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# Articles

## New Polymer Syntheses. 110. Ring-Opening Polycondensation of Two Cyclic Monomers−Polyesters from Ethylene Sulfite and Cyclic Anhydrides

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ABSTRACT: Ethylene sulfite and succinic anhydride undergo a polycondensation reaction evolving $SO_2$ when heated above 160 °C in the presence of suitable catalysts. Both quinoline and Lewis acids ($BF_3$ or $SnCl_4$) proved to be useful catalysts yielding polyesters which were characterized by IR and $^1H$ and $^{13}C$ NMR spectroscopy. Analogous polycondensations were conducted with mixtures of ethylene sulfite and glutaric anhydride, 3,3-tetramethylene glutaric anhydride, adipic anhydride, and sebacic anhydride. The resulting polyesters had number average molecular weights ($M_n$s) in the range of 5000−10 000 Da (based on PS-calibrated SEC), and the MALDI−TOF mass spectra indicated the formation of cyclic oligoesters and polyesters along with linear chains. Polycondensations of ethylene sulfite and succinyl sulfide yielded S-free polyesters, a result important for the mechanistic discussion. No polycondensations were observed for mixtures of ethylene sulfite and dicarboxylic acids, whereas oligoesters containing diethylene glycol units were obtained from acid-catalyzed polycondensations of ethylene glycol and cyclic anhydrides. The unusual thermodynamic aspects of this ring-opening polycondensation concept are also discussed.

### Introduction

Polycondensation chemistry is usually taught and technically performed on the basis of linear monomers such as diols, diphenols, diamines, $\omega$-amino acids, dicarboxylic acids and their derivatives, and so forth. In several papers[1−4] including a short review,[1] we have recently pointed out that cyclic monomers having two reactive bonds may also be used as bifunctional monomers in polycondensation processes. All examples of such ring-opening polycondensations reported so far involved the reaction between a cyclic and a linear monomer, which may be a trifunctional one (e.g., glycerol) as demonstrated in the very first reports of such a polycondensation.[5−7] Regardless of the preparative usefulness, these ring-opening polycondensations are remarkable, because their thermodynamic aspects are different from the normal case exclusively involving linear monomers.[1] What we have not found in the literature is a polycondensation based on two cyclic monomers. Therefore, it was the purpose of this study to present a first example of such a polycondensation, and combinations of ethylene sulfite with cyclic anhydrides were selected as monomers for this study.

### Experimental Section

**Materials.** Ethylene sulfite was purchased from Aldrich Co. (Milwaukee, WI) and was distilled over $P_4O_{10}$ before use. Succinic anhydride, glutaric anhydride, $P_4O_{10}$, $SnCl_4$, $BuSnCl_3$, and $ZnCl_2$ were also purchased from Aldrich Co. and used as received. $BF_3 \cdot Et_2O$, succinic acid, adipic acid, and sebacic acid were purchased from Merck and used as received. Quinoline (a gift of Bayer AG) was distilled over $CaH_2$ in vacuo. Adipic anhydride was prepared from adipic acid and acetic anhydride according to the literature[8] and used immediately after distillation. Ethylene glycol was azeotropically dried with toluene and distilled in vacuo.

**Polycondensations of Ethylene Sulfite. (A) With Succinic Anhydride and $SnCl_4$.** Ethylene sulfite (30 mmol), succinic anhydride (30 mmol), and $SnCl_4$ (0.15 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirrer, gas-inlet, and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 100 °C, and the polycondensation was conducted at 180 °C for 16 h with stirring in an athmosphere of dry nitrogen. The cold polyester was dissolved in $CH_2Cl_2$, precipitated into dry diethyl ether (methanol may cleave the ester bonds) and dried at 25 °C in vacuo.

**(B) With Glutaric Anhydride and Quinoline.** Ethylene sulfite (30 mmol), glutaric anhydride (30 mmol), and dry quinoline (0.3 mmol) were weighed into a cylindrical glass reactor and polycondensed as described above.

**(C) With Sebacic Anhydride and $BF_3 \cdot OEt$.** Bistrimethylsilyl sebacate (20 mmol), sebacoyl chloride (20 mmol), and benzyl triethylammonium chloride were polycondensed in a cylindrical glass reactor as described previously.[9] Ethylene sulfite (48 mmol) and $BF_3 \cdot OEt$ (0.48 mmol) were added to the crude sebacic anhydride, and the polycondensation was continued at 180 °C for 16 h as described for part A.

**(D) With Succinyl Sulfide.** Ethylene sulfite (30 mmol), succinyl sulfide (30 mmol), and dry quinoline (0.3 mmol) were weighed into a cylindrical glass reactor and polymerized as described for A).

