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POLYLACTONES. XXV.† POLYMERIZATIONS OF *racemic-* AND *meso-*D,L-LACTIDE WITH Zn, Pb, Sb, AND Bi SALTS—STEREOCHEMICAL ASPECTS

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ABSTRACT

Polymerizations of *racemic-* and *meso-*D,L-lactide were conducted at 120°C in xylylene or in bulk. Lead oxide (PbO), zinc stearate, antimony(III) 2-ethylhexanoate, and bismuth(III) 2-ethylhexanoate were used as initiators. With PbO and Zn stearate, bulk polymerizations were also conducted at 150°C. High yields ($\geq 90\%$) were only obtained with PbO and Bi(III) 2-ethylhexanoate, but the molecular weights were low in all cases. The stereosequences were analyzed by ^{1}H- and ^{13}C-NMR spectroscopy. A significant stereospecificity was never detected. At higher reaction temperatures the resulting stereosequences show an increasing tendency toward randomness.

INTRODUCTION

The properties of poly(L-lactide) and poly(D,L-lactide) with a random stereosequence differ largely [1]. Poly(L-lactide) is crystalline with a melting point around 175°C whereas atactic poly(D,L-lactide) is an amorphous material with a glass transition in the temperature range of 45 to 55°C. However, a poly(D,L-lactide) with long blocks of L- and D-units should show properties similar to those of poly(L-lactide). Such stereoblock copolylactides have never been synthesized from *rac.*-D,L-lactide. Therefore, it was the purpose of this work and other parts of this

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†For Part 24, see Ref. 3.

series [2, 3] to look for initiators capable of initiating a stereospecific polymerization of *rac.*-D,D,L,L-lactide. The polymerizations were extended to *meso*-D,L-lactide, because a comparison of *rac.*- and *meso*-D,L-lactide under identical conditions allows one to determine if a deviation from Bernoullian-type kinetics is the result of stereospecificity or of transesterification.

EXPERIMENTAL

Materials

rac.-D,L-Lactide and *meso*-D,L-lactide (S-grade) were gifts of Boehringer Ingelheim GmbH (Germany). They were recrystallized from ethylacetate and dried over P_4O_{10} *in vacuo*. A melting point of 125–126°C was found for the *rac.*-D,L-lactide and 52–54°C for the *meso*-D,L-lactide. Zinc stearate was purchased from Ventron GMbH (W-7500 Karlsruhe, Germany), PbO was purchased from Merck & Co. (W-6100 Darmstadt, Germany), and Sb(III) 2-ethylhexanoate and Bi(III) 2-ethylhexanoate were gifts of Hoechst AG (W-6230 Hoechst, Germany). All catalysts were dried over P_4O_{10} *in vacuo*. Xylene was distilled over P_4O_{10} followed by distillation over sodium/potassium alloy.

Polymerizations

In Xylene

A D,L-lactide (30 mmol) was dissolved in dry xylene (40 mL) in an Erlenmeyer flask (50 mL) with silanized glass walls. The catalyst was added, and the reaction vessel was closed with a glass stopper and a steel spring. The reaction mixture was then completely immersed in a thermostated oil bath. The reaction mixture was cooled, diluted with CH_2Cl_2 (30–50 mL), precipitated in cold methanol, and dried at 40°C *in vacuo*.

In Bulk

A D,L-lactide (40 mmol) and the catalyst were weighed into a 25-mL Erlenmeyer flask with silanized glass walls. The polymerization was then conducted as described above.

Measurements

The inherent viscosities were determined with an automated Ubbelohde viscometer thermostated at 20°C .

The 360-MHz ^{1}H-NMR spectra were measured in 5 mm o.d. sample tubes on a Bruker AM 360 FT spectrometer. The 90.4-MHz ^{13}C-NMR spectra were recorded with the same spectrometer using 10 mm o.d. sample tubes. $CDCl_3$ containing TMS was used as the solvent.

The optical rotations were measured with a Perkin-Elmer Md 241 polarimeter at a concentration of 10 g/L in chloroform at a wavelength of 578 nm in a cell of 100 mm length.

