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### **Polylactones. LXI. Polymerization of $\beta$ -*D,L*-Butyrolactone Initiated with 1,3-Diacetoxy-1,1,3,3-tetrabutyl-distannoxane and with 1,3-Dichloro-1,1,3,3-tetrabutyl-distannoxane**

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## **Polylactones. LXI. Polymerization of $\beta$ -D,L-Butyrolactone Initiated with 1,3-Diacetoxy-1,1,3,3-tetrabutyl-distannoxane and with 1,3-Dichloro-1,1,3,3- tetrabutyl-distannoxane**

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### **ABSTRACT**

Commercial 1,3-dichlorotetrabutyl distannoxane (DCTSO) and 1,3-diacetoxy-tetrabutyl distannoxane (DATSO) were used as initiators for the ring-opening polymerization of  $\beta$ -D,L-butyrolactone ( $\beta$ -D,L-BL). These polymerizations were conducted in bulk and in concentrated solutions at 50°C or 100°C. Regardless of initiator and reaction medium, no polymerization took place at 25°C. When the monomer/initiator (M/I) ratio was varied from 100 : 1 to 2000 : 1, polymerization was observed up to M/I ratios of 600 : 1 or 800 : 1, but never at higher ratios, and the number average molecular weights did not parallel the M/I ratios. The stereosequences were evaluated by means of <sup>13</sup>C NMR spectroscopy and a predominance of syndiotactic dyads was found. The highest percentage of syndiotactic dyads (around 75%) was found at the lower reaction temperature, and as a result, the consequence that semicrystalline polylactones with higher melting temperatures were formed than in the case of 65% or 55% syndiotactic dyads.

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*Key Words:*  $\beta$ -D,L-Butyrolactone; Ring-opening polymerization; Distannoxanes; Syndiotactic stereosequences; Enantioselectivity.

## INTRODUCTION

The present work is part of a broader study of the usefulness of tin-containing initiators for the ring-opening polymerization of  $\beta$ -D,L-butyrolactone ( $\beta$ -D,L-BL).<sup>[1–5]</sup> The copolymerization of two enantiomers may in principle yield three different types of stereosequences: a random copolymer, an isotactic stereo block copolymer and a syndiotactic polymer. In the case of  $\beta$ -D,L-BL the syndiotactic polyester is of particular interest, because it should be (slowly) biodegradable, and because its melting temperature ( $T_m$ ) should fall into the range of 140–150°C<sup>[2]</sup> which is convenient for any processing from the melt. In contrast, the isotactic poly(D-hydroxybutyrate) which is commercially available on the basis of a biotechnological process,<sup>[6,7]</sup> has a  $T_m$  of 180°C which bears the risk of thermal degradation (yielding crotonyl groups) upon processing from the melt. Tin compounds containing Sn—O bonds were the only group of initiators known so far, which allow the preparation of predominantly syndiotactic poly( $\beta$ -D,L-BL).<sup>[1,2,4,8,9]</sup> Unfortunately, the only initiator (i.e.,  $\text{Bu}_2\text{Sn}(\text{Ome})_2$ ) yielding >70% of syndiotactic dyads produces low molecular weights ( $M_n \leq 10^4$ ).<sup>[2]</sup>  $\text{Bu}_2\text{SnO}$  and  $\text{Et}_2\text{SnO}$ , which enable the preparation of rather high molecular weights ( $M_n > 50,000$ ) do not yield more than 70% syndiotactic dyads.<sup>[5]</sup>

Recently, Hori et al.<sup>[10]</sup> have reported that 1,3-disubstituted tetraalkyl distannoxanes are highly efficient initiators for the polymerization of D- or D,L-butyrolactones producing high yields and high molecular weights in a short time. However, no information on the stereosequences and melting temperatures of the resulting poly( $\beta$ -D,L-BL) was disclosed. Therefore, the present work had the purpose of studying the usefulness of the commercial initiators 1,3-dichloro-1,1,3,3-tetra-butyl-distannoxane (DCTSO) and 1,3-diacetoxy-1,1,3,3-tetra-butyl-distannoxane (DATSO) for the preparation of syndiotactic poly( $\beta$ -D,L-BL).

