Macrocycles. 3. Telechelic Polylactones via Macrocylic Polymerization

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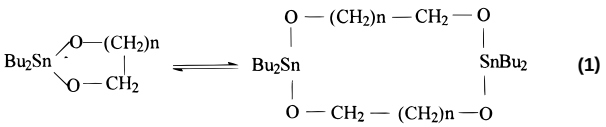
ABSTRACT: ϵ-Caprolactone (ϵ-CL) was polymerized with 2,2-dibutyl-2-stanna-1,3-dioxepane or 2,2-dibutyl-2-stanna-1,3,6-trioxocane as initiator. All polymerizations were conducted in bulk at monomer/initiator (M/I) ratios of 10/1, 20/1, 35/1, or 50/1 and yielded macrocyclic poly(ϵ-CL) with quantitative conversion. These macrocycles were reacted in situ with 4-nitrobenzoyl chloride or with thiocresyl 4-nitrobenzoate yielding the 4-nitrobenzoyl-functionalized telechelics. The completion of these ring-opening reactions was checked by ^{119}Sn NMR spectroscopy of the reaction mixture and by ^{1}H NMR spectroscopy of the isolated oligo(ϵ-CL). Analogous quantitative functionalizations of the macrocyclic oligo(ϵ-CL) were obtained with 4-bromobenzoyl chloride, 6-propargyloxynaphthoyl chloride, 3- or 4-maleimidobenzoyl chloride, cinnamoyl chloride, undecenoyl chloride, and methacrylic anhydride. The hydrogenation of the nitro groups and the thermal cross-linking of the propargyl ether groups were conducted as examples of the great versatility of the telechelic oligo(ϵ-CL)s in modification and chain extension reactions.

Introduction

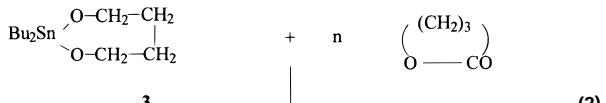
It was demonstrated in previous publications[1−3] that lactones (including lactides) react with cyclic tin alkoxides such as **1**−**3** by insertion into the Sn−O bond. Repetition of this insertion into both Sn−O bonds yielded macrocyclic oligo- or polylactones almost quantitatively (eq 2). These so-called macrocyclic polymerizations are complicated in the case of five- or six-membered cyclic initiators (**1** and **2**), because these preferentially form cyclic dimers (eq 1).[4−8] These cyclic



(1)

1a : n = 1 **1b** : n = 1

2a : n = 2 **2b** : n = 2



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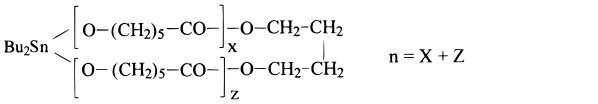

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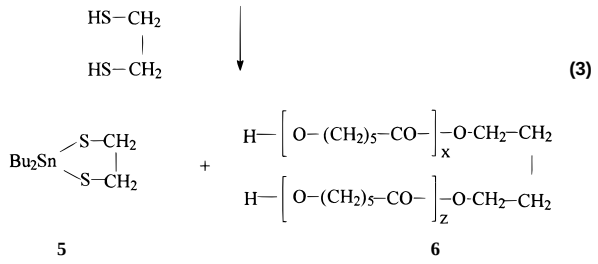
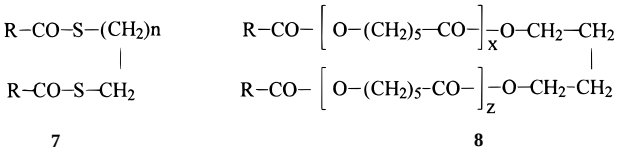


5 **6** (3)

dimers possess high melting temperatures (>200 °C) and poor solubilities in organic solvents or in the lactones. It was found that the initiation with the dimers of **1** or **2** is slower than the propagation, and thus, the molecular weight of the resulting macrocyclic lactones is difficult to control.

In contrast to **1** and **2**, the seven-membered initiator **3**, 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) is a monomeric liquid[8] that is miscible with most (if not all) lactones. DSDOP-initiated polymerizations of ϵ-CL in bulk at 80 °C were found to more or less obey the "living pattern". A rapid and quantitative conversion of the monomer was observed, and the number-average molecular weights (M_n's) followed the monomer/initiator (M/I)-ratio.[9] The polydispersities (∼1.5) were broader than in the ideal case, because the initiation step is not significantly faster than the propagation steps. Furthermore, it was found that dimercaptoethane allows an easy and mild removal of the dibutyltin group from the macrocyclic lactones **4** yielding telechelic linear oligo- or polylactones having two OH end groups (**6**, eq 3). This clean reaction prompted us to study the syntheses of further telechelic polylactones (having the general structure **8**) by the reaction of the macrocyclic



7 **8**

polylactones **4** with acyl sulfides such as **7**. The greater stability of the Sn−S bond compared to the Sn−O bond in combination with a greater stability of the CO−O relative to the CO−S ester group was assumed to provide a sufficient driving force for a quantitative functionalization. In other words, a new approach called synthesis of telechelic polylactones via macrocyclic polymerization should be elaborated.

