Research Article

Catalytic copolymerization of methyl 9,10-epoxystearate and cyclic anhydrides under neat conditions

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The solvent-free copolymerization of methyl 9,10-epoxystearate **1** with different cyclic anhydrides, such as phthalic anhydride **2**, succinic anhydride **3**, maleic anhydride **4**, or the Diels-Alder-adduct **5** of methyl α-eleostearate and maleic anhydride, using a (salen)$Cr^{III}Cl$-catalyst and n-Bu_4NCl as co-catalyst is demonstrated. In this way, polyesters ($M_n = 2000$–$10{,}000$ g/mol) with low glass transition temperatures were formed. The reaction is characterized by sustainable aspects, for instance, the use of starting materials derived from renewable resources (>60%), low catalyst loadings, and no added solvent.

Practical applications The alternating ring-opening copolymerization of epoxides such as methyl 9,10-epoxystearate with various cyclic acid anhydrides such as phthalic anhydride and succinic anhydride, respectively, afford polyesters of narrow molecular weight distributions using a (salen)$Cr^{III}Cl$ catalyst in the presence of n-Bu_4NCl. The pending long chain alkyl groups introduced in the polyesters by the fat derived substrates attribute amorphous properties to the polymers. Various fatty epoxides are easily available and open up the possibility for the synthesis of new highly branched polyesters

Keywords: Methyl 9, 10-epoxystearate / Phthalic anhydride / Polyester / Ring-opening polymerization / (salen)$Cr^{III}Cl$-catalyst

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1 Introduction

Raw materials derived from renewable resources are of growing interest for the chemical industry [1, 2]. Especially compounds synthesized from plant oils are attractive for the production of environmental friendly and in many cases biodegradable consumer products. A great challenge is the production of polymers based on renewable feedstocks and indeed, there are already numerous examples using natural oil based monomers as starting materials [3, 4]. Methyl 9,10-epoxystearate **1** and other epoxidized fatty compounds have been used for the synthesis of a variety of new oleochemicals, among those are polyethers [1, 5, 6]. The synthesis of polyesters using epoxide **1** as monomer should be promising, since the catalytic ring-opening copolymerization of epoxides with cyclic anhydrides, such as phthalic, maleic, or succinic anhydride, using different metal-complex systems is known for some time [7, 8, 9, 10] and has been intensively investigated in recent years [11, 12, 13, 14, 15]. Respective reactions of a variety of epoxides and saturated anhydrides with β-diiminate-ZnOAc as catalyst gave aliphatic polyesters in a strictly alternating copolymerization with high M_n values and narrow molecular weight distributions [11]. Unsaturated polyesters were obtained using a highly active chromium(III) salen complex for the copolymerization of terminal epoxides and maleic anhydride [12]. The high activity of the (salen) $Cr^{III}Cl$-catalyst was further confirmed by the copolymerization of a series of epoxides and cyclic anhydrides, such as propylene or cyclohexane oxide and succinic anhydride or phthalic anhydride, respectively [13]. Kinetic studies of the temperature-dependent (salen)$Cr^{III}Cl$-catalyzed reactions in the presence of n-Bu_4NCl as co-catalyst revealed that the ring-opening of the epoxide by the terminal carboxylate demonstrates the rate-determining step [13]. Further

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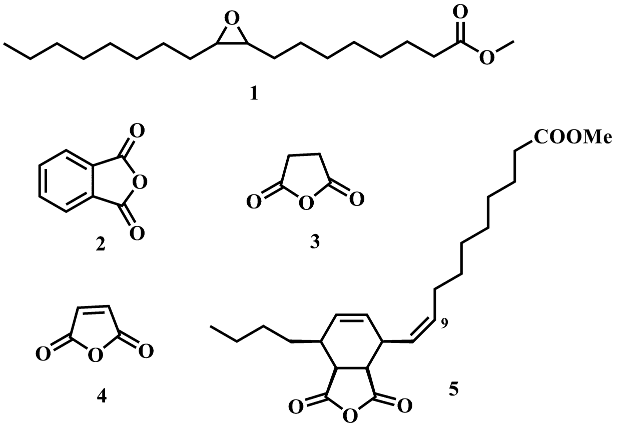
Abbreviations: DSC, differential scanning calorimetry; **GPC,** gel permeation chromatography; **TLC,** thin layer chromatography

