Multicyclic Poly(ether ester)s by Polycondensation of Oligo(ethylene glycol)s and Trimesoyl Chloride

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ABSTRACT: Monodisperse oligo(ethylene glycol)s were polycondensed with trimesoyl chloride using triethylamine as HCl acceptor. Despite nearly quantitative conversions and relatively high concentrations (0.4 mol/L), no gelation occurred with tri- and tetra(ethylene glycol), regardless of the feed ratio. With a feed ratio around 1.5/1.0 multicyclic poly(ether esters)s free of end groups were isolated and characterized by ^{1}H NMR and MALDI-TOF mass spectrometry. At concentrations of 0.2 or 0.4 mol/L di-, penta-, and hexa(ethylene glycol)s yielded gels. At concentrations $\geq$ 0.2 mol/L exclusively gels were obtained from various α,ω-dihydroxyalkanes. However, soluble multicycles were obtained from 1,8-dihydroxy-3,6-dithiaoctane and from 1,4-bis(2-hydroxyethoxy)-2-butyne. The influence of conformational differences on the cyclization tendency is discussed. The multicycles derived from tri- and tetraethylene glycol showed cryptand properties and dissolved Li-, Na-, K-, and Cs-benzoate in tetrahydrofuran.

Introduction

Polycondensation of difunctional with trifunctional monomers (so-called $a_2 + b_3$ polycondensations) were first studied and analyzed by Kienle et al.[1,2] and Flory.[3] These polycondensations were mostly conducted with feed ratios of 1.5:1.0 and yielded insoluble gels at high conversions or soluble, branched oligomers at low conversions. More recently, several authors[4−21] have reported on polycondensations with a feed ratio of 1.0:1.0 aiming at the synthesis of (hyper)branched polymers. Such a study also included 1:1 polycondensations of trimesoyl chloride with polydisperse oligo(ethylene glycol)s (number-average molecular weights, M_ns, between 200 and 3400 Da).[21] To avoid gelation, these polycondensations were conducted at low concentration conditions which, in principle, favor cyclization. However, Long et al. did not detect the expected cyclic oligomers, apparently because MALDI-TOF mass spectra were too complex below 1500 Da. We have recently reported on syntheses of multicyclic aromatic polyethers by $a_2 + b_3$ polycondensations with feed ratios around 1.5:1.0.[22−26] Despite nearly quantitative conversions, gelation was avoided by optimization of the concentration and by selection of monomers favoring cyclization. In this context, the present work served three purposes. First, it should find out if our concept of multicyclic polymers can be extended to polyesters using trimesoyl chloride as b_3 monomer (Scheme 1). Oligo(ethylene glycol)s seemed to be favorable because of a relatively high cyclization tendency due to the high concentration of gauche conformations. Second, it should be studied how the different conformational properties of aliphatic α,ω-diols (e.g., the ratio of gauche and trans conformations) influence the cyclization tendency and thus the probability that multicyclic polyesters are formed. Third, it should be elucidated if multicyclic oligomers and polymers derived from oligo(ethylene glycol)s may act as crown ethers or cryptands for cations with largely differing radii.

Experimental Section

Materials. 1,7-Heptanediol, di-, tri-, and tetra(ethylene glycol) were purchased from Aldrich Co. (Milwaukee, WI), azeotropically dried with toluene, and distilled in a vacuum of 10^{-2} mbar over a short-path apparatus. Penta- and hexa(ethylene glycol) (Aldrich Co.) were also azeotropically dried with toluene and finally dried at 100 °C in a vacuum of 10^{-2} mbar. The crystalline 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, and 1,12-dodecanediol were also purchased from Aldrich Co. and dried in desiccator in vacuo over P_4O_{10}. Trimesoyl chloride (TmsCl) was also purchased from Aldrich Co. and recrystallized from toluene. Dichloromethane was distilled over P_4O_{10}. Triethylamine was kindly supplied by BASF AG (Ludwigshafen, Germany) and distilled over powdered calcium hydride. Dioxane was refluxed and distilled over sodium.

Polycondensations (Exemplary Procedures). A. In Dichloromethane. Trimesoyl chloride (20 mmol) and a tri(ethylene glycol), TrEG, or tetra(ethylene glycol), TeEG (29 mmol), were weighed into a 150 mL Erlenmeyer flask and dissolved in dry dichloromethane (45 mL). A solution of triethylamine (61 mmol) in dry dioxane (10 mL) was added dropwise with stirring over a period of ∼30 min. The reaction mixture was stored for 24 h at 20 °C. It was then diluted with dichloromethane (200 mL) and washed twice (or five times) with water (50 mL). The organic solution was dried with Na_2SO_4 concentrated to dryness. The crude residue was characterized. Analogous polycondensations were performed in 90 or 180 mL of dichloromethane (nos. 1, 2, Table 1).

