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Polylactones. 41. Polymerizations of β-D,L-Butyrolactone with Dialkyltinoxides as Initiators

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ABSTRACT: The usefulness of dimethyl-, diethyl-, dibutyl- and dioctyltin oxide for the preparation of syndiotactic poly(β-D,L-butyrolactone) was studied. Most polymerizations were conducted in bulk and a few polymerizations in toluene or chlorobenzene. The reaction temperature was varied between 50 and 100 °C. Below 50 °C the initiatiors were not reactive enough. Me_2SnO proved to be the least reactive initiator. High yields and the highest molecular weights (M_n's up to 80 000 and M_w up to 130 000) were achieved with Bu_2SnO. These high molecular weights were obtained at low monomer/initiator ratios (M/I = 50−400). In contrast to literature data, no conversion was observed at M/I ratios >600 regardless of the reaction conditions. The highest percentage of syndiotactic diads (72%) resulted either from polymerizations with Bu_2SnO at 50 °C or with Et_2SnO at 100 °C. Transparent films with high expansibility were cast from the 63 and 70% syndiotactic polybutyrolactone samples, which may be useful as biodegradable packaging materials.

Introduction

Poly(β-D-hydroxybutyric acid) and copolyesters of β-D-hydroxybutyric acid and smaller amounts of other β-D-hydroxy acids have attracted much interest as biodegradable engineering plastics.[1,2] They are meanwhile produced by several chemical companies, a technological process involving suitable microorganisms.[1] Isotactic poly(β-D- or -L-butyrolactone) can also be obtained by ring opening polymerization of β-D- or β-L-butyrolactone.[3−6] Unfortunately, the synthesis of an optically active lactone is costly, and thus, the biotechnological production of an optically active poly(3-hydroxybutyric acid) is currently not rivaled by a fully synthetic route.

However, a mainly isotactic poly(β-hydroxybutyrolactone) can also be prepared from the relatively inexpensive β-D,L-butyrolactone (β-D,L-BL) by means of stereoselective initiators.[7−12] Such initiators are typically derivatives of aluminum or zinc. However, the products obtained in this way are usually not homogeneous. The lengths of the isotactic blocks may vary, and atactic or even partially syndiotactic chains may be formed in addition to the preferentially isotactic polyester.[12] As a source of poly(β-hydroxybutyrolactone), β-D,L-butyrolactone has the advantage that it may also enable the preparation of an amorphous atactic poly(β-D,L-BL) and a crystalline syndiotactic poly(β-D,L-BL). The only class of initiators yielding a more or less syndiotactic poly(β-D,L-BL) are tin compounds containing at least one Sn−O bond.[13−18] Tributyltin methoxide, dibutyltin dimethoxide, triphenyltin methoxide, and diphenyltin dimethoxide were preferentially used as initiators. Under optimum conditions poly(β-D,L-BL) with more than 80% of syndiotactic diads was obtained, but the molecular weights were low and rarely exceeded values of 20 000. Furthermore, no polymerization was observed at monomer/initiator (M/I) ratios > 400.

Recently, Hori et al.[6] reported on one Bu_2SnO-initiated polymerization of β-D-BL conducted with a M/I ratio of 1000 in bulk at 100 °C. A high yield (87%) and high molecular weights were apparently found (M_n 119 000, M_w 193 000).[6] In an analogous experiment racemic β-D,L-BL was polymerized in toluene at 100 °C at a M/I ratio of 2000 and again extremly high molecular weights (M_n 187 000, M_w 398 000) were found. However, numerous attempts to reproduce the Bu_2SnO initiated polymerization of β-D,L-BL in our lab failed (see below) and this result prompted us to study dialkyltin oxide-initiated polymerizations of β-D,L-BL in more detail.

Experimental Section

Materials. β-D,L-Butyrolactone was purchased from Aldrich Co. (Milwaukee, WI) either in 250-mL or in 1-L bottles. The β-D,L-BL received in 250-mL bottles proved to be colorless over a period of 8 years. However, an 1-L sample showed yellowish color and the molecular weights obtained from this yellowish monomer were inferior to those obtained from the colorless product under identical reaction conditions. As described below the monomer was purified in three ways. Regardless of the purification procedure, no impurity was detectable by GC and 400-MHz ^1H NMR spectra. Bu_2SnO was either purchased from Aldrich Co. or from ABCR GmbH (Karlsruhe, FRG). n-Oct_2SnO, Et_2SnO, and Me_2SnO were all purchased from ABCR. All initiators were activated by heating in a vacuum of 10^{-1} mbar for 24 h (see text).

