Articles

Macrocycles. 20. Cyclic Poly(ethylene glycol) Phthalates via Ring-Exchange Substitution

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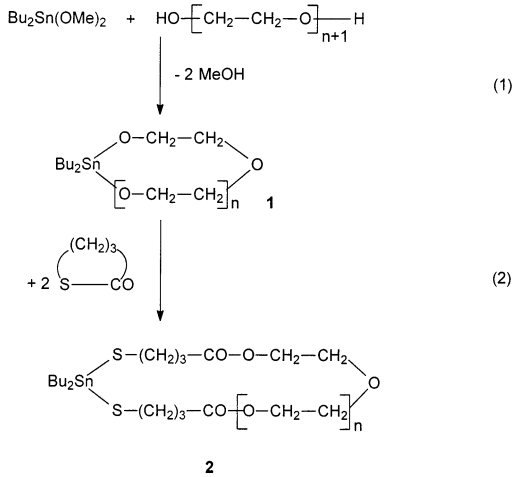
ABSTRACT: Various oligo- and poly(ethylene glycol)s were transformed into tin-containing macrocycles by "polycondensation" with dibutyltin dimethoxide. These cyclic oligo- and poly(ethylene glycol)s were heated with a spirocycle derived from phthaloyl chloride and 1,2-dimercaptoethane. This spirocycle inserts into the Sn−O bonds with subsequent elimination of 2,2-dibutyl-2-stanna-1,3-dithiolane. By this ring-insertion/ring elimination mechanism, the Bu_2Sn group in the cyclic polyethers was replaced by the phthalate unit without intermediate ring-opening. The cyclic poly(ethylene glycol) phthalates were characterized by elemental analyses by viscosity and DSC measurements, by ^1H NMR, ^{13}C NMR, and IR spectroscopy, and by MALDI−TOF mass spectrometry. Analogous experiments were conducted with a spirocycle derived from 4,5-dichlorophthalic acid which turned out to be less reactive than the unsubstituted phthalide. In summary, this new approach allows syntheses of cyclic polyether phthalates in high yields, in an "one-pot procedure" and without need of dilution.

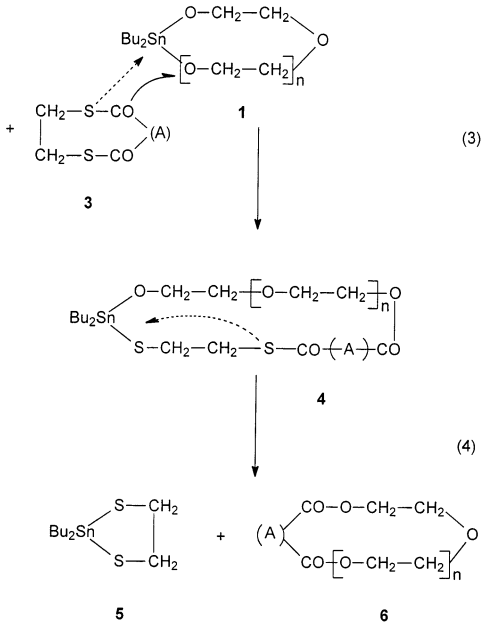
Introduction

Cyclic oligomers or polymers are usually prepared under extreme dilution according to the Ruggli−Ziegler dilution principle.[1−3] This approach is expensive and makes it difficult to synthesize larger quantities of cycles. The present work is part of a broader study[4−8] dealing with the question of how polydisperse cyclic oligomers and polymers can be prepared in bulk or in concentrated solution. The approach studied in this work is based on the finding that oligomeric or polymeric diols (e.g., poly(ethylene glycol)s, PEGs) yield tin-containing cycles (**1**) and never polymers when polycondensed with dibutyltin dimethoxide (eq 1).[7,8] This



cyclization is almost quantitative, it is thermodynamically controlled, and it is best conducted in bulk to accelerate the conversion.

In agreement with the well-known fact that Sn−S bonds are more stable than Sn−O bonds, it was found that thiolactones insert quantitatively into the Sn−O bonds of the Sn containing macrocycles (eq 2).[4,9] On this basis it was anticipated that cyclic esters of 1,2-dimercaptoethane (**3**) (or 1,3-dimercaptopropane) will also insert into Sn−O bonds (eq 3). However, in this case



the insertion product (**4**) should be unstable and undergo an intramolecular ring contraction (eq 4) with the concomitant elimination of 2-stanna 1,3-diolane (**5**) (or 2-stanna-1,3-dithiane) which is a stable and well docu-

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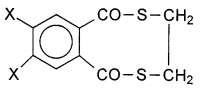
Table 1. Condensations of Cyclic Bu_2Sn PEGs with 4,5-Dichlorospirophthalide (8b)

expt no.	PEG	excess of **8b** (%)	catalyst	temp (°C)	time (d)	yield (%)	η_{inh}[a] (dL/g)	results
1	1000	1		100	1	85	0.11	no cycles
2	1000	1		100	4	85	0.12	no cycles
3	1000	5		100	4	95	0.32	cycles < 50 mol %
4	1000	10		100	4	98	0.36	cycles < 50 mol %
5	1000	1	pyridine	100	4	97	0.24	few cycles
6	1000	1	DMAP	100	4	96	0.24	few cycles
7	1000	10		160	4	95	0.38	cycles > 50 mol %
8	1000	15		160	4	97	0.49[b]	cycles > 95 mol %
9	600	15		160	4	91	0.31[c]	cycles > 95 mol %
10	2000	20		160	4	98	0.63[d]	cycles > 95 mol %

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] Mp: 23 °C. [c] Amorphous. [d] Mp: 46 °C.

mented compound.[10] This reaction sequence should give cyclic poly(ether ester)s (**6**) in high yields without intermediate ring cleavage and without any need of the Ruggli−Ziegler dilution principle. The present work had the purpose to explore the usefulness of this novel approach on the basis of the cyclic dithiophthalates **7a** and **7b**.



