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MACROCYCLES. 12. RING-OPENING POLYCONDENSATIONS OF TIN-CONTAINING MACROCYCLES WITH BIS(THIOARYLESTER)S

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MACROCYCLES. 12. RING-OPENING POLYCONDENSATIONS OF TIN-CONTAINING MACROCYCLES WITH BIS(THIOARYLESTER)S

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ABSTRACT

2,2-Dibutyl-2-stanna-1,3-dioxepane (DSDOP) was polycondensed with bis(4-chlorothiophenyl) suberat under various reaction conditions, but only moderate molecular weights ($M_n \approx 10000$) were obtained. The MALDI-TOF mass spectrometry revealed the formation of cyclic oligo- and polyesters in addition to linear species having OH, CO₂H, and unreacted 4-chlorothiophenyl ester endgroups.

Furthermore, ϵ -Caprolactone (ϵ -CL) was polymerized with DSDOP as the initiator at monomer/initiator (M/I) ratios of 20 and 50. The resulting tin-containing macrocyclic polylactones were reacted with sebacic acid bis(4-thiocresyl)ester at three different temperatures and with different reaction times. Analogous

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polycondensations were conducted with suberic acid bis(4-chlorothiophenyl) ester. The presence of thioarylester endgroups in the isolated polyesters was checked by ^1H NMR spectroscopy. The highest conversions were found at long reaction times (24 or 72 hours), or after the addition of pyridine and *N,N*-dimethylaminopyridine as catalysts. Despite high conversions, the number average molecular weights (M_n 's) did not exceed values around 20000. Even in the samples having the highest molecular weights, unreacted 4-chlorothiophenylester endgroups were detected by GPC measurements evaluated with a UV-detector. It is concluded that both factors, cyclization and incomplete conversion, contribute to the limitation of the chain growth.

INTRODUCTION

As reported in previous parts of this series, it was possible to prepare tin-containing macrocyclic polylactones **2** using 2-stanna-1,3-dioxacycloalkanes such as **1** as initiator (Equation 1) [1, 2]. Furthermore, it was found that the Sn-O bonds of these supermacrocycles react easily at temperatures above 100°C with thioarylestere of carboxylic acids (Equation 2) [2]. Moreover, the tin-containing (macro)cycles such as **1** and **2** proved to be useful difunctional monomers for polycondensations with dicarboxylic acid chlorides (Equation 3) [3]. Unfortunately, stable acid chlorides are not available from α -amino acid, β -amino acid, α -hydroxy acid or β -hydroxy acid derivatives which are of interest as monomers for syntheses of biodegradable polyesters. However, stable thioaryl esters can be prepared under mild conditions from free carboxylic acids and thiophenols by means of carbodiimides. Therefore, the present work had the purpose to study the polycondensation of 2,2-dibutyl-2-stanna-1,3-dioxepane (**1**, DSDOP) or tin-containing macrocyclic poly-(ϵ -caprolactone) with dicarboxylic acid bis(thio-aryl) esters.

Answers to the following questions should be found. First, does the lower reactivity of the thioaryl esters (when compared to acid chlorides) result in lower molecular weights of the polyesters? Second, are thioaryl ester endgroups detectable due to incomplete conversion? Third, do the isolated polyesters mainly possess a cyclic or a linear structure? The answer to this third question was of particular interest, because the oligo- and polyesters isolated from polycondensations of DSDOP and dicarboxylic acid dichlorides had a cyclic structure [3]. The formation of cyclic oligomers and polymers by direct polycondensation in the absence of equilibration and the absence of dilution has

theoretically been predicted [4, 5], but experimental proof has not been published yet (with the exception of Reference 3).

EXPERIMENTAL

Materials

4-Methylthiophenol, 4-chlorothiophenol, suberic acid, sebacic acid, dibutyltin dimethoxide, 1,4-butanediol, and ϵ -caprolactone were all purchased from Aldrich Co. (Milwaukee, Wisc.). The 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) was prepared from dibutyltin dimethoxide and dry 1,4-butanediol as described previously [2, 6]. The acid chlorides of the dicarboxylic acid were prepared in a refluxing mixture of chloroform and thionylchloride (volume ratio 1:1) and isolated by distillation. The ϵ -caprolactone was distilled over freshly powdered calcium hydride.