Experimental Section

Materials. Dibutyltin dimethoxide, 1,4-butanediol, ϵ-caprolactone, 4-nitrobenzoyl chloride, 4-bromobenzoyl chloride, unedecenyl chloride, cinnamoyl chloride, and methacrylic anhydride were purchased from Aldrich Co. (Milwaukee, WI). The 1,4-butanediol was dried by azeotropic distillation with

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Table 1. Acylation of DSDOP-Initiated Macrocylic Poly(ϵ-caprolactone) by Means of 4-Nitrobenzoyl Derivatives

expt no.	4-nitrobenzoyl derivative	M/I[a]	temp (°C)	time (h)	conv (%)	yield[b] (%)	DP (^{1}H NMR)
1	ester of 1,4-di-mercapto to butane	20/1	80	4	75	70.0	
2	ester of 1,4-di-mercapto to butane	20/1	100	6	95	81.5	
3	ester of 1,4-di-mercapto to butane	20/1	150	6	100	106.5	21
4	ester of 4-thiocresol	20/1	80	4	80	77.0	
5	ester of 4-thiocresol	20/1	100	16	100	81.0	22
6	acid chloride	10/1	80	4	100	91.0	13
7	acid chloride	20/1	80	4	100	89.5	22
8	acid chloride	40/1	80	4	100	94.5	41
9	acid chloride	60/1	80	4	100	95.0	62

[a] Molar ϵ-CL/DSDOP ratio used for the ring-opening polymerization. [b] After precipitation into cold methanol.

toluene followed by distillation in vacuo. ϵ-Caprolactone was distilled over calcium hydride in vacuo. All other chemicals were used as received. Maleic anhydride, 3-aminobenzoic acid, 4-aminobenzoic acid, and 4-hydroxybenzoic acid were gifts of Bayer AG (Leverkusen, Federal Republic of Germany). The acid chloride of 3-maleimidobenzoic acid (mp 126 °C) and the acid chloride of 4-maleimidobenzoic acid (mp 162 °C) were prepared according to the literature.[10] The 4-thiocresyl-4-nitrobenzoate (mp 98−99 °C) was synthesized according to ref 11. 6-(Propargyloxy)-2-naphthoic acid (mp 187 °C[12]) and its acid chloride (mp 117 °C [12]) were also synthesized as described previously. DSDOP and 2,2-dibutyl-2-stanna-1,3,6-trioxocane (DSTOX) were prepared from dibutyltin dimethoxide and dry 1,4-butanediol or diethylene glycol as described previously and distilled in vacuo.[8]

Bis-4-nitrobenzoate of 1,4-Dimercaptobutane. 1,4-Dimercaptobutane (0.05 mol) and 4-nitrobenzoyl chloride (0.1 mol) were dissolved in dry ethyl acetate (250 mL), and triethylamine (0.1 mol) diluted with ethyl acetate (50 mL) was added dropwise with stirring. The reaction mixture was allowed to stand at 20 °C for 20 h and was then filtered from the precipitated triethylamine hydrochloride. The filtrate was washed twice with water (300 mL) and dried over Na_2SO_4. The organic solution was concentrated in vacuo until the product began to crystallize. The crystallization was completed by dropwise addition of ligroin. Yield: 78%, mp 140−142 °C. Anal. Calcd for $C_{18}H_{16}N_2O_6S_2$ (420.45): C, 51.46; H 3.83; N, 6.66. Found: C, 51.50; H, 3.71; N, 6.42%.

Syntheses of Telechelic Oligolactones (General Procedure). ϵ-Caprolactone (50 mmol) and DSDOP (2.5 mmol) were weighed into a cylindrical glass reactor equipped with stirrer and gas inlet and gas outlet tubes. The reaction vessel was immersed in an oil bath thermostated at 80 °C, and after 4 h, the acylating reagent was added either in the form of a powder or via a syringe in the form of a 2 M solution in warm chlorobenzene. The reaction mixture was stirred in an atmosphere of dry nitrogen for 6 h at 80 °C (or higher; see tables). Afterward, the reaction product was dissolved in CH_2Cl_2 (50 mL), precipitated into cold methanol (5−6 °C), isolated by filtration, and dried at 40 °C in vacuo.

DSTOX-initiated polymerizations were conducted as described above, but the initiator was added to the ϵ-caprolactone in form of an 0.5 M solution in dry *sym*- tetrachloroethane.

6-Propargyloxy-2-naphthoyl End-Capped Polylactones. ϵ-Caprolactone (50 mmol) and DSDOP were weighed into a cylindrical glass reactor equipped with stirrer and gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 80 °C, and this temperature was maintained for 4 h. Afterward, 6-(propargyloxy)-2-naphthoyl chloride (11 mmol) was added with stirring, and the temperature was raised to 110 °C. After 36 h, the reaction product was dissolved in dichloromethane (40 mL) and precipitated into cold (4−5 °C) methanol (250 mL). The precipitated product was isolated by filtration and dried at 40 °C in vacuo. Yield: 76% mp 56 °C (DSC). The ^{1}H NMR spectra of the reaction mixture (before precipitation) indicated 95−98% conversion, and the isolated oligoester had a degree of polymerization (DP) of 22.