RESULTS AND DISCUSSION

Analytical Aspects

It is known from the work of Bero et al. [4] and from a previous part of this series [2] that both ^{1}H- and ^{13}C-NMR spectra are sensitive to the stereosequences of poly(D,L-lactide) on the level of tetrads. When polymerizations of *rac.*-D,L-lactide are conducted under mild reaction conditions so that exclusively ring-opening (without transesterification or racemization) occurs, the following five tetrads may be formed: iii, isi, iis, sii, sis. In the case of *meso*-D,L-lactide, the following five tetrads may appear: sss, sis, ssi, iss, isi. Here, in Eq. (1), and in Figs. 1-3, the symbols "i" and "s" represent isotactic and syndiotactic dyads.

As discussed previously [2], tetrad splittings of both ^{1}H and ^{13}C NMR signals could be identified for the CH group of the lactidyl unit. The peak assignments presented in Figs. 1-3 are based on a previous study [2]. Quantification of the peak intensities also allows a more quantitative characterization of the stereosequences. According to the goal of the present work, the average length of isotactic blocks, L_i (i.e., the number of directly connected L or D units), was the most useful value for the characterization of the stereosequences. These L_i values were calculated according to Eq. (1) from the intensities of the individual tetrad peaks in the ^{1}H- and ^{13}C-NMR spectra of selected poly(D,L-lactide) samples. A Bernoullian-type polymerization of *rac.*-D,L-lactide entails a stereosequence with $L_i = 4.0$. In the case of *meso*-D,L-lactide, the Bernoullian-type stereosequence is characterized by $L_i = 1.3$, whereas $L_i = 2.0$ is typical for a random sequence of L- and D-units. As a consequence, a stereospecific polymerization of *rac.*-D,L-lactide favoring isotactic blocks will result in L_i-values > 4.0. In contrast, a syndiotactic stereospecificity will lead to $L_i < 4.0$. However, in the case of $L_i < 4.0$, it is difficult to distinguish a syndiotactic stereospecificity from the influence of transesterification and racemization of individual monomer units. Therefore, it is useful to polymerize *meso*-D,L-

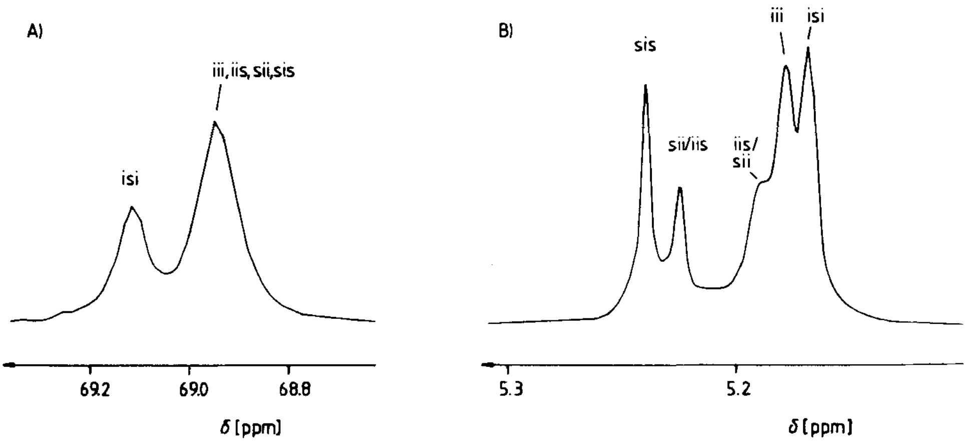

FIG. 1. 90.5 MHz ^{13}C-NMR signal (A) and 360 MHz ^{1}H-NMR signal (B) of the CH group of the poly(D,L-lactide) prepared with PbO and *rac.*-D,L-lactide in bulk at 120°C/2 h (No. 5, Table 1).