Dedicated to Professor Dieter Lenoir on the occasion of his 80th birthday mechanistic studies were carried out by Chisholm et al. using porphyrin metal(III) complexes as catalysts [16, 17]. The copolymerization of propylene oxide with different cyclic anhydrides was characterized as a catalytic cycle of two main steps including the formation of a metal-alkoxide intermediate followed by the ring-opening of the anhydride and formation of the metal-carboxylate intermediate [16].

The synthesis of (semi) bio-based polyesters using the alternating epoxide/cyclic anhydride copolymerization approach was first described by Coates et al. for the β-diiminato zinc-catalyzed copolymerization of limonene oxide with diglycolic anhydride [11]. Duchateau and coworkers carried out a screening of different catalysts for the copolymerization of limonene oxide and phthalic anhydride. The highest activity was found for chromium- and aluminium-salophen catalysts in combination with the onium salt PPN^+Cl^- [14]. Moreover, 3,4-Dihydrocoumarin (DHC)-based polyesters were obtained by copolymerization of a variety of epoxides with DHC, catalyzed by (salen)Cr(III)-complexes [18]. The resulting polyesters were characterized by high molecular weights and narrow molecular weight distributions and in case of terminal epoxides more than 90% regioselectivity for 1,2-insertion was observed.

Encouraged by these well-founded studies on the alternating ring-opening epoxide/cyclic anhydride copolymerization, our interest was focused to respective reactions using methyl 9,10-epoxystearate **1**, which is an industrially available bio-based compound, as substrate. Recently, it has been claimed that 9,10-epoxystearic acid and epoxide **1**, respectively, undergo copolymerization with *cis*-1,2-cyclohexanedicarboxylic anhydride in the presence of triethylamine, however with low molecular weight of $M_w = 2500$ g/mol [19].

Here, we report on the ring-opening alternating copolymerization of methyl 9,10-epoxystearate **1** with cyclic anhydrides **2**–**5** (Scheme 1) in the presence of (salen)$Cr^{III}Cl$ as catalyst and n-Bu_4NCl as co-catalyst using a modified protocol of Darensbourg [13].



Scheme 1. Substrates of the ring-opening copolymerization of methyl 9,10-epoxystearate **1** with phthalic anhydride **2**, succinic anhydride **3**, maleic anhydride **4**, and the Diels–Alder adduct **5** of methyl α-eleostearate and maleic anhydride.

2 Materials and methods

General: Methyl 9,10-epoxystearate **1** was synthesized as described previously [5]. Phthalic anhydride **2**, succinic anhydride **3,** and maleic anhydride **4** were purchased from Sigma–Aldrich and used as received. Diels–Alder adduct **5** was synthezised as previously described [20]. (1S,2S)-(+)-[1,2-Cyclohexanediamino-N,N′-bis(3,5-di-*tert*-butylsalicylidene)]chromium(III) chloride [(salen)$Cr^{III}Cl$] was purchased from Strem Chemicals and n-Bu_4NCl from VWR, and used as received.

Analytical equipment: ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX 500 spectrometer at 300 K using residual non-deuterated solvent (^1H NMR) or $CDCl_3$ (^{13}C NMR) as internal standards. IR spectra were recorded on a Bruker Vector 22 spectrometer.