**Polycondensations of Ethylene Glycol.** Dry ethylene glycol (100 mmol), glutaric anhydride (100 mmol), and toluenesulfonic acid (10 mg) were weighed into a 250 mL three-neck flask equipped with a mechanical stirrer and a distillation head. Chlorobenzene (100 mL) was added, and most of it (ca. 80 mL) was slowly distilled off with stirring at a bath temperature of 150−160 °C. After cooling, the reaction mixture

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**Table 1. Yields and Properties of Polyesters Prepared by Polycondensation of Ethylene Sulfite and Various Cyclic Anhydrides in Bulk at 180 °C (16 h)**

| expt no. | cyclic anhydride of (polymer) | catalyst | yield (%) | $\eta_{inh}$[a] (dL/g) | chem shifts δ (ppm)[b] ¹H NMR | chem shifts δ (ppm)[b] ¹³C NMR |
|---|---|---|---|---|---|---|
| 1 | succinic acid (**2a**) | quinoline | 86 | 0.17[c] | δ = 2.67 (s, 4H), 4.30 (s, 4H) | δ = 29.18 (2C), 62.77 (2C), 172.41 (C=O) |
| 2 | succinic acid (**2a**) | $BF_3 \cdot Et_2O$ | 91 | 0.21[d] | | |
| 3 | glutaric acid (**2b**) | quinoline | 84 | 0.16 | δ = 1.95 (m, 2H), 2.41 (t, 4H), 4.28 (s, 4H) | δ = 20.25 (1C), 33.32 (2C), 65.41 (2C), 172.99 (C=O) |
| 4 | glutaric acid (**2b**) | $BF_3 \cdot Et_2O$ | 87 | 0.15 | | |
| 5 | tetramethyleneglutaric acid (**3a**) | quinoline | 88 | 0.18[e] | δ = 1.50 (m, 8H), 2.57 (s, 4H), 4.30 (s, 4H) | δ = 24.42 (2C), 38.58 (2C), 42.27 (2C) 43.26 (1C), 172.51 (C=O) |
| 6 | tetramethyleneglutaric acid (**3a**) | $BF_3 \cdot Et_2O$ | 90 | 0.18 | | |
| 7 | adipic acid (**2c**) | quinoline | 82 | 0.13 | δ = 1.67 (s, 4H), 2.37 (s, 4H), 4.32 (s, 4H) | δ = 24.50 (2C), 34.01 (2C), 62.50 (2C), 173.50 (C=O) |
| 8 | adipic acid (**2c**) | $BF_3 \cdot Et_2O$ | 84 | 0.14 | | |
| 9 | sebacic acid (**2d**) | quinoline | 83 | 0.15 | δ = 1.29 (s, 8H), 1.61 (s, 4H), 2.31 (m, 4H),4.21 (s, 4H) | δ = 25.19 (4C), 29.44 (2C), 34.31 (2C), 62.39 (2C), 173.93 (C=O) |
| 10 | sebacic acid (**2d**) | $BF_3 \cdot Et_2O$ | 90 | 0.16 | | |
| 11 | thiosuccinic acid (**2a**) | quinoline | 84 | 0.11 | δ = 2.67 (s, 4H), 4.30 (s, 4H) | δ = 29.19 (2C), 62.77 (2C), 172.41 (C=O) |
| 12 | thiosuccinic acid (**2a**) | $BF_3 \cdot Et_2O$ | 86 | 0.12 | | |

[a] Measured at 25 °C with $c = 2$ g/L in $CH_2Cl_2$. [b] Recorded in $CDCl_3$ containing TMS as shift reference. [c] $M_n = 7000$ Da, $M_w = 15\,000$ by PS-calibrated SEC measurements, or $M_n = 5000$ Da, $M_w = 10\,500$ by Universal calibration. [d] $M_n = 10\,000$ Da, $M_w = 21\,000$ by PS-calibrated SEC measurements, or $M_n = 7000$ Da, $M_w = 15\,000$ by Universal calibration. [e] $M_n = 8000$ Da, $M_w = 17\,000$ by PS-calibrated SEC measurements, or $M_n = 5500$ Da, $M_w = 11\,000$ by Universal calibration.

was diluted with $CH_2Cl_2$ (50 mL) and precipitated into dry diethyl ether, and the isolated polyester was dried at 25 °C in vacuo.

**Measurements.** The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The GPC measurements were performed with a Kontron GPC apparatus equipped with a Waters Md 410 differential refractometer. A set of four "Ultrastyragel" column having pore sizes of $10^{-2}$, $10^{-3}$, $10^{-4}$, and $10^{-5}$ Å was used in combination with THF as eluent.