An analogous synthesis was conducted with 25 mmol of ϵ-caprolactone, and an oligoester of DP 12 was isolated in a yield of 49%.

The propargyl ether end groups showed the following ^{1}H NMR signals in $CDCl_3$/TMS: $\delta = 2.58$ (1H, t, $J = 2.0$ Hz), 4.84 (2 H, d, $J = 2.0$ Hz) ppm.

Hydrogenation of Nitro Groups. A 4-nitrobenzoyl-terminated poly-(ϵ-CL) having a DP of 22 (2 mmol ∼5 g) was dissolved in dry tetrahydrofuran (60 mL). Dry Na_2SO_4 (2 g) and 10% Pt on charcoal (1.5 g) were added. The hydrogenation was performed at 25 °C and atmospheric pressure until enough hydrogen was consumed (∼6 h). The solid "additives" were removed by filtration, the tetrahydrofuran solution was concentrated in vacuo, and the crude product was characterized. Yield 82%; for the ^{1}H NMR spectrum see Figure 1B.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The 100 MHz ^{1}H NMR spectra were obtained on a Bruker AC-100 FT NMR spectrometer in 5mm o.d. sample tubes. The 360 MHz ^{1}H NMR spectra were recorded analogously with a Bruker AM-360 FT NMR spectrometer. $CDCl_3$ containing TMS served as solvent for all NMR measurements. The 74.58 MHz ^{119}Sn NMR spectra were recorded with a Varian Gemini 200 BB spectrometer in 5mm o.d. sample tubes. The DSC measurements were conducted with a Perkin Elmer DSC-7 in aluminum pans under nitrogen.

Results and Discussion

Oligoesters Having 4-Nitrobenzoyl End Groups. As reported previously,[9] DSDOP-initiated polymerizations of ϵ-CL and the DPs of the crude macrocycles match the M/I ratio. First attempts to synthesize telechelic oligo-(ϵ-CL) were conducted in such a way that a macrocyclic oligo(ϵ-CL) (**4**, $x + z = 20$) was reacted with the bis-4-nitrobenzoyl ester of 1,4-dimercaptobutane (**9**) (the analogous 4-nitrobenzoyl esters of 1,2-dimercaptoethane or 1,3-dimercaptopropane were unfavorable due to high melting points and low solubilities).

When the reaction temperature of 80 °C used for the macrocyclic polymerization of ϵ-CL was maintained for 4 h, the acylation of the macrocyclic poly(ϵ-CL) with **9** was still far from complete. Even after 6 h at 110 °C, the conversion was incomplete and a temperature of 150 °C was needed to reach 100% (nos. 1−3, Table 1).

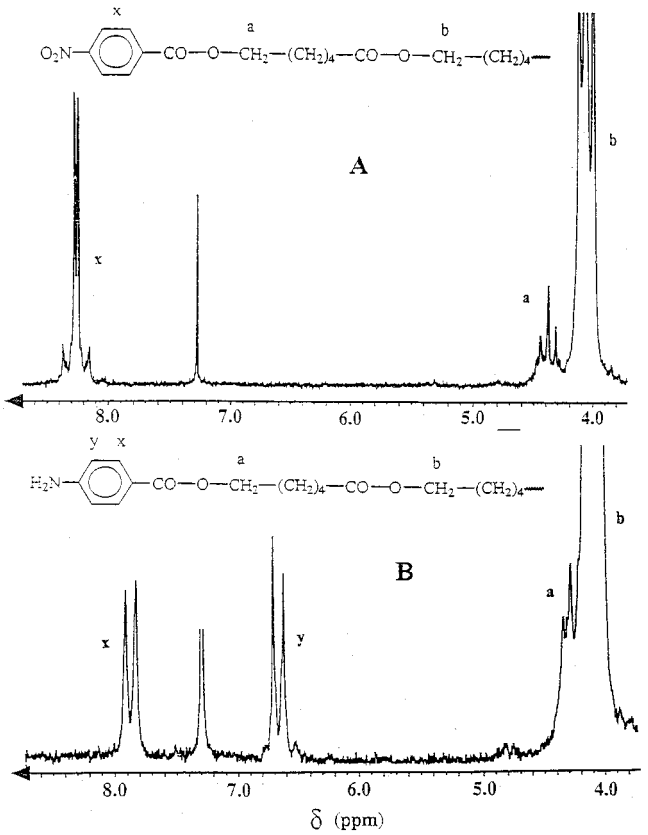
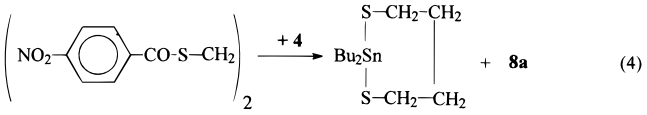


Figure 1. 100-MHz ^{1}H NMR spectra (measured in $CDCl_3$): (A) a telechelic oligo(ϵ-CL) **8a** with DP = 22; (B) the same oligo(ϵ-CL) after reduction with H_2/Pt (**8b**).

