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Polymers of carbonic acid 29. Bu_2SnOct_2—initiated polymerizations of trimethylene carbonate (TMC, 1,3-dioxanone-2)

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Abstract

Model reactions between neat Bu_2SnOct_2 and benzylalcohol suggest that no exchange occurs at temperatures ≤60°C. However, at 100°C a slow esterification process yielding benzyl octanoate and Sn–OH groups takes place. Bu_2SnOct_2 is a little less reactive than $SnOct_2$, but polymerizes trimethylene carbonate (TMC) at 80°C. Addition of benzylalcohol accelerates the polymerization process and allows controlling the molecular weight via the TMC/alcohol ratio. The resulting poly TMC contains the stoichiometric quantity of benzyl carbonate endgroups. Neat Bu_2SnOct_2 reacts above 120°C with TMC by transesterification and formation of octanoate endgroups. However, a satisfactory control of M_n via the M/I ratio is not possible, and the "backbiting" degradation competes with the polymerization process at high conversions.

Keywords: Ring-opening polymerization; Trimethylene carbonate; Dibutyltin octanoate

1. Introduction

Sn(II)2-ethylhexanoate, $SnOct_2$, is the most widely used initiator for the technical production of polylactides and copolyesters of lactic acid. Therefore, an increasing number of research groups has recently contributed numerous preparative and mechanistic studies to the application of $SnOct_2$ as initiator for lactides and lactones. Further, we have previously shown [1–7] that $SnOct_2$ is also a good and useful initiator for ring-opening polymerizations of aliphatic cyclocarbonates. In the preceding part of this series a preparative and mechanistic study dealing with $SnOct_2$ and trimethylene carbonate (TMC) was presented in Ref. [7]. $SnOct_2$-initiated copolymerizations of TMC and ϵ-caprolactone, glycolide and lactide were described by several research groups [8–15]. Further, it is known that Sn(IV) compounds such as $SnCl_4$, $BuSnCl_3$, Bu_2SnCl_2 or Bu_3SnCl are good or even better initiators for aliphatic cyclocarbonates than $SnOct_2$ [16,17]. The missing link between these Sn(IV) halides and $SnOct_2$ is Bu_2SnOct_2. To the best of our knowledge nothing has been reported on the Bu_2SnOct_2 initiated polymerization of cyclocarbonates and only little is known [18] about the Bu_2SnOct_2-initiated polymerizations of lactones. Therefore, the present work was designed as a first approach to understand the Bu_2SnOct_2-initiated polymerizations of TMC better.

2. Experimental

2.1. Materials

TMC, 1,3-dioxanone-2 was a gift of Boehringer KG (Ingelheim/Rhein, FRG). It was recrystallized from ethyl acetate and stored in a exsiccator prior to use. Bu_2SnOct_2 was purchased from Aldrich (Milwaukee, WI, USA). It was used as received because recrystallization from non-polar solvents was not successful due to the good solubility in ligroin. Distillation in a vacuum of 10^{-3} mbar over a short-path apparatus also failed. Benzylalcohol (from Aldrich) was fractionated in vacuum of 10^{-1} mbar and the high boiling fraction was used. Chlorobenzene was distilled over P_4O_{10}. Bu_2SnO and adipic acid were purchased from Aldrich and used as-received.

2.2. Time/conversion curves

1. With neat Bu_2SnOct_2 (Figs. 2 and 3) or neat $SnOct_2$ (Fig. 3). The reaction mixtures were prepared from recrystallized TMC (30 mmol) and a 1 M solution of Bu_2SnOct_2 in dry chlorobenzene (or a 1 M solution of $SnOct_2$ in dry chlorobenzene). Dry chlorobenzene was

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Table 1
Bu_2SnOct_2-initiated and Bzl–OH-coinitiated (Bu_2SnOct_2/benzylalcohol ratio 1:2) polymerizations of TMC in chlorobenzene at 80°C

Exp. no.	Mon./init.	Time (h)	Yield (%)	η_{inh} (dl/g)[a]	DP ($-CH_2-OH$)[b]	DP ($-CH_2-Ph$)[b]
1	40	48	60	0.11	60	54
2	60	48	70	0.13	80	67
3	100	48	74	0.18	95	110
4	150	48	74	0.21	110	145
5	200	48	87	0.26	130	180
6	300	48	91	0.29	155	240
7	500	48	94	0.37	240	370

[a] Measured at 20°C with c = 2 g/l in CH_2Cl_2.
[b] ^1H NMR spectroscopic endgroup analyses.

added, so that the total volume of all experiments was 8 ml (= 3.75 mol/l TMC) and the reaction mixture was thermostated at 80°C. From time to time (see Figs. 2 and 3) a sample was taken from the reaction mixture by means of a syringe (via a septum) diluted with $CDCl_3$ and a ^1H NMR spectrum was recorded immediately afterwards.

2. With a Bu_2SnOct_2/benzylalcohol mixture (Fig. 2). TMC (30 mmol), 2.0 ml chlorobenzene and 3 ml of a chlorobenzene solution 1 M in Bu_2SnOct_2 and 2 M in benzylalcohol were mixed and thermostated at 80°C. From time to time a sample was removed by means of a syringe, diluted with $CDCl_3$ (approx. 1:4 by volume) and a ^1H NMR spectrum was recorded immediately afterwards.

All reaction mixtures were prepared under dry nitrogen and reaction vessels with silanized glass walls (pretreated with Me_2SiCl_2 in CH_2Cl_2) were used.