Synthesis

Suberic Acid Bis(4-chlorothiophenyl)ester

The suberic acid chloride (0.2 mol) and the 4-chlorothiophenol (0.4 mol) were dissolved in dry THF, and pyridine (0.4 mol) was added dropwise under cooling with stirring. The reaction mixture was allowed to stand at 20°C for 20 hours and then filtered from the precipitated pyridine hydrochloride. The filtrate was concentrated *in vacuo* and poured on ice/distilled water. The precipitated crude product was filtered off, washed twice with distilled water, dissolved in dry CH_2Cl_2 and dried over Na_2SO_4 . Afterwards, the solution was concentrated *in vacuo* again until the product began to crystallize. The product was filtered off and dried at 40°C *in vacuo*.

Yield 54%, m.p. 84-85°C

$\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{O}_2\text{S}_2$ (427.4 g/mol):

Calcd.: C 56.20 H 4.72 Cl 16.59 S 15.00

Found: C 55.91 H 4.63 Cl 16.60 S 15.08

^1H NMR (CDCl_3/TMS): $\delta = 1.42$ (4H,m), 1.72 (4H,m), 2.66 (4H,t), 7.35 (8H,m).

Sebacic Acid Bis(4-methylthiophenyl)ester

This thioester was prepared by the same procedure, using sebacic acid chloride and 4-methylthiophenol as starting materials.

Yield 87%, m.p. 67-68C (m.p. 70°C in Ref. [7])

C ₂₄ H ₃₀ O ₂ S ₂ (414.6 g/mol):	Calcd.:	C 69.52	H 7.29	S 15.47
	Found:	C 69.63	H 7.26	S 15.31

¹H NMR (CDCl₃/TMS): δ = 1.32 (8H,s), 1.70 (4H,m), 2.37 (6H,s), 2.64 (4H,t), 7.29 (8H,m).

Polycondensations of DSDOP

10 mmol DSDOP and 10.0, 10.1 or 10.2 mmol bis(4-chlorothiophenyl)ester of suberic acid (that's adequate to 0, 1 or 2% excess) were weighed into a cylindrical glass-reactor equipped with a mechanical stirrer, gas-inlet and outlet tubes. The reaction vessel was immersed into an oil bath thermostated at a temperature in the range of 100-160°C (see Table 1) and the reaction mixture was stirred in an atmosphere of dry nitrogen for 24 resp. 48 hours. Afterwards, the reaction product was dissolved in dichloromethane (20 mL) and precipitated into cold (4-5°C) diethyl ether (200 mL). The precipitated product was isolated by filtration and dried at 40°C *in vacuo*. Then, the polyester was dissolved in dichloromethane again and reprecipitated into cold isopropanol.

Polycondensations of Macroyclic Poly(ε-caprolactone)

ε-Caprolactone (50 mmol) and DSDOP (2.5 or 1 mmol) were weighed into a cylindrical glass-reactor equipped with a mechanical stirrer, gas-inlet, and outlet tubes. The reaction vessel was placed into an oil bath preheated to 80°C, and this temperature was maintained for 1 hour. Afterwards, the bis(thioary)ester of sebacic acid respectively suberic acid (2.5 or 1 mmol) was added and the reaction mixture was stirred in an atmosphere of dry nitrogen for various times at a temperature between 100 and 200°C (see Tables 2-5). Then the reaction product was dissolved in dichloromethane (40 mL) and precipitated into cold (4-5°C) diethyl ether (400 mL). The precipitated product was isolated by filtration and dried at 40°C *in vacuo*.

Measurements

The viscosities were measured with an Ubbelohde viscometer thermostated at 25°C.

TABLE 1. Polycondensations of Suberic Acid Bis(4-chlorothiophenyl)ester with DSDOP 1

Polym. No.	Temp. [°C]	Time [h]	Excess of the Dithioaryl ester in %	Yield ₁ ^{b)} [%]	Yield ₂ ^{c)} [%]	η_{inh} ^{d)} [dl/g]	M_n ^{e)} [g/mol]	$\frac{M_w}{M_n}$
1	100	24	0	83	65	0.23	7,000	1.62
2	100	24	2	64	45	0.21	5,800	1.69
3	100	48	0	96	85	0.25	7,200	1.72
4	100	48	2	96	84	0.26	7,500	1.74
5	130	24	1	95	83	0.29	10,400	1.44
6	160	24	1	91	79	0.30	10,000	1.50
7 ^{a)}	100	48	0	82	68	0.25	7,800	1.63
8 ^{a)}	130	24	1	86	71	0.30	10,500	1.52

a) : these polyesters were precipitated only in dry diethylether

b) : after the (first) precipitation in moist diethylether (samples 1-6) resp. dry diethylether (samples 7 and 8)

c) : after the (second) reprecipitation in isopropanol (samples 1-6) resp. dry diethylether (samples 7 and 8)

d) : measured at 25°C with $c = 2\text{g/l}$ in CH_2Cl_2

e) : SEC measurements evaluated with the K and η values of eq. (5)

