NEW POLYMER SYNTHESES. 105. SYNTHESES OF ALIPHATIC POLY(THIOESTER)S BY RING-OPENING POLYCONDENSATION OF 2,2-DIBUTYL-2-STANNA-1,3-DITHIOLANE

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NEW POLYMER SYNTHESES. 105. SYNTHESES OF ALIPHATIC POLY(THIOESTER)S BY RING-OPENING POLYCONDENSATION OF 2,2-DIBUTYL-2-STANNA-1,3-DITHIOLANE

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ABSTRACT

2,2-Dibutyl-2-stanna-1,3-dithiolane was reacted with various aliphatic α,ω,-dicarboxylic acid dichlorides. In an exothermic reaction, the corresponding polyesters of 1,2-dimercapto ethane were obtained in high yields. These polythioesters were found to be rapidly crystallizing materials with melting temperatures in the range of 125-195°C. The DSC measurements of the polythioester derived from suberic acid suggest that this polymer undergoes a reversible first order transition resulting from a change of the crystal modification. The MALDI-TOF mass spectra indicated the formation of large amounts of cyclic oligo- and polyesters in all cases. The polythioesters proved to be useful reagents for the exchange of Bu_2Sn groups in cyclic tin-containing alkylene bisoxides, so that tin- and sulfur-free oligo or polyesters were obtained.

Key Words: Polymer syntheses; Aliphatic poly(thioester)s; Ring-opening polycondensation; 2,2-Dibutyl-2-stanna-1,3-dithiolane

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INTRODUCTION

In a previous publication [1] polycondensations of 2,2-dibutyl-2-stanna-1,3-dithiane (1) with aliphatic dicarboxyclic acid dichlorides, ADADS (Equation 1) were reported. These "ring-opening polycondensations" represent a new type of step-growth polymerizations [2], and the resulting polythioesters **2** proved to be interesting materials for two reasons. Firstly, they consisted, to a large extent, of cyclic oligomers and polymers. Secondly, some of these polythioesters showed a reversible change of crystal modifications in heating/cooling cycles which is a rare property among aliphatic polymers.

In the present work, analogous polycondensations of the 5-ring **3** should be studied for the following three reasons. Firstly, it should be elucidated, if again large amounts of cycles are formed. Secondly, the existence of reversible first order phase transitions should be elucidated. Thirdly, it was expected that the polythioesters of structure **4** are particularly useful to transform the easily accessible cyclic, tin-containing polyethers of structure **5** [3] (and analogous cyclic ethers [4]) into tin-free and sulfur-free polyesters (Equation (3)). In this connection it should be mentioned that Cort *et al*. [5] studied the condensation of the 2-stanna-1,3-dithiolane 3 with pimeloyl chloride (n=5) and azelaoyl chloride (n=7) in dilute chloroform solution. Cyclic dimers and tetramers were isolated and characterized.

EXPERIMENTAL

Materials

1,2-Dimercapto ethane, and Bu_2SnO were purchases from Aldrich Co. (Milwaukee, WI,) and used as received. Succinylchloride, Adipoyl chloride suberoyl chloride, sebacoyl chloride and 1,10 decane dicarbonyl chloride were also purchased from Aldrich Co. and distilled prior to use. 2,2-Dibutyl-2-stanna-1,3-dioxepane was prepared from $Bu_2Sn(OMe)_2$ and dry 1,4-butane diol as described previously [6]. 2,2-Dibutyl-2-stanna-1,3-dithiolane was prepared from Bu_2SnO and 1,2-dimercaptoethane in boiling toluene with azeotropic removal of water according to the literature. It had a melting point of 58-60°C in agreement with the literature data [5, 7].