Thin layer chromatography (TLC) was performed on silica gel TLC cards (silica gel, layer thickness 0.20 mm, Merck). Compounds were visualized by 2 N sulfuric acid/heat. Silica gel 60 (70–230 mesh) was used for column chromatography. Gel permeation chromatography (GPC) of the polymers was performed on the system LC-20 A from Shimadzu equipped with a SIL-20A auto sampler, RID-10A refractive index detector, main-column PSS SDV analytical (5.0 μm, 300 × 8.0 mm, 10000 Å) with a PSS SDV analytical precolumn (5.0 μm, 50 × 8.0 mm) in THF (flow rate $1\,mL \times min^{-1}$) at 50°C. All determinations of molar mass were performed relative to PMMA standards (Polymer Standards Service, M_p 1100–981000 Da). Differential scanning calorimetry (DSC) was carried out with a Mettler Toledo DSC star^e system operating under nitrogen atmosphere using about 5 mg of the respective polymer for the analysis. The glass transition (T_g) was recorded on the second heating scan by using the following method: heating from −75 to 150°C at 20°C/min, cooling from 150 to −75°C at 20°C/min and heating from −75 to 150°C at 10°C/min.

All products were identified unambiguously by ^1H and ^{13}C NMR spectroscopy.

2.1 Copolymerization of methyl 9,10-epoxystearate 1 and cyclic anhydrides 2–5

General procedure: A mixture of the respective cyclic anhydride **2–5** (5.0–10 mmol) and (salen)$Cr^{III}Cl$-catalyst (0.12–0.5 mmol) was degassed in a two-necked round-bottom flask with magnetic stirrer and flushed with nitrogen (3 cycles). After addition of co-catalyst n-Bu_4NCl (0.01–0.04 mmol), methyl 9,10-epoxystearate **1** (5.0–10 mmol) was added and the sample was degassed and flushed with nitrogen (2 cycles). The reaction mixture was stirred magnetically over night at the given temperature. The reaction was followed by TLC (petroleum ether/diethyl ether = 7:3) showing complete conversion of epoxide **1** mostly after overall 20 h. The reaction mixture was dissolved in THF (3.0 mL) and precipitated under vigorous stirring in cold methanol (25 mL). The lower brown colored phase was washed with methanol and dried in vacuo at 100°C. Detailed data are given in Tables 1 and 2.

2.1.1 Representative synthesis of polyester 6 (Table 1, entry 3)

A mixture of phthalic anhydride **2** (740.6 mg, 5.0 mmol) and methyl 9,10-epoxystearate **1** (1.69 mL, 1.56 g, 5.0 mmol) was reacted in the presence of (salen)$Cr^{III}Cl$-catalyst (16.6 mg, 0.025 mmol, 0.5%) and *n*-Bu_4NCl (11.5 mg, 0.04 mmol, 0.8%) over night at 116°C. After 20 h, TLC (petroleum ether/diethyl ether 7:3) showed complete conversion of epoxide **1**. Isolation as described above yielded 1.91 g (83%) of polyester **6**.

^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 7.68$ (m, aryl-H), 7.48 (m, aryl-H), 5.38 (m, CHOC=O), 3.67 (s, OCH_3), 2.30 (t, $J = 7.7$ Hz, CH_2CO), 1.77 (m, $C\mathit{H}_2CH$), 1.58 (m, $C\mathit{H}_2CH_2CO$), 1.43–1.20 (m, CH_2), 0.87 (t, $J = 7.4$ Hz, CH_3) ppm.

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 174.1$ ($\mathit{C}OOCH_3$), 166.6 (aryl-$\mathit{C}OO$), 132.4, 131.9, 130.0, and 129.6 (aryl), 75.0 ($\mathit{C}HOCO$), 51.3 (OCH_3), 34.0 ($\mathit{C}H_2CO$), 31.9 ($\mathit{C}H_2CHO$), 30.8, 29.6–29.1, 25.7, 25.2, 24.9, 22.7 ($\mathit{C}H_2CH_3$), 14.1 (CH_3) ppm.

Table 1. Alternating copolymerization of methyl 9,10-epoxystearate **1** and phthalic anhydride **2** in the presence of (salen)$Cr^{III}Cl$ as catalyst and *n*-Bu_4NCl as co-catalyst yielding polyester **6**.