## EXPERIMENTAL

### Materials

$\beta$ -D,L-Butyrolactone was purchased from Aldrich Co. (Milwaukee, WI) in 250 mL quantities (we have found that the 250-mL and 1-L bottles do not always contain the same quality). The  $\beta$ -D,L-BL was stirred over powdered calcium hydride for 48 h at 25°C and distilled over freshly powdered calcium hydride in vacuo. The distillation over freshly powdered  $\text{CaH}_2$  was repeated prior to use. The DCTSO was purchased from Aldrich Co. (Milwaukee, WI) and recrystallized from chloroform/ligroin. It had a mp of 111–113°C and correct elemental analyses. The 1,3-bisacetoxy-1,1,3,3-tetrabutyl-distannoxane was purchased from ABCR Chemicals (Karlsruhe, Germany) and recrystallized from toluene/ligroin. It had a mp of 57–59°C and correct elemental analyses. Toluene, chlorobenzene, and chloroform were distilled over  $\text{P}_4\text{O}_{10}$  prior to use.





### Polymerizations

#### In Bulk

$\beta$ -*D,L*-Butyrolactone (50 mmol) was weighed under dry nitrogen into a 25-mL Erlenmeyer flask having silanized glass walls. The initiator was added as a solid in an atmosphere of dry nitrogen. The reaction vessel was closed with a glass stopper and steel spring and thermostated at 50°C, 75°C, or 100°C. The cold reaction product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50–60 mL) and precipitated into cold diethylether.

#### In Solution

$\beta$ -*D,L*-Butyrolactone (40 mmol), dry toluene (3 mL) or chlorobenzene (3 mL) and the initiator were added to a 25-mL Erlenmeyer flask having silanized glass walls in an atmosphere of nitrogen. The polymerizations and work up procedure were conducted as described above.

### Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25°C. The DSC measurements were conducted with a Perkin Elmer DSC-7 in aluminum pans under nitrogen. The 100 MHz <sup>1</sup>H NMR spectra were obtained on a Bruker AC-100 FT NMR spectrometer in 5-mm od sample tubes. The 25.2 MHz <sup>13</sup>C NMR spectra were recorded with the same Bruker instrument in 10-mm od sample tubes. TMS served as an internal standard for all measurements. The GPC measurements were performed with a Kontron HPLC/GPC apparatus equipped with a Waters Md 410 differential refractometer and four Ultrastaygel columns having pore sizes of 10<sup>2</sup>, 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Å. Tetrahydrofuran served as eluent.

## RESULTS AND DISCUSSION

### 1,3-Dichloro-1,1,3,3-tetrabutyl-distannoxane-Initiated Polymerizations

Hori et al.<sup>[10]</sup> described DCTSO-initiated polymerizations of  $\beta$ -*D,L*- and  $\beta$ -*D*-butyrolactone, and thus, the first part of the present work was concentrated on this initiator. It was demonstrated<sup>[3]</sup> in our previous work that the stereoselectivity (i.e., the percentage of syndiotactic dyads) increased at lower reaction temperatures. Taking into account the reported high reactivity of the substituted distannoxanes as initiators and transesterification catalysts, the first experiments were conducted at +5°C and continued at +25°C. A M/I ratio of 100 was used and the reaction time was extended to 3 weeks. Furthermore, several polymerizations were conducted in bulk, others in chlorobenzene. Regardless of the reaction conditions, no conversion of the rac.  $\beta$ -*D,L*-Butyrolactone was observed.