The 400 MHz $^1H$ NMR spectra were recorded with a Bruker AM-400 FT NMR spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent and shift reference. The 100.4 MHz $^{13}C$ NMR spectra were recorded with the same instrument.

The MALDI−TOF mass spectra were obtained on a Bruker Biflex III in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from THF solutions using dithranol as matrix and K−trifluoroacetate as dopant.

## Results and Discussion

**Preparative Aspects.** The first series of experiments was conducted in such a way that equimolar mixtures of ethylene sulfite and succinic anhydride (the most reactive anhydride of this study) were heated for 16 h to temperatures in the range 80−180 °C. Yet, no significant conversion was found, and higher temperatures were not applicable due to the distillation of the monomers. On the basis of these negative results, two series of potential catalysts were selected, namely pyridine type amines, on one hand, and Lewis acids, on the other. Pyridine itself had the shortcoming of a low boiling point, and thus the more nucleophilic and less volatile. *N*,*N*-Dimethyl-4-aminopyridine was added (1 wt %). With this catalyst partial conversion was found at 140 °C and complete conversion at 180 °C, but the $^1H$ and $^{13}C$ NMR spectra indicated the formation of a complexe mixture of low molar mass reaction products. Therefore, the less nucleophilic, high boiling quinoline was used for the next series of experiment and again an almost quantitative conversion was obtained at 180 °C. This time IR and $^1H$ NMR and $^{13}C$ NMR spectra proved the formation of polyester **2a** (no. 1, Table 1). Quinoline was also found to be an useful catalyst when other cyclic anhydrides were used as reaction partners of ethylene sulfite (nos. 3, 5, 7, 9, and 11; Table 1).

In addition to amines, six different Lewis acids were studied as potential catalysts: $BF_3 \cdot OEt_2$, $SnCl_2$, $SnCl_4$, $BuSnCl_3$, $ZnCl_2$, and $BiCl_3$. Complete conversions (at 180 °C) were only observed for $BF_3 \cdot OEt_2$- and $SnCl_4$-catalyzed polycondensations, and in both cases polyester **2a** was formed. However, the viscosity value obtained with $SnCl_4$ was lower, and thus, $BF_3 \cdot OEt_2$ was used for all further polycondensations (nos. 4, 6, 8, 10, and 12; Table 1). Whereas in the case of succinic, glutaric, and adipic acids monodisperse cyclic anhydrides were available, a monomeric anhydride is not known from sebacic acid. In this case, a mixture of cyclic and linear oligoanhydrides was prepared from bistrimethylsilyl sebacate and sebacoyl chloride (with elimination of $ClSiMe_3$) as described previously.[9] This polydisperse mixture of anhydrides was in situ polycondensed with ethylene sulfite. The characterization of the resulting polymers by $^1H$ and $^{13}C$ NMR spectroscopy revealed that from equimolar mixtures of reactants copolymers were obtained containing an anhydride group. Obviously the partial distillation of ethylene sulfite caused a significant imbalance of the stoichiometry. Therefore, these

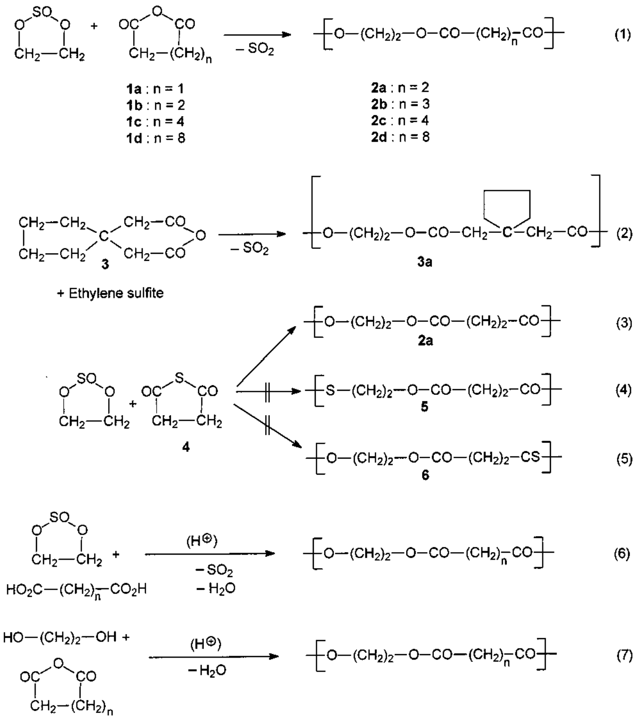


**Table 2. Polycondensations of Ethylene Glycol with Cyclic Anhydrides in Boiling Chlorobenzene Catalyzed by Toluene Sulfonic Acid**

| expt no. | monomers | yield (%) | $\eta_{\mathrm{inh}}{}^{a}$ (dL/g) | content of diethylene glycol units, mol % |
|---|---|---|---|---|
| 1 | ethylene glycol + succinic anhydride | 88 | 0.11 | 15 |
| 2 | ethylene glycol + glutaric anhydride | 85 | 0.10 | 11 |
| 3 | ethylene glycol + adipic anhydride | 82 | 0.08 | 9 |

