274.84	2313.94
5	2403.05	2442.15	2843.55	2882.65
6	2883.66	2922.76	3412.26	3451.36
7	3364.27	3403.37	3980.97	4020.07
8	3844.88	3883.98	4549.68	4588.78
9	4325.49	4364.59	5118.39	5157.49
10	4806.1	4845.2	5687.1	5726.2
11	5286.71	5325.81	6255.81	6294.91
12	5767.32	5806.42	6824.52	6863.62
13	6247.93	6287.03	7393.23	7432.33
14	6728.54	6767.64	7961.94	8001.04
15	7209.15	7248.25	8530.65	8569.75

Table 2. Polycondensations of TTSBI with Di(ethylene Glycol)tosylate (DEGT)

expt no.	reaction medium	concn of TTSBI (mol/L)	yield (%)	η_{inh}[a] (dL/g)
1	DMF	0.1	78	0.10
2	DMF[b]	0.2[b]	88	0.07
3	DMF	0.2	74	0.05
4	DMSO	0.1	99	0.16
5	DMSO	0.2	99	0.15
6	DMSO	0.3	99	0.06
7	DMSO	0.4	cross-linked	

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA 8:1. [b] Potassium *tert*-butoxide was used in an excess of 2.5 mol %.

Table 3. Polycondensation of TTSBI with Tri(ethylene glycol)tosylate (TEGT)

expt no.	reaction medium	concn of TTSBI (mol/L)	yield (%)	η_{inh}[a] (dL/g)
1	DMF	0.1	83	0.08
2	DMF	0.2	79	0.06
3	DMSO	0.1	98	0.21
4	DMSO	0.2	96	0.24
5	DMSO	0.3	98	0.06
6	DMSO	0.4	cross-linked	

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA 8:1.

100 °C. The cold reaction mixture was poured into water, and the precipitated polyether was isolated by filtration.

B. With TrEGT in DMSO (No. 5, Table 3). TTSBI (10.0 mmol) was dissolved in DMSO (45 mL) and potassium *tert*-butoxide (40 mmol) was added. After 5 min, TrEGT (20.0 mmol) was added and the reaction mixture was stirred for 1 h at 20 °C and for 5 h at 100 °C. The cold reaction mixture was poured into water and the precipitated polyether was isolated by filtration.

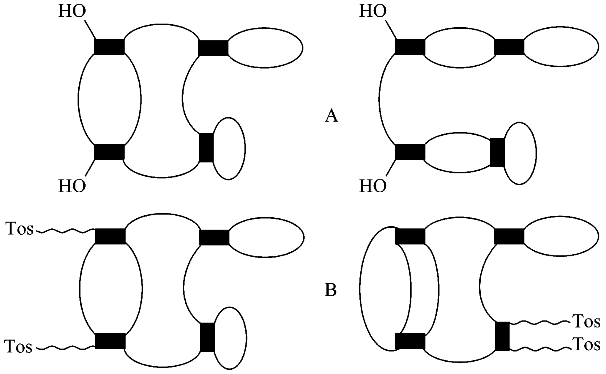
Complexation Studies. Solutions of 4.80 g of **1a** or 5.68 g of **1b** in 45 mL of THF (0.2 M) and 0.2 M solutions of commercial 18-crown-6 or tri(ethylene glycol) were prepared. Alkali metal benzoates or barium benzoate (10, 20, 30, or 50 mg each) were added to 5 mL of a ligand solution, and the suspension was shaken at 20−22 °C for 2 weeks. The alkali metal benzoates were prepared by dissolution of equimolar amounts of benzoic acid and metal hydroxides in distilled water followed by partial concentration of the resulting solutions in vacuo. Dioxane was then added and the resulting solution or suspension was again concentrated in vacuo. This treatment was repeated twice or three times to remove most of the water. The precipitated alkali metal salts were isolated by filtration and dried over P_4O_{10} in vacuo.