TABLE 2. Polycondensations of Sebacic Acid Bis(4-thiocresyl)ester with Macrocylic Poly(ϵ -CL) 2 Prepared with $M/I = 20:1$

Polym. No.	Temp. [°C]	Time [h]	Yield [%]	η_{inh} ^{d)} [dl/g]
1	100	4	95	0.40
2	130	4	93	0.44
3	160	4	92	0.47
4	100	8	94	0.40
5	130	8	90	0.44
6	160	8	88	0.45
7	100	24	91	0.38
8	130	24	86	0.42
9	160	24	83	0.42
10 ^{a)}	120	24	92	0.45
11 ^{b)}	120	24	90	0.43
12 ^{c)}	120	24	92	0.52

a) : a double molar amount (relative to S_n) of pyridine was added

b) : 10 mg of N,N -dimethylamino pyridine was added

c) : a double molar amount of pyridine + 10 mg of N,N -dimethylamino pyridine was added

d) : measured at 25°C with $c = 2\text{g/l}$ in CH_2Cl_2

TABLE 3. Polycondensations of Sebacic Acid Bis(4-thiocresyl)ester with Macrocylic Poly(ϵ -CL) 2 Prepared with M/I = 50:1

Polym. No.	Temp. [°C]	Time [h]	Yield [%]	η_{inh}^d [dl/g]
1	100	8	97	0.42
2	130	8	93	0.48
3	160	8	84	0.49
4	100	24	90	0.38
5	130	24	88	0.43
6	160	24	87	0.47
7	100	72	96	0.37
8	130	72	93	0.56
9	160	72	92	0.32
10 ^{a)}	120	24	94	0.56
11 ^{b)}	120	24	90	0.55
12 ^{c)}	120	24	95	0.72

a) : a double molar amount (relative to Sn) of pyridine was added

b) : 10 mg of N,N-dimethylamino pyridine was added

c) : a double molar amount (relative to Sn) of pyridine and 10 mg of N,N-dimethylamino pyridine were added

d) : measured at 25°C with $c = 2\text{g/l}$ in CH_2Cl_2

TABLE 4. Polycondensations of Suberic Acid Bis(4-chlorothio-phenyl)ester with Macrocylic Poly(ϵ -CL) 2 Prepared with M/I = 20:1

Polym. No.	Temp. [°C]	Time [h]	Yield [%]	η_{inh}^b [dl/g]	M_n^c [g/mol]	$\frac{M_w}{M_n}$
1	120	8	91	0.55	18,000	1.40
2	200	8	86	0.41	12,500	1.47
3 ^{a)}	120	8	93	0.46	15,000	1.70
4	120	24	92	0.55	18,000	1.45
5	200	24	89	0.42	13,500	1.62
6 ^{a)}	120	24	91	0.62	22,000	1.45

a) : a double molar amount (relative to Sn) of pyridine and 10 mg of N,N-dimethylamino pyridine were added

b) : measured at 25°C with $c = 2\text{g/l}$ in CH_2Cl_2

c) : SEC measurements evaluated with the K and η values of eq. (5)

TABLE 5. Polycondensations of Suberic Acid Bis(4-chlorothiophenyl)ester with Macrocylic Poly(ϵ -CL) 2 Prepared with M/I = 50:1

Polym. No.	Temp. [°C]	Time [h]	Yield [%]	η_{inh}^b [dl/g]	$M_n^{c)}$ [g/mol]	$\frac{M_w}{M_n}$
1	120	8	89	0.58	19,000	1.49
2	200	8	81	0.45	14,500	1.48
3 ^{a)}	120	8	88	0.57	18,500	1,37
4	120	24	86	0.60	20,000	1.39
5	200	24	80	0.48	16,000	1.40
6 ^{a)}	120	24	82	0.56	18,000	1.38

a) : a double molar amount (relative to Sn) of pyridine and 10 mg of N,N-dimethylamino pyridine were added

b) : measured at 25°C with c = 2g/l in CH₂Cl₂

c) : SEC measurements evaluated with the K and η values of eq. (5)

The 360 Mhz ¹H NMR spectra were recorded with a Bruker AM-100 FT NMR spectrometer in 5 mm o.d. sample tubes. CDCl₃ containing TMS served as solvent for all NMR measurements.