2.3. Polymerizations of Tables 1 and 2

TMC (30 mmol), a 1 M solution of Bu_2SnOct_2 in chlorobenzene, a 2 M solution of benzylalcohol in chlorobenzene and additional chlorobenzene were mixed so that the final volume of the reaction mixture reached 8 ml. The reaction vessel was closed with a glass stopper and steel spring and thermostated at 80°C. After cooling the reaction mixture was diluted with CH_2Cl_2 (30 ml) and precipitated into cold (+5°C) methanol. The polycarbonates were isolated by filtration and dried at 40°C in vacuo.

2.4. Polymerizations of Fig. 4

TMC (30 mmol) and neat Bu_2SnOct_2 were mixed and the closed reaction vessel was thermostated at 120°C for 24 h. After rapid cooling with ice a ^{13}C NMR spectrum was recorded in $CDCl_3$. Analogous experiments were conducted at 140, 160 and 180°C. ^{13}C NMR spectra were recorded directly from the virgin reaction mixtures.

2.5. Measurements

The inherent viscosities were measured with an Ubbelohde viscometer thermostated at 25°C in CH_2Cl_2. The 100 MHz ^1H NMR and the 25.2 MHz ^{13}C NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 or 10 mm o.d. sample tubes using $CDCl_3$/TMS as solvent and shift reference. The 400 MHz ^1H NMR spectra were recorded with a Bruker AM-400 FT NMR spectrometer in 5 mm o.d. sample tubes using $CDCl_3$/TMS as solvent and shift reference. The GPC measurements were conducted at 30°C with a Kontron HPLC/GPC apparatous equipped with a Waters differential diffractometer Md 410. Four polystyrene-filled columns having pore sizes of 10^2, 10^3, 10^4 and 10^5 Å were used and tetrahydrofuran served as eluent.

Table 2
Bu_2SnOct_2-initiated and Bzl–OH coinitiated polymerizations of TMC in chlorobenzene (TMC/Bu_2SnOct_2 = 500: 1)

Exp. no.	TMC/Bzl–OH	Time (h)	Yield (%)	η_{inh} (dl/g)[a]	DP ($-CH_2-OH$)[b]	DP ($-CH_2-Ph$)[b]
1	40	48	69	0.16	43	50
2	60	48	50	0.21	60	50
3	100	48	90	0.27	85	110
4	150	48	90	0.29	130	150
5	200	48	94	0.32	170	195
6	300	48	98	0.42	200	285

[a] Measured at 20°C with c = 2 g/l in CH_2Cl_2.
[b] ^1H NMR spectroscopic endgroup analyses.

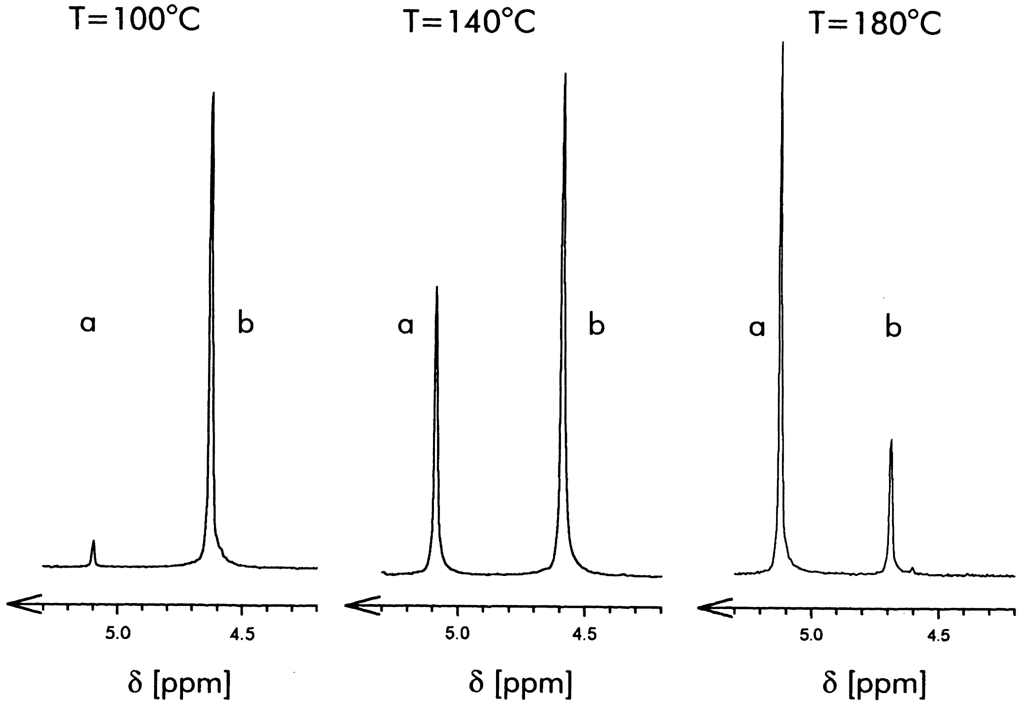


Fig. 1. ^{1}H NMR spectrum (100 MHz) of the reaction mixtures obtained from neat Bu_2SnOct_2 and benzylalcohol after 24 h. Signal "a" represents the $O{-}CH_2$ group of benzyl octanoate, signal "b" represents the $O{-}CH_2$ group of free benzyl alcohol.