Entry	Catalyst/co-catalyst (mol %)	T (°C)	t (h)	Yield (%)	M_n (g/mol^{-1})	Đ	T_g (°C)	Remarks
1	0.34/0.5	110	20	51	3950	1.17	−30	In toluene
2	0.3/1.1	110	20	71	4650	1.19	−21	b), c)
3	0.5/0.8	116	20	83	7600	1.17	−23	b), c)
4	0.24/0.38	126	20	82	9600	1.19	−23	b), 10% polyether
5	0.23/0.59	142	20	87	10150	1.22	−25	b), 13% polyether
6	0.25/0.37	116	44	80	8850	1.3	−21	b), c)
7	0.25/0.22	116	92	81	9100	1.5	−24	b), c)
8	0.12/0.12	116	19	79	7900	1.19	−27	b), c)
9	0.25/0.56	116	21	81	7600	1.27	−23	b), c)
10	0.5/0.2	116	20	77	7550	1.17	−23	b), c)
11	0.25/0	116	70	42	a)	a)	a)	b), 40% polyether
12	0/0.25	116	70	81	a)	a)	a)	b), 12% polyether

a) Not determined; b) no solvent; c) <5% polyether.

Table 2. Copolymerization of methyl 9,10-epoxystearate **1** with succinic anhydride **3**, maleic anhydride **4**, and Diels-Alder adduct **5** in the presence of (salen)$Cr^{III}Cl$ as catalyst and *n*-Bu_4NCl as co-catalyst.

Entry	Anhydride	Catalyst/co-catalyst (mol%)	T (°C)	t (h)	Yield^a (%)	M_n (g/mol^{-1})	Đ	T_g (°C)	Remarks
1	**3**	0.20/0.78	119	20	39 (**7**)	5450	1.45	−43	
2	**3**	0.18/1.0	129	20	54 (**7**)	5750	1.44	−44	
3	**4**	0.20/1.32	117	20	36 (**8**)	2400	2.91	b)	*cis*/*trans* = 5; 25% polyether
4	**4**	0.22/0.78	129	20	32 (**8**)	4750	2.63	b)	*cis*/*trans* = 2.3; 50% polyether
5	**5**	0.25/1.44	112	20	54 (**9**)	2250	1.48	b)	c)
6	**5**	0.34/0.94	130	20	40 (**9**)	2450	1.48	b)	c)
7	**5**	0.31/1.04	142	20	46 (**9**)	2500	1.46	b)	c)
8	**5**	0.25/0.30	145	20	34 (**9**)	3400	1.71	b)	c)
9	**5**	0.25/0.24	158	20	34 (**9**)	3900	1.62	−43	c)
10	**5**	0.25/0.25	198	20	50 (**9**)	5050	2.80	−40	c)

b) Could not be determined. c) <20% polyether.
^{a}Yields of copolymers 7, 8, and 9, respectively (Scheme 3).

2.1.2 ^{1}H-NMR monitored copolymerization of 1 and 2

Phthalic anhydride **2** (2.96 g, 20 mmol) and epoxide **1** (6.76 mL, 6.28 g, 20 mmol) were reacted in the presence of (salen)Cr^{III}Cl-catalyst (31.5 mg, 0.05 mmol, 0.25%) and *n*-Bu_4NCl (13.5 mg, 0.05 mmol, 0.24%) as described above at 116°C. After predetermined times, aliquots of the reaction solution were taken and dissolved without any work-up in $CDCl_3$ for ^{1}H NMR analysis.

Additionally, the molecular weight was determined by GPC analysis. The results are compiled in Fig. 1.

2.1.3 Representative synthesis of polyester 7 (Table 2, entry 2)

The reaction of epoxide **1** (1.52 mL, 1.40 g, 4.5 mmol) and succinic anhydride **3** (450.5 mg, 4.5 mmol) was carried out as described above using 5.2 mg (0.008 mmol, 0.18%) of (salen)Cr^{III}Cl-catalyst and 12.5 mg (0.045 mmol, 1.0%) of *n*-Bu_4NCl. The reaction mixture was stirred magnetically over night at 129°C and yielded after work-up as described above 1.0 g (54%) of polyester **7**.