Toluene was dried and distilled over sodium metal under argon. Chlorobenzene was first distilled over P_4O_{10} and afterwards distilled over K_2CO_3 under argon.

Polymerizations. (A) With R_2SnO ($R = CH_3$, C_2H_5, n-C_4H_9, n-C_8H_{17}) in Bulk. β-D,L-Butyrolactone (40 mmol) and the calculated amount of initiator were weighed into a 50 mL Erlenmeyer flask with silanized glass walls. The reaction vessel was closed with a glass stopper and steel spring and thermostated at the temperatures given in Tables 1−7. The reaction mixture was dissolved in CH_2Cl_2, filtered, and precipitated into cold diethyl ether. The reaction mixtures were prepared in a glovebox under dry argon.

(B) With R_2SnO ($R = CH_3$, C_2H_5, n-C_4H_9, n-C_8H_{17}) in Solution. β-D,L-Butyrolactone (40 mmol), the calculated amount of initiator, and 3 mL of a dry solvent were weighed into a 50 mL Erlenmeyer flask with silanized glass walls. The reaction vessel was closed with a glass stopper and steel spring and thermostated at the temperatures given in Tables 1−7. The reaction mixture was dissolved in CH_2Cl_2, filtered, and precipitated into cold diethyl ether. The reaction mixtures were prepared in a glovebox under dry argon.

Measurements. The viscosities were measured in an automated Ubbelohde viscosimeter thermostated at 25 °C. The 25,18-MHz ^{13}C NMR spectra were recorded on a Bruker AC-

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Table 1. Bu_2SnO[a]-Initiated Polymerizations of β-D,L-Butyrolactone[b] in Bulk at 100 °C/24 h

polym no.	source of Bu_2SnO	mon init	yield, %	η_{inh},[c] dL/g	T_g,[d] °C	T_m,[d] °C
1	ABCR	100	82	0.66	10	76
2	ABCR	200	83	0.81	8	47/76
3	Aldrich (100 g)	100	77	0.65	10	51/71
4	Aldrich (100 g)	200	79	0.77	9	50/72
5	Aldrich (500 g)	100	71	0.73	9	49/72
6	Aldrich (500 g)	200	71	0.76	8	48/71

[a] Activated at 100 °C/24 h in vacuo. [b] Purified by procedure II. [c] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2. [d] DSC measurements with a heating rate of 20 °C/min.

Table 2. Yield and Inherent Viscosities of Poly(β-D,L-Butyrolactone)[a] Polymerized with Bu_2SnO[b] at 100 °C/24 h

polym no.	reaction medium	mon. init.	yield, %	η_{inh},[c] dL/g
1	bulk	100	81	0.68
2	bulk	200	83	0.76
3	bulk	400	75	0.78
4	bulk	600	0	
5	bulk	1000	0	
6	toluene	100	75	0.26
7	toluene	200	76	0.40
8	toluene	200	75	0.37
9	toluene	400	75	0.38
10	toluene	600	0	
11	toluene	1000	0	

[a] Dried according to procedure II. [b] From Aldrich Co., activated at 100 °C/24 h in vacuo. [c] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2.

100 FT-NMR spectrometer in 10-mm-o.d. sample tubes. The DSC measurements were conducted with a Perkin-Elmer DSC-4 in aluminium pans under nitrogen. The WAXS powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered Cu Kα radiation. The GPC measurements were conducted with a Kontron HPLC 420 equipped with Waters differential refractometer 410. Four Ultrastyragel columns with pose sizes of 10^2, 10^3, 10^4, and 10^5 Å were used, and tetrahydrofurane served as eluent.