3. Results and discussion

3.1. Bu_2SnOct_2/benzylalcohol-initiated polymerizations

The commercial Bu_2SnOct_2 was used as received, because its good solubility in ligroin prevented a recrystallization from nonpolar solvents and because it decomposed upon distillation in a vacuum of 10^{-3} mbar. It also decomposed when its purity was checked by gas chromatography. However, the 400 MHz ^{1}H NMR spectrum and elemental analyses were in agreement with a pure compound of the expected structure.

In analogy with previous studies of $SnOct_2$ the reaction of Bu_2SnOct_2 with neat benzylalcohol (a potential coinitiator) was studied first. Whereas a rapid exchange of octanoic acid and benzylalcohol (Bzl–OH) was found for $SnOct_2$ at 20°C (Eqs. (1) and (2)) [7,19], such an equilibration was not detectable for Bu_2SnOct_2 in $CDCl_3$ up to 60°C. This comparison clearly demonstrates a considerably lower reactivity of the Bu_2SnOct_2 and raises the question if the higher stability of Bu_2SnOct_2 has a kinetic or a thermodynamic origin. In this connection the well-known syntheses of Bu_3Sn acetate and higher carboxylates should be mentioned [20]. The Bu_3Sn carboxylates are easily prepared from Bu_3SnCl and sodium salts of carboxylic acids in the presence of water or alcohols. These syntheses clearly demonstrate that the Bu_3Sn carboxylates are thermodynamically much more stable than the alkoxides or hydroxide. Obviously the same tendency exists for Bu_2SnOct_2.

$$SnOct_2 + BzlOH \rightleftharpoons OctSnOBzl + OctOH \quad (1)$$

$$OctSnBzl + BzlOH \rightleftharpoons Sn(OBzl)_2 + OctOH \quad (2)$$

$$Bu_2SnOct_2 + BzlOH \rightleftharpoons Bu_2Sn(Oct)OBzl + OctOH \quad (3)$$

$$Bu_2Sn(Oct)OBzl + BzlOH \rightleftharpoons Bu_2Sn(OBzl)_2 + OctOH \quad (4)$$

When mixtures of neat Bu_2SnOct_2 and Bzl–OH (molar ratio 1:2) were heated to 60, 100, 140 and 180°C for 24 h no reaction was detected at 60°C. However, at 100°C the formation of 1–2% of benzyl-2-ethylhexanoate was found and at 140 or 180°C much higher conversions were observed as demonstrated by the ^{1}H NMR spectra of Fig. 1. In this connection it should be mentioned that benzyl-2-ethylhexanoate was also synthesized from Bzl–OH and 2-ethylhexanoylchloride (with pyridine) so that both the ^{1}H and ^{13}C NMR signals were available for an unambiguous identification.

The esterification of the alcohol with octanoate groups has far reaching consequenses for the reactivity of the tin initiator. The first consequence is a formation of Sn–OH groups (Eqs. (5) and (6)) which are like Sn-alkoxides far more reactive towards lactones or cyclocarbonates than the $Sn{-}O_2C{-}R$ groups. Secondly, the tinhydroxides can undergo a variety of postreactions such as the elimination of octanoic acid (Eq. (7)) or the elimination of water (Eq. (8)). Further, an equilibration with unreacted benzylalcohol

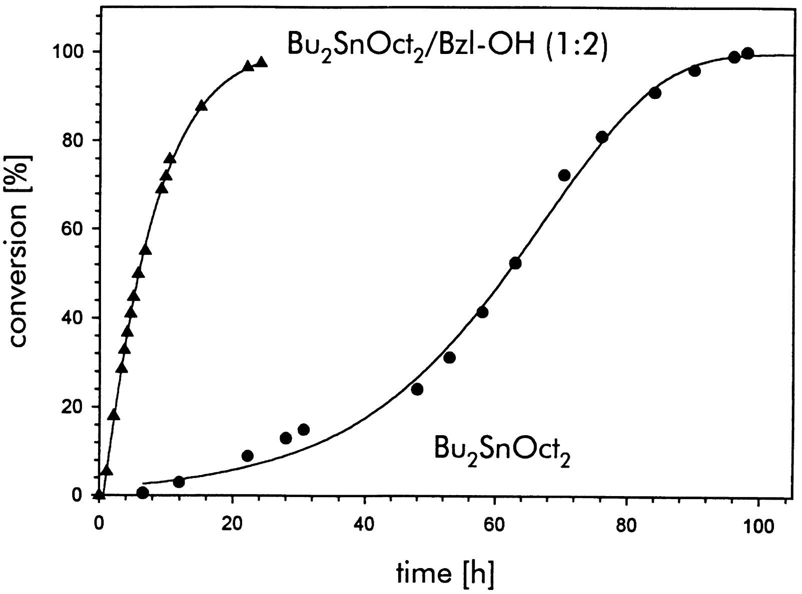


Fig. 2. Time conversion curves of Bu_2SnOct_2-initated polymerizations of TMC in chlorobenzene at 80°C with and without addition of benzyl alcohol.

