Macrocycles. 10. Macrocyclic Poly(1,4-butanediol−ester)s by Polycondensation of 2-Stanna-1,3-dioxepane with Dicarboxylic Acid Chlorides

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ABSTRACT: 2,2-Dibutyl-2-stanna-1,3-dioxepane (DSDOP) was polycondensed at 80 °C in bulk with succinyl chloride, adipoyl chloride, suberoyl chloride, sebacoyl chloride, and 1,12-dodecanedioyl chloride. In the case of adipoyl chloride the stoichiometry was varied and the temperature in the case of sebacoyl chloride. With a slight excess of the dicarboxylic acid chlorides, macrocyclic polyesters were obtained as the main reaction products in all cases. Depending on the dicarboxylic acid dichloride the ratio of polycondensation/cyclization steps was of the order of 20/1 to 100/1. The temperature had little influence provided that the reaction mixture remained liquid and homogeneous over the whole course of the polycondensation. Macrocyclic polyesters were also obtained as the main products when the noncyclic 1,3-bis(tributylstannoxy)butane was used as monomer. It is demonstrated that the cyclic oligo- and polyesters are not the result of transesterification and backbiting degradation processes.

Introduction

In previous publications of this series we have demonstrated[1−4] that cyclic tin initiators such as **1** enable a so-called macrocyclic polymerization of lactones (and cyclocarbonates) yielding tin-containing supermacrocycles of structure **2** (eq 1). Furthermore, it was shown[5] that it is possible to use these supermacrocycles as difunctional monomers for polycondensations with dicarboxylic acid chlorides (**3**, eq 2). A comparison of the molecular weights (number-average M_n) before and after the polycondensation suggested that typically 8−15 polycondensation steps occurred.

On the other hand, three publications of Shanzer and co-workers should be mentioned[6−8] describing the reaction of dimeric 2-stanna-1,3-dioxacycloalkanes (e.g., **4a** or **4b**) with dicarboxylic acid chlorides. These reactions were conducted at low concentration in refluxing chloroform, and "tetralactones" of the structure **6a** (or **6b**) were isolated by column chromatography, but those authors did not say anything about further reactions products. However, they claimed that the tetralactones were formed by a stepwise reaction of the dicarboxylic acid chlorides with the tin containing macrocycles **4a**,**b**, i.e., via the intermediates **5a**,**b**. In other words, the successful isolation of the tetralactones was ascribed to a "template effect" of the macrocycles **4a**,**b**. A later publication of Mandolini et al.[9] reported on a reinvestigation with a more complete product analysis. Using SEC and FAB MS measurements, these authors identified a full series of cyclic oligoesters up to molecular weights around 1700 Da without any preference of the cyclic tetramer. They also concluded that these cyclic oligoesters represent a thermodynamically controlled equilibrium situation.

In this connection the present work was aimed at bridging the gap between the polycondensation of the tin-containing cyclic polylactones and the oligomerization of the heterocycles **4a**,**b**. The liquid monomeric 2,2-dibutyl-2-stanna-1,3-dioxepane (**1**, DSDOP) should be polycondensed in bulk with various dicarboxylic and dichlorides to find out whether high molecular weight polyesters or just (cyclic) oligoesters are formed. Furthermore, it should be investigatedwhether the majority of the reaction products have a cyclic or linear structure. Finally, it should be elucidated whether the reaction