Measurements. The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20 °C. the 400 MHz ^{1}H NMR spectra were recorded with a Bruker “Avance 400” FT spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ (containing TMS) served as solvent. The MALDI−TOF mass spectra (MS) were measured on a Bruker Biflex III mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded on the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from polymer solutions in $CHCl_3$ with dithranol as matrix and potassium trifluoroacetate as dopant. The calculated masses of the multicycles with and without K^+ doping are listed in Table 1. The DSC measurements were performed on a Mettler-Toledo Md. 821 apparatus in aluminum pans under nitrogen with a heating rate of 20 °C/min. The SEC measurements were conducted on an apparatus of Polymer Laboratories equipped with a “Shodex RI 101” RI detector. A combination of three PL mixed-bed columns was used with chloroform as eluent (flow rate 1.0 mL/min). Commercial polystyrene standards served for calibration.

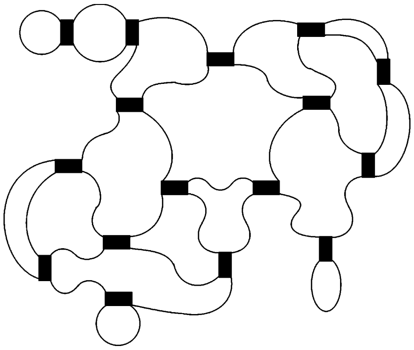
Results and Discussion

For a rapid and proper understanding of the polycondensations and MALDI−TOF mass spectra discussed below it seems to be advisable to explain at first the simplified formulas and terminology used in this publication for a short description of multicycles. This terminology is an extension of the formulas designed previously for the reaction products of “$a_2 + b_3$” polycondensations. Multicycles resulting from an ideal polycondensation with 2:1 feed ratio and 100% conversion are labeled $\mathbf{B}_N\mathbf{C}N$. Here C stands for cyclic, N is the degree of polymerization based on “b_4” monomers, and B means bridging units (based on “a_2“ monomers). Hence, the isomeric monomers of structure **1** have the general formula $\mathbf{B_1C1}$ (Scheme 2), the

Scheme 4. Two Isomers of the General Formula (A) B$_3$C4 and (B) B$_5$C4



Scheme 5. One Arbitrarily Selected Isomer of a Multicyclic Polymer B$_{16}$C16 Derived from TTBSI



isomeric dimers of **B$_2$C2** have the structures presented in Scheme 3, and Scheme 5 presents one isomer of **B$_{16}$C16** (the largest multicycle observed in a mass spectrum of this work). This structural formula and those of Scheme 4 use black rectangles as symbols of “b$_4$“ monomeric units which allow for a simple differentiation between isomers of complex multicycles. It is characteristic for **B$_N$CN** multicycles that they are free of “end groups” and that the number of cycles that can be depicted in a two-dimensional formula equals $N + 1$.

In the case of stoichiometric imbalance with an excess of “b$_4$” monomers, multicycles lacking bridging units will be formed. Their general formulas correspond to **B$_{N-1}$CN**, **B$_{N-2}$CN** etc. As illustrated in Scheme 4A, the lack of one B-unit means that the multicycles possess two “end groups” typical for the “b$_4$” monomer (in this work OH-groups of TTSBI). An excess of “a$_2$” monomers may yield **B$_{N+1}$CN** multicycles. Scheme 4B displays an illustration of such species as they may result from an excess of oligo(ethylene glycol)tosylates. The simultaneous presence of **B$_{N-1}$CN** and **B$_{N+1}$CN** multicycles in a reaction mixture indicates incomplete conversion.

The synthetic method used in this work is a normal version of “Williamson’s ether syntheses” using potassium *tert*-butoxide for the deprotonation of the phenolic OH groups. The first experiments were conducted with a concentration of 0.1 mol/L of TTSBI and DMF or DMSO served as reaction media (Nos. 1 + 4, Table 2, and Nos. 1, 3 + 4, Table 3). The ^{1}H NMR spectra indicated high conversions (>97%) because the CH$_2$-OH signal at 3.7 ppm had vanished and a new singlet signal at 4.3 ppm had appeared (Figure 1). The MALDI−TOF mass spectra proved that the desired **B$_N$CN** multicycles were the main products. Yet, **B$_{N-1}$CN** and **B$_{N+1}$CN** multicycles and unidentified byproducts were also detectable. Therefore, the polycondensations were repeated at TTSBI concentration of 0.2 mol/L and no gelation occurred (Nos. 2, 3, and 5, Table 2 and Nos. 2 and 4, Table 3). Now, the mass spectra revealed almost quantitative conversion, but small amounts of byproducts were still detectable in the mass psectra of the products prepared in DMF. Thus, the mass spectra evidenced that DMSO enabled cleaner polycondensations. Therefore, all further polycondensations using higher concentrations of TTSBI were exclusively performed in DMSO. Why DMF gave poorer results than DMSO was not studied in detail. Yet, in the presence of strong bases and nucleophiles DMF is sensitive to hydrolytic, alcoholytic or aminolytic cleavage, whereby part of the base/nucleophile is consumed and the liberated dimethylamine may cause additional side reactions.