Polycondensation

In Bulk (Table 1)

2,2-Dibutyl-2-stanna-1,3-dithiolane (20 mmol) was weighed into a 50 mL round bottom flask and an aliphatic dicarboxylic acid dichloride (20 mmol) was added. The monomers were mixed by intensive stirring with a glassrod whereby the exothermic reaction started. The reaction vessel was then closed with a glass-

Table 1. Polycondensations of 2,2-Dibutyl-2-stanna-1,3-dithiolane (**3**) and Various ADADs in Bulk

Polyc. No.	Polymer No. (n)	Yield	$\eta_{inh}{}^{a}$ (dL/g)
1	**4a** (2)	76	0.10
2	**4b** (4)	78	0.27
3	**4c** (6)	66	0.28
4	**4c** (6)	78	0.30
5	**4c** (6)	78	0.34
6	**4c** (6)	74	0.38
7	**4e** (10)	84	0.42

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 8:1).

stopper and steel spring and one minute late it was placed into an oil bath pre-heated to 110°C. After 16 hours, the reaction mixture was cooled to approximately 60°C and shaken 3 times with warm ligroin to remove most of the liberated Bu_2SnCl_2. The crude product was then dissolved in CH_2Cl_2 (containing trifluoroacetic acid when necessary) and precipitated into a mixture of diethyl ether and ligroin (volume ratio 1:1). The isolated polymer was dried at 40°C *in vacuo*.

In Chlorobenzene (Table 2)

Dry chlorobenzene (5 mL) and 2,2-dibutyl-2-stanna-1,3-dithiolane (10 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirrer, gas-inlet and gas-outlet tubes. An aliphatic dicarboxylic acid dichloride (10

Table 2. Yields and Properties of Polythioesters Prepared from ADAD and 2,2-Dibutyl-2-stanna-1,3-dithiolane in Chlorobenzene

Polymer No. (n)	Acidchlorid	Yield [%]	$\eta_{inh}{}^{a}$ [dL/g]	Tm[b] [°C]	Elemental Formel		Elemental Analyses C	H	S
4a (2)	Succinic acid	76	0.27	194 184	$C_6H_8O_2S_2$ (176.25)	calcd. found	40.89 41.50	4.58 4.67	36.38 33.45
4b (4)	Adipic acid	79	0.52	154	$C_8H_{12}O_2S_2$ 204.30)	calcd. found	47.03 47.05	5.92 5.92	31.38 31.19
4c (6)	Suberic acid	88	0.79	129, 146	$C_{10}H_{16}O_2S_2$ (232.36)	calcd. found	51.69 51.81	6.94 7.04	27.60 27.72
4d (8)	Sebacic acid	86	1.11	128	$C_{12}H_{20}O_2S_2$ (260.41)	calcd. found	55.35 55.66	7.74 7.72	24.62 24.64
4e (10)	1,12-Dodecane-dioic acid	91	0.82	126	$C_{14}H_{24}O_2S_2$ (288.46)	calcd. found	58.29 58.44	8.39 8.47	22.23 22.23

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 8:1).
[b]From DSC measurements conducted with a heating rate of 20°C/min.

mmol) was added and the reaction vessel was placed into an oil bath preheated to 110°C. The reaction mixture was worked up as described above.

Reactions with 2,2-Dibutyl-2-stanna-1,3-dioxepane (Table 3)

2,2-dibutyl-2-stanna-1,3-dioxepane (10 mmol) and a polythioester (**4b'** or **4d**, 10 mmol) were weighed into a 50 mL Erlenmeyer flask equipped with a magnetic stirrer. Dry chlorobenzene (20 mL) was added, the reaction vessel was closed with a glass stopper and steel spring and immersed into an oil bath preheated to 100°C. After 24 or 48 hours, the reaction mixture was poured into cold methanol, the precipitated product was isolated by filtration and dried at 40°C *in vacuo*.

Measurements

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

The IR spectra were recorded with a Nicolet "Impact 410" FT-IR spectrometer using KBr pellets. The 100 MHz ^{1}H NMR spectra and the 25.2 MHz ^{13}C NMR spectra were recorded on a Bruker AC-100 FT-NMR spectrometer in 5 mm o.d. sample tubes.

The MALDI-TOF mass spectra were recorded on a Bruker Biflex III mass spectrometer in the reflection mode. An acceleration voltage of 20 kV was used, dithranol served as matrix and potassium trifluoroacetate as dopant.