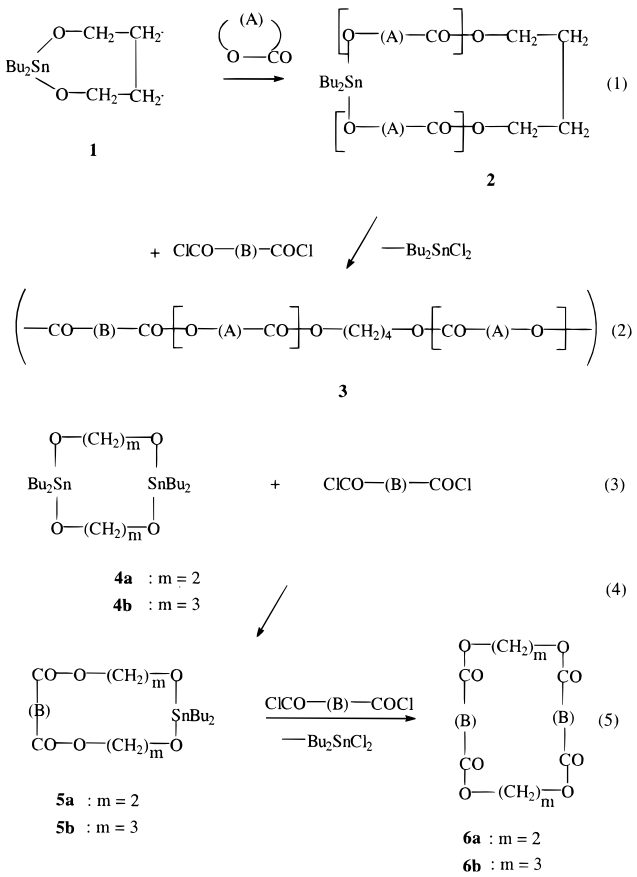

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Table 1. Reaction Conditions and Results of the Polycondensations Conducted with DSDOP and Various Dicarboxylic Acid Dichlorides in Bulk

polym no.	acid chloride	temp (C°)	time (h)	yield (%)	η_{inh}[a] (dL/g)	M_n[b] (SEC)	M_w/M_n[b]	T_m[c]
1	succinic	80	6	95	0.18			113
2	adipic	80	6	88	0.38	17 000	1.85	64
3	suberic	80	6	86	0.62	27 000	1.80	58
4	sebacic	80	1	90	0.48	20 000	2.00	
5	sebacic	80	6	87	0.49	20 000	1.90	65
6	sebacic	80	24	92	0.46	18 000	1.85	
7	sebacic	30	24	88	0.45	18 000	1.80	
8	sebacic	130	6	94	0.49	21 000	1.90	
9	sebacic	180	6	91	0.55	24 000	2.00	67
10	dodecanedioic	80	6	96	0.41	16 000	2.00	68

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] SEC measurements evaluated with the "*a*" and "*K*" values of the Mark−Houwink equation (eq 6). [c] DSC measurements (first heating) with a heating rate of 20 °C/min.

products are based on a thermodynamically controlled equilibrium or not.

Experimental Section

Materials. Dibutyltin dichloride and tributyltin chloride were purchased from Aldrich Co. (Milwaukee, WI). Dibutyltin chloride was reacted with a solution of sodium methoxide in methanol to yield dibutyltin dimethoxide, which (after distillation) was reacted with dry 1,4-butanediol to yield 2,2-dibutyl-2-stanna-1,3-dioxepane (**1**, DSDOP). Tributyltin methoxide was prepared from tributyltin chloride (Aldrich Co.) by means of sodium methoxide in methanol and purified by distillation in vacuo. Succinyl chloride, adipic acid, suberic acid, sebacic acid, and dodecanedioic acid were also purchased from Aldrich Co. The dicarboxylic acid chlorides were prepared by means of thionyl chloride and distilled twice prior to use. 1,4-Butanediol was acetylated by means of a 20% excess of acetic anhydride and a catalytic amount of pyridine.

1,4-Bis(tributyltinoxy)butane. 1,4-Bis(acetoxy)butane (0.2 mol) and tributyltin methoxide (0.4 mol) were mixed in a round-bottom flask which was then equipped with a magnetic bar and a head allowing for blowing a slow stream of nitrogen over the reaction mixture. The reaction vessel was slowly heated to 160 °C whereby most of the liberated methyl acetate was removed. Finally, the product was distilled in a short-path apparatus in a vacuum of 10^{-3} bar. A forerun (ca. 10 wt %) containing unreacted starting materials was separated from the higher boiling liquid product which was characterized by ^{1}H NMR.

Polycondensations. 2,2-Dibutyl-2-stanna-1,3-dioxepane (15 mmol) was weighted into a 50 mL round-bottom flask equipped with a magnetic bar. The reaction vessel was closed with a glass stopper and placed in an oil bath preheated to 80 °C. After 5 min a dicarboxylic acid chloride (15.1 mmol as 2 M solution in dry toluene) was added via a pipet, and the temperature was maintained for 6 h. Afterward the reaction product was dissolved in dry CH_2Cl_2 (50 mL) and precipitated into dry diethyl ether. The polyester was isolated by filtration and was intensively washed with diethyl ether and dried at 40 °C in vacuo. Correct elemental analyses were obtained in all cases.