However, the oligo(ϵ-CL) isolated from this reaction by precipitation into methanol was heavily contaminated, as indicated by its apparent yield of 106% and by ^{1}H NMR spectroscopy. The course of the reaction (eq 4)



(4)

9 **10**

was monitored by ^{119}Sn NMR spectroscopy of the crude reaction mixture. The formation of the 1,3-dithiepane (**10**) was evidenced by a signal at 130 ppm (relative to $SnMe_4$ in $CDCl_3$), whereas the macrocyclic poly(ϵ-CL) had a chemical shift of −157 ppm. The structure (and conversion) of the crude and of the isolated oligoester **8a** was checked by ^{1}H NMR spectrosopy. The acylation of the OCH_2 end groups by an aromatic acid causes the ^{1}H NMR signal to shift downfield, so that it is well separated from the $COOCH_2$ signal of the polymer

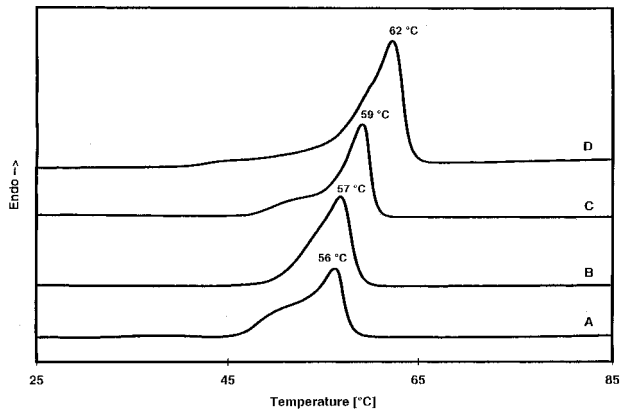
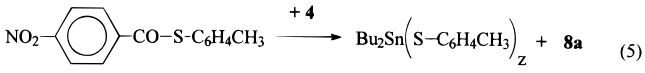


Figure 2. DSC heating curves (heating rate 20 °C/min) of telechelic oligo(ϵ-CL) having two 4-bromobenzoyl end groups (**8c**): (A) DP ∼ 22; (B) DP ∼ 37; (C) DP ∼ 52; (D) DP ∼ 81.

backbone (Figure 1A). The quantification of the OCH_2 end group signal and of aromatic protons (Figure 1A) allowed the calculation of the average degree of polymerization and, thus, a comparison with the theoretical value which is identical with the M/I. When the experimental DP measured from the crude oligoester in the reaction mixture was identical with the M/I, 100% conversion was assumed. The DPs of the isolated oligoester were slightly higher, due to the fractionation resulting from the precipitation into methanol. The completion of the acylation was also confirmed by disappearance of CH_2OSn triplet at 3.7 ± 0.1 ppm.

The insufficient reactivity of the thioester **9** prompted us to use the more electrophilic thiocresyl ester **11** (eq 5). In this case, 100% conversion was reached after 16 h at 100 °C (no. 5, Table 2), and the formation of the tin bis(tolyl sulfide) **12** was evidenced by a ^{119}Sn NMR signal at 111 ppm (in $CDCl_3$). The isolated oligoester showed the expected ^{1}H NMR spectroscopic properties (Figure 1A) corresponding to a DP of 22. Further acylation of macrocyclic oligo(ϵ-CL) was conducted with 4-nitrobenzoyl chloride, and 100% conversion was found after only 4 h at 80 °C (nos. 5−8, Table 1). For the dibutyltin dichloride formed in the course of these acylations (eq 7), a ^{119}Sn NMR signal was found at 125



(5)

11 **12**

ppm. The ^{1}H NMR spectra of the crude and of the isolated oligoesters proved their structure and confirmed that the DPs indeed parallel the M/I ratios. The increasing DPs were also reflected in the DSC measurements, which exhibited increasing melting temperatures

Table 2. Acylation of DSDOP-Initiated Macrocyclic Poly(ϵ-caprolactone) with 4−Bromobenzoyl Chloride

expt no.	M/I[a]	temp (°C)	time (h)	conv (%)	yield[b] (%)	η_{inh}[b] (dL/g)	DP		
							^{1}H NMR[b]	Br + Anal.[b]	GPC[b,c]
1	20/1	80	4	∼75	70.0	0.17			
2	20/1	80	8	∼90	84.5	0.15			
3	10/1	100	16	100	90.5	0.08	13	14	23
4	20/1	110	16	100	91.0	0.14	22	22	35
5	35/1	110	16	100	91.0	0.18	37	38	53
6	50/1	110	16	100	90.5	0.23	52	51	75
7	80/1	110	16	100	92.0	0.29	81	80	115

[a] Molar monomer/initiator ratio of ϵ-CL and DSDOP. [b] After precipitation into cold methanol. [c] From GPC measurements in tetrahydrofuran. This number average molecular weight was obtained by calibration with eq (6).

(T_m's) in the heating traces (analogous to Figure 2). Since numerous acid chlorides are commercially available or easy to synthesize, the success of these acylations open a wide field for the syntheses of telechelic oligoesters via macrocyclic polymerizations.