MALDI-TOF mass spectra were recorded with a Kratos Kompact MALDI III (Shimadzu) using a nitrogen laser source ($\lambda = 337$ nm), a positive polarity and 20 kV acceleration voltage in the reflexion mode. The samples were prepared by mixing of approximately 5 μ L of substrate dissolved in THF (1 mg/mL) with 5 μ L of matrix solution (25 mg/mL THF) before drying on the sample slide. 2,4,5-trihydroxyacetophenone or 1,8,9-trihydroxyanthracene were used as matrices. The equipment was calibrated with bovine insulin. The spectra shown in this paper have peaks (apex) after baseline subtraction. Sodium ions were present due to sodium containing glassware.

The molecular weight data listed in Tables 1, 4, and 5 were obtained by SEC measurements using a Kontron HPLC-420 apparatus equipped with a Waters differential refractometer 410. Four Ultrastyrigel[®] columns with pore sizes of 10², 10³, 10⁴, and 10⁵ Å were used, and tetrahydrofuran served as eluent. The SEC curves of the sample No. 6, Table 4 (Figures 4 and 5) were measured by equipment consisting of HPLC pump Rheos 40000/ERC, RI- and UV-(254nm)-Detector/Knauer, GPC Software, PSS, Mainz. Three PS-DVB columns (PL-gel mix E, 3 μ m, PSS 100 Å, PL 50 Å, 5 μ m,) were used. The mobile phase was THF/Licrosolve, Flow 1mL/min. 100 μ L of a 0.5% solution were injected.

All SEC and viscosity measurements were performed with precipitated polymer samples.

RESULTS AND DISCUSSION

Polycondensations of DSDOP

Bis(4-chlorothiophenyl) suberate **3** which is easy to synthesize from 4-chlorothio-phenol and suberoyl chloride was selected as reaction partner of DSDOP **1** for analytical reasons. The resulting polyester is an isomer of poly(ϵ -CL), and thus, its solubility and hydrodynamic properties were expected to be quite similar, so that SEC measurements calibrated with the Mark-Houwink-Sakurata Equation 5 determined for poly(ϵ -CL) should allow reasonable molecular weight measurements.

Whereas the polycondensation of DSDOP with suberoyl chloride is highly exothermic, no significant reaction enthalpy was detected when DSDOP was mixed and heated with the Bisester **3**. In order to achieve high conversions, the temperature and the time were varied (Table 1). Furthermore, pyridine alone or in combination with N,N-dimethylaminopyridine were added as potential catalysts. However, the inherent viscosities and the SEC-data listed in Table 1 indicate that the broad variation of the reaction conditions had rather little influence on the molecular weights. The number average molecular weights (M_n 's) were in the range of 6000-12000 Da. Therefore, even the best values of Table 1 amount to only 40-50% of the best values obtained with suberoyl chloride and sebacoyl chloride [3].

The isolated polyesters were reprecipitated and the presence of 4-chlorothiophenyl ester endgroups was checked by $^1\text{H-NMR}$ spectroscopy. As exemplified by the spectrum of Figure 1, the aromatic protons of these endgroups were detected in the spectra of four samples. In order to make sure that these aromatic protons do not result from impurities such as 4-chlorothiophenol or its dibutyltin-derivative, six samples were also characterized by MALDI-TOF mass spectrometry (Nos. 3-8, Table 1).

A typical example of such a mass spectrum is displayed in Figure 2. The MALDI-TOF mass spectra revealed, in all cases, the formation of cyclic oligo- and polyesters (structure **4**, masses of 2090, 2318 and 2546 Da in Figure 2). However, linear polyesters having hydroxyl- and carboxyl endgroups (structures **5** and **6**) respectively, unreacted 4-chlorothiophenyl endgroups (structure **7** and **8**) were also discovered. A characteristic difference was found between poly-