Fractionation. The crude polyester prepared from DSDOP and adipoyl chloride at 80 °C ($\eta_{inh} = 0.38$ dL/g) was dissolved in CH_2Cl_2 and precipitated into cold diethyl ether. The precipitated polyester was isolated by filtration with a yield of 88% of the theory (see no. 2, Table 1). Sample 1 was dissolved again in CH_2Cl_2 and precipitated into 2-propanol. The polyester isolated after 1 day amounted to 72% of the theory. Sample 2 was then precipitated into a 1:1 (by volume) mixture of 2-propanol and ethyl acetate, and a yield of 61% of the theory was obtained. The resulting sample 3 was precipitated into a 1:3 mixture of 2-propanol and ethyl acetate, whereby sample 4 was isolated in a yield of 47% of the theory. For sample 4 an inherent viscosity of 0.44 dL/g was determined. The soluble fractions were isolated by evaporation of the filtrates.

An analogous fractionation was conducted with a polyester prepared from DSDOP and sebacoyl chloride having an inherent viscosity of 0.48 dL/g. For the last precipitation neat ethyl acetate was used, and a final yield of 62% of the theory was obtained ($\eta_{inh} = 0.52$ dL/g).

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The 100 MHz ^{1}H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent and shift reference.

The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen at a heating rate of 20 °C/min.

The SEC measurements were performed on a Kontron HPLC/SEC apparatus equipped with a Waters Md 410 differential diffractometer. A combination of four Ultrastyragel colums with pore sizes of 10^2, 10^3, 10^4, and 10^5 Å were used, and tetrahydrofuran served as eluent.

The MALDI-TOF mass spectrometry was performed with a Micromass Tof Spec. E mass spectrometer equipped with a nitrogen laser (3 ns pulse time, $\lambda = 337$ nm). All mass spectra were recorded in the reflectron mode with an acceleration potential of 20 kV and a reflectron potential of 26 kV. The matrix (1,8,9-trihydroxyanthracene) was dissolved in CH_2Cl_2 (0.1 mol/L). A 10 μL aliquot of the matrix solution was mixed with 10 μL of the polymer solution (2 g/L). A 1 μL aliquot of KCO_2CF_3 solution (3 g/L) was added as cationization agent. A 1 μL sample of the resulting solution was applied to the target and air-dried immediately before use. In all cases only the potassium cationized ions ($M + K^+$) were detected. Polystyrene ($M_n = 3370$) served for calibration.

Results and Discussion

Most polycondensations were performed in such a way that the neat DSDOP (**1**) was heated to 80 °C, and the dicarboxylic acid chloride was added dropwise in the form of a 2 M solution in dry toluene. The temperature of 80 °C was selected to avoid crystallization of the resulting polyesters. Crystallization was observed in the experiment conducted with sebacoyl chloride at 30 °C (no. 7, Table 1). With sebacoyl chloride the reaction time was varied at 80 °C (nos. 4−6, Table 1), but no significant influence on the yield or on the inherent viscosity was detected. Therefore, the analogous polycondensations with succinyl chloride (no. 1, Table 1), adipoyl chloride (no. 2), and dodecane dicarbonyl chloride (no. 10) were conducted with a time of 6 h. The most conspicuous result of this series is the fact that the molecular weights pass through a maximum in the case of suberic acid. These polycondensations were repeated with redistilled acid chlorides, and a good reproducibility of the inherent viscosities (±0.02 dL/g) was found.

With sebacoyl chloride as electrophilic monomer, not only the time but also the temperature was varied.

Despite a broad variation (from 30 to 180 °C) and despite partial crystallization of the polyester, relatively little variation of the molecular weights was observed (nos. 5 and 7−9, Table 1). However, it is noteworthy that the highest molecular weight was obtained at the highest temperature. This result suggests that the liberated Bu_2SnCl_2 did not cause transesterification combined with "backbiting degradation" (see Discussion below). The same trend was observed in several series of polycondensations of tin-containing macrocyclic polylactones.[5]