The 4-nitrobenzoyl group had been selected for these studies, not only because of their reactivity and easy purification but also because an easy transformation into the 4-aminobenzoyl group was expected. Several experiments with a sample of **8a** having a DP of **22** showed that cyclohexene did not allow a quantitative hydrogenation of the nitro groups regardless of whether Pd or Pt catalysts were used. However, the combination of elemental H_2 and 10% Pt on charcoal allowed a quantitative reduction even at room temperature (Figure 1B). Surprisingly, the DP of the isolated bis(4-aminobenzoyl) oligoester **8b** was slightly higher (DP = 25) than that of the starting material, and viscosity measurements confirmed this interpretation of the ^{1}H NMR end group analyes. Since a reaction of the amino end groups with the ester groups (i.e., an aminolytic clearage) cannot change the average DP, the only explanation of this reproducible effect is the assumption that the shortest oligoester chain having the highest end group concentration remains adsorbed on the charcoal. Nonetheless, these hydrogenation experiments were successful, and the amino-terminated telechelic oligoester can be used for a broad variety of modification and chain extension reactions.

Oligoester Having 4-Bromobenzoyl End Groups. For the next stage of this study, 4-bromobenzoyl chloride was selected as acylating agent for two reasons. First, 4-bromobenzoyl end groups are useful for a variety of modification and chain extension reactions on the basis of the "Suzuki coupling" and the "Heck reactions". Second, the bromine atoms allowed an alternative determination of the DPs via elemental analyses. However, the first attempts to synthesize telechelic oligoesters of structure **8i** by acylation of the macrocycles **4** failed, because of incomplete conversion at 80 °C even after 8 h (nos. 1 and 2, Table 2); satisfactory results were then obtained at 110 °C and a reaction time of 16 h (nos. 3−7, Table 2). The DPs calculated from the ^{1}H NMR spectroscopic end group analyses closely paralleled the M/I ratios, and the DPs derived from the Br elemental analyses were in perfect agreement. Furthermore, the inherent viscosities increased with the M/I ratios, thus confirming that the above interpretaion of the end group analyses in terms of DPs (and molecular weights) are justified.

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

GPC measurements were performed and calibrated with the *a* and *K* values of the Mark−Houwink equation (6), which was reported by Schindler et al.[13] for poly(ϵ-CL) in tetrahydrofuran solution. The number-average molecular weights obtained in this way were used for the calculation of the DPs listed in Table 2. These values were almost 50% higher than those derived from end group analyses and, thus, indicate that this very indirect method considerably overestimates the true DPs. This overestimation is most likely a consequence of the fact that the Mark−Houwink equation is based on a calibration with weight-average molecular weights.

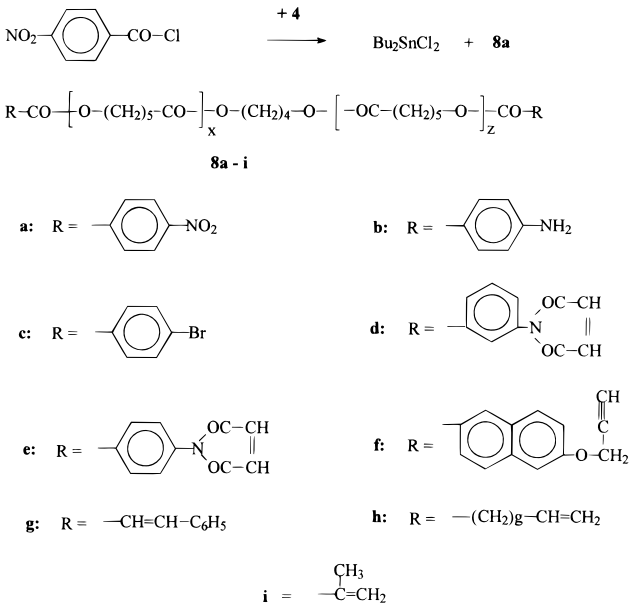
Finally, DSC measurements of samples 3−7 in Table 2 were conducted. As illustrated by the heating curves of Figure 2, the melting endotherms increase with higher DPs and, thus, represent another indirect prove of the systematic variation of the DPs via the M/I ratios of the macrocyclic polymerizations.

Table 3. Acylation of DSDOP-Initiated Macrocyclic Poly(ϵ-caprolactone) with Maleimidobenzoyl Chlorides[a]

expt no.	acid chloride	M/I[a]	temp (°C)	conv (%)	yield[c] (%)	DP[c] (^{1}H NMR)
1	3-maleimidobenzoyl	20/1	80	~60		
2	3-maleimidobenzoyl	10/1	140	100	75	11
3	3-maleimidobenzoyl	20/1	140	100	82	22
4	4-maleimidobenzoyl	10/1	140	100	83	11
5	4-maleimidobenzoyl	20/1	140	100	85	22

[a] Reaction time, 6 h. [b] Molar ϵ-CL/DSDOP ratio. [c] After precipitation into cold methanol.