may be assumed yielding Sn-alkoxide groups (Eqs. (9) and (10)). Altogether the partial esterification of an alcohol added as coinitiator has the consequence that three kinds of active species may be generated, which can initiate the polymerization of TMC (or lactones) according to the established coordination–insertion mechanism [21,22] outlined for tin alkoxides in Eqs. (11) and (12). These three kinds of active species are: Bu_2Sn-hydroxides, Bu_2Sn-alkoxides and the stannoxane bonds in the oligomeric Bu_2SnO

$$Bu_2SnOct_2 + BzlOH \rightarrow Bu_2Sn(Oct)OH + BzlOct \quad (5)$$

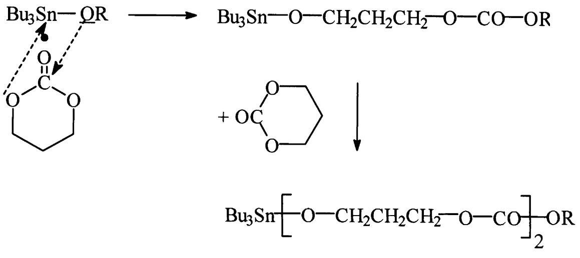
$$Bu_2Sn(Oct)OH + BzlOH \rightarrow Bu_2Sn(OH)_2 + BzlOct \quad (6)$$

$$Bu_2Sn(Oct)OH \rightarrow Bu_2SnO + OctOH \quad (7)$$

$$Bu_2Sn(OH)_2 \rightarrow Bu_2SnO + H_2O \quad (8)$$

$$Bu_2Sn(Oct)OH + BzlOH \rightleftharpoons Bu_2Sn(Oct)OBzl + H_2O \quad (9)$$

$$Bu_2Sn(OH)_2 + 2BzlOH \rightleftharpoons Bu_2Sn(OBzl)_2 + 2H_2O \quad (10)$$



(11)

(12)

In order to elucidate the role of benzylalcohol as coinitiator three series of polymerizations were conducted. The first series served as basis for time/conversion measurements and the results were summarized in Fig. 2. This figure allows a comparison between polymerizations initiated with neat Bu_2SnOct_2 and polymerizations initiated with a Bu_2SnOct_2/benzylalcohol mixture (molar ratio 1:2). All other experimental parameters were kept constant. A significant acceleration by the added benzylalcohol is clearly observable. This acceleration suggests that at 80°C at least a slow and partial exchange of octanoate versus benzyloxide groups takes place according to Eqs. (3) and (4). This suggestion is supported by the NMR-spectroscopic detection of benzyl carbonate endgroups in a poly (TMC) isolated after 80 h at 80°C. These benzyl carbonate endgroups must have been formed by a tin catalyzed reaction such as the initiation of TMC by Bu_2Sn (Oct) OBzl (analogous to Eq. (11)), because neat benzylalcohol does not attack poly TMC at 80°C within 48 h as reported in the preceding study dealing with $SnOct_2$ [7].

Another typical effect of a coinitiator is its influence on the molecular weight. Two series of polymerizations summarized in Tables 1 and 2 illustrate this influence for benzylalcohol. The polymerizations listed in Table 1 were conducted in such a way that the Bu_2SnOct_2/Bzl–OH ratio was maintained at 1:2, whereas the TMC/Bu_2SnOct_2 ratio was varied. In the ideal case the resulting degrees of polymerization calculated from the ^1H NMR end-group signals should amount to 50% of the M/I ratio. The experimental data listed in the last column of Table 1 show higher values, possibly because not all benzylalcohol has reacted. Further, a fractionation upon precipitation must be taken into account for the samples prepared with M/I ratios ≤ 150. Somewhat surprising is the observation that the DPs calculated from the ^1H NMR signals of the CH_2OH endgroups are lower. Since the methanol used for the precipiation of the poly TMC does not cleave the carbonate groups there are two potential explanations. First, a small

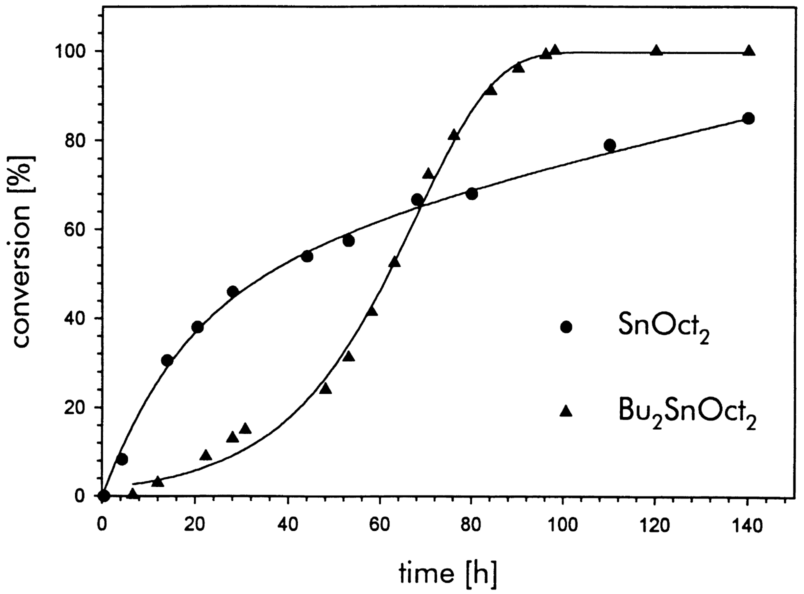


Fig. 3. Time conversion curves of $SnOct_2$ and Bu_2SnOct_2 initiated polymerizations ($M/I = 10/1$) in chlorobenzene at 80°C.

amount of humidity was present, despite the drying of all components and reactants (TMC is highly polar and may bind H_2O on its surface) so that a small percentage of poly TMC chains having the structure **1** were formed. Second, a small part of the TMC was initiated by octanoate groups (see discussion below) so that chains of structure **3** were formed in addition to those of structure **1** and **2**.