All polyesters were characterized by IR and ^{1}H NMR spectra and by elemental analyses, and in all cases satisfactory spectra and analytical data were obtained. The SEC measurements were evaluated with the "*a*" and "*K*" values of the Mark−Houwink equation (eq 6) determined for poly(ϵ-CL) in tetrahydrofuran.[10] The elution curves were also evaluated as usual with the "*a*" and "*K*" values of polystyrene (eq 7).[11] Nearly identical polydispersities were obtained from both evaluation methods. These polydispersities are slightly lower than the value of 2.0, which is typical for polycondensations under homogeneous conditions. However, the M_n values calculated via eq 7 were significantly higher than those derived from eq 6. In a previous paper dealing with poly(ϵ-CL) we have demonstrated that the lower M_n and M_w values derived from eq 6 are closer to the real values and overestimate the real molecular weights only by 5−15%. Therefore, only the lower molecular weight values based on eq 6 were listed in Table 1, and from these M_n values one can calculate that on the average 60−120 polycondensations steps occurred in the individual experiments of Table 1. These values are significantly higher than the "polycondensation factors" 8−15 observed for polycondensations of tin-containing macrocyclic polylactones.[5]

$$[\eta] = 1.395 \times 10^{-4} M^{0.786} \quad (6)$$

$$[\eta] = 1.25 \times 10^{-4} M^{0.717} \quad (7)$$

The relatively large number of polycondensation steps is a clear indication that the template effect postulated by Shanzer et al.[6−8] was not operating. This conclusion was confirmed by MALDI-TOF mass spectra. These mass spectra (Firgures 1, 3, and 5) suggest that more than 90% of the low molar mass fraction of the various samples have a cyclic structure provided that the polycondensations were conducted with a perfect stoichiometry or with a slight (1%) excess of the acid chloride. When the polycondensations were performed with a deficit of the acid chloride, the MALDI-TOF mass spectra display (in addition to the molecular peaks of the supermacrocycles) a series of mass peaks representing linear polyesters having butanediol end groups (structure **6**, m/z = 1507 and 1679 in Figure 2). The presence of CH_2−OH end groups was also detectable in the ^{1}H NMR spectra as illustrated in Figure 4. When an excess of the dicarboxylic acid dichloride was used (nos. 2−5, Table 2), the MALDI-TOF mass spectra revealed again a predominant formation of cyclic oligo- and polyesters, but the concentration of noncyclic polymers increased with increasing excess of adipoyl chloride. Consequently, it was found that a 1 mol % excess of the acid chloride is advantageous over a slight deficit, and thus, all polycondensations listed in Table 1 were conducted with a 1 mol % excess of the acid chloride. Even when only an 1% excess of the acid chlorides was

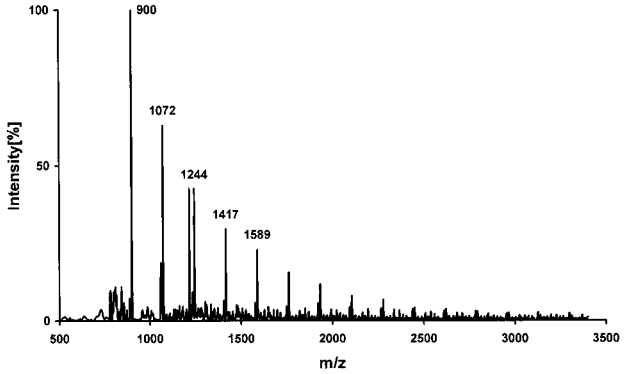


Figure 1. MALDI-TOF mass spectrum (doped with potassium) of the polycondensate of DSDOP and succinyl chloride (1 mol % in excess, no. 1, Table 1). The intensive peaks represent the cyclic oligoesters.

