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Ring-Expansion Polycondensation of 2-Stanna-1,3-dioxepane (or 1,3-dioxepene) with Dicarboxylic Acid Chlorides

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Summary: 2,2-Dibutyl-2-stanna-1,3-dioxepane 1 (or 1,3-dioxepene 2) were prepared from 1,4-butane (or 1,4-butene) diol and dibutyltin dimethoxide. They were polycondensed at 80°C in *n*-heptane with adipoyl-, suberoyl, sabacoyl chloride and with decane-1,10-dicarbonyl chloride. In the case of suberoyl chloride and 2,2-dibutyl-2-stanna-1,3-dioxepane reaction time, temperature and stoichiometry were varied to optimize both the molecular weight and the fraction of cyclic polyesters. With a slight excess of the dicarboxylic acid chlorides, only macrocyclic polyesters were obtained in all cases. The resulting cyclic polyesters were characterized by viscosity measurements, by ^{1}H and ^{13}C NMR and by MALDI-TOF mass spectrometry.

Keywords: cyclization; MALDI-TOF; polyesters; ring-expansion polycondensation

Introduction

In a previous publication [1] the ring-opening polycondensation in bulk of 2,2-dibutyl-2-stanna-1,3-dioxepane (**1**, DSDOP) with various aliphatic dicarboxylic acid chlorides was reported. The polycondensations of **1** were particularly remarkable, because it was demonstrated for the first time that the products of such a ring-opening polycondensation were mainly cyclic.[2] These results raised the question if donor-acceptor interactions between Bu_2SnO- and -COCl chain ends is responsible for the cyclization reactions or if the formation of cycles is the normal consequence of a kinetically controlled polycondensation proceeding in a homogeneous phase and in the absence of side reactions.[3-4] In almost all textbooks the theory of step-growth polymerisation is based on the work of Carothers and Flory and describes the formation of linear polymers from linear monomers via linear oligomers. However, the older "Ruggli-Ziegler Dilution Method" designed for synthesis of macrocycles assumes a permanent competition between chain growth and

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cyclization. Increasing concentration favors, of course, higher molecular weights, but the tendency of cyclization does not automatically vanish. A quantitative description of this aspect was published almost three decades ago [3-4] by two groups of british authors but it was not substantiated by experiments and it was never discussed in textbooks. Recently, we have demonstrated by numerous experiments that, in fact, cyclic oligo- and polyesters are main reaction products of any clean polycondensation proceeding in a homogeneous phase.[5]

In this connection the present work had two aims. Firstly, the reproducibility of our first study [1] concerning the polycondensation of DSDOP with various dicarboxylic acid chlorides in *n*-heptane at 80°C to optimise the formation of cyclic oligo- and polyesters (Scheme3 1). Secondly, the optimal conditions obtained with DSDOP will be used for the polycondensation of 2,2-dibutyl-2-stanna-1,3-dioxepene (DSDEN) and various dicarboxylic acid chlorides. The ring formation should provide an easy access to unsaturated cyclic oligo- and polyesters based on 1,4-butene diol (Scheme 3). These unsaturated macrocycles may be of interest for a variety of postreactions (even when containing small amounts of linear species), for instance, ring-opening polymerizations such as the metathesis copolymerization with cyclic olefins.

Results and discussion

A) Polycondensation of 2-Stanna-1,3-dioxepane (DSDOP) with Dicarboxylic Acid Chlorides

The first cyclic monomer used in this work (DSDOP, **1**) was easily prepared by condensation of dry 1,4-butane diol with dibutyltin dimethoxide. A complete conversion which can be monitored by ^{1}H-NMR spectroscopy of the reaction mixture is essential for the success of this synthesis because unreacted starting materials are difficult to separate from the product by distillation over a short-path apparatus. The DSDOP was isolated as a colorless liquid in yields of 85-90%. The polycondensations were performed in a simple way just by dropwise addition of aliphatic dicarboxylic acid chlorides (ADADs) in *n*-heptane to a solution of DSDOP in *n*-heptane with rapid mechanical stirring (Figure 1).