RESULTS AND DISCUSSION

Syntheses of Polythioesters

All polythioesters of this work were prepared by polycondensation of the 2-stanna-1,3-dithiolane 3 with various aliphatic dicarboxylic acid dichlorides (ADADs). This approach was used not only to explore a new synthetic method,

Table 3.   Spectroscopy Properties of the Polythioesters

Polymer No. (n)	IR ν_{co}[cm]	^{1}H-NMR [ppm]	^{13}C-NMR [ppm]
4a (2)	1681	3.01s, 4H; 3.14t, 4H	29.0; 38.7; 201.5
4b (4)	1684	1.73s, 4H; 2.67s, 4H; 3.13s, 4H	25.2; 29.0; 43.6; 205.3
4c (6)	1689	1.36s, 4 H; 1.67d, 4H; 2.65t, 4H;3.13s, 4H	25.9; 28.6; 29.0; 44.1; 206.8
4d (8)	1685	1.31s, 8H; 1.67s, 4H; 2.64t, 4H; 3.13s, 4H	26.2; 29.0; 29.1; 44.3; 206.8
4e (10)	1688	1.29s, 12H; 1.67q, 4H; 2.65t, 4H; 3.13s, 4H	26.3; 29.0; 29.1; 29.3; 29.5; 44.3; 207.3

but also, because it has an important advantage. The commercial 1,2-dimercaptoethane is a technical product of low purity. Because of its oxidation sensitivity , and because of its bad smell, purification by fractionated distillation is not attractive. However, its reaction with Bu_2SnO [5, 7] (with azeotropic removal of water) is an easy to perform experiment yielding the rapidly crystallizing dithiolane **3** in satisfactory purity. Further purification by recrystallization is also easy to achieve. In this way, a pure and activated monomer of 1,2-dimercaptoethane can be obtained which is stable on storage.

For the polycondensations of **3** with ADADs two different procedures were explored and compared. Firstly, the neat monomers were mixed at room temperature without the addition of a solvent, and secondly, the monomers were mixed in chlorobenzene. The first procedure is a copy of the procedure successfully used for the syntheses of the polythioesters **2**. However, this procedure was not satisfactory when the dithiolane **3** was used because the melting temperatures (T_ms) of the resulting polythioesters **4a-e** were higher than those of the polythioesters **2**. Although the reaction between monomer **3** and the ADADs was highly exothermic a completely homogeneous melt was never obtained, even when the reaction mixtures were thermostated at 110°C two minutes after the mixing of the monomers. The yields and inherent viscosities of polythioesters isolated from this procedure are listed in Table 1. A comparison with the viscosities obtained by the second procedure (see Table 2) suggests that the inhomogeneous reaction mixtures had the consequence of lower conversions, and thus, of lower molecular weights. The repetition of the polycondensations with suberoylchloride (Nos. 3-6, Table 1) also demonstrates that this procedure makes it difficult to reproduce the viscosities/molecular weights.

The second procedure is based on the mixing of monomer **3** with the ADADs at room temperature in dry chlorobenzene. Afterward, the reaction mixtures were thermostated at 110°C quite analogous to the first procedure. However, in contrast to the first procedure nearly homogeneous mixtures were obtained for the polythioesters **4b-e**. Due to the high T_m of **4a** its reaction mixture contained solid particles from the very beginning, and this product (No. 1, Table 2) showed the lowest viscosity value. Finally, it should be mentioned that three polycondensations were repeated in dry toluene (not listed in a Table). In the case of succinyl chloride, the inherent viscosity of the resulting polythioester (**4a'**) was almost identical with that isolated from chlorobenzene (**4a** in Table 2). In the case of adipoyl chloride, the inherent viscosity of **4b'** was higher (0.62 dL/g). In the case of 1,10-decane dicarbonyl chloride, the inherent viscosity of **4e'** was much lower (0.35 dL/g).

The polythioesters prepared via the second procedure had all significantly higher molecular weights than those resulting from the first procedure (Table 1), and thus, only these high molecular weight samples listed in Table 2 (plus **4b'**) were subjected to further characterizations.