A further series of polymerizations was initiated with DCTSO at 50°C either in bulk or in chlorobenzene to avoid an early precipitation (and termination) of crystalline



syndiotactic oligomers. However, it turned out that even in bulk no early precipitation of crystalline oligomers occurred. A long reaction time (14 days) was required to obtain yields around or above 90% (Table 1). With respect to the yields, the polymerizations in bulk and in solution gave similar results. Worth noting is the observation that polymerizations occurred even at a M/I ratios of 400 or 600 in contrast to previous studies of tin alkoxides.<sup>[2-4]</sup> However no conversion was detected at M/I = 800. The molecular weights achieved in bulk were somewhat higher than those obtained in solution, but they were not high enough to yield films of good mechanical properties such as those obtained from Bu<sub>2</sub>SnO—initiated polymerizations.<sup>[5]</sup>

The stereo sequences were evaluated on the basis of <sup>13</sup>C NMR spectra in analogy to previous studies,<sup>[1-5]</sup> because the CO-signal exhibits a clear splitting into two peaks representing isotactic and syndiotactic dyads. These CO-peaks were evaluated in terms of percent syndiotactic dyads and the resulting data were listed in Table 1. The percentage of syndiotactic dyads was comparable to those values obtained from dialkyltin oxides. Interestingly, the stereoselectivity was slightly higher, when the polymerizations were conducted in bulk.

Two more polymerizations series were conducted at 100°C, again in bulk, or in solution (Table 2). At this temperature, the short reaction time of 24 h sufficed to obtain conversions (detected by <sup>1</sup>H NMR spectroscopy) above 90% and yields up to 86%. The inherent viscosities were slightly higher than those achieved at 50°C (Table 1). Furthermore, successful polymerizations were achieved at a M/I ratio of 800 but not at 1000. Therefore, our results (repeated several times including the use of the virgin initiator) clearly deviate from those reported by Hori who reported polymerizations for M/I ratios as high as 5000 at 100°C. However, the most interesting results were somewhat lower percentage of syndiotactic dyads (when compared to the 50°C experiments), an effect which was clearly detectable at relatively low M/I ratios. Decreasing stereoselectivity at

**Table 1.** DCTSO-initiated polymerizations of  $\beta$ -D,L-BL, reaction conditions: 50°C/14 d.

Polym. no.	Reaction medium	Mon. Init.	Yield (%)	$\eta_{inh}^a$ (dL/g)	Percentage of synd. dyads <sup>b</sup>
1	—	100	84	0.36	65
2	—	200	91	0.47	65
3	—	400	88	0.51	65
4	—	600	93	0.53	65
5		800	0	—	—
6		1,000	0	—	—
7	Toluene	100	84	0.34	70
8	Toluene	200	88	0.37	70
9	Toluene	400	91	0.40	70
10	Toluene	600	86	0.45	70
11	Toluene	800	0	—	—

<sup>a</sup>Measured at 25°C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup>From the CO-signals of the <sup>13</sup>C NMR spectra.



**Table 2.** DCTSO-initiated polymerizations of  $\beta$ -D,L-BL, reaction conditions: 100°C/24 h.

Polym. no.	Reaction medium	Mon. Init.	Yield (%)	$\eta_{inh}^a$ (dL/g)	Percentage of synd. dyads <sup>b</sup>
1	—	100	42	0.26	55
2	—	200	56	0.35	55
3	—	400	79	0.48	60
4	—	600	81	0.55	60
5	—	800	81	0.53	65
6	—	1,000	0	—	—
7	Toluene	100	47	0.28	60
8	Toluene	200	60	0.32	60
9	Toluene	400	81	0.41	65
10	Toluene	600	84	0.48	65
11	Toluene	800	86	0.57	65

<sup>a</sup>Measured at 25°C with  $c = 2$  g/L in  $CH_2Cl_2$ .

