High Molar Mass Poly(trimethylene carbonate) by Ph2BiOEt and Ph2BiBr-Initiated Ring-Opening Polymerizations

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Trimethylene carbonate, (TMC), was polymerized in bulk with Ph_2BiOEt or Ph_2BiBr as initiators. The dependence of the molecular weight on the monomer-initiator ratio (M/I) and the MALDI-TOF (MT) mass spectra suggest that these polymerizations obey a coordination-insertion mechanism. Due to "back-biting" cyclic oligomers were also formed. With Ph_2BiBr particularly high molecular weights were achieved (number averages, M_ns, up to 340×10^3 Da), but the M_ns were significantly higher than the M/Is. However, a satisfactory control of M_n was achieved by addition of tetraethylene glycol as coinitiator. In the case of Ph_2BiOEt the M_ns fell below the M/Is and only a crude control of the M_ns was achieved. Both Bi-compounds were more reactive than Sn(II)2-ethylhexanoate ($SnOct_2$) activated with ethanol. This difference was particularly conspicuous at temperatures below 100°C.

Keywords: poly(trimethylene carbonate), ring-opening polymerization, bismuth catalysts

1 Introduction

Aliphatic carbonates differ from aliphatic polyesters by a lower electrophilicity of the CO group what means that they are less sensitive to hydrolytic degradation. This property entails two applications. Amorphous homo- or copolycarbonates serve as soft segments in thermoplastic elastomers designed for application in hot humid climates (aliphatic polyethers are even less sensitive to hydrolysis, but they are more hygroscopic and more sensitive to oxidation). The lower sensitivity to hydrolysis may also be useful for pharmaceutical and biomedical application, when a slow resorption in the human body is desired. Copolymers containing aliphatic carbonate and ester groups allow for a fine tuning of the rate of biodegradation. For all these reasons ring-opening polymerization of trimethylene carbonate, TMC, (and other cyclocarbonates) has been studied by several research groups (1–20).

In this context, the present work has the purpose to report on Ph_2BiOEt- and Ph_2BiBr-initiated homopolymerizations of TMC. Ring-opening polymerizations of lactones initiated (or catalyzed) by Bi(III) salts were studied by Kricheldorf and coworkers over the past five years

(21–28). Bi(III) salts such as $BiCl_3$, Bi_2O_3, Bi-acetate or Bi-subsalicylate combine three important advantages: they are commercial, stable on storage and possess the lowest toxicity of all heavy metal salts. However, all attempts to prepare high molar mass polylactones (meaning number average molecular weights, M_ns, > 50 000 Da) failed. In contrast, Ph_2BiOEt(27) and Ph_2BiBr(28) (the toxicity of which in unknown) were recently found to allow for the preparation of poly(ε-caprolactone)s with M_ns in the range of 10^{-5} to 5×10^5 Da (and M_w up to 8×10^5 Da). Furthermore, it was surprisingly found that Ph_2BiOEt is below 90°C more reactive than $SnOct_2$, which is the standard initiator for the technical production of polylactide and polylactones. Therefore, it was the purpose of this work to find out, if Ph_2BiOEt and Ph_2BiBr also allow for the preparation of high molar mass poly-TMC, and if Ph_2BiOEt is again more reactive than $SnOct_2$, when TMC is used as monomer.

2 Experimental

2.1 Materials

TMC was kindly supplied by Boehringer Ingelheim GmbH (Ingelheim, Germany), twice recrystallized from ethyl acetate and stored over P_4O_{10}. Ph_2BiBr and Ph_2BiOET were prepared from Ph_3Bi according to the literature (29, 30). $SnOct_2$ was purchased from Aldrich Co. (Milwaukee, WI, USA) and purified as described previously (31).