[a] Measured at 25 °C with $c = 2$ g/L in $CH_2Cl_2$. [b] Recorded in $CDCl_3$ containing TMS as shift reference.

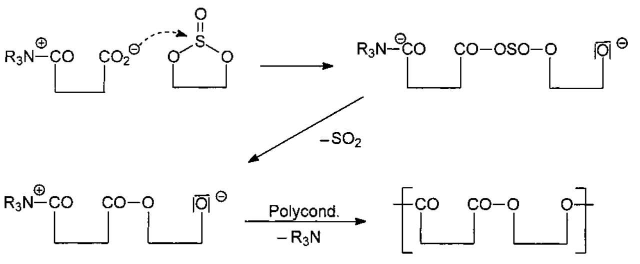
syntheses were repeated with 5, 10, 15, and 20 mol % excesses of ethylene sulfite, and with a 20% excess, a perfect polyester was indeed obtained.

Another interesting result discussed below (see mechanistic aspects) in more detail is the isolation of the polyester **2a** from polycondensations of ethylene sulfite with succinyl sulfide (**4**). Regardless which catalyst was used, polythioesters of structure **5** or **6** were not obtained (nos. 11 and 12; Table 1).

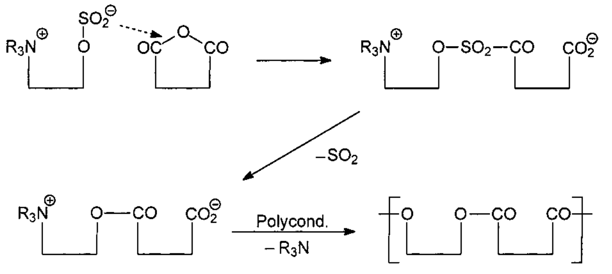
The inherent viscosities listed in Table 1 and the molecular weight measurements presented in the footnotes of Table 1 indicate that polycondensations of ethylenes sulfite with cyclic anhydrides are not the ideal method to prepare high molecular weight polyesters. The number average molecular weights ($M_n$s) obtained from SEC measurements calibrated with polystyrene were higher than those resulting from the "universal calibration". This difference agrees with the fact that PS-calibrated SEC measurements overestimate the $M_n$s of poly($\epsilon$-caprolactone)s.[10-12] This point prompted us to study alternative ring-opening polycondensations theoretically yielding the same polyesters. The first approach is based on the acid-catalyzed polycondensation of ethylene sulfite with free dicarboxylic acids (eq 6). An acidic catalyst is necessary in this case, because in addition to the elimination of $SO_2$ a normal esterification of $CO_2H$ and OH end groups is required. Yet, despite the addition of toluenesulfonic acid, no reaction was observed, either in refluxing toluene or in refluxing chlorobenzene.

The alternative approach consisted of the polycondensation of ethylene glycol with cyclic anhydrides again catalyzed by toluenesulfonic acid (eq 7). Under the relatively mild conditions of refluxing 1,2-dichloroethane, no polycondensations occurred with succinic anhydride. In refluxing chlorobenzene, the polycondensations of all cyclic anhydrides proceeded, but the yields and inherent viscosities (Table 2) were even lower than those obtained from polycondensations of both cycles (eq 1 and Table 1). The reason for these poor results was detected by $^1H$ and $^{13}C$ NMR spectroscopy of the virgin reaction mixture. Up to 15 mol % of the ethylene glycol had undergone an etherification process yielding diethylene glycol, which not only alters the structure of the polyesters, but also affects the stoichiometry of the reaction mixture. All these poor results together demonstrate that the polycondensations according to eq 1 are not as bad as they may look at first glance. This conclusion is supported by the results of Carothers and co-workers[13,14] who prepared poly(ethylene succinate) from succinic acid or bis(2-hydroxy ethyl) succinate in various ways. The $M_n$s of their polyesters never exceeded 3000 Da. In this connection, it should be mentioned that poly(ethylene succinate) is a commercial (biodegradable) material, but its relatively high molecular weight with $M_n$s > 20 000 Da is based on a posttreatment (chain extension) of low molar mass polyesters with 1,6-diisocyanatohexane. This fact indicates again that it is pretty difficult to obtain a high molecular weight poly(ethylene succinate) by an one-step polycondensation regardless of the synthetic method.