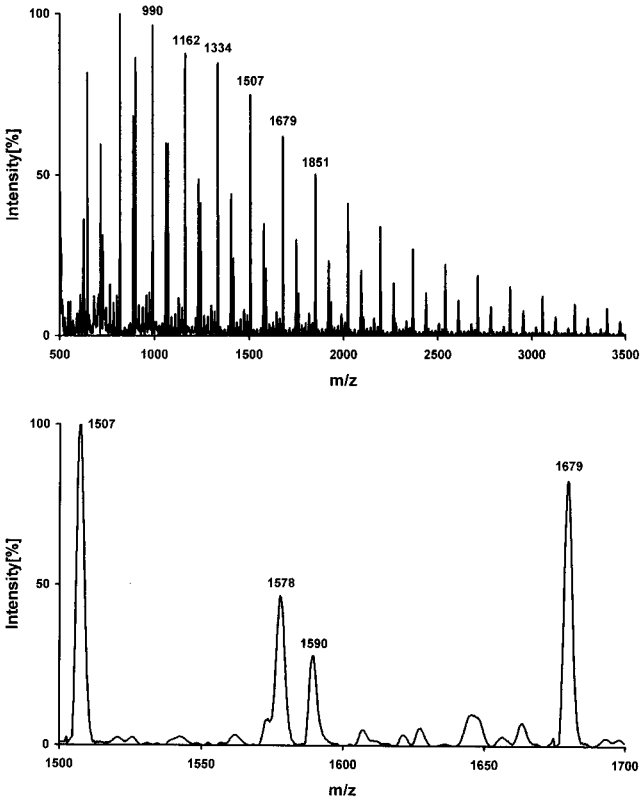


Figure 2. MALDI-TOF mass spectrum (doped with potassium) of the polyester prepared from DSDOP with a deficiency of succinyl chloride. The most intensive peaks represent linear oligoester of structure **6**.

used, the MALDI-TOF mass spectra revealed peaks of noncyclic oligoesters having a low intensity. Surprisingly, the masses of most of these peaks did not agree with structures **6**−**9** which were expected as the most probable linear species. For instance, the peak of m/z = 1578 in Figure 2 and the peak of m/z = 2003 in Figure 3 correspond to the masses of the cyclic oligoesters plus a residual mass of 161 ± 1 Da. Surprisingly, the intensities of these peaks in Figure 3 do not vary with their mass. In the mass spectra of the products obtained from suberoyl chloride, sebacoyl chloride, and 1,10-decanedicarbonyl chloride, a series of weak peaks having other residual masses were observed. Even when a reaction with the matrix (trihydroxyanthracene), acid chloride groups, or an additional doping with sodium ions were taken into account, these peaks could not be assigned. However, this unsatisfactory result does not

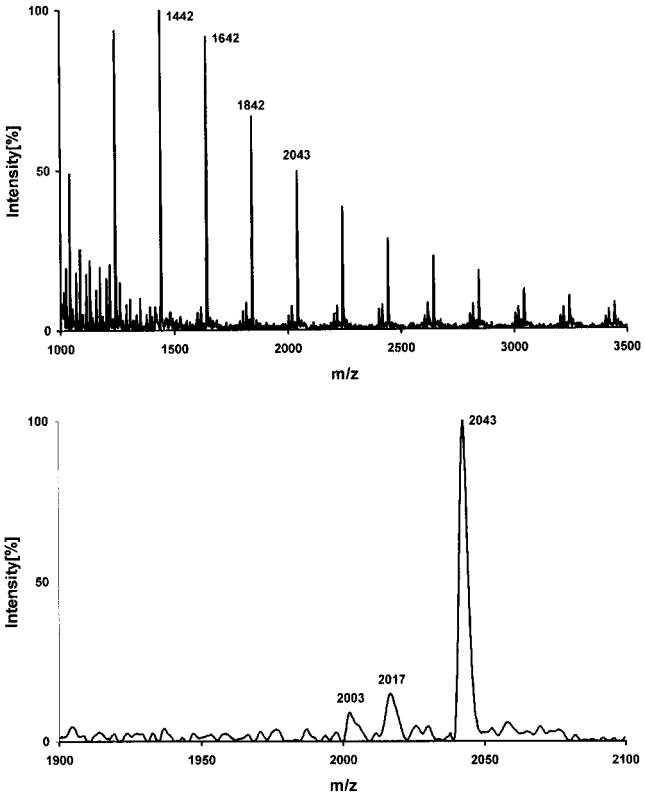
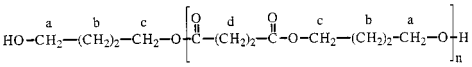


Figure 3. MALDI-TOF mass spectrum (doped with potassium) of the polycondensate of DSDOP and adipoyl chloride (1 mol % in excess, no. 2, Table 1). The intensive peaks represent the cyclic oligoesters.



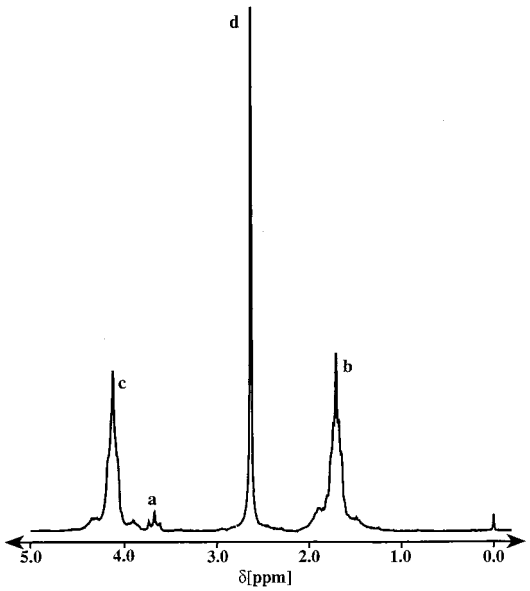


Figure 4. The 100 MHz ^{1}H NMR spectrum of a polycondensate prepared at 80 °C from DSDOP.

affect the main purpose of this study and the conclusions drawn from it.