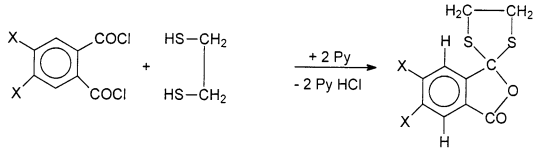
7a : X = H

7b : X = Cl

Experimental Section

Materials. $Bu_2Sn(OMe)_2$, phthaloyl chloride, 4,5-dichlorophthalic acid, 1,2-dimercaptoethane and all poly(ethylene glycol)s, PEGs, were purchased from Aldrich Co. (Milwaukee, WI). The 4,5-dichlorophthaloyl chloride was prepared in refluxing thionyl chloride with dropwise addition of a 10% solution of dimethylformamide in chloroform. It was purified by two subsequent distillations in vacuo. The PEGs were dried by azeotropic distillation of toluene, and the residual toluene was removed at 100 °C in a vacuum of 10^{-1} bar. The Bu_2SO was dried over P_4O_{10} in vacuo prior to use. The pyridine was distilled over freshly powdered CaH_2, and the toluene was distilled over sodium.

Spirophthalides 8a and 8b. Crude, commercial 1,2-dimercaptoethane (20.1 mmol) and dry pyridine (40.5 mmol) were dissolved in dry toluene (100 mL). Phthaloyl chloride (20.0 mmol) diluted with dry toluene (30 mL) was added dropwise with stirring. Afterward the reaction mixture was refluxed for 2 h. The cold solution was three times washed with water, dried over Na_2SO_4, and concentrated in vacuo to a volume around 50 mL. The concentrated solution was stored in a refrigerator, and the crystallized product was filtered off after 20 h. The crude spirophthalide **8a** was recrystallized from



8a: X = H
8b: X = Cl

toluene: yield 36%; mp 167−169 °C. Anal. Calcd for $C_{10}H_8O_2S_2$ (224.3): C, 53.55; H, 3.60; S, 28.59. Found: C, 53.28; H, 3.48; S, 28.50. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.70$ (m, 2H), 3.80 (m, 2H), 7.49−7.89 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$/TMS): $\delta = 42.1$, 107.9, 124.4, 125.7, 126.7, 131.0, 135.2, 147.5, 167.9 ppm. The 4,5-dichlorospirophthalide **8b** was prepared analogously: yield 34%; mp 198−201 °C. Anal. Calcd for $C_{10}H_6Cl_2O_2S_2$ (293.18): C, 40.97; H, 2.06; Cl, 24.18; S, 21.87. Found: C, 40.74; H, 1.86; Cl, 24.31; S, 21.71. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.70$ (m, 2H), 3.80 (m, 2H), 7.83 (S, 1H), 7.93 (S, 1H) ppm. ^{13}C NMR ($CDCl_3$/TMS): $\delta = 42.3$, 107.2, 126.3, 126.4, 127.2, 136.2, 140.3, 146.9, 165.7 ppm.

Ring-Exchange Substitution with 8b by "Method II". Dry PEG-1000 (5.0 mmol) and $Bu_2Sn(OMe)_2$ (5.25 mmol) were weighed (under dry nitrogen) into 50 mL round-bottom flask equipped with gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 80 °C and the temperature was raised to 100, 120, and 140 °C in time intervals of 1 h. The liberated methanol was removed with a slow stream of nitrogen. The temperature was then lowered to 100 °C, and a vacuum of 10^{-2} mbar was applied, whereby the temperature was raised again to 140 °C. After ventilation with dry nitrogen, the 4,5-dichlorospirophthalide **8b** (5.7 mmol) was added. The reaction mixture was stirred with a magnetic stirrer at 160 °C for 4 d under a slow stream of dry nitrogen. The cold reaction mixture was then three times extracted with a 20 mL portion of warm (approximately 50 °C) ligroin by rigorous shaking. Finally, the product was dissolved in dry CH_2Cl_2 and precipitated into a mixture of ligroin and diethyl ether (volume ratio 1:1). The solvent mixture was decanted, and the product was dried at 25 °C in a vacuum of 10−2 mbar. Yield: >95% mp 23 °C. $\eta_{inh} = 0.49$ dL/g. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.61$ (s, broad), 3.75 (s, 4H), 4.42 (t, 4H), 7.80 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$/TMS): $\delta = 65.57$, 69.13, 70.92, 131.36, 131.82, 136.0, 165.78 ppm. An analogous synthesis was performed with PEG-600 and PEG-2000 (see Table 1).