Results and Discussion

Polymerizations Initiated with Bu_2SnO. It is obvious that the preparation of high molecular weight polymers requires dry and pure monomers, and thus, particular attention was paid to the purification of β-D,L-BL. Calcium hydride is known to be most reactive commercial product which can be used for the purification of β-D,L-BL without the risk of side reaction. Therefore, all previous reports[14−19] mention a distillation of β-D,L-BL over CaH_2. More reactive drying agents, such as Na,NaH, $LiAlH_4$, or P_4O_{10} react readily with β-D,L-BL. In the present work three slightly different purification procedures were compared (which were all conducted under argon):

(I) Stirring over freshly powdered CaH_2 at 25 °C for 48 h and distillation in vacuo around 60 °C. (II) Stirring over freshly powdered CaH_2 at 25 °C for 48 h and distillation followed by redistillation over a second batch of freshly powdered CaH_2. (III) Dilution of the β-D,L-BL with dry Et_2O (volume ratio 1:3) and stirring with dry $NaHCO_3$ for 1 h followed by filtration. Afterward stirring with dry Na_2SO_4 for 2 h followed by filtration, evaporation of the diethyl ether, stirring over freshly powdered CaH_2 at 25 °C for 48 h, and distillation plus redistillation in vacuo at 60 °C.

This procedure was described in a patent of Hori et al.[19]

The best results were obtained by polymerization of β-D,L-BL purified by procedure II. Although there were only slight differences all polymerizations mentioned in Tables 1−7 were conducted on the basis of the purification method II.

Furthermore, it was found in this work that the pretreatment of the initiator plays a role in its activity. Heating in vacuo over P_4O_{10} activates Bu_2SnO unless the temperature is too high. At temperatures ≥130 °C, sintering and partial desactivation was observed. The best results were obtained after drying at 60−100 °C for 24 h in vacuo, and thus, this activation of Bu_2SnO was used for all polymerizations listed in the present work. Moreover, three different batches of Bu_2SnO were compared. One batch was purchased from ABCR GmbH and two batches (100 and 500 g) from Aldrich Co. The polymerizations conducted under identical conditions are compiled in Table 1. The highest yield and highest viscosity resulted from the ABCR catalyst but the differences were not significant (this conclusion was confirmed by the experiments and results summarized in Tables 3 and 4).

Two series of polymerizations (listed in Table 2) were designed to study the influence of the monomer/initiator (M/I) ratio on both yield and molecular weight. The temperature was fixed at 100 °C the temperature selected by Hori et al.[6] The reaction time was fixed at 24 h and, thus, 50% longer than the 16 h used by Hori et al.[6] One series of polymerizations was performed in bulk and the M/I was varied between 100 and 8000. However, all polymerizations with M/I's above 1000 were not listed in Table 2. An analogous series of polymerizations was conducted in toluene at a concentration corresponding to that used by Hori et al.[6] However, again all experiments with M/I ratios above 400 failed again to yield poly(β-D,L-BL). These results perfectly agree with those of previous studies based on dibutyl-, diphenyl-, tributyl-, and triphenyltin methoxides. Regardless of the initiator no polymerization was observed at M/I ratios above 400. Therefore, it is difficult to understand how Hori et al. have succeeded to obtain a high yield of poly(β-butyrolactone) at a M/I of 2000 in 16 h. In this connection it should be emphasized that an additional 16 attempts were made to reproduce the experiment of Hori et al. (toluene, 100 °C, 16 h)[6] exactly. Two different batches of β-D,L-butyrolactone were used, all three purification procedures were applied, and both the ABCR and the Aldrich catalyst were used. Furthermore a second experienced co-worker (Soo-Ran Lee) was involved. However, all these attempts to reproduce the results reported by Hori et al.[6] failed completely in our lab.

Unfortunately Hori et al.[6] did not make any comment on the origin and purity of their β-D,L-BL. The purified Aldrich β-D,L-BL used in this work did not show any impurity in 400 MHz ^1H NMR spectra or in GC analyses. However, we have also observed that the quality of β-D,L-BL batches purchased from Aldrich Co. over a period of several years may vary, so that the molecular weights of the resulting poly (β-D,L-BL) are not well reproducible, even when the identical purification and polymerization procedures were used (see below). The β-D,L-BL used for the experiments of Tables 1−7 was the best sample we had purchased in a period of 5 years. In other words, we cannot exclude that the β-D,L-BL used by Hori et al.[6] had a higher degree of purity.