B. In Dioxane. Trimesoyl chloride (20 mmol) and tri(ethylene glycol) or tetra(ethylene glycol) (29 mmol) were weighed into a 100 mL round-bottom flask and dissolved in dry dioxane (40 mL). A solution of triethylamine (61 mmol) in dry dioxane (5 mL) was added dropwise with stirring (using a magnetic stirrer). The reaction mixture was stored for 24 h at 20 °C.

Dissolution of Metal Salts. A solution of the tri(ethylene glycol)-based multicycle (5 g) in dry tetryhydrofuran (50 mL) was prepared and subdivided into 10 portions. Powdered Li-, Na-, K-, Cs-, and Ba-benzoate (10 or 50 mg) were added to the polymer solutions, and these suspensions were slowly shaken in 10 mL test tubes for a period of 2 weeks. During this period the 10 mg samples of Li-, Na-, K-, and Cs-benzoate went into solution, whereas part of the 50 mg samples remained insoluble.

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 on a Bruker "Avance 400" spectrometer in 5 mm o.d. sample tubes. Chloroform containing TMS served as solvent and shift reference. The MALDI-TOF mass spectra (MS) were measured with a Bruker "Biflex III" 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 chloroform solutions with dithranol as matrix and potassium trifluoroacetate as dopent.

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Scheme 1. Sytheses of Multicyclic Poly(ether ester)s from Trimesoyl Chloride and Monodisperse Oligo(ethylene glycol)s

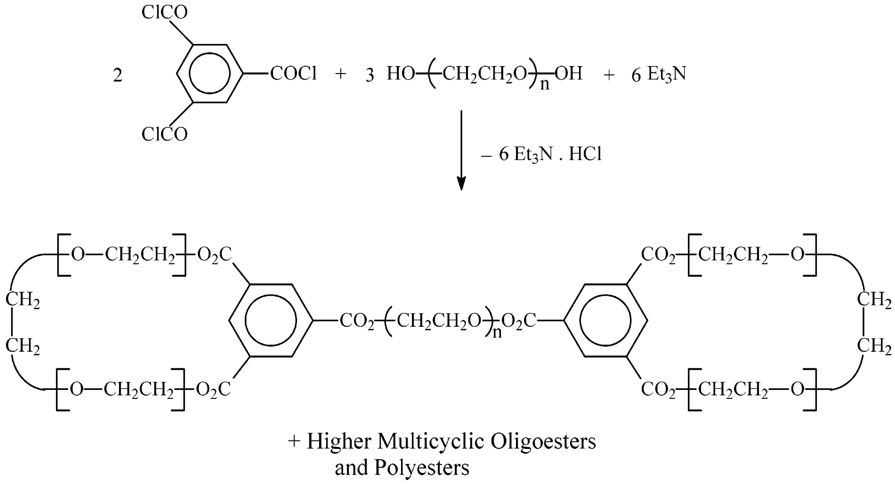
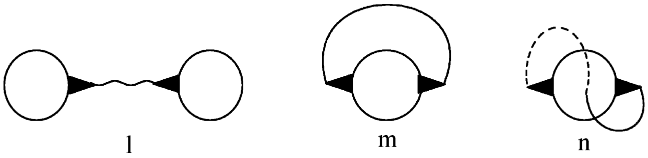


Table 1. Polycondensations of Tri(ethylene glycol), TrEG, with Trimesoyl Chloride (TMC)

expt no.	reaction medium	method of purification	concn of TMC (mol/L)	feed ratio	yield[a,b] (%)	η_{inh}[c] (dL/g)
1	CH_2Cl_2	A	0.1	1.45/1.0	40[a]	0.04
2	CH_2Cl_2	A	0.2	1.45/1.0	42[a]	0.05
3	CH_2Cl_2	A	0.4	1.45/1.0	41[a]	0.18
4	CH_2Cl_2	B	0.4	1.45/1.0	85[b]	0.17
5	CH_2Cl_2	A	0.4	1.50/1.0	cross-linked	
6	CH_2Cl_2	A	0.4	1.40/1.0	cross-linked	
7	dioxane	C	0.2	1.45/1.0	cross-linked	
8	dioxane	C	0.4	1.45/1.0	cross-linked	

[a] After 5 times washing with water. [b] After twice washing with water. [c] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2.