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Table 1. Ph$_2$BiOEt-initiated polymerizations of TMC in bulk at 120°C

Expt. no.	$\frac{\text{Mon.}}{\text{Init.}}$	Time (h)	Conversion^a (%)	Yield (%)	η_{inh}^b (dL/g)	M_n (k Da)^c (calcd.)	M_n (k Da)^d (SEC)	M_w^d (SEC)
1	50/1	0.5	98.5	80.0	0.24	5	—	—
2	100/1	2.0	99.5	79.0	0.30	10	—	—
3	200/1	4.0	99.0	82.0	0.50	20	21	52
4	400/1	2.0	99.0	86.5	0.72	40	38	91
5	600/1	2.0	99.0	85.0	0.87	60	45	135
6	1000/1	2.0	98.0	86.0	1.16	100	—	—
7^e	1000/1^e	4.0	99.0	95.5	1.18	100	60	210

^{a}As determined by ^{1}H NMR spectroscopy.
^{b}Measured at 20°C with $c = 2$ g/L in CH$_2$Cl$_2$.
^{c}Calculated from M/I and 100% conversion.
^{d}SEC measurements in chloroform calibrated with polystyrene.
^{e}Crude TMC was used, whereas the TMC for all other experiments was twice recrystallized.

Tetra(ethylene glycol), TEG, was azeotropically dried with toluene and distilled in a vacuum of 10^{-2} mbar.

2.2 Ph$_2$BiOET-Initiated Polymerizations (no. 2, Table 1)

TMC (50 mmol) was weighed into a 25 mL Erlenmeyer flask having silanized glass walls and Ph$_2$BiOEt (0.5 mmol) was added under an atmosphere of argon. The reaction vessel was closed with glass-stopper and steel spring and immersed into an oil bath preheated to 120°C. The polymerization was stopped after 2.0 h, the cold reaction product was dissolved in CH$_2$Cl$_2$ and precipitated into cold (0–2°C) diethyl ether. After filtration the poly TMC was dried at 20-25°C *in vacuo*.

All other polymerizations of Table 1 were performed analogously.

2.3 Ph$_2$BiBr-Initiated Polymerizations (no. 2, Table 2)

TMC (50 mmol) and Ph$_2$BiBr (0.125 mmol) were weighed into a 25 mL Erlenmeyer flask having silanized glass walls. The polymerization was conducted for 7 h at 120°C and worked up as described above.

All other polymerizations of Table 2 were conducted analogously. The polymerizations designed for the calibra-

tion of time conversion curve were performed as described above, but the reaction vessels were opened from time-to-time under an atmosphere of argon and small samples were taken for ^{1}H-NMR measurements.

2.4 TEG-Coinitiated Polymerizations (no. 3, Table 3)

TMC (50 mmol), Ph$_2$BiBr (0.05 mmol) and TEG (0.5 mmol) were weighed under argon into a 25 mL Erlenmeyer flask having silanized glass walls. After 20 h at 120°C the conversion was determined by ^{1}H-NMR spectroscopy and the product was precipitated from its CH$_2$Cl$_2$ solution into methanol.

2.5 Measurements

The inherent viscosities were measured in CH$_2$Cl$_2$ with an automated Ubbelohde viscometer thermostated at 20°C. The 400 MHz ^{1}H-NMR spectra were recorded on a Bruker "Avance 400" FT spectrometer using 5 mm o.d. sample tubes. CDCl$_3$ containing TMS served as solvent. The MALDI-TOF mass spectra were measured with a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 330$ nm). All spectra were recorded in the reflection mode with an

Table 2. Ph$_2$BiBr-initiated polymerizations of TMC in bulk at 120°C

Expt. No.	$\frac{\text{Mon.}}{\text{Init.}}$	Time (h)	Convers. (%)	η_{inh}^a (dL/g)	M_n (k Da)^b (calcd.)	M_v (k Da)^c (viscosim.)	M_n (k Da)^d (SEC)	M_w (k Da)^d (SEC)
1	50	4	97.5	0.80	5	—	70	145
2	400	7	98.5	0.97	40	135	77	170
3	1 000	6	67.0	2.18	68	270	200	350
4	1 000	17	99.0	3.36	100	470	345	600
5	2 000	17	98.0	2.63	200	335	250	450

^{a}Measured at 20°C with $c = 2$ g/L in CH$_2$Cl$_2$.
^{b}Calculated from M/I and 100% conversion.
^{c}Determined from the intrinsic viscosities via the Mark-Houwink equation, measured at 25°C, $\alpha = 0.85$, K $= 5.48*10^5$.
^{d}SEC measurements in chloroform calibrated with polystyrene.