<sup>b</sup>From the CO-signals of the  $^{13}C$  NMR spectra.

higher temperatures was also observed for  $Bu_2Sn(OMe)_2$ -initiated polymerizations. Yet with  $Bu_2Sn(OMe)_2$  only random stereosequences were obtained at 100°C.

### 1,3-Diacetoxy-1,1,3,3-tetra-butyldistannoxane-Initiated Polymerizations

In contrast to DCTSO, DATSO has never been used as initiator of  $\beta$ -butyrolactone. Therefore, it was not clear if this distannoxane is more or less reactive than DCTSO. Hence, the first polymerizations were again conducted at +5°C. Regardless, if the experiments were performed in bulk or in chlorobenzene no polymerization was observed. The same negative results were obtained at 25°C, despite a reaction time of 21 days. At 50°C, DATSO was finally active enough to initiate the polymerization of  $\beta$ -D,L-BL at a M/I ratio of 100. A yield of 72% was obtained and an inherent viscosity of 24 g/L. These experiments were repeated to check the reproducibility, in as much as no polymerization was observed when the M/I ratio was raised to 200 or 400 at 50°C. From this point of view, DATSO proved to be somewhat less reactive than DCTSO.

Polymerizations in bulk at 50°C may have the disadvantage that the resulting partially syndiotactic poly( $\beta$ -D,L-BL) crystallizes and buries the active chain end, so that the chain growth is seriously hindered. Therefore, further polymerizations were performed at 50°C in three different inert solvents, and in all three solvents, the M/I ratio was varied (Table 3). With a M/I of 100 the results obtained in chlorobenzene or toluene were almost identical with those obtained in bulk. However, the most interesting result is the finding that higher yields and viscosities were obtained in all three solvents, when the M/I ratio was raised to 200, 400, and 600. Surprisingly, the yields dropped to 0 when the M/I ratio was raised to 800. At first glance, such a sharp change looks unlikely, but the same trend was found in all three solvents. Furthermore, these results agree with those of the DCTSO-initiated polymerizations (Table 1) and with our previous studies,<sup>[3,4]</sup> which demonstrated that



**Table 3.** DATSO-initiated polymerizations of  $\beta$ -D,L-BL in various solvents at 50°C/21 d.

Polym. no.	Reaction medium	Mon. Init.	Yield (%)	$\eta_{inh}^a$ (dL/g)	$T_g^b$ (°C)	$T_m^b$ (°C)	Percentage of synd. dyads <sup>c</sup>
1	Chlorob.	100	71	0.24	5	72/121	75
2	Chlorob.	200	73	0.32	7	71/114	75
3	Chlorob.	400	81	0.36	8	68/115	75
4	Chlorob.	600	85	0.40	9	69/112	75
5	Chlorob.	800	0	—	—	—	—
6	Toluene	100	75	0.25	8	86/110	70
7	Toluene	200	80	0.30	9	108	70
8	Toluene	400	77	0.34	9	84/108/121	75
9	Toluene	600	81	0.36	—	—	—
10	<i>n</i> -Hexane	100	81	0.31	7	65/84	65
11	<i>n</i> -Hexane	200	83	0.37	10	46/70	65
12	<i>n</i> -Hexane	400	83	0.40	11	47/74	65
13	<i>n</i> -Hexane	600	85	0.43	11	55/88	70

<sup>a</sup>Measured at 25°C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup>From DSC measurements with a heating rate of 20°C/min (1st heat).