Scheme 2. Schematic Structures of Isomeric B_1C2 Multicycles



Results and Discussion

Nomenclature. Our recent studies of multicyclic aromatic polyethers suggested to design a new nomenclature which allows for a simple symbolization and presentation of their complex structure. Two sets of formulas were designed, namely formulas allowing for a precise two-dimensional description of ring sizes, degrees of polymerization (DPs), and mutual connection of all rings in one molecule. The triangles in these two-dimensional formulas exemplarily illustrated in Schemes 1−3 represent the building blocks resulting from b_3 monomers. Furthermore, "one-dimensional" formulas were designed for the text. In these formulas C stands for cycle, and the number behind C indicates the DP. The letter B stands for a "bridge unit" which either connects two cycles (illustrated by B_1C2 a in Scheme 1) or forms a bridge across a cycle (e.g., B_1C2 "m" in Scheme 2). The total number of cycles which can be formulated in a two-dimensional formula is then given by B_n+1.

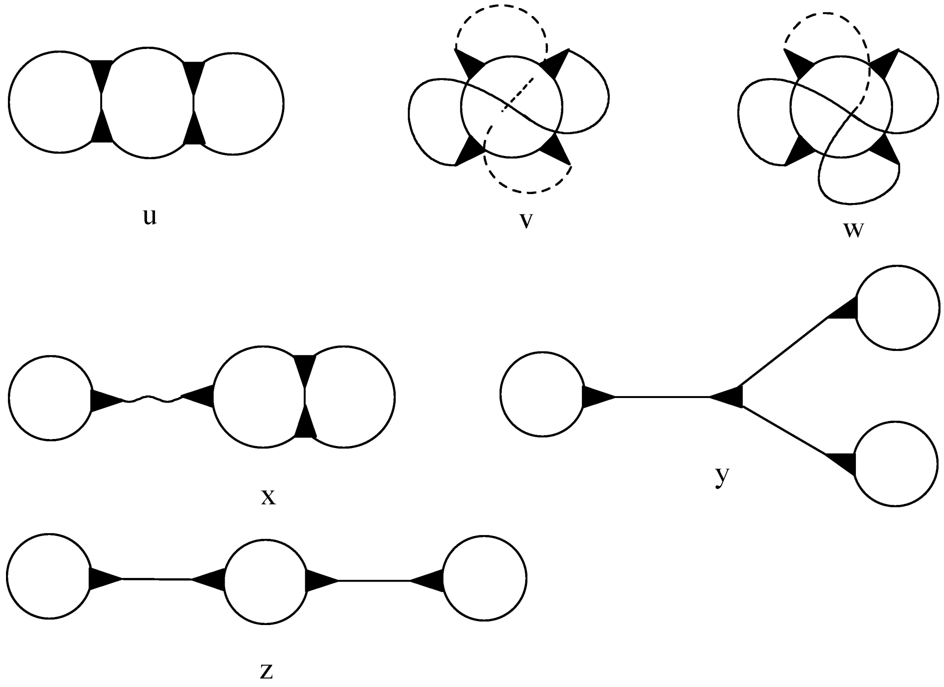
This nomenclature was taken over from our previous publication, but in addition to clarification the present paper requires short discussion of the correlation between isomerism and chain flexibility. In all previous studies of multicyclic polymers fully aromatic polyethers were prepared which possess a more restricted segment mobility than the oligo(ethylene oxide) units of the multicycles described in the present work. This difference has consequences for the number and structure of the isomers which can be formed. For instance, three isomers of the B_1C2 type can, in principle, be formed, when the a_2 monomers are sufficiently long and flexible, whereas the relatively rigid aromatic polymers can only yield the "b-isomers". In the case B_2C4 (Scheme 3) the "u" and "v" isomers can be formed by fully aromatic polymers, but with flexible aliphatic chain segments the isomers "w"−"z" should also be accessible. The B_8C16 isomers of Scheme 4 were formulated for two reasons. First, they illustrate that higher multicycles can exist in relatively open star-shaped or branched structures or in rather compact, globular structures. Second, B_8C16 multicycles were largest molecules detected by MALDI-TOF mass spectroscopy in the spectrum of Figure 1. However, in the less clean mass spectrum of sample no. 5, Table 2, even $B_{10}C20$ (8948.5 Da) was detected.