Three more series of polymerizations were performed with the purpose of elucidating the influence of the temperature on the molecular weight and on the ste-

Table 3. Bu_2SnO-Initiated Polymerizations of β-D,L-Butyrolactone[a] (M/I = 50) Conducted in Bulk and Solution

polym no.	source and activ of Bu_2SnO	reaction medium	temp, °C	time, days	yield, %	η_{inh},[b] dL/g	T_g,[c] °C	T_m,[c] °C	% synd diads[d]
1	ABCR activated at 100 °C for 24 h in vacuo	bulk	100	1	91	0.61	9	50/70	60
2		bulk	75	1	78	0.63	11	51/74	63
3		bulk	50	21	52	0.21	7	66	nd
4		toluene	50	21	91	0.44	11	64	70
5		toluene	25	21	0				
6		chlorobenzene	50	21	88	0.28	5	65/87	70
7		chlorobenzene	25	21	0				

[a] Purified by procedure II. [b] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2. [c] DSC measurements with a heating rate of 20 °C/min. [d] Calculated from the i/s ratio in the CO peaks in the ^{13}C NMR spectra.

Table 4. Bu_2SnO-Initiated Polymerizations of β-D,L-Butyrolactone[a] Conducted with M/I = 50 at Various Temperatures

polym no.	source and activ. of Bu_2SnO	reaction medium	temp, °C	time, days	yield, %	η_{inh},[b] dL/g	T_g,[c] °C	T_m,[c] °C	% synd diads[d]
1	Aldrich Co. activated at 100 °C for 24 h in vacuo	bulk	100	1	85	0.54	12	50/74	58
2		bulk	75	1	89	0.71	11	47/73	62
3		bulk	50	21	83	0.28	12	77	64
4		toluene	50	21	90	0.41	14	75	69
5		toluene	25	21	0				
6		chlorobenzene	50	21	78	0.26	5	66/88	71
7		chlorobenzene	25	21	0				
8	Aldrich Co. activated at 60 °C for 24 h in vactuo	bulk	100	1	89	0.52	8	46/70	58
9		bulk	75	1	89	0.74	10	68	62
10		bulk	50	21	58	0.21	9	48/76	nd
11		toluene	50	21	94	0.46	11	65	70
12		toluene	25	21	0				
13		chlorobenzene	50	21	81	0.30	7	64/85	71
14		chlorobenzene	25	21	0				

[a] Purified by procedure II. [b] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2. [c] DSC measurements with a heating rate of 20 °C/min [d] Calculated from the i/s ratio of the CO peaks in the ^{13}C NMR spectra.

Table 5. Oct_2SnO-Initiated Polymerizations of β-D,L-Butyrolactone[a] Conducted with M/I = 50 in Bulk

polym no.	Activation of Oct_2SnO	temp, °C	time, days	yield, %	η_{inh},[b] dL/g	T_g,[c] °C	T_m,[c] °C	% synd diads[d]
1	100 °C/24 h in vacuo	100	1	70	0.30	8	44/79	58
2	100 °C/24 h in vacuo	75	8	44	0.24	8	74	60
3	100 °C/24 h in vacuo	50	21	50	0.17	7	45/80	65
4	50 °C/24 h in vacuo	100	1	73	0.31	9	49/75	nd
5	50 °C/24 h in vacuo	75	1	78	0.31	12	51/74	nd
6	50 °C/24 h in vacuo	50	21	9	0.11	1	53/78	nd

[a] Dried according procedure II. [b] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2. [c] DSC measurements with a heating rate of 20 °C/min. [d] Calculated from the i/s ratio of the CO peaks in the ^{13}C NMR spectra.

Table 6. Me_2SnO-Initiated Polymerizations of β-D,L-Butyrolactone[a] Conducted with M/I = 50 at Various Temperatures

polym no.	reaction medium	temp, °C	time, days	yield, %	η_{inh},[c] dL/g	T_g,[d] °C	T_m,[d] °C	% synd diads[e]
1	bulk	100	1	63	0.68	12	83	61
2	bulk	75	1	2				
3	bulk	50	21	0				
4	toluene	50	21	0				

[a] Activated at 100 °C/24 h in vacuo. [b] Purified by procedure II. [c] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2. [d] DSC measurements with a heating rate of 20 °C/min. [e] Calculated from the i/s ratio of the CO peaks in the ^{13}C NMR spectra.