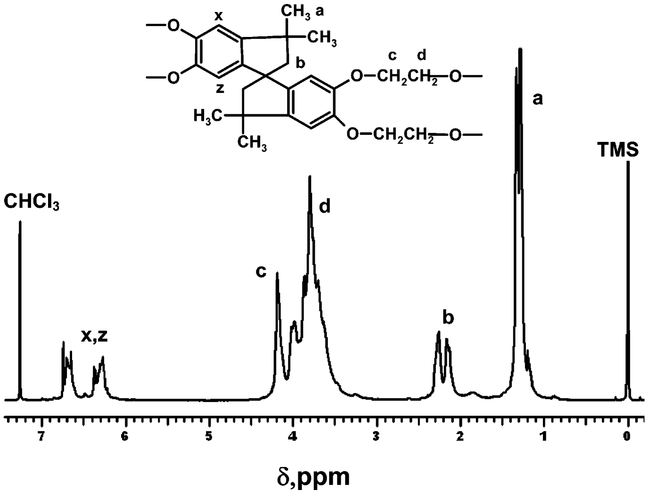


Figure 1. ^{1}H NMR spectrum of the multicyclic polyether derived from DEG (No. 4, Table 2).

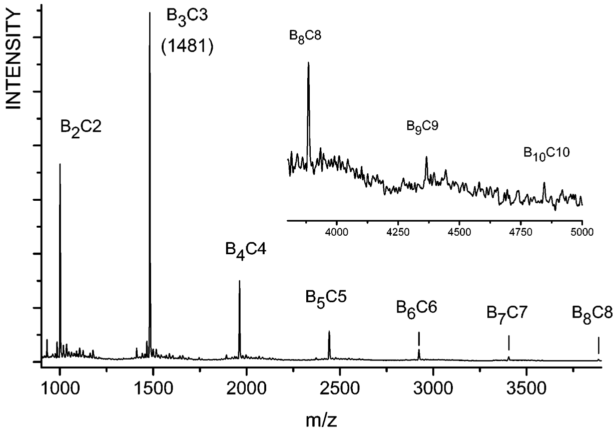


Figure 2. MALDI−TOF mass spectrum of the multicyclic polyether **1a**, No. 4, Table 2.

When TTSBI was polycondensed in DMSO at a concentration of 0.3 mol/L, cross-linking was still avoided but stirring proved to be difficult and a perfect homogenization of the reactants was not achieved. Therefore, the solution viscosities were low and the MALDI−TOF mass spectra indicated incomplete conversion. At a concentration of 0.4 mol/L both experiments (No. 7 in Tables 2 and 3) ended up with total gelation. The best MALDI−TOF mass spectra were obtained from the products prepared at a concentration of 0.2 mol/L as exemplarily illustrated in Figures 2 and 3. The multicycles with the highest mass which were detectable (in the mass spectrum of sample No. 3, Table 3) obeyed the general formula **B$_{16}$C16**, and one arbitrarily selected isomer of this species was depicted in Scheme 5 to illustrate the compact multicyclic structure. This example also demonstrates that not only **B$_{16}$C16** polyethers having a mass of 9100 Da, but also larger multicycles, possess

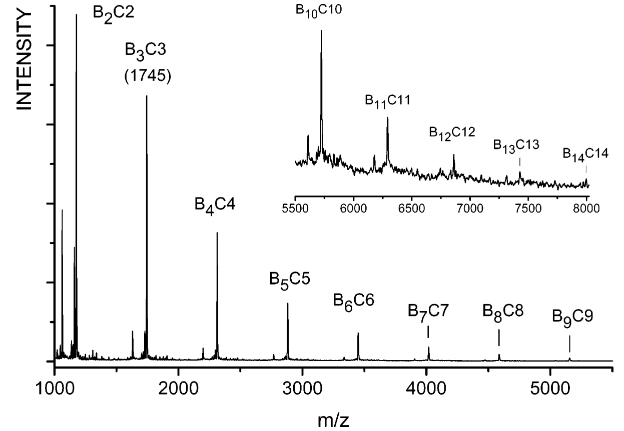


Figure 3. MALDI−TOF mass spectrum of the multicyclic polyether **1b** (No. 4, Table 3).