Ring-Exchange Substitution with 8a by "Method I". Dry PEG-1000 (10 mmol) and $Bu_2Sn(OMe)_2$ (10 mmol) were weighed into a 50 mL round-bottom flask (having silanized glass walls) equipped with a magnetic stirrer and a head allowing for the passage of nitrogen. The reaction vessel was placed into an oil bath preheated to 80 °C. The temperature was raised to 140 °C in steps of 20 °C and maintained for 1 h at each temperature. After 1 h at 140 °C, dry toluene (1 mL) was added, and the heating under a slow stream of nitrogen was continued for 1 h more. Afterward, the temperature was lowered to 100 °C, the spirophthalide **8a** (10.1 mmol) was added, and the reaction mixture was stirred for **4d** at 100 °C. The product was then three times extracted with hot ligroin (50−60 °C) by stirring for 30 min. The remaining product was dissolved in CH_2Cl_2 (5 mL) and precipitated into an 1:1 mixture of ligroin and diethyl ether (together 200 mL). The supernatant liquid was decanted and the remaining product was dried at 25 °C in vacuo. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.64$ (s, 87H), 3.79 (t, 4H), 4.46 (t, 4H), 7.53 (q, 2H), 7.74 (q, 2H) ppm. ^{13}C NMR ($CDCl_3$/TMS): $\delta = 64.3$, 68.4, 70.0, 128.5, 130.7, 131.5, 166.9 ppm.

Ring-Exchange Substitution with 8a by "Method II". Dry PEG-600 (10 mmol) and $Bu_2Sn(OMe)_2$ (10.5 mmol) were reacted at temperatures up to 140 °C (as described above for **8b**). The spirophthalide **8a** (11.5 mmol) was then added and the reaction mixture was stirred at 160 °C for 1 d, whereby a slow stream of dry nitrogen was blown over the reaction mixture. The cold reaction mixture was worked up as described above.

Acetylation of the Polycondensation Product. A poly(ethylene glycol) phthalate (1.0 g) was dissolved in 10 mL of dry chloroform. Acetic anhydride (1.0 g) and three drops of pyridine were added. The solution was heated at 60 °C for 8 h. After cooling the solution was poured into a 1:1 mixture of ligroin and ether. The solvent was decanted, and the product was dried at 40 °C in vacuo.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20

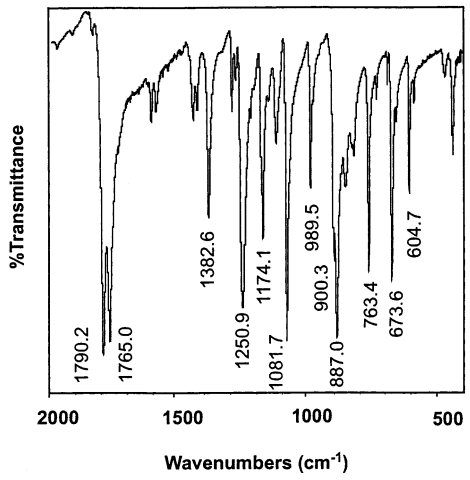


Figure 1. IR spectrum of the spirophthalide **8b**.

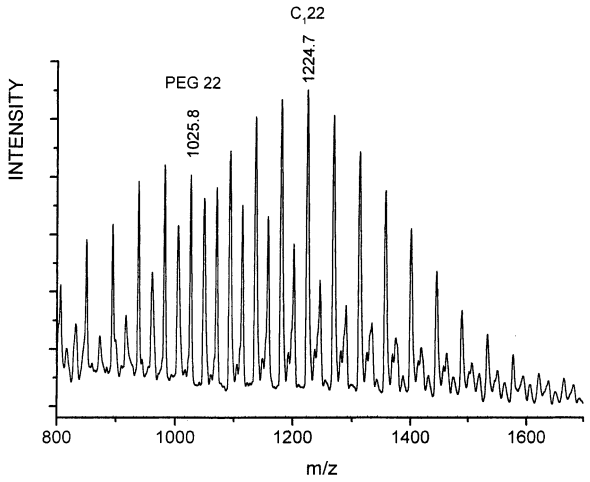


Figure 2. MALDI−TOF mass spectra of the PEG-1000 4,5-dichlorophthalates prepared by "method I" (no. 4, Table 1).

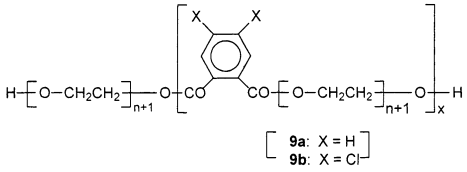
°C. The DSC measurements were conducted on a Perkin-Elmer DSC-7 in aluminum under nitrogen. A heating and cooling rate of 20 °C/min was used. The 400 MHz ^{1}H NMR spectra and the 100.4 MHz ^{13}C NMR spectra were recorded with Bruker AM 400 FT NMR spectrometer in 5 mm o.d. sample tubes using $CDCl_3$/TMS as solvent and shift reference. The IR spectra were recorded from KBr pellets on a Nicolet "Impact 410" FT IR spectrometer. The mass spectra were recorded with a V6.70 SE spectrometer using the "electron impact" ionization and detection method. The MALDI−TOF mass spectra were obtained on a Bruker Biflex III mass spectrometer in the reflectron mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from CH_2Cl_2 solutions using dithranol as matrix and potassium trifluoroacetate as dopant. A total of 200−1000 scans were accumulated. The SEC measurements were performed on a Knaur apparatus using THF as eluent at 25 °C. A combination of three PLG columns was applied and commercial PEG and PS standards were used for calibration.