reoselectivity. The source of the initiator was varied (Table 3 versus Table 4) and its activation temperature was varied (Table 4). However, the results of all three series of polymerizations show a satisfactory agreement. When the temperature of the bulk polymerizations was reduced from 100 to 50 °C both yields and inherent viscosities decreased. When concentrated solutions of the monomer in toluene were polymerized at 50 °C, higher yields and viscosities were obtained than in bulk, presumably due to a higher mobility of the polymer chains and active chain ends. However, when toluene was replaced by chlorobenzene, which is a better solvent for poly(β-D,L-butyrolactone), no further progress was detectable. For the stereoselectivities a slight increase was found up to values of 71 ± 2% of syndiotactic diads. High degrees of tacticities at lower temperatures were also found for $Bu_2Sn(OMe)_2$-initiated polymerizations and are an obvious trend. Unfortunately, all attempts to polymerize β-D,L-butyrolactone at 25 °C failed regardless of if the experiments were conducted in bulk or in solution.

The ^{13}C NMR signals and the WAXS powder pattern of the poly(β-D,L-butyrolactone) with the highest level of syndiotactic stereosequences (no. 6, Table 4) agree with those of sample no. 5, Table 7, illustrated in Figures 1 and 2. Furthermore, the results of DSC measurements are worth discussing. All samples of poly(β-D,L-BL) initiated by Bu_2SnO at 100 °C (or lower temperatures) proved to be semicrystalline with melting temperatures T_m's in the range 47−77 °C. In most cases two endotherms appeared in the first heating trace (Figure 3A), but the low temperature endotherm disappeared after annealing between T_{m1} and T_{m2}. When the crude reaction products prepared with M/I ratios of 50 or 100 were characterized, two additional endotherms in the range 75−85 °C and 110−130 °C were observed (Figure 3B). The endotherm at higher temperature has been reported for highly syndiotactic poly(β-D,L-butyrolactone) prepared with $Bu_2Sn(OMe)_2$ at low temperatures (≤25 °C).[16] However, when the samples obtained

Table 7. Et_2SnO-Initiated Polymerizations of β-D,L-Butyrolactone[a] (M/I = 50) Conducted in Bulk at Various Temperatures

polym no.	activation of Et_2SnO	temp, °C	time, days	yield, %	η_{inh},[b] dL/g	T_g,[c] °C	T_m,[c] °C	% synd diads[d]
1	100 °C/24 h in vacuo	100	1	91	0.59	11	49/73	61
2	100 °C/24 h in vacuo	75	1	92	0.69	10	73	61
3	100 °C/24 h in vacuo	50	21	89	0.61	13	70	59
4	100 °C/24 h in vacuo	25	21	0				
5	140 °C/24 h in vacuo	100	1	85	0.57	11	50/71	72
6	140 °C/24 h in vacuo	75	1	87	0.63	10	71	70
7	140 °C/24 h in vacuo	50	21	84	0.37	10	67	65
8	140 °C/24 h in vacuo	25	21	0				

[a] Dried according to procedure II. [b] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2. [c] DSC measurements with a heating rate of 20 °C/min. [d] Calculated from the i/s ratio of the CO peaks in the ^{13}C NMR spectra.

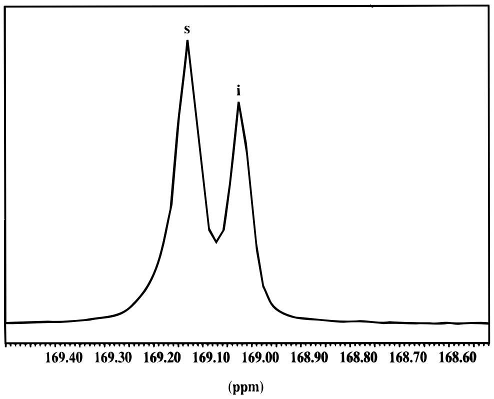

Figure 1. 25.18 MHz ^{13}C NMR spectrum (CO signals) of poly(β-D,L-HBu) (Table 7, no. 5); i/s ratio = 72%.