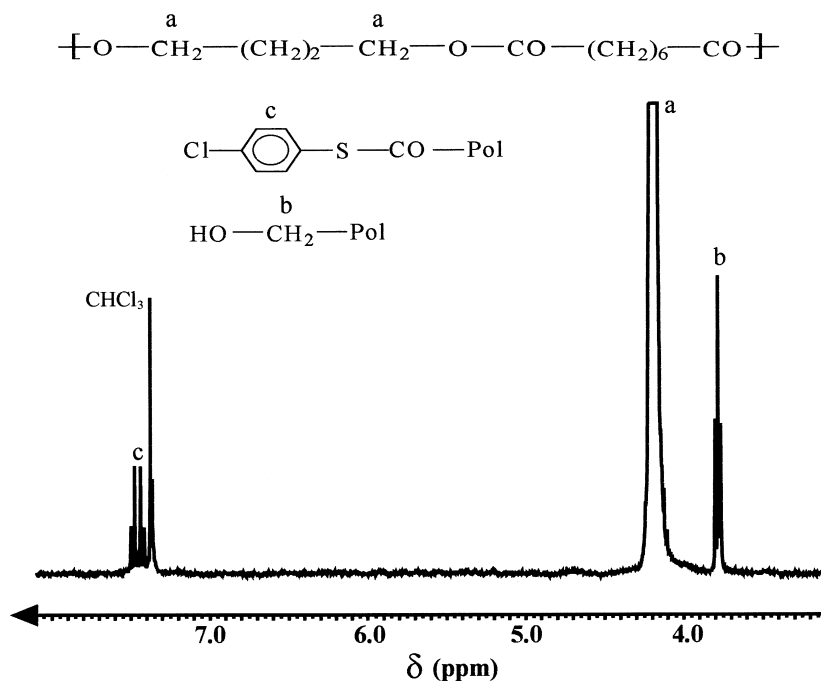


Figure 1. 360 MHz ^1H NMR spectrum (recorded in CDCl_3 / TMS) of a reprecipitated polyester prepared by ring-opening polycondensation of DSDOP with **3** (No. 2, Table 1).

esters precipitated into moist diethyl ether and dry diethyl ether. In the former case, OH-terminated oligoesters (**5** and **6**) were found resulting from the hydrolysis of the macrocyclic oligoesters (Figure 2).

These OH-terminated oligomers were absent when dry diethyl ether was used for the precipitation and the content of cyclic oligo- and polyesters was significantly higher (Figure 3). The cyclic polyesters were detectable up to molecular weights around 7000 Da. The concentration of these large cycles were considerably higher than observable on the MALDI-TOF mass spectra, because the MALDI-TOF method is known to underestimate the high molar mass fraction. Taking into account the low average M_n 's of all samples the MALDI-TOF spectra definite prove that more than 50% of the polyester had a cyclic structure, and then, the cyclization is a limiting factor for the chain growth. However, in contrast to analogous polycondensations of dicarboxylic acid dichlorides [3] the lower reactivity of the bithioaryl esters is another limiting factor.

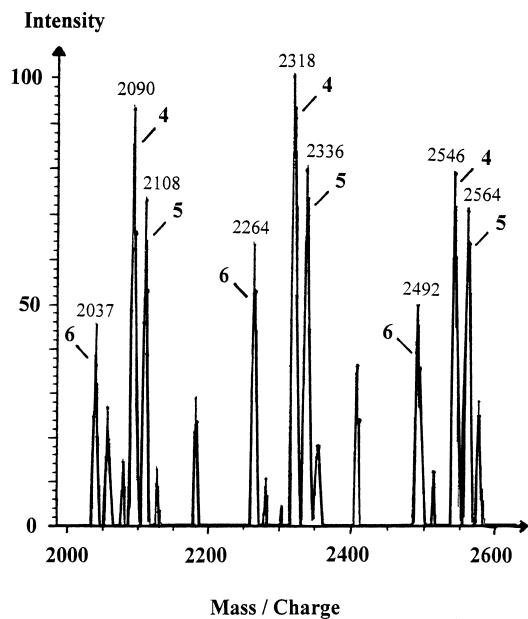


Figure 2. MALDI-TOF mass spectrum of a polyester prepared by ring-opening polycondensation of DSDOP with **3** (No. 6, Table 1) and precipitated in moist diethylether.