Results and Discussion

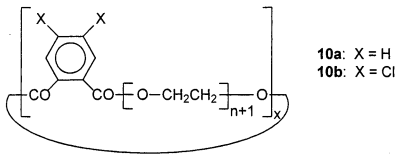
Synthesis of Spirophthalides. For the purpose of this study cyclic esters of 1,2-dimercaptoethane (structure **3**) were needed. When succinyl chloride or adipoyl chloride were used as reaction partners (in combination with pyridine) complex mixtures of oligoesters were obtained despite dilution of the reaction mixture. However, with phthaloyl chloride and 4,5-dichlorophthaloyl chloride crystalline compounds were isolated which had a monomeric structure as confirmed by mass spectrometry. Surprisingly, the IR spectra and the ^{1}H NMR and the ^{13}C NMR spectra proved that these crystalline heterocycles did not have the symmetrical structure **3** but the spirophthalide structure **8**. The IR-spectra exhibited CO-stretch vibrations typical for an anhydride ring: a broad band at 1775 cm^{-1} in the case of **8a** and two sharp bands at 1790 and 1765 cm^{-1} in the case of **8b** (Figure 1). For the cyclic thioesters of structure **7a**,**b** significant bathochromic shift of the wavenumber is expected (<1720 cm^{-1}). The ^{1}H NMR spectra of **8a** and **8b** showed two pairs of nonequivalent aliphatic protons. Furthermore, the aromatic protons of **8b** were not equivalent. Finally, the ^{13}C NMR spectra displayed six signals of aromatic carbons, which is an unambiguous proof of the nonsymmetrical spirocyclic structure.

As reported elsewhere,[11] the same spirocycles were obtained by a completely different synthetic method regardless of the reaction temperature. This alternative approach consists of the exothermic condensation of 2,2-dibutyl-2-stanna-1,3-dithiolane (**5**) with phthaloyl chlorides. All these results together suggest that the spirocycles **8a**,**b** are the thermodynamically more stable isomers compared to the symmetrical cyclic esters **7a**,**b**. Although the isolated phthalic acid derivatives of 1,2-dimercaptoethane had not the expected cyclic structure **7a** or **7b**, this study was continued, because it was found that the spirophthalides **8a** and **8b** also react with stannylenated PEGs (**1**) at elevated temperatures.

Condensations of 4,5-Dichlorospirophthalide. Because of the electronegative character of Cl-atoms it was expected that the 4,5-dichlorospirophthalide **8b** is more reactive than the spirophthalide **8a**, and therefore, the first reaction with stannylenated PEGs were performed with **8b**. Preliminary experiments had shown that temperatures below 100 °C were too low, and thus, the first series of condensations (listed in Table 1) was conducted at 100 °C on the basis of PEG-1000. After a reaction time of 1 d only a moderate conversion was observed and the MALDI−TOF mass spectrum (MS) revealed a large amount of free PEGs resulting from the hydrolysis of unreacted stannylenated PEG-1000 (**1**). After 4 days a higher fraction of linear oligoesters (formula **9b**) was obtained and addition of pyridine or



4-(*N*,*N*-dimethylamino)pyridine improved the conversion further, but the fraction of cyclic oligo(ether ester)s (formula **10b**) was still low. With a 15 mol % excess of



8b, the cycles turned to the main products (no. 4, Table 1), but as demonstrated by the MALDI−TOF MS of Figure 2, a significant amount of linear oligomers (**9b**) were still present. The molar masses of selected PEGs and cyclic ether-esters listed in Table 2 indicate that it

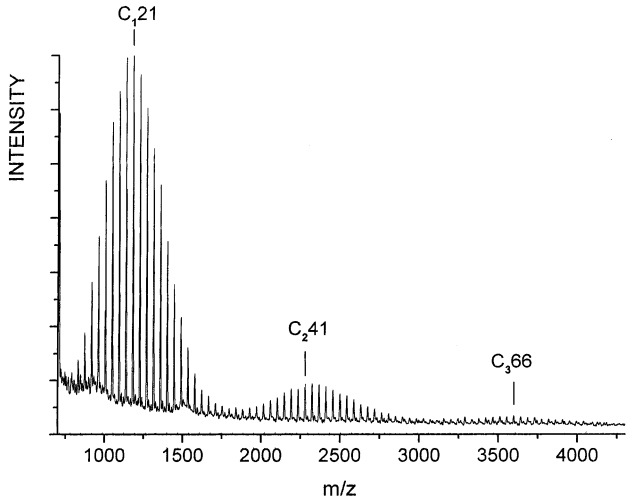


Figure 3. MALDI−TOF mass spectrum of the PEG-1000 4,5-dichlorophthalate prepared by "method II" (no. 8, Table 1).