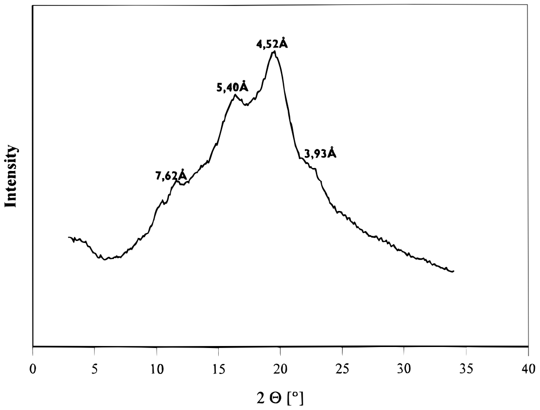

Figure 2. WAXS powder pattern of poly(β-D,L-HBu) (Table 7, no. 5).

from initiation with Bu_2SnO were dissolved again, filtered, and precipitated into cold diethyl ether, the endotherm >100 °C had disappeared. This endotherm was also almost absent in the crude products obtained with a M/I ratio of 400 in that temperature range. Therefore, it is obvious that the presence of the initiator is responsible for this endotherm. Also the neat initiator exhibited an endotherm.

Initiation with Oct_2SnO, Me_2SnO, and Et_2SnO. The interesting results obtained by initiation with Bu_2SnO justified the investigation of the effects a variation of the alkyl groups of the initiator might have. Since Bu_2SnO is insoluble in the monomer (or in a toluene monomer mixture), the longer alkyl groups of Oct_2SnO were supposed to favor a more rapid reaction and dissolution of this initiator. However, also Oct_2SnO was insoluble in the monomer, and at least a part of it remained insoluble at polymerization temperatures ≤75 °C if it was activated at 50 °C. However, activation of Oct_2SnO at 100 °C or a polymerization temperature of 100 °C had the consequence that the initiator gradually dissolved in the reaction mixture. Nonetheless, the results of Oct_2SnO-initiated polymerizations summarized in Table 5 were disappointing. Regardless, if Oct_2SnO was activated at 50 or at 100 °C the yields and inherent viscosities were considerably lower than those of anologous polymerizations initiated with Bu_2SnO, and even the percentage of syndiodactic diads was lower.

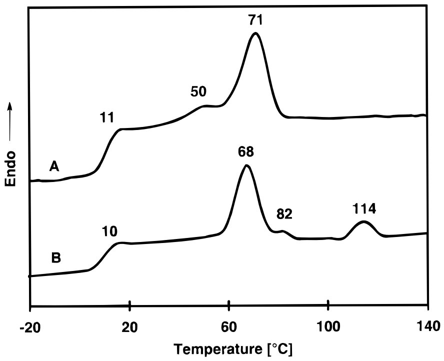

Figure 3. DSC heating curve (heating rate 20 °C/min) of poly(β-D,L-HBu) (Table 7, no. 5). (B) DSC heating curve (heating rate 20 °C/min) of crude poly(β-D,L-HBu) (Table 4, no. 9) with traces of Bu_2SnO.

Me_2SnO was the initiator with the shortest alkyl groups and lowest tendency to react with the monomer. As illustrated by the data listed in Table 6, the low tendency to react is reflected in the absence of any polymerization, when the reaction temperature was reduced from 100 °C. The yields obtained at 100 °C were lower than those of Bu_2SnO initiation under identical condition (no. 1, Tables 3 and 4) but the inherent viscosities were higher. The tacticities were almost identical with those resulting from initiation with Bu_2SnO at 100 °C. In other words, Me_2SnO is clearly more attractive as initiator than Oct_2SnO but is not advantageous over Bu_2SnO.

Finally, two series of polymerizations were conducted with Et_2SnO as initiator, which was activated either at 100 °C (nos. 1−4, Table 7) or 140 °C (nos. 5−8). Both series show slight but remarkable differences. The yields and viscosities were higher after the activation of Et_2SnO at 100 °C, but the percentage of syndiotactic diads was higher after activation at 140 °C. Both series agree in that no polymerization takes place at 25 °C. Hence, the performance of Et_2SnO as initiator resembles largely that of Bu_2SnO, but one result is particularly remarkable, and that is the fact that 72 ± 1% syndiotactic diads were formed at 100 °C (no. 5, Table 7). No other tin initiator studied so far has yielded such a high level of stereoselectivity at 100 °C. In the case of Bu_3SnOMe, $Bu_2Sn(OMe)_2$, or Bu_2SnO a reaction temperature of 40 or 50 °C is required to obtain 70% syndiotactic diads, but these lower temperatures entail much longer reaction times. In the case of Et_2SnO a reaction time of 24 h was found to suffice for a yield of 87% even at 75 °C (no. 6, Table 7), and the stereoselectivity is as high as 70% syndiotactic diads. Thus, the Et_2SnO-initiated polymerizations at 75 or 100 °C in bulk are quite attractive from a preparative point of view.