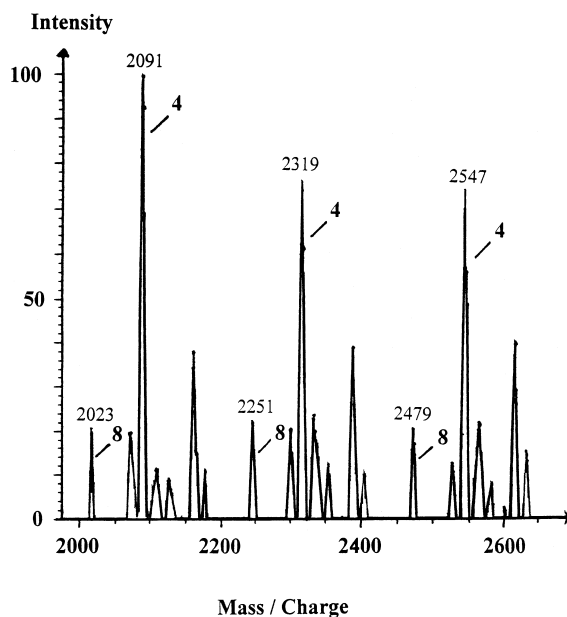


Figure 3. MALDI-TOF mass spectrum of a polyester prepared by ring-opening polycondensation of DSDOP with **3** (No. 8, Table 1) and precipitated in dry diethylether.

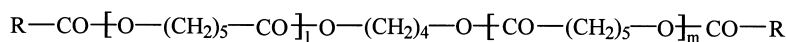
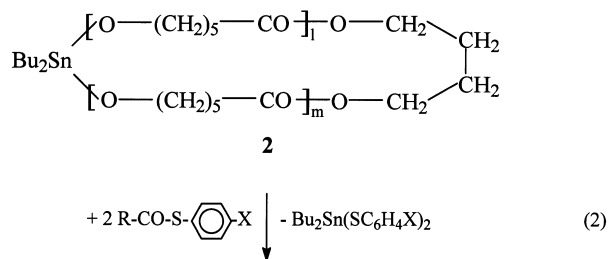
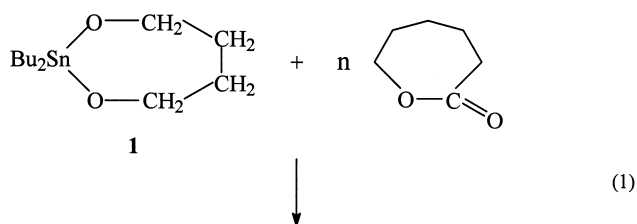
Polycondensations of Macrocylic Poly(ϵ -caprolactone)

In a previous publication [3], tin-containing macrocylic poly(ϵ -caprolactone) (poly(ϵ -CL)) was reacted with sebacoyl chloride in bulk at 80°C. The number average molecular weights (M_n 's) of the resulting polyesters varied with the M_n 's of the parent macrocylic polylactones **2** and fell into the range of 30000 to 90000 Da. In order to find out if the considerably low reactivity (electrophilicity) of arylthioesters compared to acid chlorides has negative consequences for the conversion, and thus, for the molecular weights a bis(4-thiocresyl)ester of sebacic acid was prepared and used as reaction partner of **2**, so that a direct comparison with the previous results was feasible. Furthermore, it was observed in two previous studies that reaction temperatures above 80°C (the standard temperature used for the macrocylic polymerization of ϵ -CL) favor higher molecular weights. Therefore, all polycondensations of this work were conducted at temperatures in the range of 100-200°C.

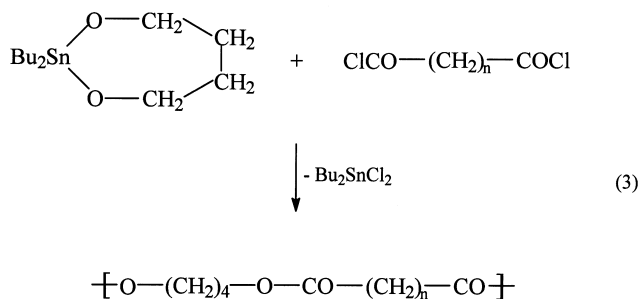
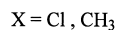
A first series of polycondensations was performed with macrocylic poly(ϵ -CL) prepared according to Equation 1 at a M/I ratio of 20:1 (Table 2). Three different temperatures were applied (100, 130, and 160°C) and the time of the polycondensation process was varied from 4 to 8 and 24 hours. Two major results were obtained. First, all molecular weights were considerably lower than those obtained with sebacoyl chloride. Second, the variation of the reaction conditions had little influence on the molecular weights. A slight decrease of the yields with higher reaction temperature was observed. Three additional polycondensations were conducted in such a way that pyridine (2 equivalent relative to Sn), a catalytic amount of N,N-dimethyl-4-aminopyridine or both amines were added (Nos. 10-12, Table 2). Only the combination of both pyridines produced a slight increase of the molecular weight. This effect was confirmed in the second series of polycondensations (Table 3).