Characterization

When the polythioesters were characterized by C- and H elemental analyses good results were obtained for **4b-e**, whereas the C-value of **4a** was less satisfactory in agreement with a relatively low molecular weight (Table 2). The IR spectra displayed an intensive CO-stretch vibration in the range of 1680–1690 cm^{-1} as exemplarily illustrated by Figure 1 (see also Table 3). This wave number is about 50-60 cm^{-1} lower than the CO vibrations of normal ester groups (R-CO-O-R'). This bathochromic shift suggests a more extensive delocalization of the n-electrons of the sulfur atoms and a higher dipolmoment of the CO-S group (relative to CO-O). The ^{1}H NMR spectra were in perfect agreement with the expected structures, and did not show any unexpected feature (Table 3). In the case of the ^{13}C NMR spectra, the CO-signals appear around $\delta = 203 \pm 3$ ppm a shift value which is about 30 ppm further downfield of the CO-signals is typical for normal aliphatic ester groups. This downfield shift is another consequence of the extensive delocalization of the n-electrons of the S-atoms. These spectroscopic features are, in principle, known from low molar mass esters and thioesters. However, the third consequence of the stronger delocalization and the higher dipole moment of CO-S groups are the relatively high melting temperatures (T$_m$s, see Table 2) and high rates of crystallization. The T$_m$s of the polythioesters **4a-e** are roughly 50-70°C higher than those of the corresponding S-free polyesters of ethyleneglycol.

Another interesting aspect of the polythioesters prepared in this work was revealed by MALDI-TOF mass spectroscopy. All the polythioesters listed in Table 2 contained high fractions of cycles which were the dominant species at least in the mass range up to 3000 Da. In the case of **4a** we were not able to detect peaks at higher masses (Figure 2). In the case of **4c-4e** the mass peaks of linear chains such
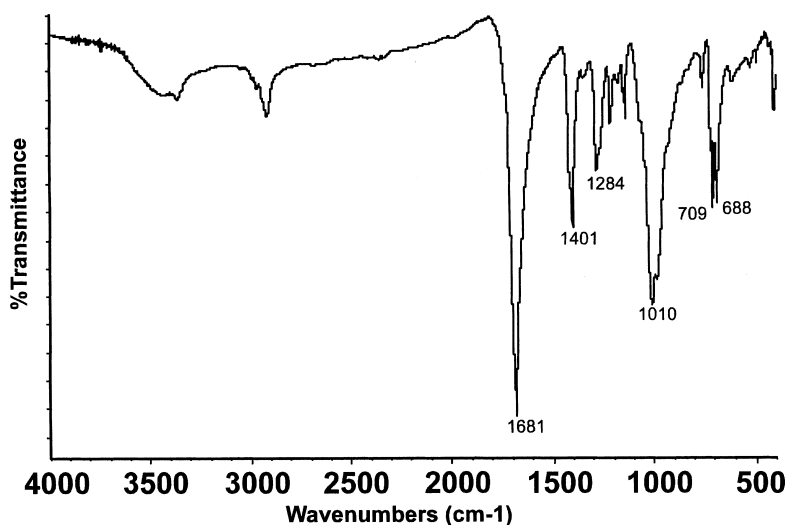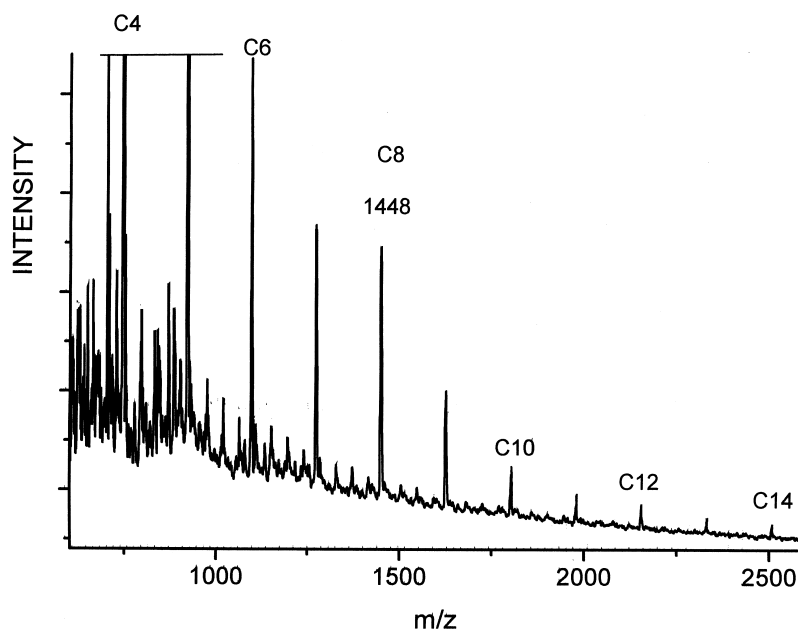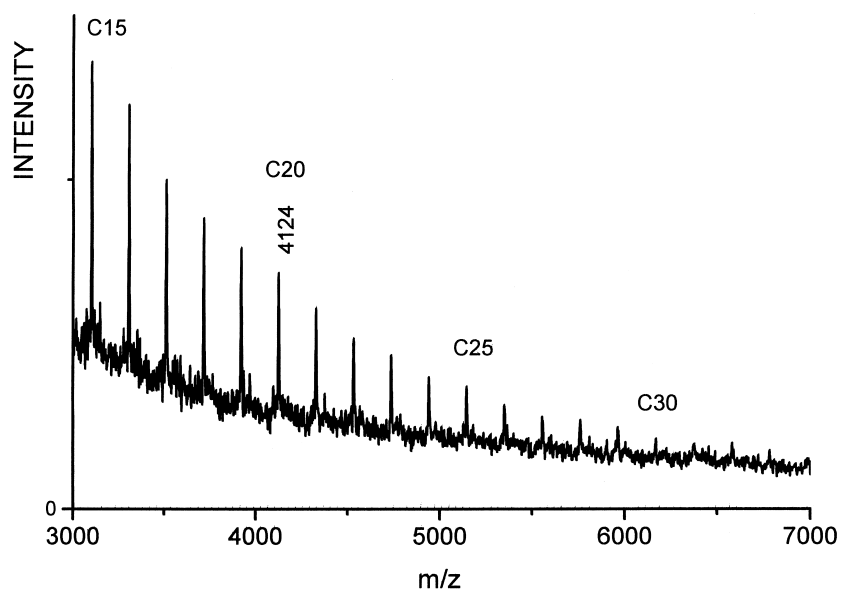