The polymerizations compiled in Table 2 are based on a TMC/Bu_2SnOct_2 ratio fixed at 500:1 were as the TMC/BzlOH ratio was varied. These polymerizations yielded a satisfactory agreement between the DPs calculated from the benzyl carbonate endgroups and the feed ratio of TMC and BzlOH. However, the DPs calculated from the CH_2OH endgroups were again lower, proving the reproducibility of the trend derived from the data of Table 1. None the less, all these results clearly demonstrate that the alcohol plays the role of a coinitiator allowing for a certain control of the molecular weight.

$HO–(CH_2)_3–O–[–OC–O–(CH_2)_3–O–]–H$

1

$HO–(CH_2)_3–O–[–CO–O–(CH_2)_3–O–]–CO–O–CH_2C_6H_5$

2

$HO–(CH_2)_3–O–[–CO–O–(CH_2)_3–O–]–CO–C_7H_{15}$

3

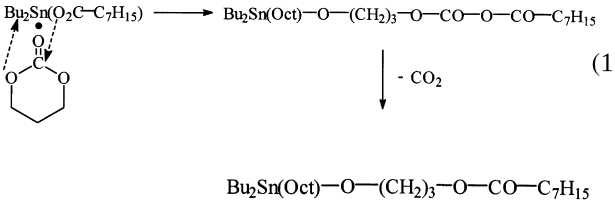
$HO–(CH_2)_3–O–[–OC–O–(CH_2)_3–O–]_x–CO–C_7H_{15}$

4

3.2. Initiation by neat Bu_2SnOct_2

The time conversion curve presented in Fig. 3 already demonstrates that neat Bu_2SnOct_2 is reactive enough to initiate a polymerization of TMC at 80°C in the absence of a purposely added coinitiator. In a previous study dealing with polymerizations of L-lactide in bulk at 120°C [18] Bu_2SnOct_2 was found to be less reactive than $SnOct_2$ and at M/I ratios > 20 the conversion was far from completion after 24 h. In the present work a more accurate comparison was conducted. A $SnOct_2$ initiated polymerization of TMC was performed at 80°C in chlorobenzene under exactly the same conditions. The resulting time conversion curve is displayed in Fig. 3 together with the time conversion curve of the Bu_2SnOct_2-initiated polymerization. Both curves show an amazing difference in the kinetic course of these polymerizations. Bu_2SnOct_2 is considerably less reactive in the early stage of the polymerization ($<20\%$ conversion) but a tremendous acceleration has the consequence that above 50% conversion the Bu_2SnOct_2-initiated polymerization is more rapid.

The relatively slow initiation combined with a conspicuous acceleration of the Bu_2SnOct_2 polymerization may be explained by the following hypothesis. In the case of $SnOct_2$ HO-containing impurities may play the role of coinitiators, so that the initiation and propagation follow the scheme in Eqs. (1), (11) and (12). In the case of Bu_2SnOct_2 which is less reactive towards R–OH compounds another initiation step may play a predominant role namely the insertion of the TMC into the Sn-carboxylate bond (which is covalent, Eq. (13)). The decarboxylation of the resulting mixed anhydride (Eq. (14)) renders this step irreversible. The insertion of TMC into the resulting Sn-alkoxide bond (according to Eq. (11)) has a lower energy of activation. Hence, this process is slow in the beginning but the increasing number of Sn-alkoxide bonds causes acceleration.



(13)

(14)

If this hypothesis is correct, the poly TMC resulting from the initiaton process of Eqs. (13) and (14) should contain octanoate ester endgroups (structure **4**). In order to check the formation of those endgroups a series of model reactions was performed. TMC and Bu_2SnOct_2 were mixed in a molar ratio of 10: 1 and heated in bulk either to 80, to 100, 120, 140, 160 or 180°C. The low *M*/*I* ratio was selected to allow for a ^{13}C NMR spectroscopic inspection of the reaction mixture (the ^{13}C NMR chemical shifts are listed in Table 3). At 80, 100 and 120°C no octanoate groups were detected after 24 h and the most of the initiator was unchanged (Fig. 4). However, at 140°C a small amount (approx. 10%) of ester groups was detectable and at 160 or 180°C a complete conversion was obtained. These measurements suggest the existence of an insertion mechanism according to Eqs. (13) and (14) at high temperatures, but they do not prove it for low temperatures such as 80°C. However, the sensitivity of the ^{13}C NMR measurements was relatively low and even 4% of ester groups were certainly not detectable. Therefore, the results of Fig. 4 do not disprove a slow initiation according to Eqs. (13) and (14) at 80°C.

Table 3
Chemical shifts (δ) of ^{13}C NMR CO-signals (in $CDCl_3$/TMS)

Compound	δ (ppm)
Bu_2Sn(2-ethylhexanoate)	187.0
2-Ethylhexanoic acid	183.6
Benzyloctanoate	175.7
Octanoate endgroups	176.2
TMC	148.4
Poly TMC	154.8

The quantitative formation of octanoate endgroups at 160°C prompted us to study Bu_2SnOct_2-initiated polymerizations of TMC at 160°C in bulk with variation of the *M*/*I* ratio. The conditions and results of these polymerizations were summarized in Tables 4 and 5. Nearly identical yields corresponding to conversions around 95% were obtained in all experiments. The viscosities (Table 4) and the number average molecular weights (M_ns, Table 5) show a continuous increase with the *M*/*I* ratio, but the slope is much more