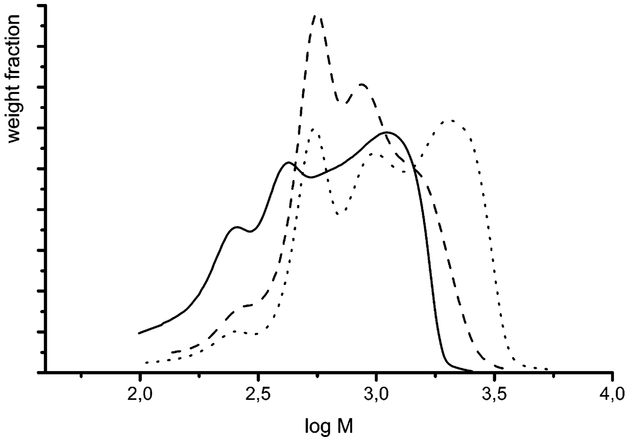


Figure 4. SEC elution curve of the multicyclic polyether: (A) **1a**, No. 5, Table 2; (B) **1b**, No. 3, Table 3; (C) **1b**, No. 4, Table 3.

an architecture which is absolutely unfavorable for entanglement. Therefore, it was found for all previously studied multicycles that even those samples with high polydispersities and high weight-average molecular weights showed low solution viscosities.

When analogous polycondensation experiments were conducted with α,*ω*-dibromoalkanes at a TTSBI concentration of 0.1 mol/L gelation occurred or the conversions were incomplete. This observation underlines that the successful syntheses of multicycles **1a** and **1b** is not trivial, but a characteristic consequence of the high cyclization tendency inherent in oligo(ethylene glycol)s. The repulsive interaction between the lone electronic pairs of the O atoms and the C−H σ-bonds in β-position has the consequence that oligo- and poly(ethylene oxide)s possess a high content of gauche conformations which favor the formation of loops and cycles. This characteristic conformational property is, for instance, reflected in the easy synthesis of crown ethers and in the previously published syntheses of multicyclic poly(ether ester)s.[14] In contrast, the all-trans conformation is the energetically most favorable state of an alkane chain, and this conformation favors chain growth (and thus gelation) over cyclization.

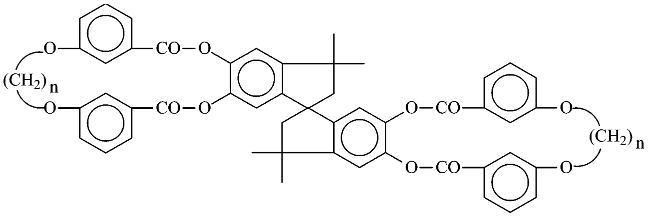
SEC measurements of the polyethers with the highest solution viscosities (No. 4, Table 2, and Nos. 3 and 4, Table 3) were performed in chloroform and calibrated with polystyrene. From such a calibration highly accurate molecular weights were, of course, not expected, but nonetheless, the SEC curves revealed two interesting aspects, as illustrated in Figure 4. All three curves indicate relatively low molar masses with number-average molecular weights (M_ns in the range of 1500−2000 Da). They also indicate rather narrow molecular weight distributions with polydispersities below 2.0. These findings disagree with the following observations. Other multicyclic polyethers having similarly low solution viscosities show higher molecular weight[10,13−17] and higher polydispersities (typically in the range of 3−8). Polydispersities in the range of 3−10 are characteristic for all polycondensates with high contents of cycles.[18] Such comparison is particularly informative, when the multicyclic polyesters of TTSBI (**2**) are taken into account.[19] These polyesters had solution viscosities in the range of 0.17−0.22 dL/g measured under the same conditions as those of the polyethers **1**. Yet, their SEC elution curves ended at masses of 10^5−10^6 Da and the polydispersities fell into the range 3.5−5.0. Furthermore, the MALDI−TOF mass spectra of **1b** display mass peaks of multicycles up to 9100 Da. Taking into account that higher molar masses are considerably discriminated in these mass spectra[20−22] multicycles with masses >9000 Da should be present in the **1b** samples and the mass peaks above 2000 Da should be more intensive to match their real frequency. Furthermore, it must be taken into account that in a SEC curve multicycles with a mass of 10 000 Da appear with a nearly 20-fold intensity relative to an equal number of **B$_1$C1** cycles which form the first peak in all elution curves. In other words, at least the **1b** samples should contain a significant mass fraction above 5000 Da, whereas the SEC curves fade away around 5000 Da. On the other hand, two results indicate that the calibration with polystyrene is not responsible for this problem. First, SEC measurements of commercial linear poly(ethylene oxide)s overestimated not underestimated the real M_ns by 20−50%. Second, a mass of 500 Da was determined for the first peak in the SEC curve A of **1a** and a mass of 600 Da for the first peak in the SEC curves of both **1b** samples. These masses agree well with those calculated for **B$_1$C1** (Table 1). Taken together, these results suggest that the observation of the high molar mass multicyclic polyethers (>4000 Da) is suppressed in the SEC curves, possibly by association of the multicycles with the polystyrene gels. Possibly the aromatic ring plays the role of a host in the oligoether cycles.