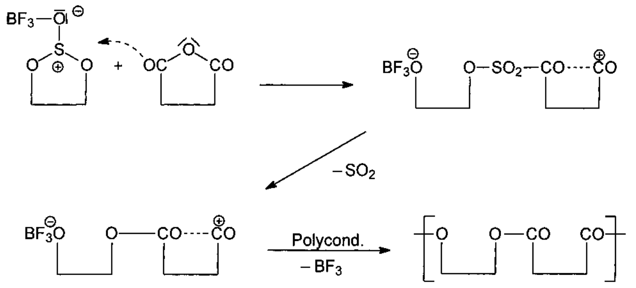
**Scheme 1**



**Scheme 2**



**Scheme 3**



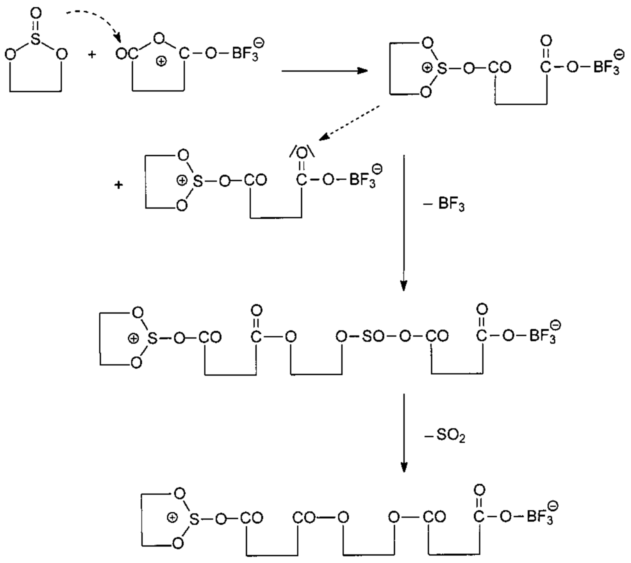
**Mechanistic Aspects.** A detailed mechanistic study including most side reactions was not the purpose of this work, but the main propagation step should be elucidated. A series of five reaction mechanisms is formulated in Schemes 1−5, which are not an exhaustive description of all theoretically imaginable reactions but suffice for the discussion of this work. Two fundamentally different growing steps should be distinguished:

(1) the sulfinylation of the cyclic anhydride involving the formation of a mixed anhydride followed by the formation of an ester group by elimination of $SO_2$ (Schemes 1, 2, and 3);

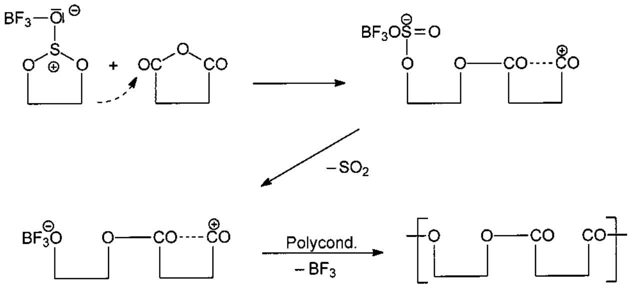
(2) an alkylation of the cyclic anhydride with direct formation of an ester group (Schemes 4 and 5).

In this connection, the polycondensation of ethylene sulfite with succinyl sulfide (**4**) yielded an important piece of information, because any alkylation of succinyl sulfide should yield thioester groups of structure **5** or **6**. The absence of these thioester groups definitely proves that the propagation exclusively proceeded via mixed anhydride groups (Schemes 1−3). This finding is also satisfactory, when taking into account that it is

**Scheme 4**



**Scheme 5**



difficult to formulate a reasonable “alkylation mechanism”, when quinoline is used as catalyst.

Furthermore, attemps were made to elucidate the first step of the reaction between quinoline and both monomers and the first step in the reaction between BF$_3$·OEt and both monomers. It is well-known that pyridine type amines react (reversibly) with anhydrides by a heterolytic cleavage as illustrated in the first formula of Scheme 1. Therefore, it was of interest to find out if quinoline reacts also with ethylene sulfite by heterolytic cleavage as illustrated by the first formula in Scheme 2. When equimolar amounts of quinoline and ethylene sulfite were heated, reactions were observed at temperatures ≥140 °C. However, both $^1$H NMR and $^{13}$C NMR spectra proved the formation of complex reaction mixtures and not a clear formation of a zwitterion. This observation suggests that the activation of the cyclic anhydride is the first step in the polycondensation experiments. Finally, the interaction of BF$_3$·OEt$_2$ with ethylene sulfite or succinic anhydride and with equimolar mixtures of both monomers was studied by $^1$H and $^{13}$C NMR spectroscopy at 20 °C, but no significant downfield shifts were found.