The second series of polycondensations was performed with a macrocylic poly(ϵ -CL) prepared at a M/I of 50:1. In order to compensate the lower concentration of Sn-O bonds in the reaction mixture, longer reaction times (8, 24, and, 72 hours) were used. On the average, the same yields and viscosity values were obtained as in the first series. Furthermore, the same trends were observed. For instance, higher temperatures yielded slightly higher molecular weights, when the time did not exceed 24 hours. A time of 72 hours at 160°C seems to induce a degradation of the initially formed poly-(ϵ -CL). Furthermore, the highest yields were obtained at lowest temperatures, a result typical for both series (Tables 2 and 3).

The viscosity measurements revealed that the molecular weights obtained with the suberic acid ester (Tables 4 and 5) were quite similar to those



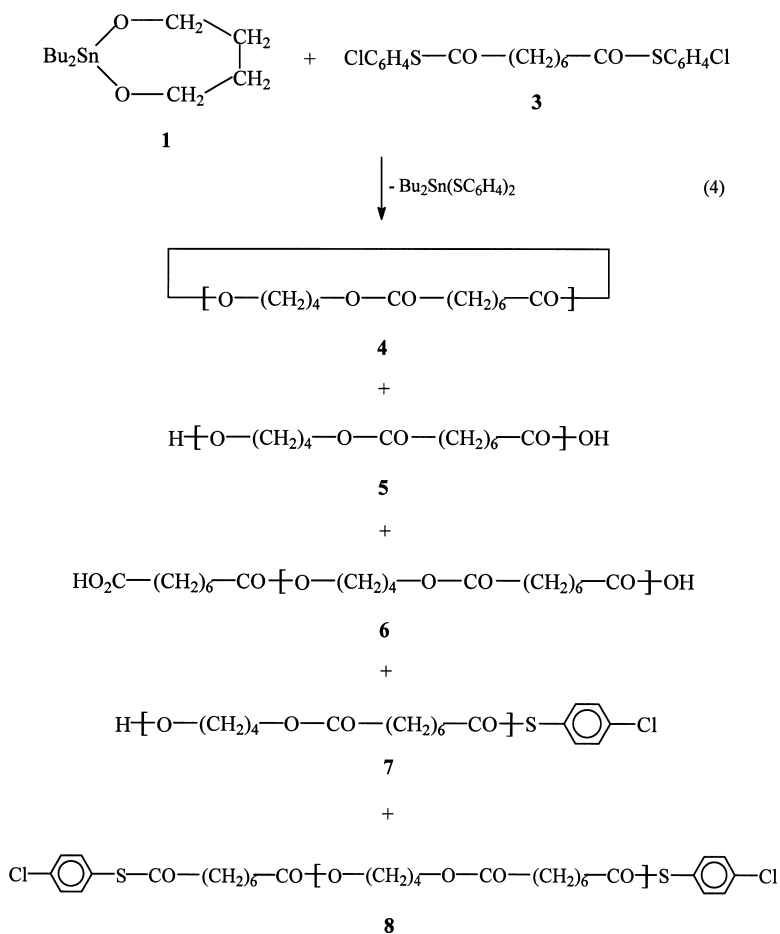
$$n = l + m$$



achieved with the sebacic acid ester (Tables 2 and 3). Therefore, the SEC-measurements were limited to the samples containing suberic acid. The best M_n values were in the range of 19000 to 22000 Da. This means a ring-opening polycondensation of the macrocyclic poly(ϵ -CL) **2** has certainly taken place, but their molecular weights had only increased by the factor 4-8. Taking into account the results obtained with DSDOP as macrocyclic comonomer (Equation 4), it may be concluded that the limitation of the molecular weights has again two reasons: cyclization and incomplete reaction.

In order to detect unreacted thioaryl ester endgroups the polyesters listed in Tables 4 and 5 were examined via 360 MHz ^1H NMR spectra recorded with a

signal-to-noise ratio of $>10^4:1$. Yet, 4-chlorothiophenol groups were only detected in those samples having the lowest molecular weights (No. 2, Tables 4 and 5). Furthermore, attempts were made to obtain MALDI-TOF mass spectra of the samples No. 4 and 6, Table 4. Despite a variation of both matrix and MALDI-TOF apparatus, no signals were obtained. Obviously, the high molecular weights prevented successful measurements, since the lower molecular weight samples obtained from the polycondensations of DSDOP were successfully analyzed under the same experimental conditions (Figures 2 and 3). It is well known that the MALDI-TOF method may yield mass peaks above 20000



$$[\eta] = 1.395 \cdot 10^{-4} \times M_w^{0.786} \text{ (ref. } ^8\text{)} \qquad \qquad \qquad (5)$$

Da, but such measurements were only performed for monodisperse proteins, but not for polydisperse polymers.