Table 3. Ph$_2$BiBr-initiated polymerizations of TMC (M/I = 1000/1) in bulk at 120°C (24 h) coinitiated with tetra(ethylene glycol), TEG

Expt. No.	$\frac{TMC^a}{TEG}$	Convers. (%)	η_{inh}^b (dL/g)	M_n (k Da)^c (calcd.)	M_n (k Da)^d (SEC)	M_w (k Da)^d (SEC)
1	40/1	99.0	0.17	4	7	15
2	60/1	97.5	0.20	6	9	19
3	100/1	98.0	0.36	10	14	37
4	200/1	98.5	0.56	20	21	57
5	500/1	98.5	0.77	50	45	98
6		>99.0	3.40	–	340	

^{a}Molar feed ratio.
^{b}Measured at 20°C with c = 2 g/L in CH$_2$Cl$_2$.
^{c}Calculated from the TMC/TEG feed ratio and 100% conversion.
^{d}SEC measurements in chloroform calibrated with polystyrene.

acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions with dithranol as matrix and potassium trifluoroacetate as dopant. The SEC measurements with an apparatus of Polymer Laboratories equipped with a RI detector "Shodex RI 101". A combination of three mixed bed columns was used with chloroform as eluent (flow rate 1.0 mL/min.). Commercial polystyrene standards served for calibration.

3 Results and Discussion

3.1 Preparative Polymerizations

Two series of polymerizations were performed, the first one based on Ph$_2$BiOEt as initiator and the second one based on Ph$_2$BiBr. Both series of polymerizations were conducted in bulk at a temperature of 120°C. With Ph$_2$BiOEt as initiator the monomer-initiator ratio (M/I) was varied from 50/1 to 1000/1 (Table 1). The reaction time was varied from 0.5 h to 4.0 h and the conversions were determined by ^{1}H NMR spectroscopy. Since in all experiments conversions ⩾ 98% were found, these results indicate a quite rapid polymerization process. The yields, inherent viscosities and molecular weights (M_n = number average, M_w = weight average) were determined after precipitation of the crude polycarbonate (dissolved in CH$_2$Cl$_2$) into diethyl ether.

The inherent viscosities roughly paralleled the M/I ratio, but the M_n values derived from polystyrene (PS)-calibrated SEC measurements were lower than calculated from the M/I ratios at least for M/Is ⩾ 200/1. At this point it should be mentioned that PS-calibrated SEC measurements overestimate the real M_ns of unsubstituted aliphatic polyesters such as poly(ε-caprolactone) by approximately 50% above 10 000 Da (33–39). This means the hydrodynamic volume of the polyesters is higher than that of PS or, in other words, their coil density is lower. However, the carbonate group is significantly more polar than aliphatic ester groups (e.g. evidenced by stable Lewis acid complexes (40)), and thus, the coil density should be lower in less