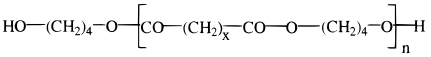
Furthermore, it should be mentioned that the MALDI-TOF mass spectra of the crude polyesters only represent a low molar mass fraction of the entire samples. The MALDI-TOF mass spectra do not represent the original mass distribution due to discrimination effects of the high molar mass fraction of a polydisperse polymer sample. Up to now only several instrumental reasons for these discrimination effects have been discussed, but without a final solution of the problem.[12−14] To check the structure of the higher molar mass fraction, a larger sample of a polyester prepared with adipoyl chloride was fractionated by repeated precipitation into different solvent mixtures. As a final result, a "higher molecular weight fraction" making up 47% of the theoretical yield was isolated. The soluble fractions and the final insoluble fractions were characterized by MALDI-TOF mass spectrometry, and in all cases the cyclic polyesters were found to be the main products. The mass spectrum of the final insoluble fraction is displayed in Figure 5. Cyclic polyesters up to a mass of approximately 5000 Da were detected (degree of polymerization ∼ 25). This result proves that far more than 50% of the original reaction product consisted of cyclic polyesters. An analogous fractionation and characterization was performed with a polyester prepared from sebacoyl chloride (no. 5, Table 1). The final insoluble fraction represented a yield of 62% of the theory, and again the cyclic polyesters were the main reaction products.

At this point the question arises whether the cyclic oligo- and polyesters represent a thermodynamic equilibrium situation resulting from rapid transesterifica-

Table 2. Polycondensations[a] of DSDOP and Adipoyl Chloride in Bulk with Variation of the Stoichiometry

polym. no.	deficiency (−) or excess (+) of adipoyl chloride (mol %)	yield (%)	η_{inh}[a] (dL/g)	comment[b]
1	−2	92	0.25	predom linear
2	+1	88	0.38	predom cycles
3	+2	90	0.39	predom cycles
4	+6	89	0.31	predom cycles
5	+10	96	0.32	predom cycles

[a] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [b] Based on MALDI-TOF mass spectrometry.



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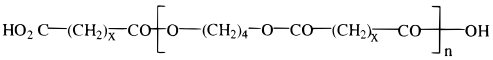

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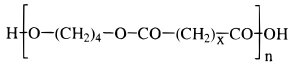

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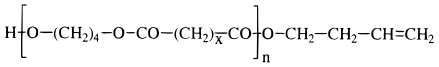

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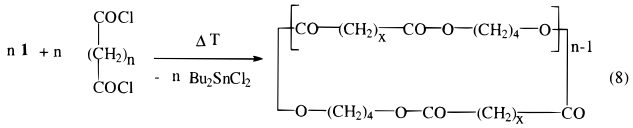


10a - e

a : x = 2 **d** : x = 8
b : x = 4 **e** : x = 10
c : x = 6

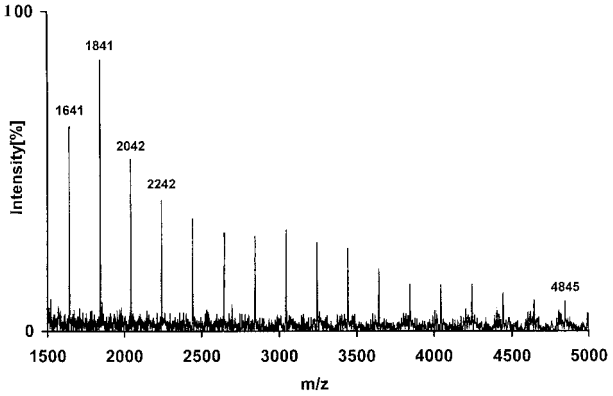


Figure 5. MALDI-TOF mass spectrum of the "high molecular weight fraction (47%) of a fractionated polyester **10b** (no. 2, Table 1). The intensive peaks represent cyclic polyesters.