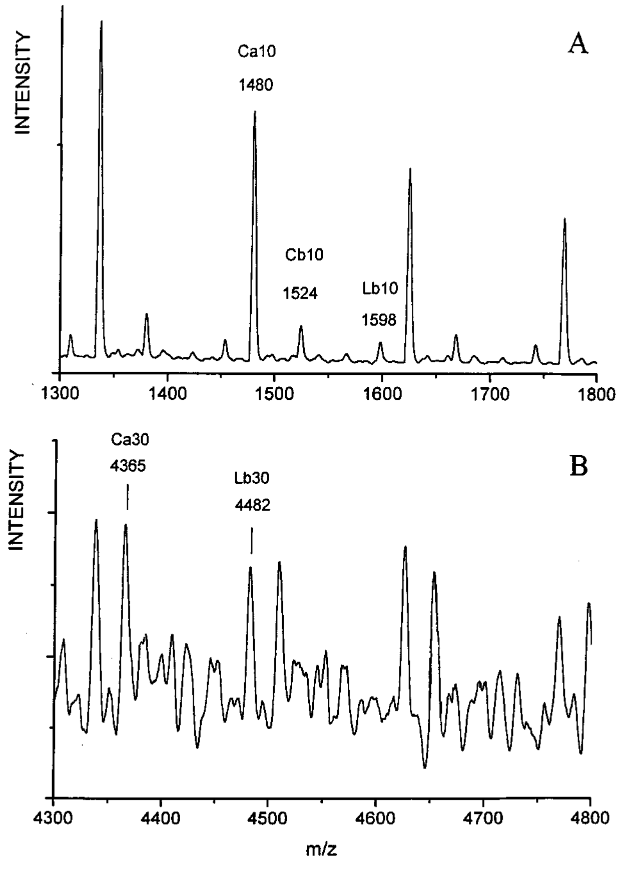
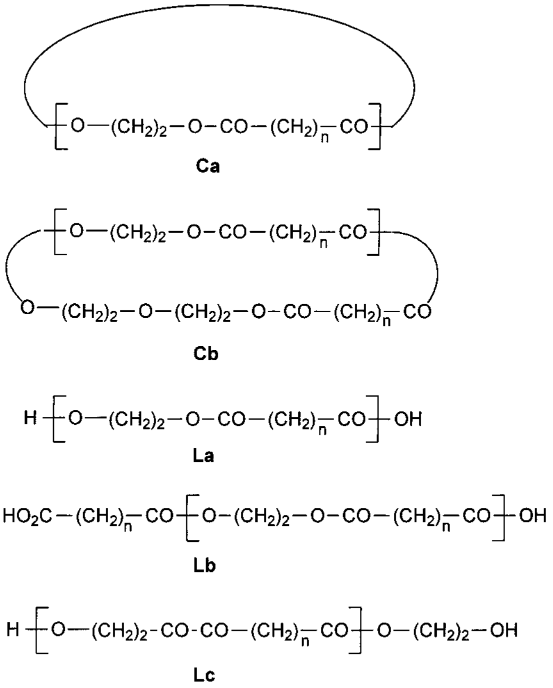


**Figure 1.** MALDI−TOF mass spectrum of poly(ethylene succinate) prepared at 180 °C (16 h) by means of BF$_3$·OEt$_2$.

**Scheme 6**



The characterization of the polyesters listed in Table 1 by MALDI−TOF mass spectrometry gave the following information. All reaction products contained cyclic oligoesters and cyclic polyesters of structure **Ca** (Scheme 6). The content of cycles in BF$_3$-catalyzed polycondensations was higher than in quinoline-catalyzed ones. The mass spectrum of the BF$_3$-catalyzed poly(ethylene succinate) exhibited the peaks of the cycles **Ca** up to masses around 5000 Da (Figure 1). Furthermore, cycles of structure **Cb** (Scheme 6) containing one diethylene glycol unit were detectable (Figure 1). The $^1$H NMR confirmed that in all polyesters 2−4 mol % of diethylene glycol was present regardless, if BF$_3$·OEt$_2$ or quinoline were used as catalyst. Cycles containing two diethylene glycol units may also have been formed, but their concentrations were so low that they were not detectable. A rather frequent type of linear chain in all products were polyesters terminated by two dicarboxylic