Oligoesters Having Unsaturated End Groups. Stimulated by the successful syntheses of telechelic oligoesters having nitro or bromobenzoyl end groups, further oligoesters with a broader variety of functional end groups were prepared. A first series of such functionalization experiments had the purpose of introducing maleimide end groups (structures **8d** and **8e**). The maleimide end groups allow a thermal cure just by heating above 200 °C. Furthermore, maleimide end groups allow the addition of various nucleophilic reagents, and such addition reactions may include chain extension or cross-linking. 3- and 4−maleimidobenzoyl chloride, which were known in the literature and easy to synthesize, were used as acylating reagents. The lower melting point of the meta compound promised a more rapid and complete mixing with the macrocyclic oligo(ϵ-CL) and was used at first. However, only a moderate conversion was obtained at 80 °C/6 h (no. 1, Table 3) and even a temperature of 110 °C did not result in 100% conversion. Therefore, the temperature was raised to 140 °C, and under those relatively harsh conditions, satisfactory results were obtained with both acylating reagents (Table 3). The ^{1}H NMR spectra proved the incorporation of the maleimido end groups, by a singlet signal at 6.90 ppm. Nonetheless, no exotherm from a thermal cross-linking process was detectable in the DSC heating curve (Figure 3A). Possibly the concentration of the end groups was too low for a rapid reaction.



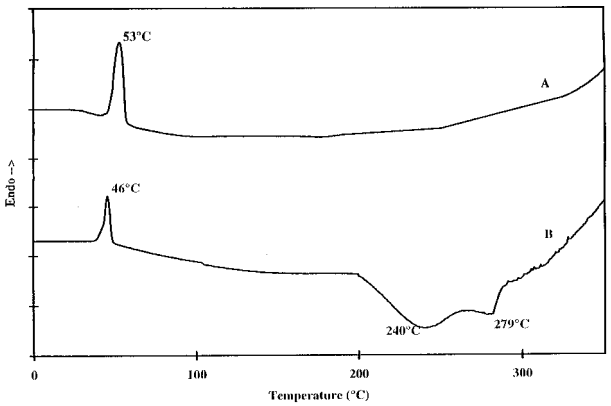


Figure 3. DSC heating curves (first heating, rate 20 °C/min): (A) telechelic oligo(ϵ-CL) **8e** having two 4-maleimidobenzoyl end groups and DP = 12; (B) telechelic oligo(ϵ-CL) of structure **8f** and DP = 20.

Table 4. Acylation of DSDOP-Initiated Macrocyclic Poly(ϵ-caprolactones)s with Cinnamoyl Derivatives

expt no.	acylating agent	M/I[a]	temp (°C)	time (h)	conv (%)	yield[b] (%)	DP[b] (^{1}H NMR)
1	cinnamoyl chloride	20/1	80	2	~80	71	
2	cinnamoyl chloride	10/1	80	6	100	79	15
3	cinnamoyl chloride	20/1	80	6	100	88	22
4	cinnamoyl chloride	50/1	80	6	100	92	52
5	cinnamic anhydride	20/1	80	6	100	86.5	21
6	cinnamic anhydride	50/1	80	6	100	93.0	51

[a] Molar ratio of ϵ-CL and DSDOP. [b] After precipitation into methanol.

Telechelic oligo(ϵ-CL) end-capped with propargyl ether groups (structure **8f**) were prepared by acylation of **4** (M/I = 10 or 20) with 6-(propargyloxy)-2-naphthoyl chloride. A reaction temperature of 80 °C did not suffice to raise the conversion above 70%, and even after 16 h at 110 °C, the conversion was only of the order of 85−90%. After 30 h at 110 °C, conversions around 95% were achieved, and oligoesters having DPs of 14 and 22 were isolated (see Experimental Section). The 6-(propargyloxy)naphthoyl group was selected for two reasons. First, we found quite recently that this end group allows a thermal cure of telechelic oligoesters in the temperature range of 200−250 °C whereas other propargyl ether groups require 50−60 °C higher temperatures. Second, telechelic oligomers having propargyl ether end groups allow an oxidative coupling, so that segmented polylactones containing diacetylene units may be prepared. Such syntheses are in progress and will be reported in a future publication. The successful thermal cure of the telechelic oligoesters **8f** is documented by the exotherms observed above 200 °C in the DSC heating curve of Figure 3B.

Telechelic oligoesters bearing photoreactive cinnamoyl end groups (structure **8g**) were prepared using cinnamoyl chloride. A first experiment conducted at 80 °C with a reaction time of 2 h was not satisfactory (no. 1, Table 4), but with a prolonged reaction time of 6 h, the desired results were obtained. Further acylation reactions were conducted with cinnamic anhydride at 80 °C (nos. 5 and 6, Table 4). The success of these reactions was evidenced by ^{119}Sn NMR spectra of the reaction mixtures exhibiting one signal at −146 ppm. Furthermore, telechelic oligoesters with the expected structure **8g** were isolated. The driving force for the acylation has two sources. First, the change of an anhydride group to the more stable ester group and second, the formation of a tin carboxylate group which is more stable than a tin alkoxide or a tin chloride bond. Hence, from the thermodynamic point of view an anhydride may be as good or even a better acylating agent than an acid chloride. However, the high melting points of aromatic anhydrides and the availability of only a few commercial anhydrides are the limiting factors. The relatively low melting point of cinnamic anhydride (135−136 °C) and its easy purification were the reasons why this anhydride was selected for the experiments in this work.

Further, telechelic oligoesters were prepared by means of undecenoyl chloride (nos. 1−3, Table 5). Again, a temperature of 80 °C sufficed to isolate the desired oligoesters **8h**. The olefinic end groups of these oligoesters may be useful for chain extension via metathesis (ADMET) polycondensation and for a variety of addition reactions, particularly for the addition of SiH silanes.