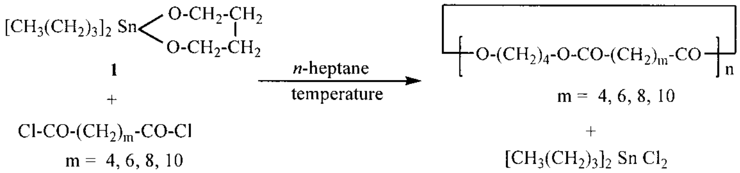
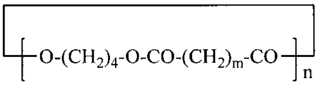


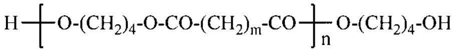
Figure 1. Polycondensation of DSDOP with various dicarboxylic acid chlorides

The first reactions were performed with equimolecular quantities of DSDOP and suberoyl chloride at 40°C. After 24 hours of reaction time, the MALDI mass spectrometry analysis of the resulting polyesters indicated the presence of three structures, one cyclic polyester (**C** = 55%) and two linear species corresponding to the linear structures **Lb** = 21%, having the 1,4-butane diol as chain end and **Lc** = 24% having the suberoyl chloride as chain end. This result was confirmed by ^{1}H-NMR where we clearly evidenced the presence of CH_2-OH and CH_2-COOH groups as chain ends (Figure 2).



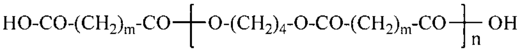
$$\left[O\text{-}(CH_2)_4\text{-}O\text{-}CO\text{-}(CH_2)_m\text{-}CO \right]_n$$

C



$$H\left[O\text{-}(CH_2)_4\text{-}O\text{-}CO\text{-}(CH_2)_m\text{-}CO \right]_n O\text{-}(CH_2)_4\text{-}OH$$

Lb



$$HO\text{-}CO\text{-}(CH_2)_m\text{-}CO\left[O\text{-}(CH_2)_4\text{-}O\text{-}CO\text{-}(CH_2)_m\text{-}CO \right]_n OH$$

Lc

Figure 2. Structures of different polyesters obtained as a result of the polycondensation reaction between DSDOP and suberoyl chloride at 40°C during 24 hours

When +1% excess of acid dichloride was used, a significant improvement of the MALDI spectrum was noticed, and in this case only two structures were obtained, one of the cyclic polyester **C** and the other one of the linear polymer **Lb**. This mixture of cyclic and linear products has an inherent viscosity of 0.48 dL\g. When the reaction temperature was raised to 80°C with +1% excess of acid dichloride and a reaction time of 24 hours, the MALDI mass spectrum shows the exclusive presence of the cyclic polyester **C,** with a higher inherent viscosity of 0.76 dL\g. Considering these results, we noticed that when we worked above the melting point of the polyester based on DSDOP and suberoyl chloride (Tm = 58°C)[1], we have a better and higher reactivity of the active centers and, as a consequence, less secondary reactions. Under these conditions a quasi-total conversion and 100% cyclic polyester were obtained (Figure 3A and 3B) in agreement with our new theory of step growth-polymerization.

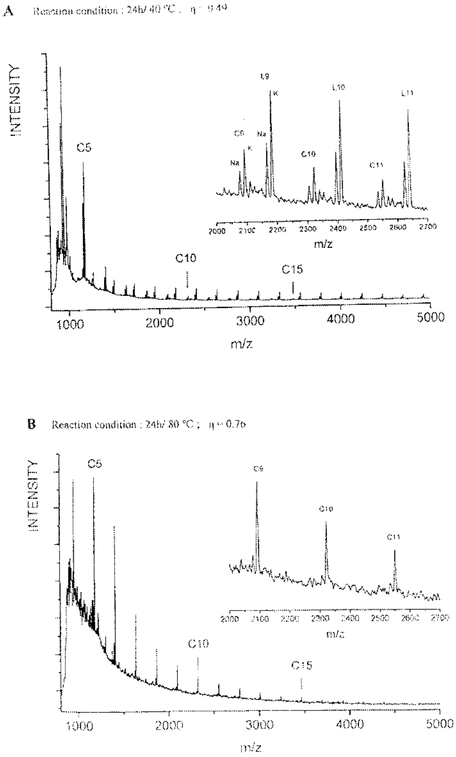


Figure 3. MALDI-TOF spectra showing the influence of reaction conditions on formation of cyclic polyesters derived of DSDOP and suberoyl chloride

The optimum conditions found with suberoyl chloride were subsequently used for the polycondensation of DSDOP with other acid dichlorides (Table 1).