Table 2. Molar Masses of Neat PEGs, Their Bisacetates, Cyclic Phthalates, and Cyclic 4,5-Dichlorophthalates

Compound	Molar mass (Da)	Molar mass + $K^{\oplus}$ (+ 39)
$H-(O-CH_2CH_2)_{24}-OH$	1075.2	1114.2
$H-(O-CH_2CH_2)_{25}-OH$	1119.2	1158.2
$H-(O-CH_2CH_2)_{26}-OH$	1163.2	1202.2
$CH_3CO-(O-CH_2CH_2)_{22}-O-COCH_3$	1071.2	1110.2
$CH_3CO-(O-CH_2CH_2)_{23}-O-COCH_3$	1115.2	1154.2
$CH_3CO-(O-CH_2CH_2)_{20}-O-CO-C_6H_3(CO_2H)$	1089.3	1128.2
$CH_3CO-(O-CH_2CH_2)_{21}-O-CO-C_6H_3(CO_2H)$	1133.3	1172.3
$C_6H_4(CO-(O-CH_2CH_2)_{20}-CO-O-CH_2-CH_2-O)_2$	1073.3	1112.3
$C_6H_4(CO-(O-CH_2CH_2)_{21}-CO-O-CH_2-CH_2-O)_2$	1117.2	1156.3
$C_6H_2Cl_2(CO-(O-CH_2CH_2)_{20}-CO-O-CH_2-CH_2-O)_2$	1141.3	1180.3
$C_6H_2Cl_2(CO-(O-CH_2CH_2)_{21}-CO-O-CH_2-CH_2-O)_2$	1185.3	1224.3

is indeed easy to distinguish the OH-terminated linear chains (**9b**) from the cycles of structure **10b**.

A higher temperature of 160 °C did not improve the conversion (no. 7) unless dry argon or highly purified nitrogen was blown over the reaction mixture and removed the majority of the liberated 2,2-dibutyl-2-stanna dithiaepane. The MALDI−TOF MS of the resulting reaction product (Figure 3) and the ^{1}H NMR spectrum of the acetylated product (see discussion of **8a** below) suggested that the molar fraction of cyclic oligo(ether-ester)s was now above 95 mol %. For the interpretation of the MS spectra and for the labeling of mass peaks it is necessary to realize that the reaction product combine two different and independent modes of polydispersity. The cycles may contain one, two, three, or more phthalate groups and larger variable amounts of ethylene oxide units. Therefore, the symbol C_XY was used for the labeling of individual cycles, where X indicates the number of phthalate groups and Y the number of ethylene oxide units.

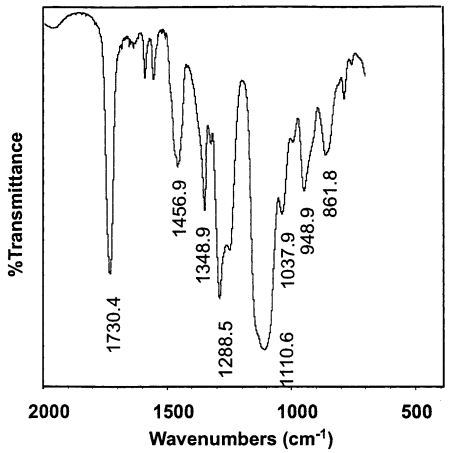


Figure 4. IR spectrum (KBr pellet) of the PEG-1000 4,5-dichlorophthalate prepared by "method II" (no. 8, Table 1).

Product no. 8, Table 2, was also characterized by IR spectroscopy, which exhibited the expected CO-stretch vibration at 1,730 cm^{-1} (Figure 4), a wavenumber quite different from that of **8b** (Figure 1). The 400 MHz ^{1}H NMR spectrum displayed one sharp singlet of the aromatic protons (7.75 ppm in $CDCl_3$/TMS) indicating a symmetrical structure of the phthalate group according to formula **10b**. This symmetrical structure was confirmed by the ^{13}C NMR spectrum displaying one CO signal (165.4 ppm) and three signals of aromatic carbons (135.7, 131.4, and 131.0 ppm).

Finally, two more cyclic PEG 4,5-dichlorophthalates were prepared using PEG-600 or PEG-2000 as starting materials (nos. 9 and 10, Table 1). Again the ^{1}H NMR, ^{13}C NMR, and MALDI−TOF mass spectra proved that the products mainly consisted of cycles (>95 mol %). As indicated by the viscosities listed in Table 1 and by footnotes b−d, both the molecular weights and the melting temperatures increased with the lengths of the PEG segments.

Condensations of Spirophthalide 8a. When stannylenated PEG-300, PEG-400, PEG-600, and PEG-1000 were reacted with the unsubstituted spirophthalide **8a** at 100 °C/4 d (method I) the virgin reaction mixtures contained high fractions of cyclic phthalates (80−85%). These results proved unexpectedly that the spirophthalide **8a** was more reactive than the dichloro analogue **8b**. To improve the yield of cycles a stepwise optimization of the procedure was studied. It was found that a 5 mol % excess of $Bu_2Sn(OMe)_2$ is advantageous for a quantitative synthesis of the stannacycles **1**, obviously because a small amount of this compound distills off together with the eliminated methanol. Furthermore, a reaction temperature of 160 °C with an excess of **8a** around 15 mol % proved to be useful. In other words, the "method II" elaborated for **8b** also proved to be favorable for the ring-exchange reaction of **8a**. In this way, the fraction of cyclic PEG phthalates indeed increased to values ≥95%. The yields and a couple of properties of isolated products were compiled in Table 3 together with viscosity and melting temperatures (T_ms) of the parent PEGs and their bisacetates. A comparison of these data revealed that the T_ms of the cyclic phthalates were almost identical with those of the bisacetates. The T_ms of the low molar mass PEGs were