Table 3. DSDOP-Initiated Degradation of Poly(butanediol sebacate)[a,b]

exp. no	temp (°C)	time (h)	yield (%)	η_{inh} (dL/g)
1	80	6	74	0.30
2	80	20	86	0.26
3	80	48	85	0.19
4	120	6	71	0.27
5	160	6	70	0.24
6	200	6	74	0.22

[a] $\eta_{inh} = 0.48$ dL/g. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2.

tion of any kind (e.g., ester−ester interchange and backbiting degradation). In their reinvestigation of Shanzer's work, Mandolini et al.[9] interpreted the identified cyclooligoesters as components of a thermodynamic equilibrium. However, in the present work several observations vote against an equilibration via transesterification.

1. The polyester structure is sensitive to slight variation of the stoichiometry. The linear species carrying CH_2OH end groups are particularly sensitive to backbiting degradation, but they are the predominant reaction products, when a slight deficit of acid chlorides is used.

2. A larger amount of mainly cyclic poly(butylene sebacate) having $\eta_{inh} = 0.48$ dL/g was mixed with DSDOP at a molar ratio of 100:1 and thermostated at various temperatures and for various times. The results compiled in Table 3 clearly demonstrate that significant degradation takes place under all circumstances. The effect of the degradation increases with the temperature, whereas the molecular weights of the polycondensation products (Table 1) are not affected by higher temperatures.

3. During the first minutes of the standard polycondensation procedure (Table 1) the unreacted DSDOP may produce a small amount of oligomeric macrocycles by transesterification. However, the Bu_2SnCl_2 formed as byproduct is a very poor transesterification catalyst as reported previously.[15] This classification is underlined by two experiments with a linear poly(ϵ-caprolactone) having dead chain ends. When heated with DSDOP (10:1) to 80 °C for 6 h, rapid degradation occurred, whereas in a parallel experiment with Bu_2SnCl_2 replacing the DSDOP no degradation was detectable.

4. In two recent publications[16,17] dealing with the synthesis of multiblock copolyesters from Sn-containing cyclic polylactones, it was demonstrated that no transesterification occurred below 240 °C.

Table 4. Polycondensations of 1,4-Bis(tributyltinoxy)butane with Dicarboxylic Acid Chloride in Bulk[a]

polym no.	acid chloride	yield (%)	η_{inh}[b] (dL/g)	M_n[c]	M_w/M_n[c]
1	succinic	85	0.12	1500	
2	adipic	82	0.17	3500	1.90
3	suberic	79	0.18	4000	1.90
4	sebacic	83	0.21	6000	1.95

[a] Temperature 80 °C; time 6 h. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] SEC measurements in tetrahydrofuran calibrated with polystyrene.

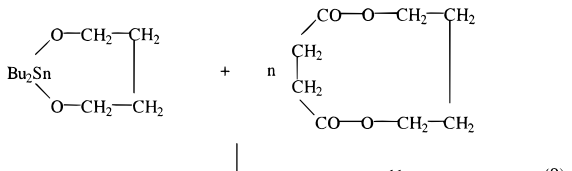
In summary, these experimental findings provide compelling evidence that the product of the polycondensations listed in Tables 1 and 2 do not represent an equilibrium but that they are the primary products of the polycondensation process.

To shorten the time, when unreacted Sn−O bonds may cause transesterification, and thus the formation of cyclic oligoesters, two more polycondensation experiments were conducted. Neat DSDOP and neat adipoyl chloride (or sebacoyl chloride) were mixed at 20 °C within a few seconds. In the case of adipoyl chloride the temperature rose to 140 °C within 50 s and began to drop 10 s later. With sebacoyl chloride the temperature rose to 135 °C, and in both experiments the reaction mixtures turned black. Because of this highly exothermic character and the discoloration, a procedure with a slower mixing of the monomers was used for the standard experiments listed in Tables 1 and 2. The polyesters recovered from the "flash mixing" of the monomers had $\eta_{inh} = 0.22$ and 0.40 dL/g, respectively. Furthermore, the MALDI-TOF mass spectra were comparable to those obtained from the products of Table 1. Therefore, these results provide additional evidence for the conclusion that in the standard polycondensation experiments both structure and molar ratios of the reactive products are little affected by tranesterification.