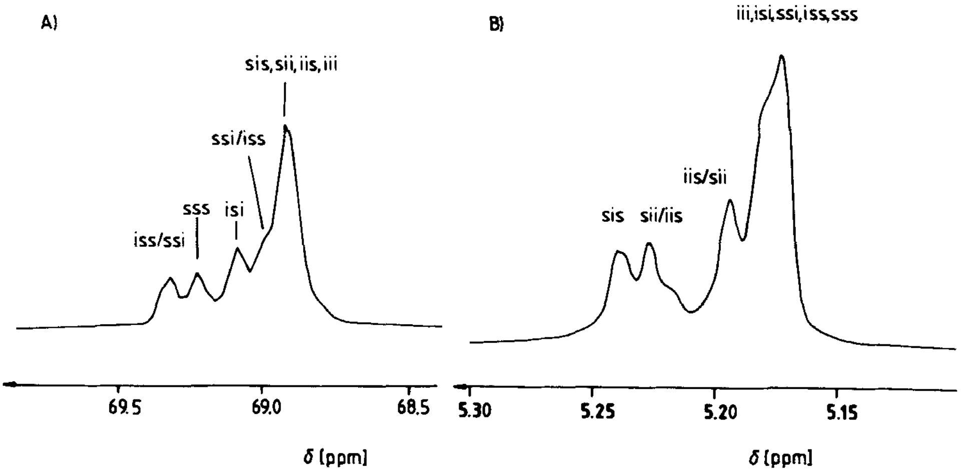

FIG. 2. 90.5 MHz ^{13}C-NMR signal (A) and 360 MHz ^{1}H-NMR signal (B) of the CH group of the poly(D,L-lactide) prepared with PbO and *rac.*-D,L-lactide on bulk at 180°C/24 h (No. 19, Table 1).

lactide under the same reaction conditions. If transesterification or racemization are operating, the L_i values of both poly(*rac.*-D,L-lactide) and poly(*meso*-D,L-lactide) will approach a value of 2.0 in contrast to a situation with syndiotactic stereospecificity.

$$L_i = \frac{3I_{iii} + 2I_{isi} + 2I_{sii} + 2I_{iis} + I_{sis} + I_{ssi} + I_{iss}}{I_{isi} + I_{iis} + I_{ssi} + 2I_{sis} + 2I_{ssi} + 2I_{iss} + 3I_{sss}} + 1 \qquad (1)$$

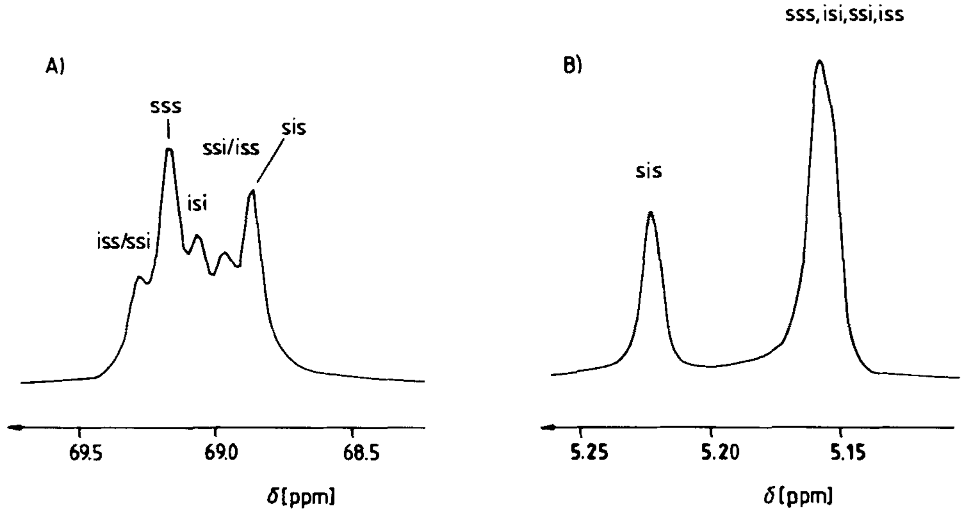

FIG. 3. 90.5 MHz ^{13}C-NMR signal (A) and 360 MHz ^{1}H-NMR signal (B) of the CH group of the poly(D,L-lactide) prepared with Bi(III) 2-ethylhexanoate and *rac.*-D,L-lactide in xylene at 120°C/4 h (No. 1, Table 4).

Results of Polymerizations

Previous studies [2, 3] of the stereospecific polymerization of *rac.*-D,L-lactide have concentrated on aluminum and tin catalysts. Further polymerizations conducted with L-lactide [5] have shown that PbO, Sb(III) 2-ethylhexanoate Zn(II)-stearate, and Bi(III) 2-ethylhexanoate are good initiators which give high yields and high molecular weights with little or no racemization. Therefore, these four metal salts were used in the present work. Relatively high initiator concentrations were used to obtain high conversions at relatively low temperatures (e.g., 120°C). Low temperatures were of interest to reduce the influence of transesterification and racemization on the stereosequences.