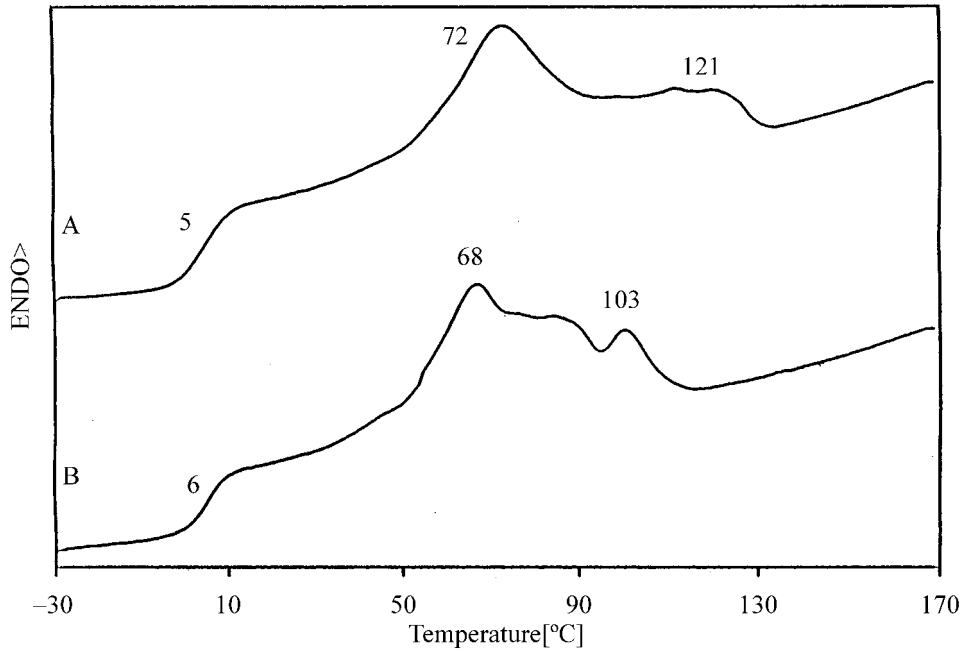
<sup>c</sup>From the CO-signals of the <sup>13</sup>C NMR spectra.

almost all tin initiators studied so far were inactive at M/I ratios above 400. Finally it should be mentioned that the viscosity values obtained with DATSO were slightly lower than those obtained with DCTSO.

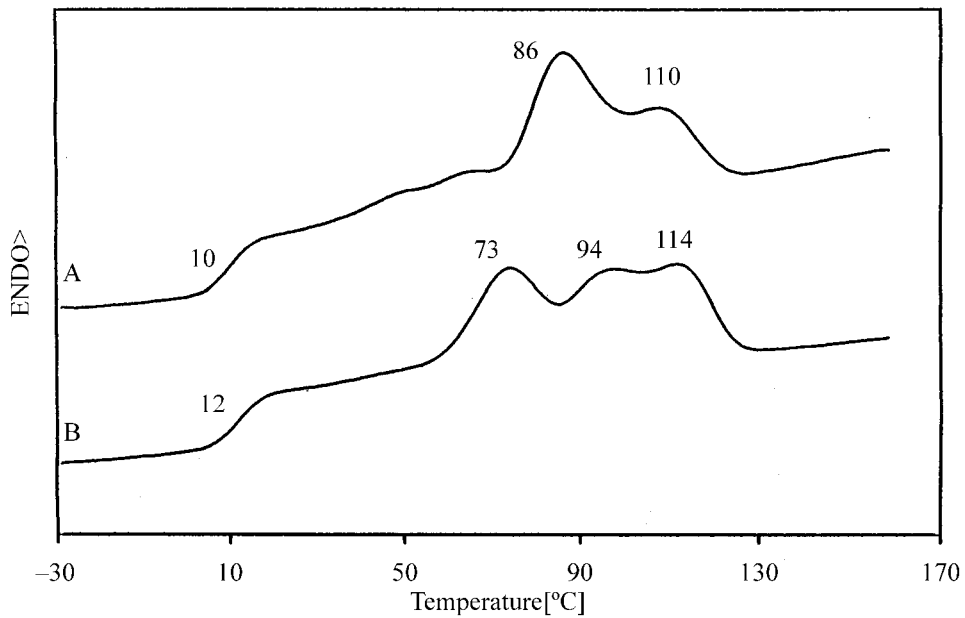
The evaluation of the stereosequences revealed slight differences between the three solvents (Table 3). The highest percentage of syndiotactic dyads was found for polymerizations in chlorobenzene (Nos. 1–5, Table 3) and these values were also slightly higher than the best values obtained with DCTSO (Table 1). Particularly noteworthy, is the influence of the stereosequences on the thermal properties as determined by DSC measurements (Table 3). On the average, a higher percentage of syndiotactic dyads leads to higher melting temperatures. A similar trend was observed for Bu<sub>2</sub>Sn(OMe)<sub>2</sub>-initiated polymerizations.<sup>[2]</sup> Also in agreement with our previous studies is the existence of two endotherms. Figures 1 and 2 exemplarily illustrate the DSC-heating curves of poly( $\beta$ -D,L-BL) samples initiated with DATSO at 50°C in solution.