Finally, several attempts were made to synthesize methacrylate-terminated telechelic oligoesters (**8i**). A first experiment using methacryloyl chloride at 80 °C yielded a gel (no. 4, Table 5). After addition of 1,4-dimethoxybenzene as a radical inhibitor and shortening of the time, a soluble oligoester was obtained, but its inherent viscosity (0.25 dL/g in CH_2Cl_2) was considerably higher than that of the parent macrocycle (0.14 dL/g), suggesting that "coupling reactions" via the methacrylate end groups had occurred. Therefore, commercial methacrylic anhydride was used (in combination with 1,4-dimethoxybenzene) for further experiments. At 60 °C, the conversion was not absolutely complete after 4 h and the DP was a little too high (no. 6). At 80 °C/4, h a satisfactory result was obtained. A viscosity value of 0.18 dL/g is acceptable, considering that the precipitation into methanol removes the Bu_2SnCl_2 and leads

Table 5. Acylation of DSDOP-Initiated Macrocyclic Poly(ϵ-caprolactone) with Undecenoyl Chloride or Methacrylic Acid Derivatives

expt no.	acylating agent	M/I[a]	ηinh[b] (dL/g)	temp (°C)	time (h)	conv (%)	yield[c] (%)	DP[c] (^{1}H NMR)	ηinh[b] (dL/g)
1	undecanoyl chloride	10/1	0.09	80	6	100	86.5	12	
2	undecanoyl chloride	20/1	0.14	80	6	100	90.5	21	
3	undecanoyl chloride	50/1	0.23	80	6	100	90.0	51	
4	methacryloyol chloride	20/1	0.14	80	8	100	part	crossl	
5	methacryloyl chloride	20/1	0.14	80	4	100	81	23	0.25
6	methacrylic anhydride	20/1	0.14	60	4	95−98	86	24	0.19
7	methacrylic anhydride	20/1	0.14	80	4	100	90	21	0.18
	methacrylic anhydride	20/1	0.14	110	4	100	92.5	21	0.23

[a] Molar ϵ-CL/DSDOP ratio. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [c] After precipitation into methanol.

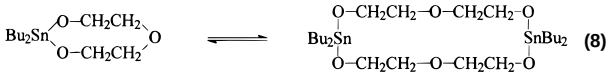
Table 6. Acylation of DSTOX-Initiated Macrocyclic Poly(ϵ-caprolactones) with 4-Bromobenzoyl Chloride

expt no.	catalyst added as	M/I[a]	temp (°C)	time (h)	conv (%)	yield[b] (%)	DP		
							^{1}H NMR[b]	Br + Anal.[b]	GPC[b,c]
1	solid	10/1	80	16	100	66.5	16		
2	solid	20/1	80	16	100	84.5	25		
3	solid	35/1	80	16	100	88.0	50		
4	solid	50/1	80	16	100	90.5	65		
5	solution	10/1	110	16	100	67.5	13	12	16
6	solution	20/1	110	16	100	77.0	23	23	30
7	solution	35/1	110	16	100	84.0	38	38	45
8	solution	50/1	110	16	100	89.0	52	51	70

[a] Molar ϵ-Cl/DSTOX ratio used for the macrocyclic polymerizations. [b] After precipitation into cold methanol. [c] From GPC measurements in tetrahydrofuran. The number-average molecular weight was obtained by calibration with eq 6.

to partial fractionation. A similar viscosity was obtained from the analogous experiment with undecenoyl chloride (no. 2). When methacrylic anhydride was used at 110 °C, the yield and the viscosity were higher, suggesting again coupling reactions of the methacrylate end groups. Taken together, a functionalization with two methacrylate groups is feasible, but the temperature/time window is narrow, and methacrylic anhydride is advantageous over methacryloyl chloride.

2,2-Dibutyl-2-stanna-1,3-6-trioxecane as Initiator. The key point for the success of the approach presented in this work is the quantitative funcionalization of Sn−O bonds. In the case of DSDOP-initiated polymerizations, the conversion was determined by a comparison of the weak end group signals with the strong signals of the repeating unit. The accuracy of this method decreases with increasing M/I (or DP). A more accurate method independent of the M/I is a comparison of the end group signals with a signal of the initiator fragment. Unfortunately the ^{1}H NMR signals of 1,4-dioxybutane units in DSDOP-initiated poly(ϵ-CL) are completely obscured by the signals of the ϵ-CL units even in the case of a 500-MHz spectrum. In order to overcome this problem, the eight-membered DSTOX (**13a**) was synthesized and used as initiator. This tin



13a **13b** (8)

compound was known in the literature, but poorly characterized. The freshly prepared heterocycle can be purified by distillation in vacuo, but the sirupy distillate solidifies upon storage, and this process includes a dimerization (eq 8). This dimerization (not reported in the literature) is evident from the high melting point (180−185 °C) and from the poor solubility in organic solvents. Furthermore, the molecule peak of the dimer was detected in the mass spectrum of **13a**,**b**.