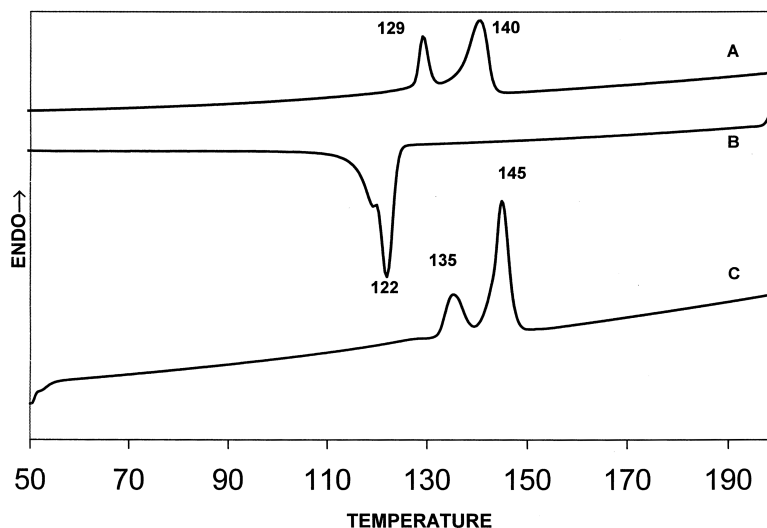*Figure 1.* IR spectrum (KBr pellets) of the polythioester **4a**.

Figure 2.   MALDI-TOF mass spectrum of the polythioester **4a**.