Two more series of DATSO-initiated polymerizations were performed at 100°C either in bulk (Table 4) or in toluene (Table 5). The results obtained by polymerization in bulk were remarkable for two reasons. Firstly, the highest viscosity value (i.e., molecular weights, see below) of this work was obtained in this series. Secondly, the polymerizations proceeded even at a M/I ratio of 800 (Nos. 5 and 6, Table 4). However, the percentages of syndiotactic dyads were slightly lower than the best values achieved at 50°C in solution, and thus, the melting temperatures were likewise lower. The polymerizations performed in toluene at 100°C were in all aspects less successful than those conducted in bulk. Particularly noteworthy is the finding that all attempts to polymerize  $\beta$ -D,L-BL at M/I ratios above 600 failed. With regard to the stereosequences, the results obtained with DATSO confirm the trend that higher temperatures reduce the stereoselectivity.





**Figure 1.** DSC measurements (1st heating, rate 20°C/min) of: (A) sample No.1, Table 5, (B) sample No.3, Table 3.



**Figure 2.** DSC measurements (1st heating, rate 20°C/min) of: (A) sample No.6, Table 3, (B) the same sample after reprecipitation from methanol.





**Table 4.** DATSO-initiated polymerizations of  $\beta$ -D,L-BL in bulk at 100°C.

Polym. no.	Mon. Init.	Time (d)	Yield (%)	$\eta_{inh}^a$ (dL/g)	$T_g^b$ (°C)	$T_m^b$ (°C)	Percentage of synd. dyads <sup>c</sup>
1	100	1	56	0.26	8	48/70	65
2	200	1	71	0.34	7	46/71	65
3	400	1	78	0.41	9	47/72	65
4	600	1	87	0.50	9	45/75	65
5	800	1	87	0.61	9	44/71	60
6	800	2	62	0.45	9	43/70	65
7	1,000	1	0	—	—	—	—
8	1,000	2	0	—	—	—	—

<sup>a</sup>Measured at 25°C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>.<sup>b</sup>From DSC measurements with a heating rate of 20°C/min (1st heat).<sup>c</sup>From the CO-signals of the <sup>13</sup>C NMR spectra.

Finally, the molecular weights need a short discussion. Six representative samples having different inherent viscosities were characterized with regard to their absolute molecular weights and polydispersities (Table 6). The GPC measurements were evaluated either via the Mark–Houwink Eq. (1) which was determined for poly( $\epsilon$ -caprolactone) in tetrahydrofuran<sup>[11]</sup> or via the M–HEq. (2) published for polystyrene in tetrahydrofuran.<sup>[12]</sup> Typically, the values obtained via calibration with polystyrene are higher by 40–50% and a maximum number average ( $M_n$ ) of 45,000 was found on the basis of this most widely used calibration. More consistent and reliable data were obtained for the polydispersities, which indicate moderately broad molecular weight distribution. This finding and the lack