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 5.05$ (m, CHOC=O), 4.86 (m, CHOH), 3.64 (s, OCH_3), 2.65 (m, $COCH_2CH_2CO$), 2.25 (m, CH_2CO), 1.77 (m, CH_2CH), 1.50–1.08 (m, CH_2), 0.83 (t, $J = 7.4$ Hz, CH_3) ppm.

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 174.2$ ($COOCH_3$), 171.9 (COOCH), 74.0 (CHOCO), 72.4 (CHOCO), 51.3 (OCH_3), 34.0 (CH_2CO), 31.8 (CH_2CHO), 30.7, 29.5–28.9, 25.4, 22.7 (CH_2CH_3), 14.1 (CH_3) ppm.

2.1.4 Representative synthesis of polymer 8 (Table 2, entry 3)

The reaction of epoxide **1** (1.52 mL, 1.40 g, 4.5 mmol) and maleic anhydride **4** (440.7 mg, 4.5 mmol) was carried out as described above using 5.9 mg (0.09 mmol, 0.2%) of (salen) Cr^{III}Cl-catalyst and 16.5 mg (0.06 mmol, 1.32%) of *n*-Bu_4NCl. The reaction mixture was stirred magnetically over night at 117°C and yielded after work-up as described above 0.68 g (36%) of polyester **8**.

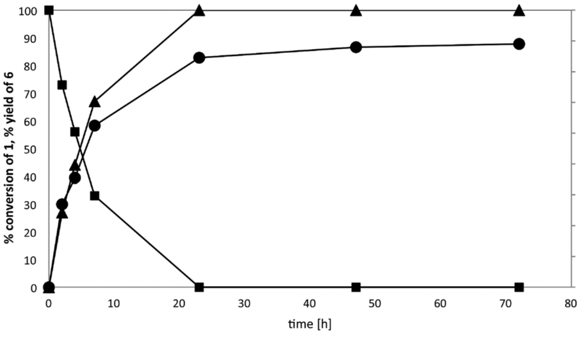


Figure 1. Copolymerization of methyl 9,10-epoxystearate **1** and phthalic anhydride **2** followed in time. Conversion of **1** (square) and formation of polyester **6** (triangle) were determined by ^{1}H NMR spectroscopy. Molecular weight (M_n) of formed polyester was determined by GPC (circle).

^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 6.83$ (m, CH=CH, *trans*), 6.20 (m, CH=CH, *cis*), 5.10 (m, CHOC=O), 4.98 (m, CHOH), 3.61 (s, OCH_3), 2.25 (m, CH_2CO), 1.77 (m, CH_2CH), 1.50–1.08 (m, CH_2), 0.83 (t, $J = 7.4$ Hz, CH_3) ppm.

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 174.1$ ($COOCH_3$), 164.4 (COOCH), 134.0, and 133.5 (CH=CH, *trans*), 129.9 (CH=CH, *cis*), 74.5 (CHOCO, *cis*), 72.3 (CHOCO, *trans*), 51.3 (OCH_3), 34.0 (CH_2CO), 31.8 (CH_2CHO), 30.4, 29.6–29.0, 25.4, 22.7 (CH_2CH_3), 14.1 (CH_3) ppm.

2.1.5 Representative synthesis of polymer 9 (Table 2, entry 7)

The reaction of epoxide **1** (1.01 mL, 0.92 g, 3.0 mmol) and Diels–Alder adduct **5** (1.22 g, 3.0 mmol) was carried out as described above using 5.8 mg (0.0092 mmol, 0.31%) of (salen)Cr^{III}Cl-catalyst and 8.7 mg (0.031 mmol, 1.04%) of *n*-Bu_4NCl. The reaction mixture was stirred magnetically over night at 142°C and yielded after work-up as described above 0.99 g (46%) of polyester **9**.