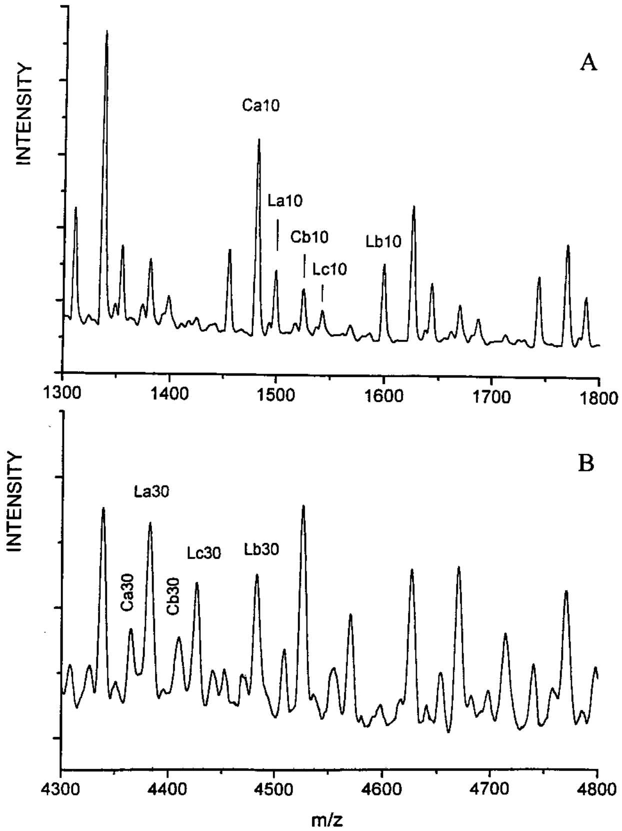


**Figure 2.** MALDI–TOF mass spectrum of poly(ethylene succinate) prepared at 180 °C (16 h) by means of quinoline.

acids (**Lb** in Schme 6). In quinoline-catalyzed polyesters, linear chains having one OH and one $CO_2H$ end group (**La**) and chains having two ethylene glycol end groups (**Lc**) were more frequent than in $BF_3$-catalyzed polyesters (Figure 2). Where the protons of the end groups came from (despite intensive drying of the monomers) was not elucidated, in a much, as vinyl ester end groups resulting from a thermal $\beta$-elimination were not detected.

These results raised the question if the large amounts of cycles present in $BF_3$-catalyzed polyesters are the result of transesterification/back-biting degradation or the products of a kinetically controlled cyclization of zwitterionic chains (Schemes 3–5). To shed more light on this problem an alternating copolyester of structure **3** (published recently[15]) was heated with $BF_3$ or quinoline to 180 °C for 16 h. The "quinoline product" was still crystalline, and both the $^1H$ and $^{13}C$ NMR spectra proved that only little transesterification had taken place. In contrast, the "$BF_3$ product" was amorphous and four intensive $CH_2$ signals were found in the $^1H$ NMR spectrum (Figure 3B), proving a far-reaching randomization of the copolyester. This interpretation was confirmed by the $^{13}C$ NMR spectrum displaying four signals (63.62, 63.41, 62.38, and 62.16 ppm in $CDCl_3$) of the ethylene glycol unit, whereas two signals are typical for the alternating sequence. These findings suggest that the majority of cycles in the $BF_3$-catalyzed polyesters of Table 1 were the results of a ring-chain equilibrium involving "back-biting". In summary, the above results indicate that the chain growth of quinoline-catalyzed polycondensations is limited by a combination of various side reactions, whereas in the case of $BF_3$ the ring-chain equilibration makes a major contribution to the limitation of the molecular weights.

**Thermodynamical Aspects.** The thermodynamical properties of a normal polycondensation based on linear monomers is characterized by $\Delta S \approx 0$. Therefore, even the slightest negative reaction enthalpy suffices to create a negative $\Delta G$, or in other words a sufficient driving force. $\Delta S \approx 0$ is a consequence of the fact that each growing step liberates a byproduct which compensates for the loss of translational motion and external rotation characteristic for the monomers. When two cyclic monomers undergo a polycondensation, the thermodynamic situation is quite different. The liberation of one molecule of byproduct (here $SO_2$) requires two propagation steps so that the compensation of lost translational and rotational motion amounts to only 50% of the normal case (linear monomers). However, the ring-opening of two cycles may result in a gain of rotational motion when the cycles are so small that rotation of the ring members in the cycles is sterically hindered. Depending on the chemical structure the