Finally, it should be mentioned that multicycles complying to the formula B_nC2n (Schemes 2−4) may be expected as reaction products, when an a_2/b_3 feed ratio of 1.5/1.0 is applied and when the reaction conditions allow for nearly quantitative conversions. For all other feed ratios and for lower conversions less perfect multicycles having one or more end groups will be the main products.

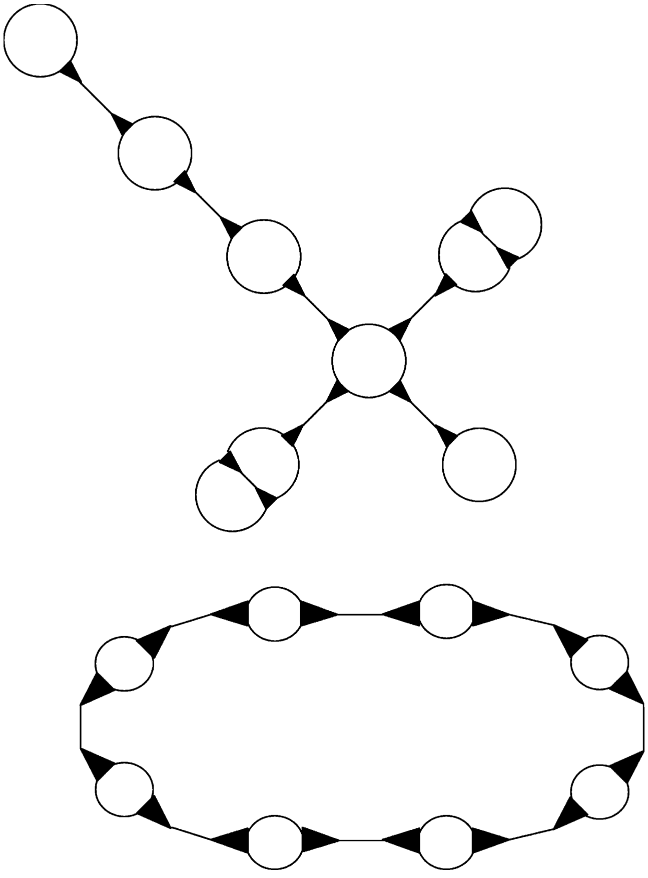
Polycondensations of Oligo(ethylene glycol)s. The first polycondensations of TmsCl with TrEG were conducted at a TmsCl concentration around 0.1 mol/L in dichloroethane (no. 1 in Tables 1 and 2), whereby triethylamine served as HCl acceptor. Despite a relatively long reaction time of 24 h both ^1H NMR spectra and MALDI-TOF mass spectra of the isolated syrupy reaction products indicated that the conversion was only of the order of 90%. When these polycondensations were repeated at the concentration of 0.2 mol/L again soluble polyesters were obtained, but the conversion was above 98%. Therefore, all further polycondensations were performed at the higher concentrations of 0.2 or 0.4 mol/L of TmsCl.

Two different reaction media and two different workup procedures were used. Either dichloromethane served as solvent and the triethylamine hydrochloride was removed by washing with neutral water (methods A and B) or dioxane served as solvent and the reaction mixture was poured into water after

Scheme 3. Schematic Structures of Isomeric B_2C4 Multicycles



Scheme 4. Two Arbitrarily Selected Isomers of B_8C16



concentration (method C). For dichloromethane as reaction medium the influence of the washing process on yield and purity was studied. One experiment was performed with 30 mmol of TmsCl and TrEG as comonomers and a parallel experiment with TeEG as comonomers. Both reaction mixtures were subdivided into four equal parts. One part was washed twice, the second part three times, the third part four times, and the fourth part five times. The isolated poly(ether ester)s were characterized by viscosity and ^{1}H NMR spectroscopic measurements. Whereas the viscosities were not significantly influenced by repeated washing, the contamination with $Et_3N{\cdot}HCl$ decreased from values around 5 to 1 wt %, and the yields decreased from values around 80% to values around 40%. The results obtained with twice washing (method B) and five times washing (method A) are summarized in Table 1 for TrEG and Table 2 for TeEG. The polycondensations in dioxane gave the interesting result that with TrEG a gel was obtained (nos. 7 + 8 in Table 1), but not with TeEG. This observation indicates that the efficiency of cyclization was significantly influenced by the reaction medium, most likely due to its influence on the population of different conformations.