Table 3. Properties of Cyclic PEG Phthalates Prepared by "Method II" Properties of Neat PEGs and PEG−Bisacetates

	cyclic PEG phthalates					PEG bisacetates	
molar mass of PEGs	yield (%)	η_{inh}[a] (dL/g)	M_n[b] (Da)	T_m[c] (T_g[c]) (°C)	neat PEG T_m[c] (°C)	η_{inh}[a] (dL/g)	T_m[c] (T_g)[c] (°C)
PEG-300	91	0.21	4200	−38		0.03	−38
PEG-400	90	0.29	5800	−33	7	0.03	−34
PEG-600	93	0.35	8300	12	21	0.04	13
PEG-1000	94	0.44	10 000	32	40	0.06	35

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] SEC measurements in tetrahydrofuran calibrated with PEG standards. The polydispersities were 1.6 ± 0.1. [c] DSC measurements with a heating rate of 20 °C.

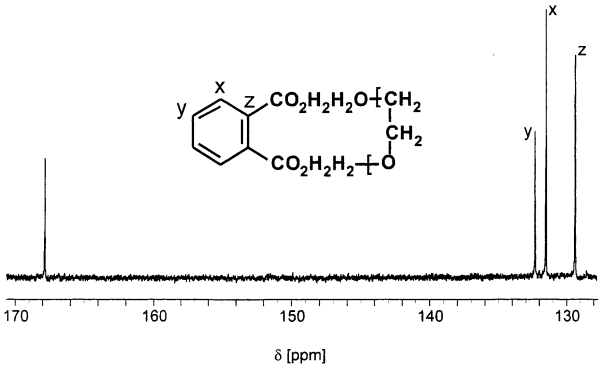


Figure 5. 100.4 MHz ^{13}C NMR spectrum of the PEG-400 phthalate prepared by "method II" (no. 2, Table 3).

higher obviously due to the existence of H-bonds. For reasons discussed below the molecular weights of the cyclic PEG phthalates **10a** were considerably higher than those of the bisacetates or of the stannylenated PEGs.

The cyclic PEGs **10a** were characterized by IR spectra which displayed the presence of a "CO-band" at 1725 cm^{-1} quite analogous to the example presented in Figure 4. The ^1H NMR spectra (see discussion below) and ^{13}C NMR spectra (Figure 5) agreed with the symmetrical structure presented in formula **10a**. A particular problem proved to check the purity of the cycles, i.e., the presence or absence of linear chains having OH end groups, such as unreacted PEG or oligoesters of structure **9a**. As demonstrated by the values listed in Table 2 the molar masses of PEGs (and higher linear oligomers) differ from those of the cyclic phthalates **10a** by only 2 g/mol. In principle, the MALDI−TOF mass spectroscopy allows for a resolution of mass peaks differing by 1 g/mol, but the isotope pattern makes it difficult to detect and to quantify byproducts having slightly higher masses than the main product. Furthermore, the ^1H NMR signal of the CH_2-OH end groups is obscured by the far more intensive signal of the ether groups.

To overcome these difficulties attempts were made to modify the CH_2OH end groups quantitatively. For this purpose, model reactions with PEG-1000 were studied using tosylisocyanate, trifluoroacetic anhydride, or acetic anhydride + pyridine as acylating reagents. The ^1H NMR spectra of the virgin reaction mixtures indicated quantitative reactions in all three cases. However, the bisurethanes (formula **11**) were difficult to volatilize under the MALDI−TOF conditions and the bis(trifluoroacetate) of PEG-1000 hydrolyzed during the preparation of the irradiation targets. The PEG bisacetate "flew"

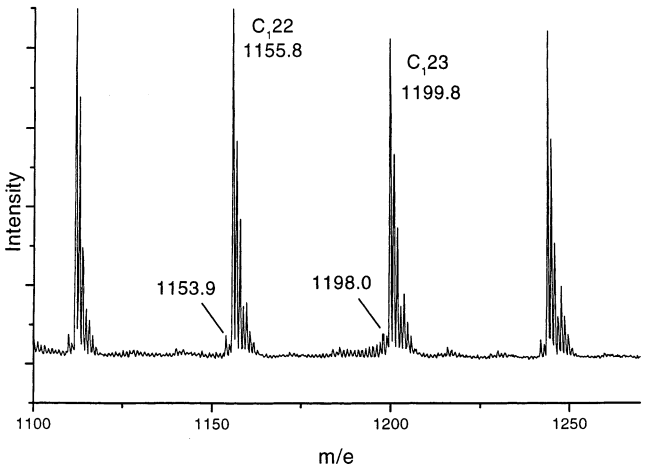


Figure 6. MALDI−TOF mass spectrum of PEG-400 phthalate prepared by "method I" after acetylation with acetic anhydride in pyridine at 20 °C. The signals at $m/z = 1153.9$ and 1198.0 Da represent linear chains with acetylated OH end groups.