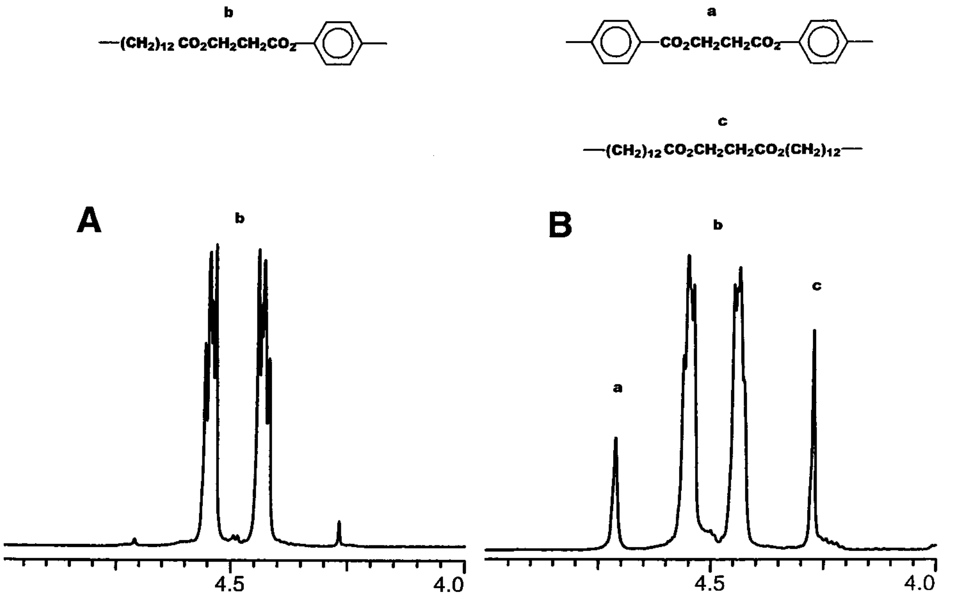


**Figure 3.** 400 MHz $^1H$ NMR spectra of the ethylene glycol unit of polyester **3**: A) original sample, B) after heating with $BF_3$ (1 mol %) at 180 °C/16 h.

borderline case for hindered rotation is a ring size of nine to ten ring members. Larger rings typically possess a rather free rotation of all ring members. The consequences for the entropy change of ring-opening polycondensation should be discussed here in the form of three simplified model calculations.

**Case I: Two Five-Membered Rings.** Characteristic for all polycondensations in solution or in the melt is the total loss of translational motion amounts to 3 × $^{3}/_{2}R$ ($R$ = gas constant) for each monomer. Furthermore, a loss of external rotational motion corresponding to 3 × $^{1}/_{2}R$ has to be considered for each monomer. Therefore, the total loss of entropy corresponds to $^{24}/_{2}R$. The liberated byproduct provides a compensation for $^{9}/_{2}R$ of translational motion and $^{3}/_{2}R$ for external rotation. The ring-opening of both cycles produces a gain of $^{10}/_{2}$R by unfreezing of external motion. Hence, the final balance is a loss of $^{2}/_{2}R$, which means that $\Delta S$ is close to zero, and a weakly exothermic reaction suffices to generate a negative $\Delta G$.

**Case II: Two Nine-Membered Rings.** The only difference compared to case I is a larger gain of entropy by unfreezing of internal motion which amounts to $^{9}/_{2}R$ for each ring. The total balance of entropy of the polycondensation process amounts to a gain of $^{6}/_{2}R$. This means that polycondensations of two seven-, eight- or nine-membered rings are thermodynamically favored at any temperature provided $\Delta H$ is close to zero or negative. This is a particular rare case among all kinds of polymerizations.

**Case III: Two 15-Membered Rings.** When two macrocycles with unhindered internal rotation are used as monomers, the net entropy change of the polycondensation corresponds to a loss of $^{12}/_{2}R$, and thus, this is the least favorable case in this series.

In summary, the above model calculations demonstrate that the change of entropy in polycondensations may cover a broad range from positive to negative values depending on the ring size. As discussed previously,[1] one cycle with one linear monomer represent another thermodynamic situation, and in the optimum case $\Delta S$ may come close to zero but can never turn positive.

## Conclusion

The results presented above demonstrate for the first time (to the best of our knowledge) that polycondensations may be conducted with two heterocycles as monomers. Regardless of the catalyst only moderate molecular weights were obtained. Thus, this approach is not particularly attractive from the preparative point of view. However, it is remarkable that two heterocycles which cannot undergo any homopolymerization are capable of a “copolycondensation” yielding a well defined homopolyester. Furthermore, polycondensations of two heterocycles are remarkable for their thermodynamical properties which are quite different from the classical case involving two linear monomers. This new concept may also stimulate further studies of ring-opening polycondensations, and polycondensations of cyclic carbonates with cyclic anhydrides are currently under investigation in our laboratory.

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