Figure 3.   MALDI-TOF mass spectrum of the polythioester **4b'** (prepared in toluene).
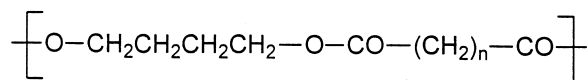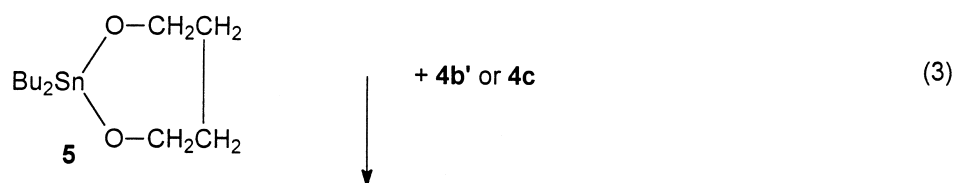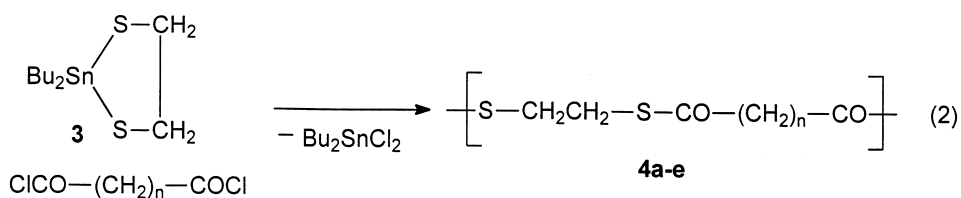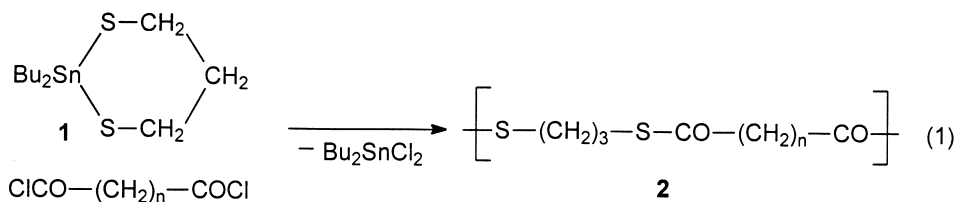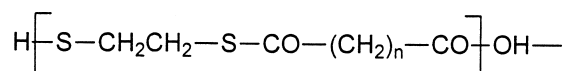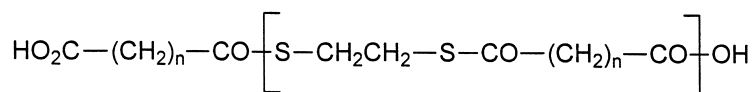
Figure 4. DSC measurements of the polythioester **4c**: A) 1st heating; B) 1st cooling; C) 2nd heating (heating/cooling rate ± 20°C/min).
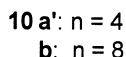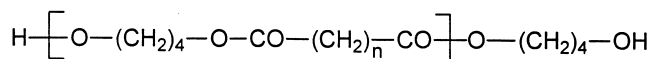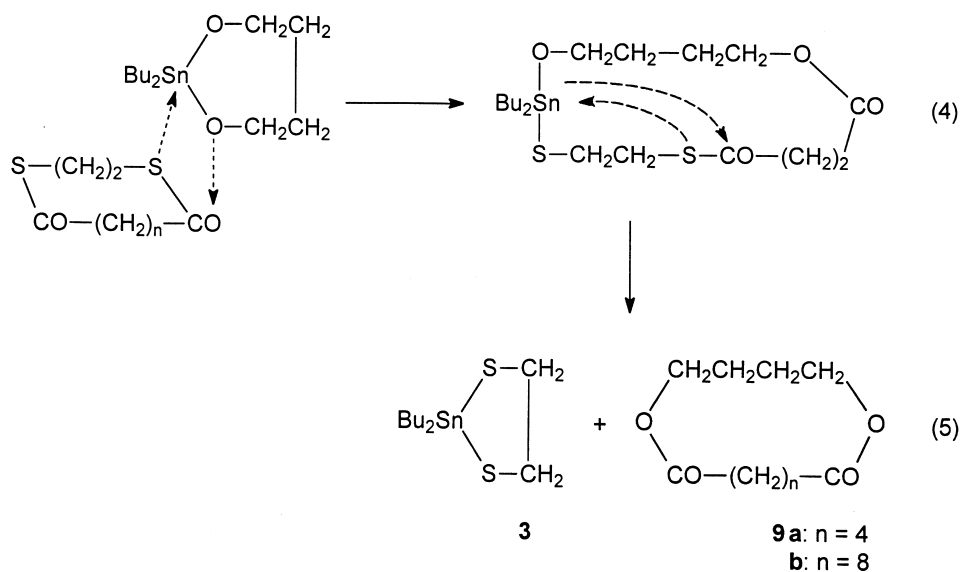
as **7** or **8** were prevailing in the mass range above 3000 or 3500 Da. However, in the case of **4b'** (prepared in toluene) the MALDI-TOF mass spectrum exclusively displayed peaks of cycles up to masses around 7000 Da (Figure 3). These results parallel those recently obtained from polycondensations of monomer **1** [1]. As extensively explained in two recent publications [8, 9], the formation of cyclic oligomers and polymers is a quite normal consequence of any clean kinetically controlled polycondensation (no side reactions, no equilibration reactions). High fractions of cycles can only be obtained with perfect stoichiometry and high conversions (> 99.9%) and such ideal conditions can, of course, not be realized in all small scale experiments. However, the mass spectra presented in Figures 3 and 4 prove that the ring-opening polycondensations studied in this work also follow our concept of kinetically controlled polycondensations.