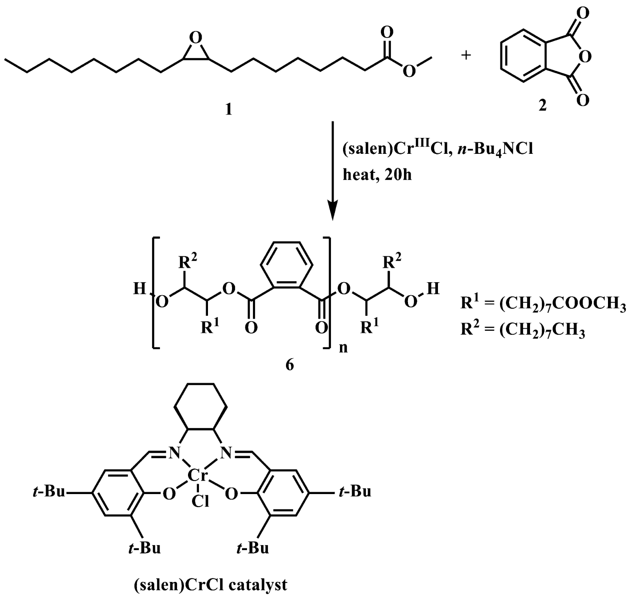
^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 5.72$–5.40 (m, CH=CH), 5.15 (m, CH=CH), 5.00 (m, CHOC=O), 4.85 (m, CHOH), 3.63 (s, OCH_3), 3.00–2.62 (m, CH=CHCHCH=CH), 2.29 (m, CH_2CO), 2.15 (m, CH=$CHCH_2$), 1.65 (m, CH_2), 1.49–1.12 (m, CH_2), 0.87 (t, $J = 7.4$ Hz, CH_3) ppm.

^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 174.1$ ($COOCH_3$), 172.5 (COOCH), 131.5, 129.0, 73.7 (CHOCO), 51.4 (OCH_3), 34.1 (CH_2CO), 31.9 (CH_2CHO), 30.5, 29.5–29.1 (CH_2), 27.8, 25.1, 22.7 (CH_2CH_3), 14.1 (CH_3) ppm.

3 Results and Discussion

The ring-opening copolymerization of equimolar amounts of methyl 9,10-epoxystearate **1** and phthalic anhydride **2** dissolved in toluene was carried out with (salen)Cr^{III}Cl as catalyst and *n*-Bu_4NCl as co-catalyst using the protocol of Darensbourg and coworkers (Scheme 2) [13]. At a reaction temperature of 80°C (used by Darensbourg) no conversion was observed after 24 h. Thus, the temperature was increased to 110°C and after 20 h reaction time polyester **6** was obtained in a yield of 51% (Table 1, entry 1).

This first result indicated that the ring-opening copolymerization of simple epoxides and cyclic anhydrides can also be applied to long chain fatty epoxides such as epoxide **1** with an ester functionality. However, the higher steric demand compared to cyclohexane oxide seems to decrease the reaction rate [13]. Thus, the copolymerization was performed without any additional solvent in order to enhance the reaction rate [14, 21]. In this case, polyester **6** was



Scheme 2. (Salen)Cr^{III}Cl-catalyzed copolymerization of methyl 9,10-epoxystearate **1** with phthalic anhydride **2**.

obtained after a reaction time of 20 h as perfectly alternating copolymer as shown by ^{1}H-NMR spectroscopy in higher yield of 71% (Table 1, entry 2). The molecular weight $M_n = 4650$ g/mol was moderately higher and dispersity of $Đ = 1.19$ was similar compared to the reaction in toluene (Table 1, entries 1 and 2). Moreover, the formation of poly(ester-*co*-ether)s, as reported by Duchateau in bulk reactions [14], was not observed by NMR spectroscopy. Thus, all following reactions were performed without solvent allowing to broaden the temperature window of the reaction significantly.