From a theoretical point of view the optimum stoichiometry for complete conversion should result from a feed ration of 1.5/1.0 (a_2/b_3). However, it was found in numerous polycondensations evaluated by means of MALDI-TOF mass spectrometry that optimum results require in fact a slight excess (typically 1−2 mol %) of the electrophilic reaction partner (exemplarily illustrated in refs 26−28). Therefore, both polycondensations of TrEG and TeEG were performed with variation of the feed ratio from 1.40/1.00 to 1.45/1.00 and 1.50/1.00. The mass spectra evidenced that the lowest content of byproducts was

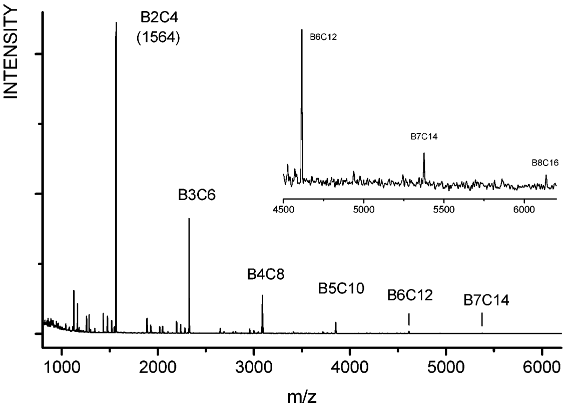


Figure 1. MALDI-TOF mass spectrum of multicyclic polyesters obtained from TrEG (no. 3, Table 1).

Table 2. Polycondensations of Tetra(ethylene glycol), TeEG, with Trimesoyl Chloride (TMC)

expt no.	reaction medium	method of purification	concn of TMC (mol/L)	feed ratio	yield (%)	$\eta_{inh}{}^{d}$ (dL/g)
1	CH_2Cl_2	A	0.1	1.45/1.0	36^a	0.05
2	CH_2Cl_2	A	0.2	1.45/1.0	34^a	0.07
3	CH_2Cl_2	A	0.4	1.45/1.0	36^a	0.19
4	CH_2Cl_2	A	0.4	1.40/1.0	35^a	0.12
5	CH_2Cl_2	A	0.4	1.50/1.0	35^a	0.20
6	CH_2Cl_2	B	0.4	1.50/1.0	78^b	0.18
7	dioxane	C	0.2	1.45/1.0	65^c	0.12
8	dioxane	C	0.4	1.45/1.0	83^c	0.15

[a] After five times washing with water. [b] After twice washing with water. [c] After precipitation into water. [d] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2.

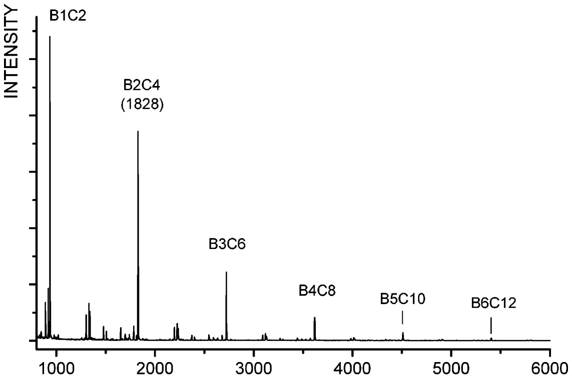


Figure 2. MALDI-TOF mass spectrum of a multicyclic polyester obtained from TeEG (no. 3, Table 2).

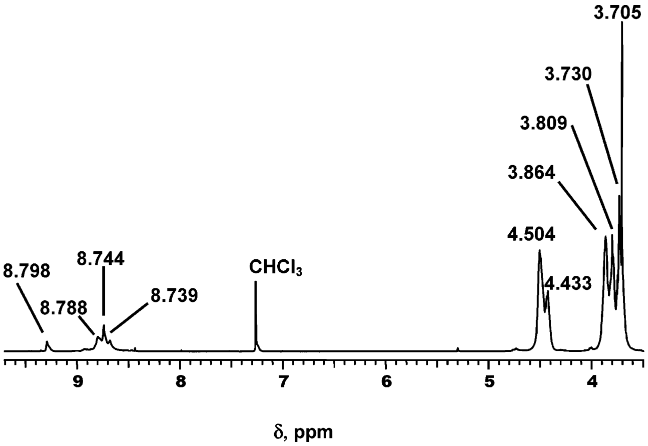


Figure 3. 400 MHz ^1H NMR spectrum of a multicyclic polyester obtained from TrEG (no. 3, Table 1).