The DSC measurements revealed for the polythioester **4b, 4b', 4d, and 4e** only one melting endotherm and the corresponding crystallization exotherm (see Table 2). Variation of the cooling rate between –10°C/min. and –80°C/min also revealed that these polythioesters are rapidly crystallizing materials in close analogy with the previously described polythioesters of structure 2. In the case of 4a one weak endotherm was detectable in addition to the main endotherm (194°C). This weak endotherm disappeared upon annealing immediately below the main endotherm (15 minutes at 187°C), and was obviously the result of less perfect crystallites. However, two well separated endotherms, which did not change upon annealing, were observable in the heating traces of **4c** (Figure 4). Therefore, it is obvious that in this case a reversible modification of the crystall lattice occurs below the melting temperature. Similar thermal properties were also found for several polythioesters of structure 2 [1].

Reactions with 2,2-Dibutyl-2-stanna-1,3-dioxapane

In contrast to silicon or carbon, the bond to sulfur is in the case of tin more stable than the bond to oxygen. Furthermore, the low energy difference between LUMO and HOMO reduces the energy of activation for any interchange reaction. Therefore, it was expected that the polythioesters **4a-e** will react with cyclic tin alkoxides such as the 2,2-dibutyl-2-stanna-1,3-dioxepane (**5**, DSDOP). In the present work, no detailed study, but only a few preliminary experiments should be

$$
\text{1} \xrightarrow[-\ Bu_2SnCl_2]{} \left[S-(CH_2)_3-S-CO-(CH_2)_n-CO \right] \quad \text{2} \tag{1}
$$

ClCO—(CH$_2$)$_n$—COCl

$$
\text{3} \xrightarrow[-\ Bu_2SnCl_2]{} \left[S-CH_2CH_2-S-CO-(CH_2)_n-CO \right] \quad \text{4a-e} \tag{2}
$$

ClCO—(CH$_2$)$_n$—COCl

$$
\text{5} \xrightarrow{+\ \textbf{4b'} \text{ or } \textbf{4c}} \tag{3}
$$

$$
\left[O-CH_2CH_2CH_2CH_2-O-CO-(CH_2)_n-CO \right]
$$

6a: n = 4   **6b**: n = 8

$$
H\left[S-CH_2CH_2-S-CO-(CH_2)_n-CO \right]OH—
$$

7

$$
HO_2C-(CH_2)_n-CO\left[S-CH_2CH_2-S-CO-(CH_2)_n-CO \right]OH
$$

8

$$
\text{(4)}
$$

$$
\text{(5)}
$$

$$
\mathbf{3} \qquad\qquad \mathbf{9\,a}: n = 4
$$
$$
\mathbf{b}: n = 8
$$

$$
H\!\!-\!\!\left[\,O\!-\!(CH_2)_4\!-\!O\!-\!CO\!-\!(CH_2)_n\!-\!CO\,\right]\!\!-\!O\!-\!(CH_2)_4\!-\!OH
$$