polar solvents such as THF or chloroform. Hence, the PS-calibrated SEC measurements should be more realistic, and for reasons discussed below, the overestimation of the M_ns should be limited to 15-20%. Regardless, if the overestimation amounts to 10 or 20% the measured M_ns listed in Table 1 are lower than those calculated from the M/I (considering 99% conversion). The reasons why the real M_ns fell below the calculated ones were revealed by the MALDI-TOF mass spectra of samples Nos. 1–3 (see Table 1). Three series of peaks were detectable as illustrated by Figure 1. The series labeled **C** represents cyclic oligomers which were certainly formed by "back-biting" as its true for all polymerizations of lactones initiated y metal alkoxides at temperatures > 60°C. The series labeled **La** represents the expected linear chains having ethylester and one CH$_2$OH endgroup (see Scheme 1). The third series labeled **Lb** contains two CH$_2$OH endgroups. For the following reasons this finding is difficult to explain. The TMC was recrystallized and stored over P$_4$O$_{10}$ and gave high molecular weights (M_ns up to 340, 000 Da, see below), when Ph$_2$BiBr
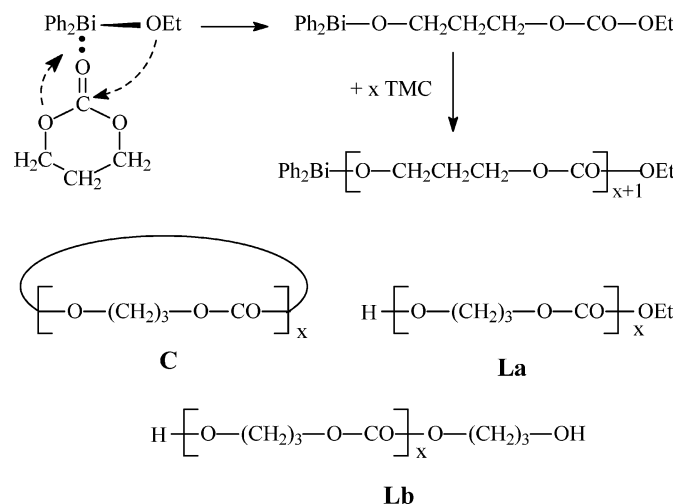
Sch. 1. Ph$_2$BiOEt-initiated polymerization of TMC and potential reaction products.
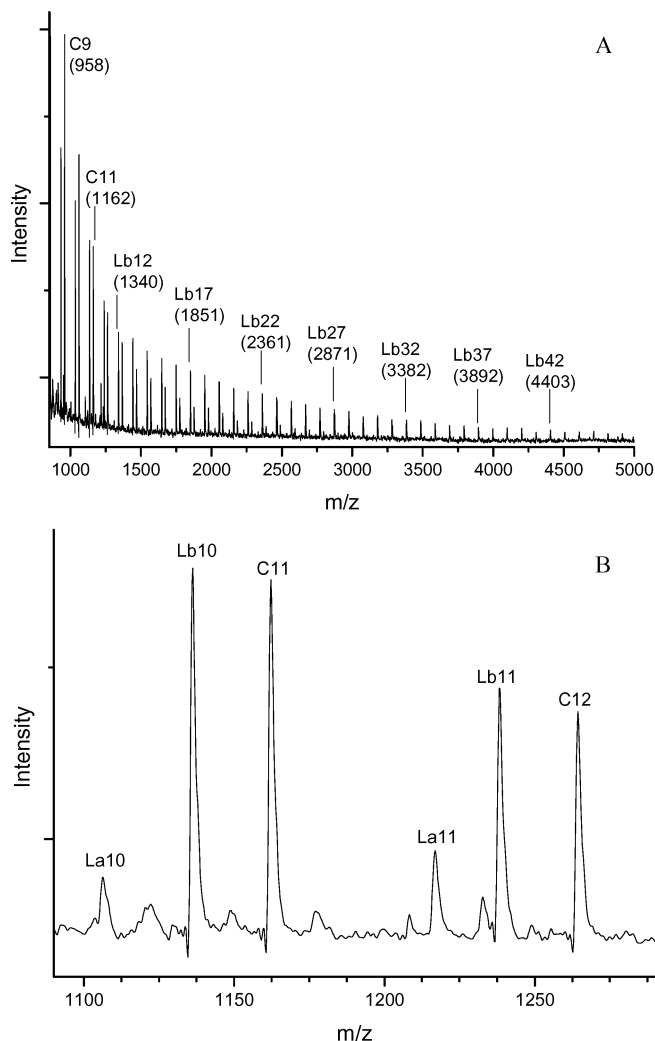
Fig. 1. MALDI-TOF mass spectrum of the Ph_2BiOEt-initiated poly TMC sample No. 7, Table 1.

was used as initiator. The glass wall of the reaction vessels were silanized (i.e. pretreated with $(CH_3)_2SiCl_2$) and the reactants were weighed into the reaction vessels under dry argon. When ε-caprolactone was polymerized under these conditions with the same Ph_2BiOEt initiator (27), all chains had ethyl ester endgroups and higher M_ns, what indicates that our reaction conditions allowed for clean and dry polymerizations.

Five polymerizations of TMC were conducted with Ph_2BiBr as initiator in bulk at 120°C (see Table 2). With the exception of experiment no. 3 where the reaction time was too short conversions above 97.5% were achieved in all cases. A comparison with the Ph_2BiOEt-initiated polymerizations indicates a lower reactivity of Ph_2BiBr as it was also found for polymerizations of ε-caprolactone (28). Yet, despite the lower reactivity (also discussed below) Ph_2BiBr-initiated polymerizations yielded considerably higher molecular weights than Ph_2BiOEt. The M_ns were also significantly higher than those calculated from the M/Is. From

four samples the intrinsic viscosities were determined and the viscosity average molecular weights (M_ws) were calculated via the Mark-Houwink Equation (1) which was elaborated in a previous publication (10). For flexible chains, M_v typically amounts to 85–90% of the M_w values. Taking this relationship into account the M_v and M_w data in Table 2 suggest the PS-calibrated SEC measurements overestimate the real molecular weights by 15–20%. Nonetheless, the measured M_ns are higher than the calculated ones with exception of experiment 5, in close analogy to Ph_2BiBr-initiated polymerizations of ε-caprolactone (28).