With regard to an application as initiator, the dimerization of **13a** has the disadvantage that DSTOX is poorly soluble in lactones. Consequently, the initiation process is slow and the resulting DPs are significantly higher than expected from the M/I ratio. This relationship is documented by the results of experiments 1−4 in Table 6, which include a functionalization of the macrocyclic oligoesters by means of 4-bromobenzoyl chloride. Fortunately, it was found that DSTOX is completely soluble in 1,1,2,2-tetrachloroethane, which is itself inert under the reaction conditions used in this work. When solutions of DSTOX were added to ϵ-CL, both the macrocyclic polymerizations and the acylactones of the Sn−O bonds took the desired course (nos. 5−8, Table 6). The ^{1}H NMR spectra of the isolated oligoesters (Figure 4) illustrated the analytical advantage of DSTOX as initiator for ϵ-CL. The signal of the CH_2OCH_2 group is well separated from the stronger signal of the ϵ-CL units and allows a rather accurate comparison with end group signals. The accuracy of these comparisons is almost independent of the M/I ratio and DP. In this connection it should be emphazied that the analytical disadvantage of DSDOP as initiator is limited to ϵ-CL or δ-valerolactone as monomers. The 1,4-dioxybutane fragment displays well-resolved ^{1}H NMR signals in combination with other lactones.

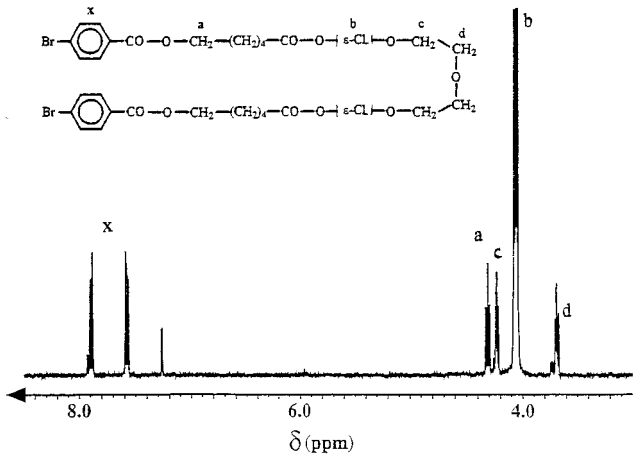
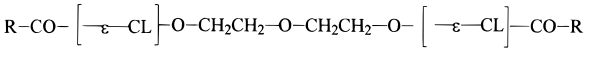
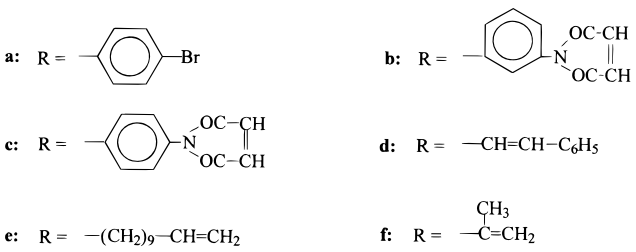


Figure 4. 400-MH$_z$ ^{1}H NMR spectrum of a DSTOX-initiated poly(ϵ-CL) functionalized by acylation with 4-bromobenzoyl chloride (no. 6, Table 6).

The successful syntheses of the telechelic oligoesters **14a**−**e** by means of dissolved DSTOX has two positive



14a - e



consequences. They prove the usefulness of DSTOX as initiator of macrocyclic polymerizations and they confirm the results obtained with DSDOP. In order to utilize the analytical advantage of DSTOX and to confirm the conclusions drawn from the experiments nos. 5−8, Table 6, five more telechelic oligoesters having

Table 7. Acylation of DSTOX-Initiated Macrocyclic Poly(ϵ-caprolactone) with Various Acylating Agents (Reaction Time 6 h)

expt no.	acylating agent	M/I[a]	temp (°C)	conv (%)	yield[b] (%)	DP[b] (^{1}H NMR)
1	3-maleimidobenzoyl chloride	20/1	140	100	77.0	21
2	4-maleimidobenzoly chloride	20/1	140	100	77.5	21
3	cinnamoyl chloride	20/1	80	100	80.5	21
4	undecenoyl chloride	10/1	80	100	80.0	14
5	undecenoyl chloride	20/1	80	100	84.0	22
6	undecenoyl chloride	50/1	80	100	86.5	51
7	methacrylic anhydride	20/1	80	100	86.0	21.5

[a] Molar ϵ-CL/DSTOX ratio used for the macrocyclic polymerizations. [b] After precipitation into cold methanol.

different functional end groups (**14b**−**f**) were prepared. The reaction conditions and results are compiled in Table 7. In all cases, the hoped for functionalization and the expected DPs were obtained.

Conclusion

The results of this work allow the conclusion that macrocyclic polymerizations of lactones by means of cyclic tin initiators offer a broad and useful access to the synthesis of telechelic oligo- and polyesters. The DP can be varied over a broad range and the structure of the polymer chain can be varied via the structure of the lactone (to be reported in future publications). The groups that can be introduced by acylation of the SnO "end groups" allow numerous modification, chain extension, and cross-linking reactions. The synthesis of more or less biodegradable multiblock copolymers is of particular interest in this connection. A noteworthy advantage of this novel approach is the fact that it can be performed in a straight forward one-pot procedure.

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