**Table 5.** DATSO-initiated polymerizations of  $\beta$ -D,L-BL in toluene at 100°C.

Polym. no.	Mon. Init.	Time (d)	Yield (%)	$\eta_{inh}^a$ (dL/g)	$T_g^b$ (°C)	$T_m^b$ (°C)	Percentage of synd. dyads <sup>c</sup>
1	100	1	55	0.25	5	70	65
2	200	1	70	0.32	8	45/71	65
3	400	1	82	0.40	9	43/70	65
4	600	1	80	0.45	9	44/70	65
5	800	1	0	—	—	—	—
6	800	2	0	—	—	—	—
7	1,000	1	0	—	—	—	—
8	1,000	2	0	—	—	—	—

<sup>a</sup>Measured at 25°C with  $c = 2$  g/L in CH<sub>2</sub>Cl<sub>2</sub>.<sup>b</sup>From DSC measurements with a heating rate of 20°C/min (1st heat).<sup>c</sup>From the CO-signals of the <sup>13</sup>C NMR spectra.



**Table 6.** Correlations of viscosity and molecular weight measurements (by GPC) of selected samples of poly( $\beta$ -D,L-BL).

Sample no.	$\eta_{inh}^a$ (dL/g)	$M_n^b$ (GPC)	$M_w^b/M_n$	$M_n^c$ (GPC)	$M_w^c/M_n$
No.5, Table 4	0.61	45,000	1.47	30,000	1.45
No.3, Table 5	0.40	25,000	1.65	17,000	1.60
No.2, Table 7	0.35	22,000	1.23	15,000	1.20
No.2, Table 4	0.34	22,000	1.35	15,000	1.34
No.7, Table 2	0.29	18,000	1.47	13,000	1.43
No.6, Table 3	0.25	16,000	1.33	12,000	1.30

<sup>a</sup>Measured at 25°C with  $c = 2$  g/L in  $CH_2Cl_2$ .

<sup>b</sup>GPC measurements evaluated via the M-H Eq. (2).

<sup>c</sup>GPC measurements evaluated via the M-H Eq. (1).

of a parallel between  $M_n$ s and M/I ratios prove that these polymerizations do not have a “living character.”

$$[\eta] = 1.395 \times 10^{-4} \times M_w^{0.786} \quad (1)$$

$$[\eta] = 1.25 \times 10^{-4} \times M_w^{0.717} \quad (2)$$

## CONCLUSION

The present study allows several interesting conclusions. When compared to previously described tin initiators, such as dialkyl tin oxides or  $Bu_2Sn(OMe)$ , DCTSO and DATSO have the advantage to initiate polymerizations at M/I ratios above 400 (up to 800) which means at relatively low concentrations. However, this finding does not mean that DCTSO and DATSO are more reactive in terms of polymerization rates. Previous systematic studies and comparisons<sup>[13,14]</sup> have revealed that these stannoxanes are more reactive than dibutyltin dicarboxylates, but far less reactive than dibutyltin bisalkoxides. Unfortunately, the polymerizations at higher M/I ratios do not result in particularly high molecular weights (i.e.,  $\geq 10^5$  Da). The molecular weights slightly increase with the M/I ratios, but they do not parallel them. This finding and the broad polydispersities indicate that these polymerizations do not obey the “living pattern.” The results of Hori et al.<sup>[10]</sup> namely, syntheses of high molecular weight poly( $\beta$ -D,L-BL) at M/I ratios around 5000 were not reproducible on the basis of our commercial chemicals. The degree of syndiotacticity increases slightly with lower temperatures, but the highest values found at 50°C do not exceed the best values obtained from other tin initiators at 50°C.<sup>[2-5]</sup> However, the stereoelectivity at 100°C was higher than that found in dibutyltin bisalkoxide-initiated polymerizations<sup>[2,4]</sup> regardless whether DCTSO or DATSO were used. In agreement with previous studies<sup>[1-5]</sup> a higher percentage of syndiotactic dyads enhanced the crystallinity and raised the melting temperatures to values around 120°C.