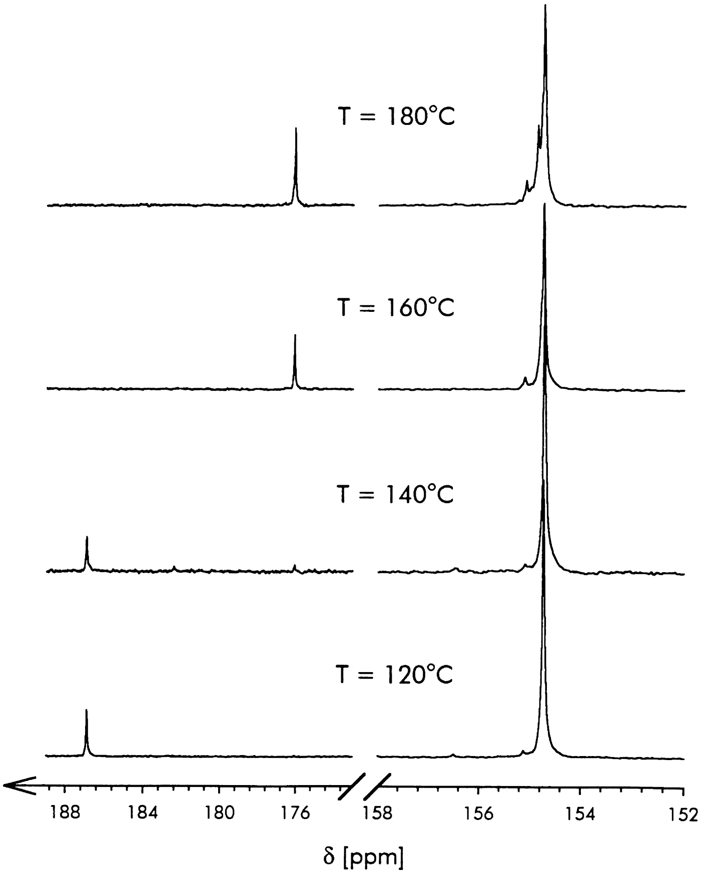


Fig. 4. ^{13}C NMR spectra (CO-signals) of the virgin reaction mixtures of TMC and neat Bu_2SnOct_2 (molar ratio 10: 1) recorded after 24 h.

Table 4
Bu_2SnOct_2-initiated polymerizations of TMC in bulk at 160°C

Exp. no.	Mon./init.	Time (h)	Yield (%)	η_{inh} (dl/g)[a]	DP ($-CH_2-OH$)[b]	DP ($-CH_3$)[b]
1	50	1.5	93	0.44	270	230
2	100	1.5	90	0.48	275	450
3	150	1.5	93	0.52	310	380
4	200	2.0	88	0.54	270	680
5	300	2.5	88	0.55	350	770
6	500	3.0	90	0.57	360	900
7	1000	3.0	90	0.58	350	920

[a] Measured at 20°C with $c = 2$ g/l in CH_2Cl_2.
[b] ^1H NMR spectroscopic endgroup analyses.

Table 5
GPC measurements of the poly TMC samples listed in Table 4

Exp. no.	Mon./init.	M_n (theor.)[a]	M_n (GPC)[b]	M_w/M_n (GPC)[b]	M_n (GPC)[c]	M_w/M_n (GPC)[c]
1	50	2650	19 900	1.68	16 200	1.66
2	100	5200	22 400	1.69	17 700	1.71
3	150	7800	24 800	1.60	19 600	1.63
4	200	10 300	26 700	1.56	21 800	1.54
5	300	15 400	28 000	1.57	22 000	1.57
6	500	25 600	30 000	1.49	23 900	1.51
7	1000	51 000	32 100	1.45	24 600	1.51

[a] Calculated from the M/I ratio and 100% conversion.
[b] GPC measurements in THF at 30°C calibrated with Eq. (15) [21].
[c] GPC measurements in THF at 30°C calibrated with Eq. (16) [22].

Table 6
Bu_2SnOct_2-initiated polymerizations of TMC in bulk at 160°C with variation of the reaction time

Exp. no.	Time (h)	Yield (%)	η_{inh} (dl/g)[a]	DP ($-CH_2-OH$)[b]	DP ($-CH_3$)[b]
1	1	92	0.65	430	760
2	2	93	0.79	560	1200
3	4	92	0.59	410	820
4	8	86	0.49	300	780
5	16	84	0.41	230	590
6	24	79	0.31	160	430

[a] Measured at 25°C with $c = 2$ g/l in CH_2Cl_2.
[b] ^1H NMR spectroscopic endgroup analyses.

Table 7
Molecular weight measurements of the poly TMC samples listed in Table 6

Exp. no.	Time (h)	M_n (theor.)[a]	M_n (GPC)[b]	M_w/M_n (GPC)[b]	M_n (GPC)[c]	M_w/M_n (GPC)[c]
1	1	25 600	38 800	1.54	31 400	1.62
2	2	25 600	40 800	1.51	34 300	1.49
3	4	25 600	27 000	1.64	27 000	1.50
4	8	25 600	26 400	1.43	20 700	1.46
5	16	25 600	21 100	1.46	16 300	1.47
6	24	25 600	14 000	1.55	10 700	1.58

[a] Calculated from the M/I ratio with 100% conversion.
[b] GPC measurements in THF at 30°C calibrated with Eq. (15) [21].
[c] GPC measurements in THF at 30°C calibrated with Eq. (16) [22].