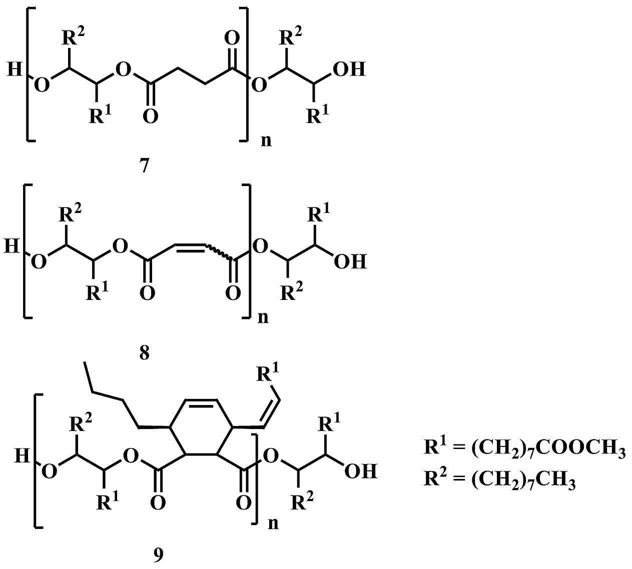
Increasing the reaction temperature to 116, 126, and 142°C gave higher M_n values of 7600, 9600, and up to 10150 g/mol as well as slightly higher dispersities of 1.17, 1.19, and 1.22, respectively, and polyether formation of up to 13% (Table 1, entries 3–5). Elongated reaction times from 20 over 44 up to 92 h gave mostly the same yields of polyester **6**, but increased the molecular weight (M_n) from 7600 to 8850 or even 9100 g/mol. The accompanying higher dispersities of up to 1.5 indicate that after some time and to a very small extent, transesterifications of the pending methyl esters and terminal alcohols intermolecularly take place (Table 1, entries 3, 6, and 7). This observation was confirmed by following the reaction course at 116°C during 72 h by NMR spectroscopy (Figure 1). Epoxide **1** was completely consumed after a reaction time of < 23 h, whereas the M_n increased from 7450 over 7800 to 7900 g/mol after 47 and 72 h reaction time, respectively. The increase in M_n can only be caused by those intermolecular transesterification reactions. The concentration of catalyst and co-catalyst in the range of 0.1–0.5% and 0.1–0.8%, respectively, had only a minor effect on yield, M_n and $Đ$ (Table 1, entries 3, 8–10) as was reported as well by Darensbourg and coworkers [13]. Performing the reaction with only the (salen)Cr^{III}Cl-catalyst or with only n-Bu_4NCl resulted after 70 h in polymers as well, however with 40 or 12% polyether amount, respectively (Table 1, entries 11 and 12). These results have to be contrasted with previous literature reports, where the partial formation of polyethers using either the catalyst [11, 12] or the co-catalyst [13] alone has not been reported.

Thermal analysis of the different synthesized polyesters **6** via DSC revealed only glass transition temperatures, which are summarized in Table 1. Due to the long chain pending groups $R^1 = (CH_2)_7COOCH_3$ and $R^2 = (CH_2)_7CH_3$ low T_g values in the range of −30 up to −21°C were determined.

^{1}H NMR analysis of **6** showed an alternating polyester containing a ratio of [**1**]:[**2**] = 1:1, since the ratio of the integrals of the signals of the four aromatic protons of the phthalate group compared to the two methylene protons at C2-position of the fatty acid methyl ester of R^1 was 2:1. A ratio lower than 2:1 gave clear evidence of the formation of some polyether (Table 1, entries 4, 5, 11, and 12). The two protons of the newly formed secondary esters of the polyester backbone appeared at 5.38 ppm. [13]. Moreover, at 5.15 ppm an additional low intensity signal (<10%) appeared, which can be attributed to the secondary ester proton vicinal to a hydroxyl end group and/or a secondary alkyl ester formed by intermolecular transesterification mentioned above. Interestingly, no carboxy end-group could be observed in the ^{13}C NMR spectra. Thus, polyester **6** exhibits two secondary hydroxyl end-groups as given in Scheme 2.