Table 1. Reaction conditions and results of the polycondensations conducted with DSDOP and various dicarboxylic acid chlorides

exp. no.	acid dichloride (1% excess)	time	temperature	yields	η_{inh} [a]	results of MALDI-TOF intensity	
		hours	°C	%	dL/g	%	
						C	La
1	adipic [b]	24	80	87	0.64	100.0	0.0
2	suberic	24	40	91	0.48	15.0	85.0
3	suberic	24	80	96	0.76	100.0	0.0
4	sebacic	24	80	81	0.18	77.0	23.0
5	dodecane-dioic	24	80	91	1.22	100.0	0.0

[a] Measured at 20°C with c = 2 g/L in CH_2Cl_2
[b] 3% excess

For the poycondensation of DSDOP with adipoyl chloride with +1% excess of the acic dichloride, the MALDI mass spectrum indicated the presence of a mixture of cyclic (**C**) and linear (**Lb** and **Lc**) polyesters in equal proportions. When +3% excess of adipoyl chloride was used, the MALDI spectrum indicated the presence of the cyclic polyester **C** with an inherent viscosity of 0.64 dL\g.

The same optimum conditions were used in the case of sabacoyl chloride, but a mixture of cyclic polyester (**C** = 77 %) and linear polyester with hydroxyl chain ends (**Lb** = 23%) were obtained. This mixture of cyclic and linear polyesters has a low inherent viscosity of only 0.18 dL/g. This result is a bit surprising, because viscosity should be higher than those obtained with suberoyl chloride, where we have an inherent viscosity of 0.76 dL/g. We noticed that neither a longer reaction time nor a higher excess of acid dichloride did not allow a significant improvement in percentage of cyclic polyesters or molecular weights.

Finally the polycondensation of DSDOP with decane-1,10-dicarbonyl chloride gave only cyclic polyesters (**C** = 100%) with a higher inherent viscosity of 1.22 dL/g.

B) Polycondensation of 2-Stanna-1,3-dioxepene (DSDEN) with Dicarboxylic Acid Chlorides

The second cyclic monomer used in this work (DSDEN, **2**) was easily prepared by condensation of dry 1,4-butene diol with dibutyltin dimethoxide under the same procedure used with DSDOP. The DSDEN was isolated as a yellow liquid in yields of 80-85%.

The polycondensations were performed again by dropwise addition of dicarboxylic acid dichlorides (ADADs) in *n*-heptane to a solution of DSDOP and *n*-heptane with rapid mechanical stirring (Figure 4, Table 2).

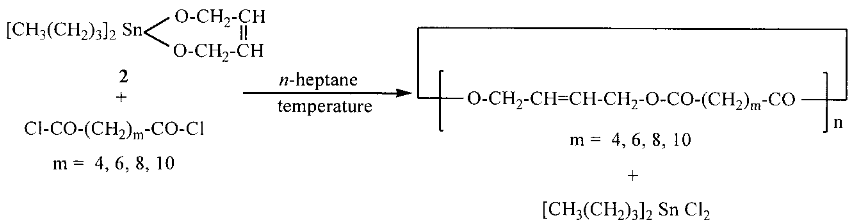


Figure 4. Polycondensation of DSDEN with various dicarboxylic acid chlorides

Table 2. Reaction conditions and results of the polycondensations conducted with DSDEN and various dicarboxylic acid chlorides

exp.	acid chloride	time	temperature	yields	η_{inh} [a]	results of MALDI-TOF intensity		
no.	(1% excess)	hours	°C	%	dL/g	%		
						C	Lb	Lc
1	adipic	24	80	88	0.57	89.0	0.0	11.0
2	suberic	24	80	89	0.49	60.0	40.0	0.0
3	sebacic	24	80	93	0.58	25.0	76.0	0.0
4	dodecane-dioic	24	80	95	0.65	93.0	0.0	07.0