$$
\mathbf{10\,a'}: n = 4
$$
$$
\mathbf{b}: \ n = 8
$$

performed to find out, if and to what extend the interchange reaction outlined in Equation (3) will take place. For this purpose DSDOP, (**5**) was heated with the polythioester **4b'** in chlorobenzene to 100°C. The reaction time was varied from 24 to 48 hours (Table 4). The crude reaction mixture was poured into methanol, and the crude insoluble reaction product was characterized by viscosity measurements, IR-spectroscopy, ^{1}H NMR- and ^{13}C NMR-spectroscopy and by MALDI-TOF mass spectrometry. The results were independent of the reaction time, and proved that polyesters of low molecular weight were obtained. These polyesters were free of tin and sulfur and had the expected structure (**6**). Characteristic for these normal polyester structures is the CO-striting vibration at 1733 cm^{-1} and a ^{13}C NMR CO-signal in the range of 173-174 ppm (in CDCl$_3$/TMS). Analogous experiments were performed with DSDOP and the polythioesters **4d** (Table 4). The results were in perfect agreement with those obtained from **4b'**. The MALDI-TOF mass spectra revealed that all four polyesters contained cyclic oligoesters (9) in the mass range below 3000 Da, but the main reaction products were linear chains having two 1,4-butanediol endgroups (structure **10**). A further optimization of the reaction conditions was not intended in this work. Nonetheless, these results demonstrate that an almost quantitative reaction between tin heterocyclic and polythioester has taken place.

Table 4. Reactions of 2,2-Dibutyl-2-stanna-1,3-dithiolane with Polythioesters Derived from Adipic Acid or Sebacic Acid at 100°C in Chlorobenzene

Exp. No.	Polythioester (No.)	Time (h)	Yield [%]	η_{inh}[a] [dL/g]	υ_{co}[b] (IR)	^{13}C-NMR Chemical Shifts[c] δ [ppm]
1	Adipic a. **(10a)**	24	31	0.21	1733	173,7, 64.2, 34.2, 25.7, 24.7
2	Adipic a. **(10a)**	48	47	0.20		
3	Sebacic a. **(10b)**	24	80	0.18	1733	174.2, 64.1, 34.6, 29.5, 25.7, 25.3
4	Sebacic a. **(10b)**	48	71	0.20		

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2.
[b]IR spectra recorded from KBr pellets.
[c]Measured in $CDCl_3$ containing TMS.

CONCLUSION

The results obtained in this work largely confirm the expectations based on the previously described polythioesters **2**. The polycondensations of the 2,2-dibutyl-2-stanna-1,3-dithiolane with ADADS are exothermic reactions yielding high molecular weight polythioesters of structure **4a-e** which contain high fractions of cyclic oligomers and polymers. The polythioesters **4a-e** are rapidly crystallizing materials with melting temperatures 50-60°C above those of the S-free analogous polyesters. The polythioesters **4a-e** react at elevated temperatures with tin alkoxides. When cyclic tin alkoxides are used as reaction partners S- and Sn-free polyesters are formed. Further studies in this direction are currently in progress.

REFERENCES

1. Kricheldorf, H.R.; Probst, N.; Schwarz, G.; Schulz, G.; Krüger, R.P. J.Polym.Sci., Part A, Polym. Chem. **2000**, *38*, 3656.
2. Kricheldorf, H.R. Macromol. Chem. Rapid Commun. **2000**, *21*, 528.
3. Kricheldorf, H.R.; Langanke, D. Macromol. Chem. Phys. **1999**, *200*, 1174.
4. Kricheldorf; H.R.; Langanke, D. Macromol. Chem. Phys. **1999**, *200*, 1183.
5. Cort, A.D.; Mandolini, L.; Roelens, S. J .Org. Chem. **1992**, *57*, 766.
6. Kricheldorf; H.R.; Eggerstedt, S. Macromol. Chem. Phys. **1998**, *199*, 283.
7. Finck, A.; Poller, R.; Steele, S. Trans Faraday Soc. **1965**, *61*, 2628.
8. Kricheldorf, H.R.; Rabenstein, M.; Schmidt, M.; Maskos, M. Macromolecules **2001**, *34*, 713.
9. Kricheldorf, H.R.; Böhme, S.; Schwarz, G. Macromolecules, in press.