$$[\eta] = 5.48 \times 10 - 5 \times M_w^{0.825} \quad (1)$$

$$Ph_2BiBr + HOR \rightleftharpoons Ph_2Bi - OR + HBr \quad (2)$$

$$Oct_2Sn + HOR \rightleftharpoons Oct_2Sn - OR + HOct \quad (3)$$

Five more polymerizations were conducted in such a way that tetraethylene glycol (TEG) was added as coinitiator (Table 3). The ^{1}H-NMR spectra proved the covalent incorporation of the TEG units (signals at 4.25 and 3.65 ppm in chloroform). Both the viscosity and SEC measurements demonstrated that the molecular weights roughly paralleled the monomer/coinitiator ratio. Hence, it may be concluded that Ph_2BiBr is a more attractive catalyst than Ph_2BiOEt for preparative purposes, because it may yield higher molecular weights, because it allows for an easy control of the molecular weight by addition of a coinitiator and because it is easier to synthesize.

3.2 Mechanistic Aspects

A handful of time-conversion measurements were performed to obtain at least a crude idea about the reactivities of Ph_2BiOEt and Ph_2BiBr relative to each other and relative to other initiators (Figures 2–4). For ε-caprolactone as
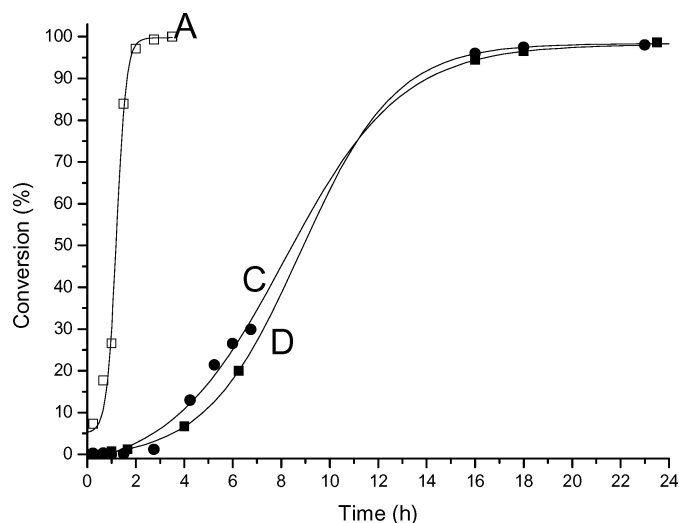

Fig. 2. Time-conversion curves measured for polymerizations of TMC in bulk at 120°C with three different initiators (M/I = 50/1): A) Ph_2BiOEt, C) Ph_2BiBr, D) $BiBr_3$.
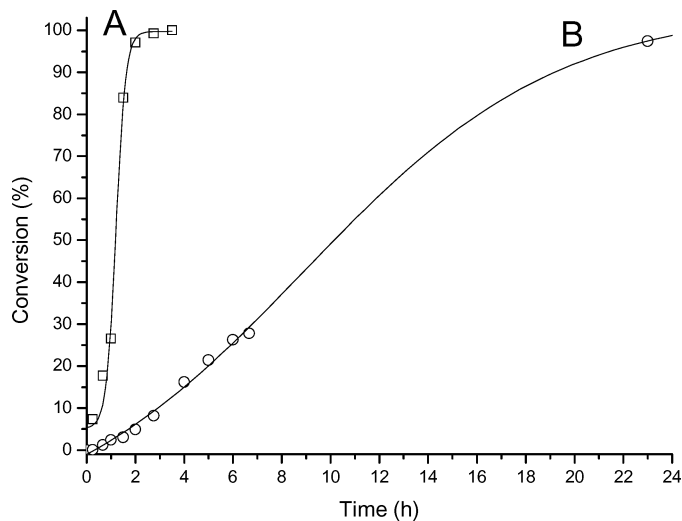
Fig. 3. Time-conversion curves measured for polymerizations in TMC in bulk at 120°C with M/I = 50/1: A) Ph$_2$BiOEt and B) SnOct$_2$+ EtOH.