Studies of Films. In order to obtain at least a crude idea of the absolute molecular weights of the poly (β-D,L-BL) prepared in this work, several samples were characterized by GPC measurements in tetrahydrofuran. The GPC curves were calibrated with *a* and *K* values of the Mark−Houwink equation (1), which was published for solutions of polystyrene in tetrahydrofuran.[20] The calibration is possibly not identical with the calibration used by other authors, so that the molecular weight data are not directly comparable. Viscosity data which allow a more reliable comparison were never published by other authors. Most number average and weight average molecular weights (M_n and M_w) obtained in this way were listed in Table 2. Furthermore, the sample with the highest viscosity value (no. 2, Table 1) was measured, and a M_n of 80 000 with a M_w of 130 000 were found. Therefore, it may be said that polydispersities in the range of 1.6−1.7 are typical for polymerization conducted in this work.

$$[\eta] = (1.25 \times 10^{-4})M^{0.717} \qquad (1)$$

Finally, the samples no. 9, Table 4 (M_n = 68 000, M_w = 11 000), and no. 6, Table 7 (M_n = 55 000, M_w = 93 000), were characterized, because in both cases relatively high molecular weights are combined with a high percentage of syndiotactic diads. Such samples were of interest for the casting and mechanical characterization of films. For this purpose larger quantities of poly(β-D,L-BL) were prepared under the same reaction conditions used for samples no. 9, Table 4, and no. 6, Table 7. Despite an identical purification and polymerization procedure the inherent viscosities of the larger samples were 10−15% lower. However, these poorer results were obtained from another batch of β-D,L-BL. This means that the quality of the commercial β-D,L-BL may vary, even when purchased from the same source, so that the molecular weights are not exactly reproducible.

The larger quantities of poly(β-D,L-BL) were then used to cast films from CH_2Cl_2 with a thickness of 0.5 and 1 mm. These films proved to be slightly less transparent than films cast from entirely atactic and amorphous poly(D,L-lactides). This oberservation is remarkable, because in the case of poly(β-D,L-BL) the mechanical strength of the films is a consequence of their crystallinity. In the absence of crystallinity poly(β-D,L-BL) is a liquid above 10 °C in contrast to poly(D,L-lactide), which has a glass transition temperature (T_g) on the order of 50−55 °C. In general, the semicrystalline polymers are not transparent because the crystallites are optically more dense than the surrounding amorphous matrix and cause diffuse light-scattering. In the case of poly(β-D,L-BL) films, only the short syndiotactic block can crystallize, and obviously, their crystallites are so small and imperfect that no significant light scattering occurs.

Mechanical measurements of doggy-bone type test bars proved that the elastic modulus of poly(β-D,L-Hbu) with 62 ± 2% syndiotactic diads is as low as 9.5 MPa and that of the sample with 70% syndiotactic diads around 13.4 MPa. However, both samples were extremely extensible, and after annealing at 25 °C for 36 h the elongation at break reached 450−500%. Freshly prepared films showed elongations up to 850%. Taken together, the best poly(β-D,L-Hbu) samples prepared in this work are certainly not useful as engineering plastics, but they have a certain potential as biodegradable films for packaging purposes.

Conclusion

From the comparison of polymerizations involving four different dialkyl tin oxides as initiators, the following interesting conclusions may be drawn. No polymerizations are feasible at temperatures around 25 °C or below. No polymerizations are feasible with M/I ratios above 400. Bu_2SnO and Et_2SnO are superior to Oct_2SnO and Me_2SnO. With Bu_2SnO and Et_2SnO syndiotactic diads are preferentially formed (up to 72%) even at temperatures up to 100 °C. Furthermore high yields (85−94%) and weight average molecular weights above 100 000 can be obtained even at low M/I ratios. The molecular weights do not significantly depend on the M/I ratio. Such preferentially syndiotactic poly(β-D,L-butyrolactone)s yield flexible transparent films which may be useful as biodegradable packaging materials.

References and Notes

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