The DSC measurements indicated that these multicyclic polyethers are amorphous with much higher glass transition temperatures than those of the linear poly(ethylene oxide)s which possess T_gs in the range of −40 to −60 °C. Yet, quite unexpected is the finding of two T_gs for each sample, namely T_gs of 79 and 170 °C for **1a** (No. 5, Table 2) and T_gs of 70 and 102 °C for **1b** (No. 4, Table 3). At first glance one might interpret the lower T_gs to result from the **B$_1$C1** isomers and the higher T_gs for the higher oligomers. However, two or more T_gs were also observed for high molar mass multicyclic poly(ether sulfone)s, whereas all other multicyclic polymers studied so far showed only one T_g. Therefore, a straightforward explanation cannot be given at this time.

Finally, the crown ether or kryptand properties of the multicycles **1a** and **1b** respectively were studied with 0.2 M solutions of the multicycles in tetrahydrofuran. At 20−25 °C, 5 mL of such a solution dissolved 10 mg of lithium, sodium, potassium, rubidium, and cesium benzoate (and about 5 mg of barium benzoate). About 20 mg of these benzoates were not completely dissolved. For comparison, analogous solubility studies were performed with an equimolar solution of 18-crown-6 (corresponding to an equal number of oligoether cycles). This standard crown ether dissolved more than 30 mg of K-benzoate, whereas 10 mg samples of all other metal salts were not dissolved. Furthermore, the solubility of the aforementioned benzoates in a 0.2 M solution of neat tri(ethylene glycol) in THF was examined at 20 °C. The 10 mg samples of sodium and potassium salts were dissolved, but all other salts remained insoluble. In summary, these results demonstrate the expected high selectivity of the crown ether and a total lack of selectivity of the multicyclic polyethers which may be useful as kryptands or phase-transfer catalysts when a high selectivity for a certain cation is not desirable.

Conclusion

The polycondensation experiments performed in this work demonstrated that it is feasible to synthesize soluble multicyclic polyether from TTSBI and DEG or TrEG tosylate when the concentration of TTSBI is kept below 0.3 mol/L. The efficient cyclization reactions which prevent cross-linking are characteristic for oligo(ethylene oxide)s and not paralleled by *n*-alkane chains. Similar structure−property relationships were found for syntheses of soluble multicyclic polyesters of TTSBI. With aliphatic dicarboxylic acids such as adipic or sebacic acid (used as their dichlorides) only cross-linked products were obtained, and similar negative results were obtained with various other dicarboxylic acids. Only a few “ether diacids” derived from resorcinol and short alkane chains yielded soluble multicyclic polyesters (structure **2**). Characteristic for the multicyclic polyethers based on the structures **1a** and **1b** is their capability to complex all alkali cations and help to dissolve them in organic solvents. Their lack of selectivity results from the presence of cycles and cavities of various diameters. Therefore, they may be called multipotent kryptands.



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