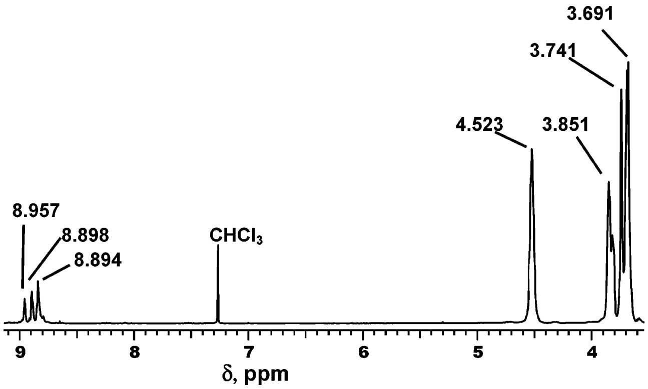


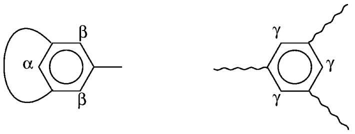
Figure 4. 400 MHz ^1H NMR spectrum of a multicyclic polyester obtained from TeEG (no. 5, Table 2).

Table 3. Polycondensations of 1,4-Bis(2-hydroxyethoxy)-2-butyne, HEB, with Trimesoyl Chloride, TmsCl

expt no.	reaction medium	concn of TmsCl (mol/L)	feed ratio	yield^a (%)	$\eta_{inh}{}^{b}$ (dL/g)
1	CH_2Cl_2	0.2	1.50/1.0	91	0.08
2	CH_2Cl_2	0.4	1.50/1.0	cross-linked	
3	CH_2Cl_2	0.4	1.45/1.0	cross-linked	
4	dioxane	0.4	1.45/1.0	cross-linked	

[a] After twice washing with water. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2.

Scheme 5. Illustration of Aromatic Protons with Slightly Different Chemical and Magnetic Environment



indeed achieved with a feed ratio of 1.45/1.00 (Figures 1 and 2). The mass spectra also revealed that the multicycles of the formula B_nC2n were the main products regardless of the feed ratio. For the reaction products of TrEG B_8C16 was the largest multicycle which was detectable in our mass spectra (Figure 1). Two isomers of this composition are presented in Scheme 4 as illustration for the broad variation of the structures which may exist behind a general formula such as B_8C16.

The ^1H NMR spectra contributed the following information. The CH_2 signal of the $-CH_2OH$ groups experienced a downfield shift of 0.7−0.8 ppm upon esterification with TmsCl (signals at 4.5 ppm in Figures 3 and 4). Quantification of the signal intensities allowed for the calculation of conversions, but the accuracy of this method does not allow one to distinguish between 99.0 and 99.5% conversion. Interestingly, the aromatic protons display a splitting which does not exist in the NMR spectra of perfectly symmetrical esters such as triethyl trimesate. Obviously, this splitting reflects the difference between smaller and larger cycles. The three signals of the TeEG-based multicycles (Figure 4) may be interpreted as a result of the α-, β-, and γ-structures presented in Scheme 5. In the case of TrEG-based multicycles the splitting is more complex and indicates a greater sensitivity to cycles of different diameter, as illustrated in Schemes 3 and 4. Hence, the ^1H NMR spectra support our interpretation of the mass spectra assuming multicycles B_nC2n as the main product.

Polycondensations of Various Diols. The successful syntheses of multicyclic poly(ether ester)s from TrEG and TeEG prompted us to study analogous polycondensations of diols having similar distances of the OH groups. At first, hydroxyethylated hydroquinone (**1**) and hydroxyethylated 1,4-dioxabutyne (**2**) were used as comonomers of TmsCl. These polycondensations were performed with feed ratios of 1.45/1.0 and 1.50/1.0 in dichloromethane and dioxane. Molar concentrations of TmsCl around 0.2 and 0.4 mol/L were selected. Yet, regardless of solvent and concentration only gels were obtained, when **1** was used as reaction partner of TmsCl. With **2** again cross-