monomer it was found that Ph$_2$BiBr is clearly less reactive than Ph$_2$BiOEt by a factor of 2 (when compared at 50% conversion and a temperature of 120°C). An analogous comparison for TMC as monomer is presented in Figure 2. Ph$_2$BiBr proved again to be less reactive, so that at 50% conversion the polymerization was slower by a factor of 7. A comparison with BiBr$_3$ (curve D) showed relatively similar reactivity. This result is different from what was found for εCL, because the BiBr$_3$-initiated polymerization of εCL was much slower than that initiated by Ph$_2$BiBr. The carbonate group is more basic and more nucleophilic than an ester group having similar substituents, and thus, is more prone to coordinate a Lewis acid (40). BiBr$_3$ is certainly
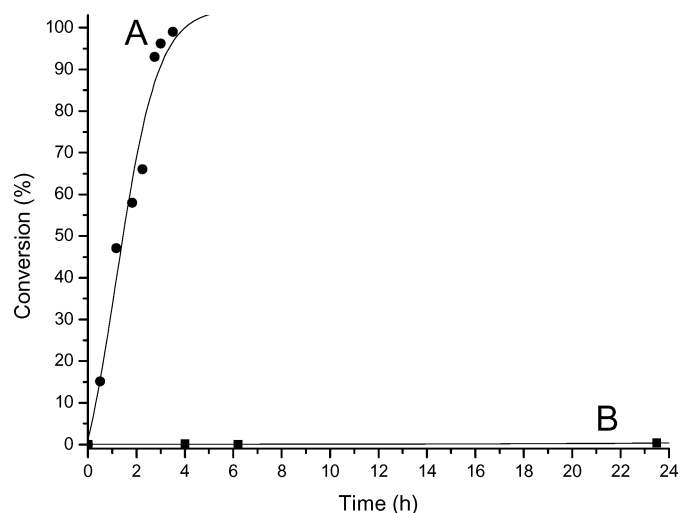
a stronger Lewis acid than Ph$_2$BiBr, but the similarity of the time-conversion curves alone does not give any reliable information about the polymerization mechanism. In a recent study of BiCl$_3$, BiBr$_3$ and BiJ$_3$-catalyzed polymerizations of εCL (41) the kinetic results and endgroup analyses suggest that the coordination-insertion mechanism via X$_2$Bi-OCH$_2 \sim$ endgroups was involved and not a cationic mechanism. In the present work, a Ph$_2$BiBr-catalyzed polymerization of TMC was performed in bulk with a M/I ratio of 20/1 and the endgroups were characterized by ^{1}H-NMR spectroscopy and MT mass spectrometry. As illustrated in Figure 5A, the triplet signal of CH$_2$OH endgroups is detectable at 3.7 ppm. Its identification was confirmed by esterification with trifluoroacetic anhydride, which shifts this triplet to 4.6 ppm (Figure 5B). A weak signal at 3.5 ppm might result from a CH$_2$Br endgroup. The mass spectrum confirmed the presence of cyclic oligomers and **La** chains terminated by two CH$_2$OH groups. Therefore, these results suggest that a coordination-insertion mechanism was operating based on a Ph$_2$Bi-OCH$_2 \sim$