Finally, the samples No. 4, Table 5 and No. 6, Table 4 (selected because of their high M_n 's) were subjected to additional SEC measurements analyzed by an UV detector, when a refractive index (RI) detector was used, no oligomers were detected (Figure 4). This means that cyclic oligocaprolactones which are usually formed by back-biting degradation, when tin-based initiators are used, were not present in quantities above 1 wt%. However, when an UV detector was used (Figure 5), the existence of linear oligomers having 4-chlorothioaryl ester endgroups were detected and unreacted thioaryl ester groups were also found in the high molecular weight fraction. This finding indicates that despite long reaction times and addition of pyridine-type catalysts, the incomplete reaction of the thioaryl ester groups was a limiting factor for the molecular weights.

CONCLUSION

The experimental results of the work allow us to answer the questions raised in the introduction. First, the molecular weights of all polyesters obtained in this work are lower than those prepared from dicarboxylic acid chlorides under similar conditions. Second, unreacted thioaryl ester endgroups were

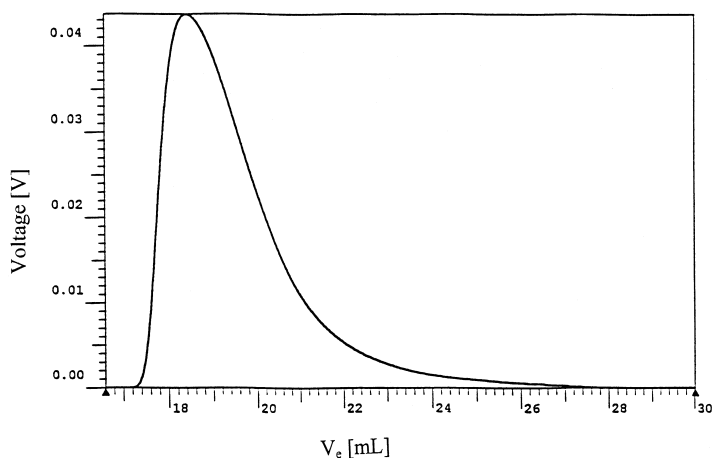


Figure 4. SEC curve of sample No. 6, Table 4 recorded with an R.I. detector.

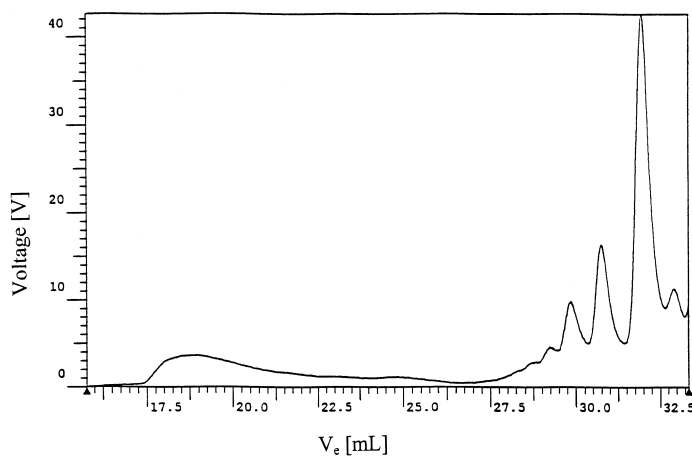


Figure 5. SEC curve of sample No. 6, Table 4 recorded with a UV detector.

detected in numerous samples, and thus, it is obvious that their lower reactivity (compared to acid chlorides) is one factor limiting the effective chain growth. Third, at least in the case of polyesters prepared from DSDOP a high fraction ($\geq 50\%$) of cyclic oligo- and polyesters were detected indicating that the cyclization even in bulk is another limiting factor for the chain growth. This result agrees with theories published 25 years ago [4, 5] and this is the most interesting aspect of the present study. Finally, it should be mentioned that the present work represents another example for our new synthetic strategy called ring-opening polycondensation of macrocyclic monomers and polymers.

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