[a] Measured at 20°C with c = 2 g/L in CH_2Cl_2

We proceeded in the same manner as in the case of DSDOP, that is using +1% excess of acid dichloride at 80°C during 24 hours. The best results were obtained in the case of adipoyl chloride and decane-1,10-dicarbonyl chloride. Practically only unsaturated cyclic polyesters were obtained (**C** = 93-89%) with inherent viscosities between 0.57 and 0.65 dL/g. In Figure 5 is presented the MALDI mass spectrometry spectrum obtained for the polycondensation of DSDEN with adipoyl chloride. We can notice the majority presence of cyclic polyesters (**C** = 89%) and a minority presence of the linear polyester (**Lc** = 11%).

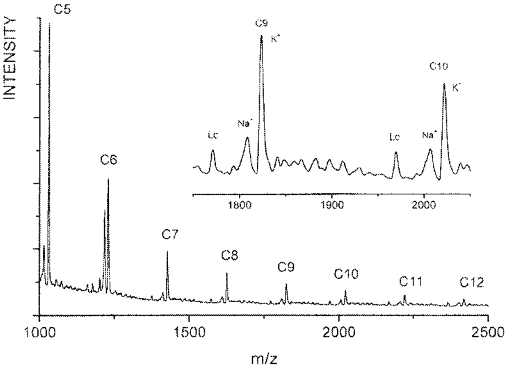


Figure 5. MALDI-TOF spectrum obtained after polycondensation of DSDEN with adipoyl chloride a 80°C during 24 hours

Due to the fact that we have an acidic chain end, we performed the same reaction with an equimolecular mixture of DSDEN and adipoyl chloride at 80°C during 24 hours. Unfortunately, the analysis of the reaction product by MALDI mass spectrometry showed a mixture of cyclic (**C** = 70%) and linear (**Lb** + **Lc** = 30%) polyesters. An increase of the reaction time did not lead in any improvement concerning the percentage of cyclic polyesters. For the polycondensation of DSDEN with suberoyl and sabacoyl chloride we did not succeed in obtaining a high percentage of unsaturated cyclic polyesters. The best results were obtained in the case of suberoyl chloride, 60% of cyclic polyesters **C** and 40% of linear polyesters **Lb**. The ^{1}H-NMR spectrum of this compound showed the presence of CH_2-OH group as chain end and confirmed the result of the MALDI mass spectroscopy. In order to improve these results we varied the excess of acid chloride between +2% and +5%, but we noticed the constant presence of a non-negligible quantity of linear polyesters (20-30%) with acidic chain ends **Lc**. In the same time, higher reaction times (7 days) did not determined a significant increase of the percentage of cyclic polyesters or of the molecular weight of these unsaturated polyesters derived from DSDEN.

Conclusion

The results of this work represent a satisfactory reproducibility of the previous study dealing with polycondensations of DSDOP (**1**). Firstly, only cyclic oligo- and polyesters (**C = 100%**) were formed in all polycondensations of DSDOP (**1**) with aliphatic dicarboxylic acid chlorides when we are working in *n*-heptane at 80°C. Particularly important is the observation that any optimisation of the reaction conditions favouring higher molecular weights enhances the fraction of cyclic products at the expense of the linear species. Therefore, the cyclizations become themselves a decisive limiting factor of the chain growth. This finding is in perfect agreement with our interpretation of kinetically controlled polycondensation according to the "Ruggli-Ziegler Dilution Method" which is based on the assumption of a permanent competition between ring-closure and propagation. Secondly, the optimal conditions obtained with DSDOP were used for the polycondensation of 2,2-dibutyl-2-stanna-1,3-dioxepene (DSDEN) and various dicarboxylic acid chlorides. Large fractions of cyclic oligo- and polyesters (approximately **C = 90%**) were formed in all polycondensations of DSDEN (**2**) with aliphatic dicarboxylic acid chlorides. These unsaturated macrocycles may be of interest for a variety of postreactions (even when containing small amounts of linear species), for instance, ring-opening polymerizations such as the metathesis copolymerization with cyclic olefins.

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