Polycondensation of Bis(tributyltinoxy)butane. The results discussed above raise now the question if the cyclic structure of the monomer **1** plays a decisive role for the formation of the macrocyclic polyesters **10a**−**e**. A potential explanation is presented in eq 9. One may assume that initially the 10-membered cyclic monomer **11** is preferentially formed which undergoes a macrocyclic polymerization initiated by a small amount of unreacted DSDOP (**1**). The resulting cyclic polyesters **12** can then react with remaining dicarboxylic acid chloride, so that the cyclic polyesters **10a**−**e** are formed.

To check the validity of this hypothesis, polycondensations of 1,4-bis(tributylstannoxy)butane (**14**) with various dicarboxylic acid chlorides were conducted. The monomer **14** is know in the literature,[18] but its synthesis from 1,4-butanediol, sodium powder, and tributyltin chloride is not attractive. Therefore, we have elaborated a new route which consists of the transesterification of 1,4-bis(acetoxy)butane (**13**) with tributyltin methoxide (eq 10).

The polycondensations of monomer **14** were conducted in bulk under the same conditions as the polycondensation of monomer **1** (i.e., 80 °C/6 h). The results are summarized in Table 4 and show that high yields of polyesters with low molecular weights were formed. The polydispersities agree with those found for the polycondensates of DSDOP (**1**). The MALDI-TOF analyses of the four polyesters revealed that in all cases macrocyclic polyesters of structure **10** were preferentially formed.



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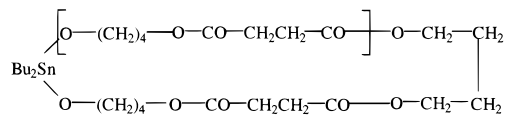

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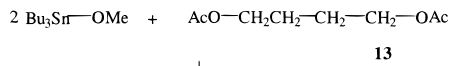
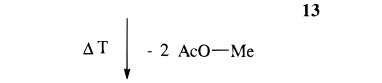
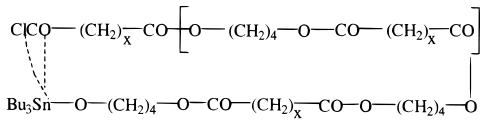


13



14 (10)



15

The MALDI-TOF mass spectra were nearly identical with those of Figures 1A and 2A, suggesting that more than 50% of the polyesters were cycles. These results clearly demonstrate that the hypothesis outlined in eq 9 does not provide a satisfactory interpretation of the course taken by the polycondensations of monomer **1**. This situation suggests a study of the following two hypotheses:

(I) The high efficiency of cyclization observed in this work is a consequence of special interactions between the ractive end groups (involving the free d-orbitals of tin) as illustrated schematically by formula **15**.

(II) The formation of supermacrocycles is the normal result of all polycondensations (A) when a conversion close to 100% is kinetically and thermodynamically feasible and (B) when no "backbiting degradation" or any other ring−chain equilibration takes place.

A detailed mathematical treatment of step growth polymerizations by two research groups has shown more than two decades ago[19,20] that such ideal and irreversible polycondensations should in fact yield 100% cyclic oligomers and polymers when the conversion reaches 100%. To the best of our knowledge, experimental results confirming this theory and based on polycondensations in bulk have not been published yet. However, the first results of our ongoing research using tin-free monomers suggest that this theory and hypothesis II provide the correct interpretation of the result obtained in the present study.

Conclusion

The results of this work demonstrate that DSDOP can be used as a difunctional monomer for polycondensations. Average degrees of polymerizations (DPs) of 30−100 were found, but there was no evidence for a template effect. When sufficient reaction time and a satisfactory stoichiometry of the reaction partners are given, the main reaction products are macrocyclic polyesters. The cyclic structure of DSDOP is not a basic requirement for this result, because noncyclic stannylated 1,4-butanediol also yields macrocyclic polyester. Furthermore, it may be concluded that the cyclic oligo- and polyesters are mainly the direct (or primary) reaction products and not the components of a thermodynamically controlled equilibration process. The high cyclization tendency observed in these polycondensations can be explained by two hypotheses. Either the cyclization is a normal result of a high conversion in the absence of side reactions or the active end groups from loose complexes favoring the cyclization. At this time a decision as to which hypothesis is correct cannot be made. Regardless of the mechanistic details, it could be demonstrated that the formation of cyclic polyesters is a kinetic result and not based on a thermodynamically controlled equilibration. When further studies confirm these results and their interpretation, the polycondensation of tin-containing cyclic alkoxides in bulk offers easy access to the synthesis of cyclic polyesters.

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