Fig. 4. Time-conversion curves measured for polymerizations in TMC in bulk at 60°C with M/I = 50/1: A) Ph$_2$BiOEt and B) SnOct$_2$+ EtOH.
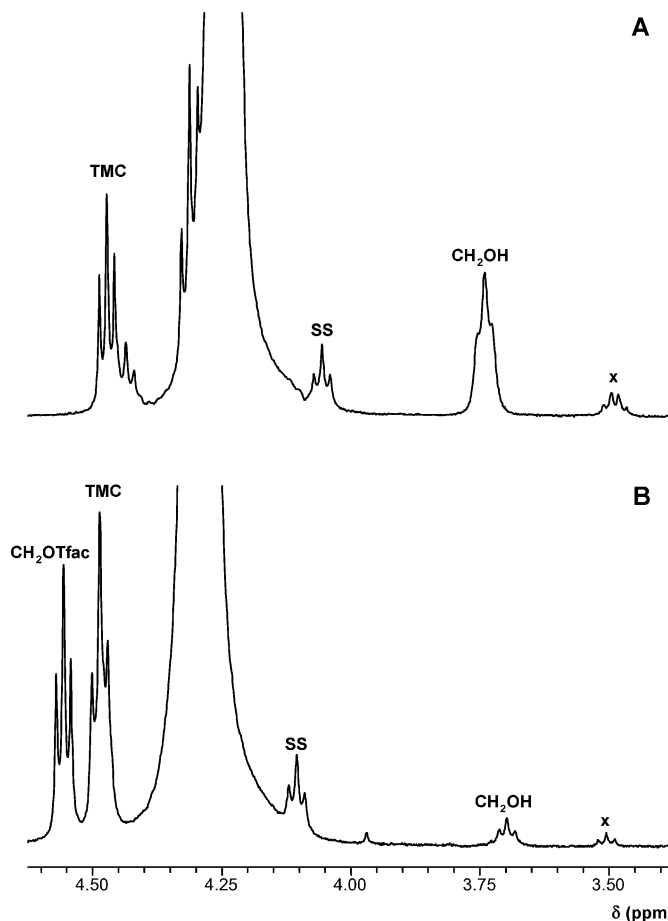
Fig. 5. 400 MHz ^{1}H NMR spectrum of Ph$_2$BiBr-initiated poly TMC prepared in bulk at 60°C with M/I = 20/1: A) virgin product and B) measured after addition of one drop of trifluoroacetic anhydride to the solution in CDCl

endgroup and was operating in agreement with the BiX$_3$-catalyzed polymerization of εCL. The lower reactivity of Ph$_2$BiBr relative to Ph$_2$Bi-OEt is understandable on the basis of the coordination-insertion mechanism outlined in Scheme 1. The reactive Bi-OR groups is missing in the case of Ph$_2$BiBr and needs to be formed by a side reaction such as that outlined in Equation 2.

Another interesting comparison based on time-conversion measurements concerns Ph$_2$BiOEt and SnOct$_2$. SnOct$_2$ is the most widely used initiator for lactones and lactides in both areas fundamental research and technical production of biodegradable polyesters. It is characteristic for SnOct$_2$ that addition of an alcohol significantly enhances its reactivity, because according to Equation 3 a reactive Sn-O alkyl group is formed via an exchange reaction (31, 32). Therefore, the kinetic comparison with Ph$_2$BiOEt is based on an equimolar combination of SnOct$_2$ and ethanol. In the case of εCL Ph$_2$BiOEt proved to be less reactive at 120°C, but surprisingly it was more reactive at 60 and 40°C (and equally reactive at 90°C). Figures 3 and 4 demonstrate that the situation is different for TMC as monomer. Ph$_2$BiOEt is significantly more reactive than SnOct$_2$+ ethanol even at 120°C. At 60°C the Ph$_2$BiOE-initiated polymerization of TMC is only slightly slower than that at 120°C, whereas the initiation with SnOct$_2$+ ethanol is so slow that this system is useless for any preparative purposes. The summary of these results demonstrate that Ph$_2$BiOEt is for TMC a highly reactive single site initiator for all temperatures above the melting point of TMC. This result was unpredictable, but it is useful for preparative applications.

4 Conclusions

Both Ph$_2$BiOEt and Ph$_2$BiBr proved to be efficient initiators of ring-opening polymerizations of TMC. In the case of Ph$_2$BiOEt, the M$_n$s roughly parallel the M/Is, but fall below the theoretical values. Ph$_2$BiBr allows for the preparation of particularly high poly TMC and the M$_n$ around 300,000 Da (corrected value) is to the best of our knowledge the highest molecular weight reported so far. However, a direct control of the M$_n$ via the M/I ratio is not feasible, but by addtion of a mono- or bifunctional alcohol this control is easily achieved. Therefore, Ph$_2$BiBr is the most attractive initiator from the preparative point of view, in as much as it is easier to synthesize. However, Ph$_2$BiOEt proved to be more reactive than Ph$_2$BiBr in agreement with a coordination-insertion mechanism involving Bi-alkoxide groups as reactive species. Yet, surprising is the observation that Ph$_2$BiOEt is more reactive than the combination SnOct$_2$+ ethanol, a difference which strongly increases at lower temperatures (e.g. 60°C).

In summary, the excellent results obtained from Ph$_2$BiOEt and Ph$_2$BiBr-initiated polymerization of ε-

caprolactone (27, 28) were largely paralleled by the results obtained with TMC in this work.

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