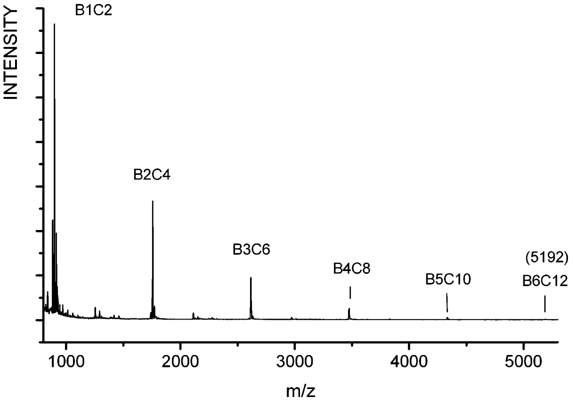


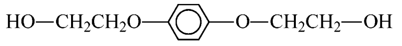
Figure 5. MALDI-TOF mass spectrum of a multicyclic polyester prepared from 1,8-dihydroxy-3,6-dithiaoctane (**3**) at a concentration of 0.2 mol/L TmsCl (no. 1, Table 4).

Table 4. Polycondensations of 1,8-Dihydroxy-3,6-dithiaoctane, DDO, with Trimesoyl Chloride

expt no.	reaction medium	concn of TmsCl (mol/L)	feed ratio	yield[a] (%)	η_{inh}[b] (dL/g)
1	CH_2Cl_2	0.2	1.50/1.0	85	0.08
2	CH_2Cl_2	0.4	1.50/1.0	cross-linked	
3	CH_2Cl_2	0.4	1.45/1.0	cross-linked	
4	dioxane	0.4	1.45/1.0	cross-linked	

[a] After twice washing with water. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2.

linking occurred at the concentration of 0.4 mol/L, whereas a completely soluble product was obtained at 0.2 mol/L (see Table 3). The ^1H NMR spectrum of this product confirmed almost quantitative esterification of the CH_2OH groups. In the mass spectrum the peaks of B_nC2n multicycles were largely prevailing over those of functional multicycles quite analogous to the spectrum of Figure 2.



1

$$HO{-}CH_2CH_2O{-}CH_2C{\equiv}C{-}CH_2O{-}CH_2CH_2{-}OH \qquad \mathbf{2}$$

$$HO{-}CH_2CH_2S{-}CH_2CH_2S{-}CH_2CH_2{-}OH \qquad \mathbf{3}$$

Further polycondensations were conducted with 1,8-dihydroxy-3,6-dithiaoctane (**3**). Again, dichloromethane and dioxane were used as reaction media at a concentration of 0.4 mol/L. However, with feed ratios of 1.45/1.0 or 1.5/1.0 gels were obtained in all experiments. Yet, an additional polycondensation performed in dichloromethane at a concentration of 0.2 mol/L with a feed ratio of 1.50/1.0 yielded a soluble product which was isolated in the form of a white powder. The ^1H NMR spectrum indicated nearly quantitative esterification and the MALDI-TOF MS proved the formation of B_nC2n multicycles as the main reaction products as illustrated in Figure 5. The bond angle of the sulfide groups in **3** amounts to approximately 99°[25] and is thus significantly smaller than the bond angle of 113°[25] typical for aliphatic ethers. Therefore, one might a priori expect that diol such as **3** is more favorable for cyclization than oligo(ethylene glycol)s, but the experiments of this work demonstrate that the contrary is true. Nonetheless, the "disulfide" **3** proved to be more useful than ω-alkanediols. When 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,-10-decanediol, and 1,12-dodecanediol were used as comonomers of TmsCl gels were obtained under all circumstances. Since the alkane chains exclusively consist of CH_2 groups with bond angles around 109.5° which are between those of the dialkyl ethers and dialkyl sulfides, the results demonstrate that the bond angles are not decisive for the efficiency of cyclization reactions. However, these results can be rationalized by considering that the energetically most favorable conformation of linear alkanes is the all-trans conformation, which is in turn unfavorable for cyclization. In contrast, aliphatic ethers prefer a gauche conformation in the bond neighboring the oxygen because the free electron pairs of the O atom interfere with the σ-electrons of the CH bonds in the β-position in an all-trans conformation. Therefore, poly(ethylene glycol)s are particularly favorable for cyclization reactions. The enormous difference between alkanediols and oligo(ethylene glycol)s with respect to cyclization has previously been demonstrated in thermodynamically controlled polycondensations with $Ge(OEt)_4$.[28] Here again, only oligo(ethylene glycol)s yielded soluble multicyclic oligomers.