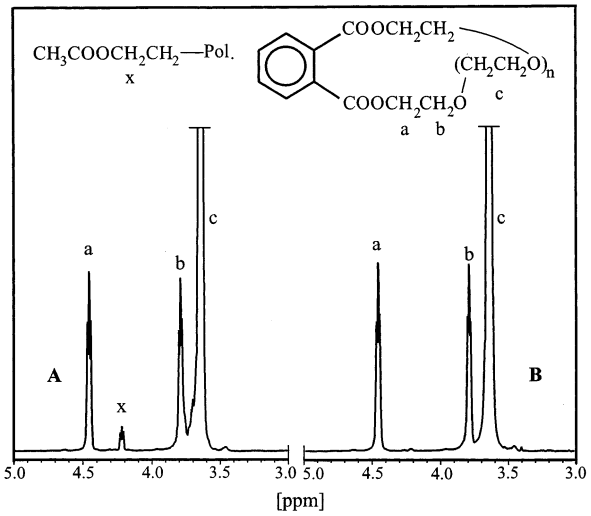
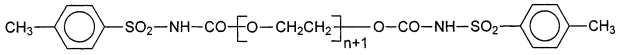


Figure 7. 400 MHz ^1H NMR spectrum of PEG−1000 phthalate prepared by "method I" after acetylation (A) and prepared by method II after acetylation (B).

well under the MALDI−TOF conditions, but as demonstrated in Table 2, their molar masses were only 2 g/mol lower than those of the cyclic phthalates. They were easy to detect, when the products were prepared by "method I". However, when the reaction products of "method II" (Table 3) were acetylated, mass peaks of bisacetates were barely detectable in the MS (Figure 6).



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More sensitive and better suited for quantification proved the ^1H NMR spectra, as demonstrated in Figure 7 for a reaction product of "method I". The signals of acetate end groups were easy to identify and to quantify. They indicated a molar fraction of 10−15% of linear chains. However, only weak signals of acetate end groups corresponding to 2−5 mol % of linear chains (PEGs or **9a**) were detected, when "method II" was used.

Mechanistic Aspects. It is well-known[12−14] that cyclic anhydrides react and insert into the Sn−O bonds of tin alkoxides. Therefore, it was originally expected

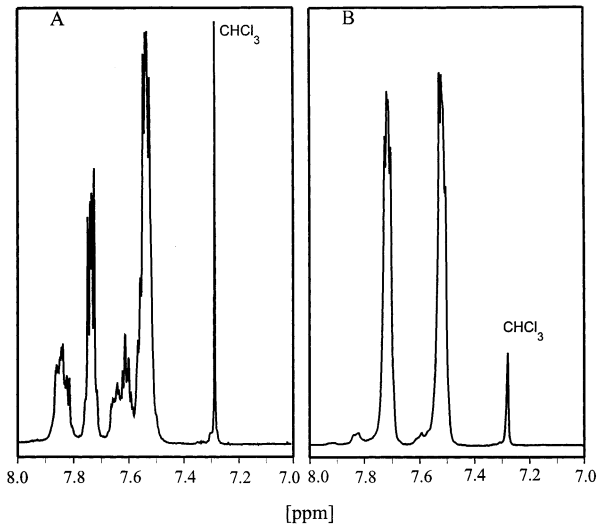
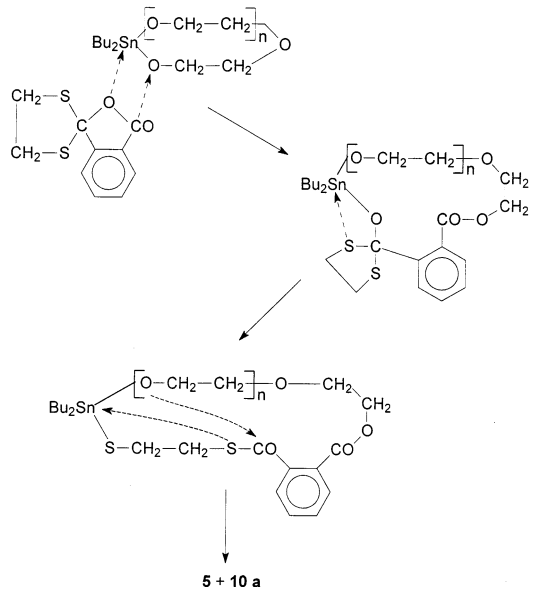


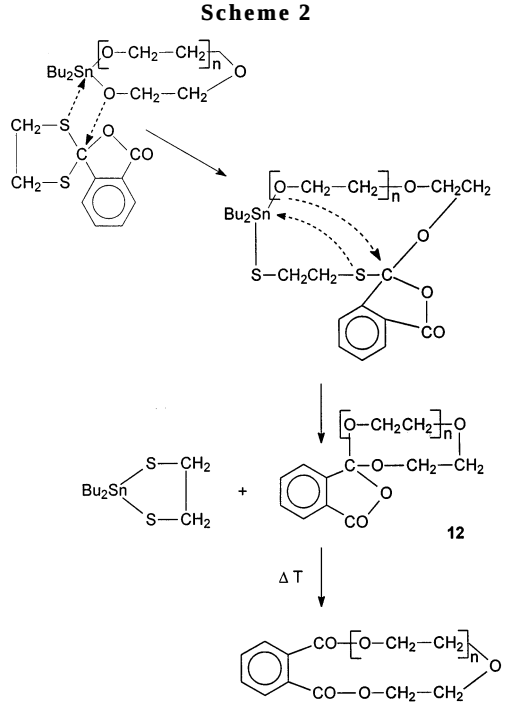
Figure 8. 400 MHz ^{1}H NMR spectra (aromatic protons only): (A) PEG phthalate prepared by "method I"; (B) PEG phthalate prepared by "method II".