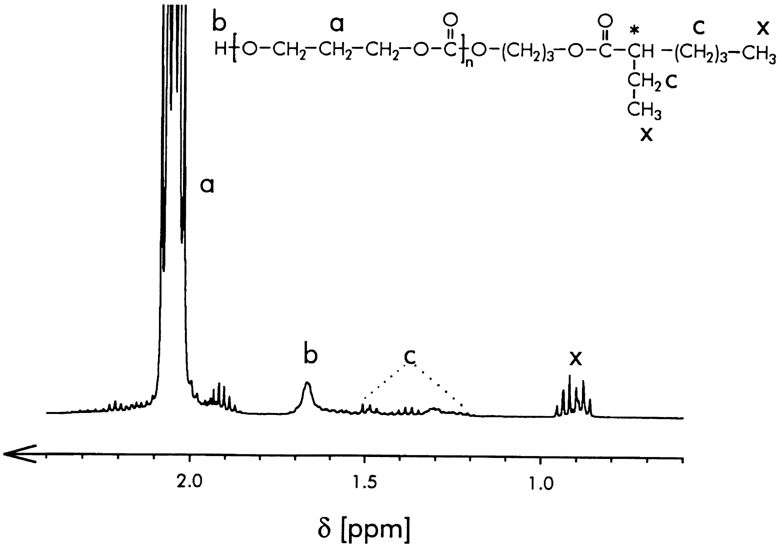


Fig. 5. ${}^{1}H$ NMR spectrum (400 MHz) of a Bu_2SnOct_2 initiated poly TMC prepared with *M/I* = 50 in bulk at 160°C (No. 1, Table 4).

flat. In this connection it should be explained that the GPC measurements were calibrated in two ways, firstly with polystyrene using the K and a values of the Mark Houwink equation (15) [23]; and secondly, with the Mark Houwink equation (16) [24] published for poly TMC. Calibration with polystyrene is the international standard procedure, but in the case of poly TMC (and poly caprolactone) calibration with pertinent Mark Houwink equations seems to give more realistic lower molecular weight data.

$$[\eta] = 1.25 \times 10^{-4} \times M^{0.717} \quad (15)$$

$$[\eta] = 2.77 \times 10^{-4} \times M^{0.677} \quad (16)$$

All poly TMC samples listed in Table 4 contained octanoate endgroups as revealed by ${}^{1}H$ NMR spectroscopy and illustrated in Fig. 5. The ${}^{1}H$ NMR endgroups analyses and the DPs derived from them confirmed an upward trend with incrasing *M/I* ratios (Table 4), but it does not parallel the *M/I* ratios (Fig. 6). Further, the content of octanaote was considerably lower than expected from a quantitative reaction of both Oct. groups of the initiator. In contrast the DPs and M_ns determined from the CH_2OH endgroups showed an acceptable agreement with the M_ns derived from polystyrene calibrated GPC measurements. These endgroup analyses confirmed the relatively flat increase of the M_ns and clear deviation from a parallel to the *M/I* ratio (see Fig. 6). Obviously, the entire

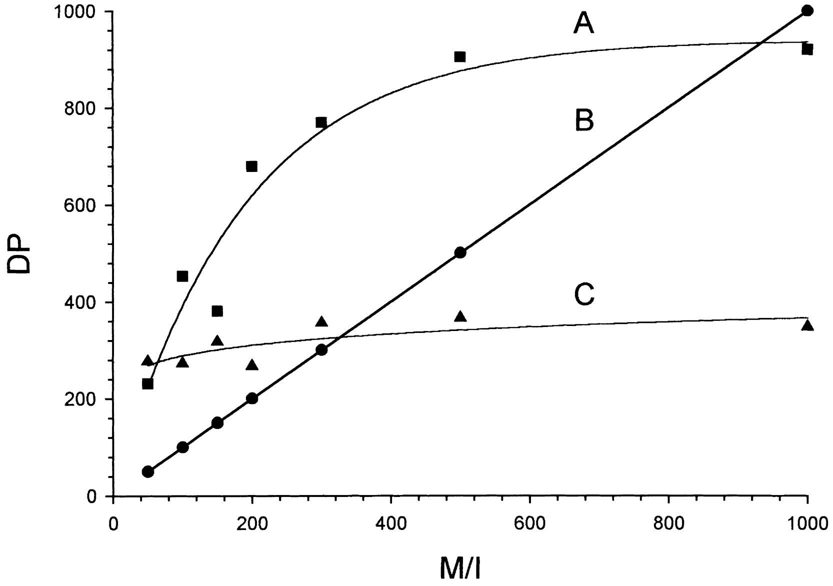


Fig. 6. Bu_2SnOct_2-inititated polymerizations of TMC in bulk at 160°C (Table 4). Dependency of $\overline{DP}$'s determined from ${}^{1}H$ NMR spectroscopic endgroup analyses. A: $\overline{DP}$ calculated from CH_2–OH endgroups. B: $\overline{DP}$ calculated from the *M/I* ratio and 100% conversion. C: $\overline{DP}$ calculated from CH_3 endgroups.