Dissolution of Metal Salts. Although the individual cycles of the poly(ether ester)s synthesized in this work are quite different from an ideal crown ether, the multicylic oligomers and polymers may contain cavities capable of complexing cations. Since the oligoether segments are flexible and since individual cycles with various diameters exist, complexation of various metal ions might be possible, if cavities having the properties of cryptands exist at all. To elucidate this aspect, at least qualitatively four metal salts, namely the benzoates of lithium, sodium, potassium, cesium, and barium, were prepared for probes. These metal salts were added to 10 wt % solutions of TrEG and TeEG multicycles in tetrahydrofuran. Two series based on different feed ratios were studied, namely multicycle/salt ratios of 10:1 and 50:1. After 2 weeks of shaking the suspensions at 20 °C, the salts of the 10:1 series were not completely dissolved. Yet, clear solutions of Li-, Na-, K-, and Cs-benzoate were obtained from the 50:1 series. Hence, this preliminary study proves that the multicyclic poly(ether ester)s of this work possess cryptand properties for alkali metal ions of any size. For comparison, the complexing capacity and selectivity of TrEG and TeEG in TAF were studied under identical conditions. These free diols dissolved 10 mg of sodium and potassium benzoate but neither the benzoates of lithium, cesium, or barium. This comparison indicates that the complexing properties of the multicyclic poly(ether ester)s are quite different from those of the free diols. The high hydrolytic stability against neutral water (tested for 8 days at 20 °C) which agrees with that of poly(ethylene terephthalate) allows for potential applications as cryptands even in the presence of water.

Molecular Weight Measurements. Even under optimized conditions the inherent viscosities were as low as 0.18 dL/g (Table 1) or 0.20 dL/g (Table 2). When compared to linear polyesters, such solution viscosities indicate number-average molecular weights around 2500−5000 Da and polydispersities around 2. However, the hydrodynamic volume of multicyclic polymers is considerably more compact, and low solution viscosities may be compatible with rather high molecular weights. Therefore, the samples with the highest viscosity values (no. 3, Table 1; no. 5, Table 2) were subject to SEC measurements in chloroform. Although, a calibration with polystyrene will certainly not provide exact molecular weights, the elution curves yielded three interesting pieces of information. First, as illustrated in Figure 6 the mass distribution were multimodal. Second, a significant mass fraction had molecular weights above 10^5 Da. Such a correlation, low solution viscosities and large fractions of high molar mass multicycles, was also found for two classes of multicyclic aromatic polyethers.[25,26] These results also indicate that indeed high conversions were achieved, and they justify to call the multicycles of this work polymers. Third,

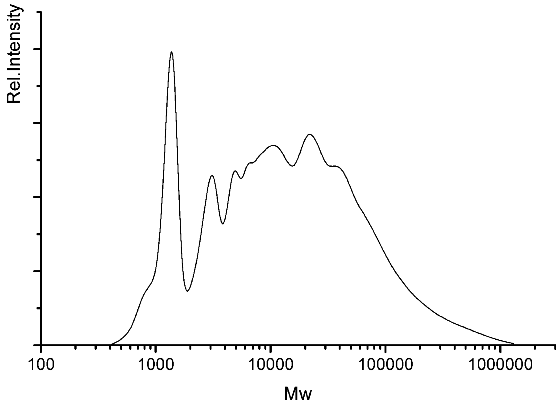


Figure 6. SEC measurement of a multicyclic polyester prepared from TrEG (no. 3, Table 1).

high polydispersities, around 8 for no. 3, Table 1, and around 10 for no. 5, Table 2, were measured. Such high polydispersities are not only characteristic for multicyclic polymers but also found for the products of "linear polycondensations", when large fractions of cycles were formed. On the basis of the work of Flory,[3] a polydispersity of 2.0 is reported in textbooks to be typical for polycondensates, but Flory ignored the influence of cyclization.

Conclusion

The polycondensations studied in this work allow for two important conclusions. First, syntheses of multicyclic polymers on the basis of "$a_2 + b_3$" polycondensations, first elaborated for aromatic polyethers, may be extended to polyesters. Second, multicyclic polymers derived from oligo(ethylene oxide)s may possess the properties of nonspecific cryptands, enabling complexation of various cations. Another interesting aspect is the high sensitivity of the reaction conditions optimized for successful synthesis of multicyclic poly(ether ester)s to variations of numerous experimental parameters. The chain length of the oligo(ethylene glycol)s, their concentration, the reaction medium, and the chemical structure of other diols are all decisive for the success. Further studies concern multicyclic aliphatic polyethers being more potent ligands (cryptands) for a variety of cations.

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