Scheme 1



that the spirophthalates react with the stannylenated PEGs according to Scheme 1. However, when the ^{1}H NMR spectra of the reaction products of **8a** obtained at 100 °C by "method I" were examined, the ^{1}H NMR signal patterns of the aromatic protons looked more complex than expected (Figure 8A). Weaker signals appeared downfield of the strong signals characteristic of the symmetrical phthalate group. Such chemical shifts were also observed for the spirophthalide **8a**. When this compound was heated to 160 °C, these weaker signals almost completely disappeared (Figure 8B) and the products of "method II" displayed a spectrum like the one of Figure 8B. This transformation did not cause any change in the MS and, thus, should be an isomerization. Hence, it may be concluded that the reaction of stannylenated PEGs with spirophthalide **8a** follows the reaction pathway of Scheme 2 involving the intermediate formation of spirocyclic PEG phthalate **12**. This interpretation is supported by the ^{13}C NMR spectra of "method I" products which show two weak signals in the neighborhood of the CO-signal representing the symmetrical phthalate (167.0 ppm in $CDCl_3$/TMS).

Scheme 2



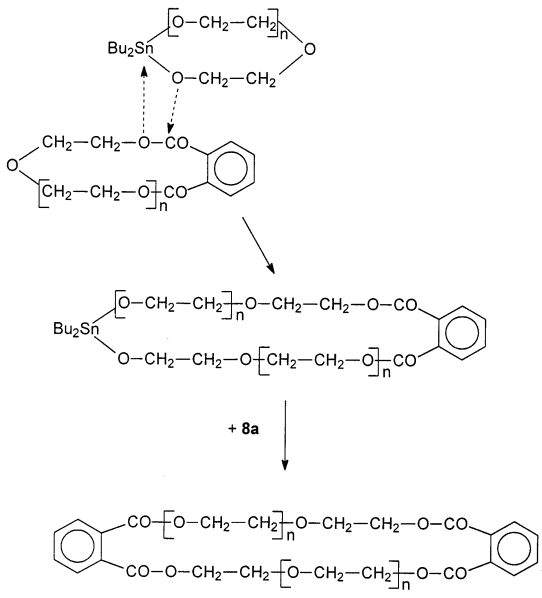
Furthermore, six weak signals typical for a nonsymmetrical aromatic ring were found between 125 and 135 ppm. After this was heated to 160 °C, only the three aromatic signals (128.3, 130.4, and 131.3 ppm) of the symmetrical phthalate group remained.

Finally, the question needs to be discussed, why the cyclic PEG phthalates have higher molar masses than the stannylenated PEGs. Taking into account that the exponents in the Mark−Houwink equations of flexible polymers typically fall into the range of 0.7−0.9 it may be concluded from the inherent viscosities listed in Tables 1 and 3 that the number-average molecular weights increased by a factor 10−12 compared to the PEGs used as starting materials. SEC measurements calibrated with commercial PEG standards are in good agreement with this estimation (Table 3). We have previously demonstrated[7−9] for numerous cyclic dibutyltin alkoxides including stannylenated PEGs that these cycles can initiate the ring-expansion polymerization of lactones and cyclic diesters. If the cyclic PEG phthalates react as monomers and insert into initially unreacted stannylenated PEGs (which play the role of cyclic initiators), higher cyclic oligomers and polymers will be the result (Scheme 3). This reaction pathway presents the most obvious explanation of the higher molar masses.

Conclusion

The experiments of this work suggest that condensations of phthaloyl chlorides (substituted or unsubstituted ones) with 1,2-dimercaptoethane yield the spirocycles of structure **8** as the thermodynamically most stable form of cyclic bis(thiophthalates). These spirocycles are reactive enough to insert into Sn−O bonds of cyclic tin alkoxides. Because this insertion is immediately followed by elimination of 2,2-dibutyl-2-stanna-1,2-dithiolane (**5**), this ring-exchange substitution allows the transformation of Sn-containing macrocycles and cyclic polymers into cyclic phthalates. However, the reaction conditions need to be optimized for an almost complete conversion. Both ^{1}H and ^{13}C NMR

Scheme 3



spectroscopy prove that the cyclic PEG phthalates obtained at high temperatures have a symmetrical structure in agreement with bis(alkylphthalates). This ring-exchange substitution of the Bu_2Sn group is accompanied by a ring-expansion polymerization which raises the molecular weights by a factor of 10. Because these reactions are thermodynamically controlled, high yields and high quantitaties of cycles can be prepared without dilution in a rather simple "one-pot procedure".

The smallest cycles, i.e., the PEG-300 phthalates, were found to have crown ether properties in combination with large cations such as Cs^+ but not in combination with Na^+ (details will be reported in a future publication). The stability of the PEG phthalates toward neutral water or methanol (tested for 1 week at 20 °C) may indeed allow a potential application as crown ethers or phase-transfer catalysts.

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