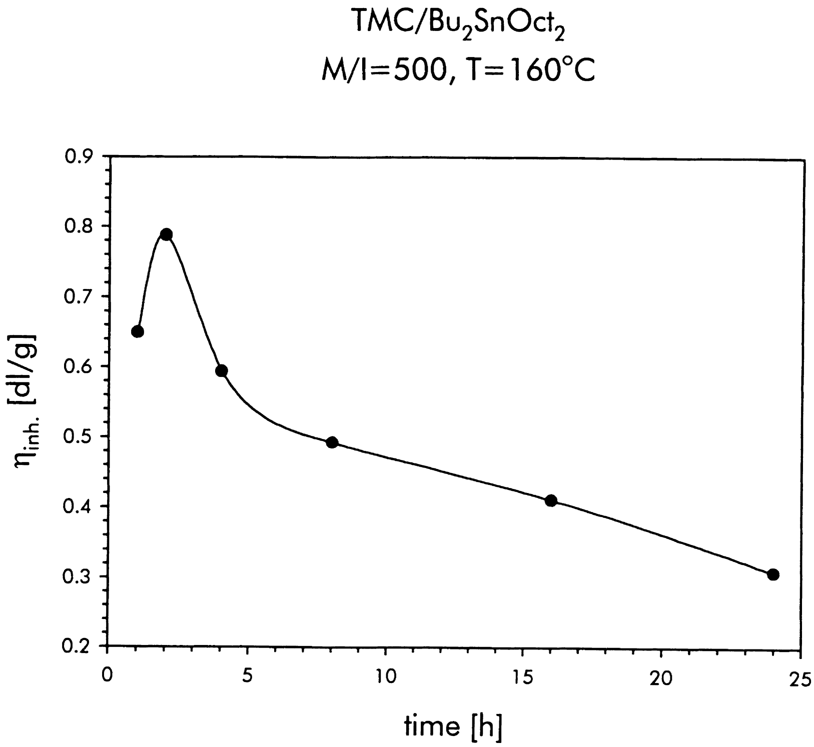
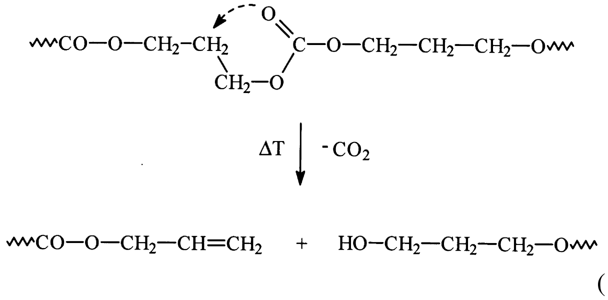


Fig. 7. Bu_2SnOct_2-inititated polymerizations of TMC in bulk at 160°C. Influence of the reaction time on the viscosity.

polymerization process is relative complex and not in good agreement with the simple scheme in Eqs. (11)–(14).

In this connection it should be mentioned that a similar study based on $SnOct_2$ as initiator was reported in the proceeding part of this series [7]. In that study the M_ns derived from both endgroup analyses and GPC measurements displayed a nearly perfect parallel to the *M*/*I* ratio. Therefore, the results presented here in Table 4 and 5 demonstrate again that the kinetic course of $SnOct_2$ and Bu_2SnOct_2 initiated polymerizations of TMC are different despite similar reactivities. The high reactivity of Bu_2SnOct_2 towards TMC is underlined by the short reactive times (1.5–2.0 h) needed for almost complete conversions (Table 4).

In order to elucidate to what extent polymerizations of TMC at 160°C are affected by backbiting degradation an additional series of polymerization was performed. Again neat Bu_2SnOct_2 was used in bulk at 160°C and the *M*/*I* ratio was fixed at 500:1. Now the reaction time was varied and its influence on the viscosities and molecular weights (from GPC measurements) was determined (Tables 6 and 7). Fig. 7 and the data of Tables 6 and 7 indicate that the molecular weights peak around 2 h followed by a steady decrease with longer times. On the basis of these results the times selected for the polymerizations of Tables 4 and 5 were restricted to a range of 1.5–3.0 h. Similar results were previously found for $SnOct_2$ illustrating again similar reactivities of the Sn–O–CH_2 endgroups in the TMC/poly TMC system. However, the most surprising result of this series of polymerizations is the finding that the number of CH_2–OH endgroups seemingly increases. A formal loss of endgroups due to the fractionation upon precipitation of the poly TMC does not explain the steep decrease of the $\overline{DP}$ determined from CH_2–OH endgroups, because the yields only decrease by 15%. In other words a degradation reaction generating CH_2–OH endgroups seems to exist. The *cis*-β-elimination outlined in Eq. (17) offers a hypothetical explanation, but the allyl ether endgroup resulting from this elimination was not detected in the ^{1}H NMR spectra. In summary, this first study of Bu_2Sn carboxylate-initiated polymerizations of TMC (or other cyclocarbonates) raises more questions about the mechanism than it can answer, but this is typical for a first step into a complex area.



(17)

4. Conclusions

From the present work it may be concluded that

Bu_2SnOct_2 is a reactive initiator for the ring-opening polymerization of TMC. Its reactivity is in principle comparable with that of $Sn(II)Oct_2$, but details of the initiation process and of the kinetic course of the polymerization are quite different. Polymerizations conducted below 100°C are coinitiated by alcohols that accelerate the entire polymerization process and allow for a control of the molecular weights. The resulting polycarbonates contain carbonate endgroups derived from the coinitiator, but no octanoate endgroups. Above 120°C the polymerizations take a different course and rapid esterification of octanoate residues yields polycarbonates having nearly stoichiometric amounts of octanoate endgroups. However, the M_ns do not parallel the monomer/initiator ratio indicating a complex polymerization mechanism which certainly deserves further investigations.

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