In analogy, copolymerization reaction of **1** was performed with succinic anhydride **3**, a renewable cyclic anhydride (Table 2, entries 1 and 2; Scheme 3). However, only moderate yields of the corresponding polyester **7** were obtained, showing an average molecular weight (M_n) of 5450 g/mol. Compared to the higher yields as well as higher M_n values of polymer **6**, obtained by the analogous reaction of **1** with phthalic anhydride **2**, it could be assumed that the ring-opening of **2** is favored by a stabilizing effect caused by the conjugated aromatic system, also observed by Duchateau when copolymerizing cyclohexene oxide [14]. Moreover, higher dispersities of 1.45 were observed for copolymer **7**. The glass transition temperature of polyester **7** is about −44°C (Table 2, entries 1 and 2) and thus lower compared to polyester **6**, which has a more rigid backbone due to the aromatic ring.

Maleic anhydride **4** was also copolymerized with epoxide **1** giving polymer **8** with low yield and molecular weight (M_n) of 2400–4750 g/mol and high dispersity of 2.6–2.9 (Table 2, entries 3 and 4; Scheme 3). Polymer **8** was not a pure alternating copolymer but contained polyether in amount of 25–50%, as revealed by ^{1}H NMR analysis. Darensbourg also reported a higher $Đ$ of 2.3 and attributed this observation to a spontaneous photo-dimerization reaction [13]. Interestingly, the *cis*-configured double bond of maleic anhydride was



Scheme 3. Polyesters **7**, **8**, and **9** obtained by copolymerization reactions of methyl 9,10-epoxystearate **1** and succinic anhydride **3**, maleic anhydride **4**, and Diels–Alder adduct **5**, respectively (Scheme 1).

isomerized during the reaction to a [*cis*]/[*trans*]-mixture in -polyester **8** (Table 2, entries 3 and 4). This isomerization had not been observed in typical polymerizations of epoxides and anhydrides, but can be ascribed to the relatively high temperature used in our experiments [12] [13].

Diels–Alder adduct **5** was synthesized by addition of maleic anhydride to the conjugated *trans*-double bonds of methyl α-eleostearate (methyl 9-*cis*, 11, 13-*trans*-octadecatrienoate) [20], and was used as a bio-based cyclic anhydride in the copolymerization with epoxide **1**. The reaction was performed at temperatures in the range of 112–198°C and a reaction time of 20 h (Table 2, entries 5–10). However, the isolated yields were only moderate. The steric effect of the long chain alkyl groups in both substrates seems to hinder the reaction considerably, though the reaction proceeds smoothly at higher temperature of 198°C, however, forming some polyether (<20%). The obtained molecular weight (M_n) doubled from $M_n = 2250$ g/mol at 112°C to $M_n = 5050$ g/mol at 198°C (Table 2, entries 5 and 10). The glass transition temperature could not be determined for all samples due to their low molecular weight (Table 2, entries 5–8). Nevertheless, polymers obtained at higher reaction temperatures of 158 and 198°C showed a T_g of about -40 and thus 20°C, lower than polymer **6** because of pending alkyl groups in both monomers.

4 Conclusions

We have reported the alternating ring-opening copolymerization of methyl 9,10-epoxystearate **1** with various cyclic acid anhydrides **2**–**5** to afford polyesters of narrow molecular weight distributions using a (salen)Cr^{III}Cl-catalyst in the presence of *n*-Bu_4NCl. The polyesters are made up of a high percentage of renewable carbon, from 66% in polyester **6** over 76% in polyester **9** to 95% in polyester **7**. The pending long chain alkyl groups introduced in the polyesters by the fat derived substrates attribute amorphous properties to the polymers. Various fatty epoxides are easily available and open up the possibility for the synthesis of new highly branched polyesters.

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