## REFERENCES

1. Kricheldorf, H.R.; Kreiser-Saunders, I.; Scharnagl, N. Anionic and pseudoanionic polymerization of lactones – a comparison. *Macromol. Chem. Macromol. Symp.* **1990**, *32*, 285.
2. Kricheldorf, H.R.; Lee, S.-R.; Scharnagl, N. Polyactones. 28. Syndiotactic poly(beta-D,L-hydroxybutyrate) by ring-opening polymerization of beta-D,L-butyrolactone with butyltin methoxides. *Macromolecules* **1994**, *27*, 3139.
3. Kricheldorf, H.R.; Lee, S.-R. Polyactones. 29. Preferentially syndiotactic poly(beta-(R-S)-butyrolactone) obtained by ring-opening polymerization with triphenyltin methoxide or diphenyltin dimethoxide. *Macromol. Chem. Phys.* **1994**, *195*, 2299.
4. Kricheldorf, H.R.; Lee, V. Polyactones. 35. Macrocyclic and stereoselective polymerization of beta-D,L-butyrolactone with cyclic dibutyltin initiators. *Macromolecules* **1995**, *28*, 6718.
5. Kricheldorf, H.R.; Eggerstedt, S. Polyactones. 41. Polymerizations of beta-D,L-butyrolactone with dialkyltin oxides as initiators. *Macromolecules* **1997**, *30*, 5693.
6. Byrom, V. Polyhydroxyalkanoates. In *Plastics from Microbes*; Mobley, D.P., Ed.; Hanser Publishers: Munich, Vienna, New York, 1994; Chap. 2.
7. Hocking, P.J.; Marchessault, R.H.; Timmins, M.R.; Lenz, R.W.; Fuller, R.C. Enzymatic degradation of single crystals of bacterial and synthetic poly(beta-hydroxybutyrate). *Macromolecules* **1996**, *29*, 2472 and literature cited therein.
8. Kemnitzer, J.E.; McCarthy, S.P.; Gross, R.A. Preparation of predominantly syndiotactic poly(beta-hydroxybutyrate) by the tributyltin methoxide catalysed ring-opening polymerization of racemic beta-butyrolactone. *Macromolecules* **1993**, *26*, 1221.
9. Kemnitzer, J.E.; McCarthy, S.P.; Gross, R.A. Syndiospecific ring-opening polymerisation of beta-butyrolactone to form predominantly syndiotactic poly(beta-hydroxybutyrate) using tin(IV) catalysts. *Macromolecules* **1993**, *26*, 6143.
10. Hori, Y.; Suzuki, M.; Yamaguchi, A.; Nishishita, T. Ring-opening polymerisation of optically active beta-butyrolactone using distannoxane catalysts: synthesis of high-molecular-weight poly(3-hydroxybutyrate). *Macromolecules* **1993**, *26*, 5533.
11. Schindler, A.; Hibionada, Y.M.; Pitt, C.G. Aliphatic polyesters. III. Molecular weight and molecular weight distribution in alcohol-initiated polymerizations of epsilon-caprolactone. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 319.
12. van Dijk, I.A.P.P.; Smit, J.A.M.; Kohn, F.G.; Feijen, I. Characterization of poly(D,L-lactic acid) by gel permeation chromatography. *J. Polym. Sci. Polym. Ed.* **1983**, *21*, 197.
13. Kricheldorf, H.R.; Stricker, A.; Langanke, D. Polyactones. 50. The reactivity of cyclic and non-cyclic dibutyltin bisalkoxides as initiators of lactones. *Macromol. Chem. Phys.* **2001**, *202*, 2525.
14. Kricheldorf, H.R.; Stricker, A.; Langanke, D. Polyactones. 52. Tin carboxylates as initiators of epsilon-caprolactone. *Macromol. Chem. Phys.* **2001**, *202*, 2963.

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