TABLE 1. Polymerizations Conducted in Xylylene or in Bulk with Lead Oxide (PbO), (M/I = 100:1)[a]

			racemic-D,L-Lactide			*meso*-D,L-Lactide		
No.	Temperature, °C	Time, h	Yield, %	η_{inh}, dL/g[c]	L_i[d]	Yield, %	η_{inh}, dL/g	L_i[d]
1	120 X[b]	4	50	0.12	3.7	65	0.06	1.33
2	120 X[b]	8	51	0.04	–	67	0.10	–
3	120 X[b]	16	72	0.04	–	64	0.08	–
4	120 X[b]	24	98	0.05	3.0	62	0.03	1.4
5	120	2	93	0.13	3.3	30	0.11	1.3
6	120	4	85	0.06	–	70	0.05	–
7	120	8	95	0.06	–	90	0.06	–
8	120	16	86	0.06	–	68	0.10	–
9	120	24	86	0.06	2.8	82	0.07	1.4
10	150	2	72	0.05	3.1	61	0.04	1.4
11	150	4	84	0.06	–	79	0.05	–
12	150	8	75	0.07	–	69	0.07	–
13	150	16	73	0.18	–	66	0.12	–
14	150	24	77	0.12	2.00	60	0.07	2.0
15	180	2	79	0.12	2.50	71	0.06	1.5
16	180	4	73	0.14	–	45	0.12	–
17	180	8	44	0.10	–	32	0.13	–
18	180	16	39	0.14	–	28	0.18	–
19	180	24	50	0.15	2.00	66	0.24	2.0

[a] Initial molar monomer/initiator ratio.

[b] In xylene.

[c] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2.

[d] Average lengths of the isotactic blocks as calculated from NMR spectra according to Eq. (1).

The results obtained with PbO are compiled in Table 1 and allow the following conclusions. Although high yields can be obtained at 120°C in xylene, the yields are even higher in bulk polymerizations. The stereosequences formed after short reaction times show L_i-values typical for the Bernoullian-type of kinetics (No. 1, Table 1). With increasing reaction time and temperature, the L_i-values of both *rac.*- and *meso*-D,L-lactide tend to 2.0. This tendency indicates the expected randomization by transsesterification and racemization (of individual monomer units). These tendencies are illustrated by ^{1}H- and ^{13}C-NMR spectra of Figs. 1 and 2.

The results obtained with Zn(II)stearate, Sb(III) 2-ethylhexanoate, and Bi(III) 2-ethylhexanoate are listed in Tables 2–4. In the case of Zn(II) stearate, it is conspicuous that the yields of poly(*meso*-D,L-lactide)s prepared at 150°C are higher than those of poly(*rac.*-D,L-lactide) although the polymerization of *meso*-D,L-lactide is thermodynamically less favorable for steric reasons. The stereosequences are of the "Bernoullian type" when the polymerizations are conducted at 120°C. The randomness increases at the higher reaction temperature of 150°C, although to a lesser extent than in the case of PbO_2. Possibly the lower basicity of the stearate anions compared to the oxide anions is responsible for this difference. The results compiled in Table 3 indicate that the catalytic activity of Sb(III) 2-ethylhexanoate is comparable with that of Zn(II) stearate. The yields, inherent viscosities, and L_i-values are similar.

More interesting are the results obtained with Bi(III) 2-ethylhexanoate (Table 4 and Fig. 3). In addition to high yields, the highest molecular weights of this work were obtained with this catalyst. Furthermore, conspicuous are the relatively low L_i-values found for Bi-initiated polymerizations of *rac.*-D,L-lactide. These L_i-values do not vary at all with the reaction time, and the L_i-values of polymerized *meso*-D,L-

TABLE 2. Bulk Polymerizations Conducted with Zinc Stearate as Initiator (M/I = 100:1)[a]

			racemic-D,L-Lactide			*meso*-D,L-Lactide		
No.	Temperature, °C	Time, h	Yield, %	η_{inh},[b] dL/g	L_i[c]	Yield, %	η_{inh},[b] dL/g	L_i[c]
1	120	24	20	0.12	3.6	0	–	–
2	120	48	33	0.13	–	11	0.12	–
3	120	72	44	0.14	3.6	35	0.14	1.3
4	150	4	11	0.21	3.5	70	0.12	1.3
5	150	8	14	0.20	–	79	0.13	–
6	150	16	28	0.21	–	81	0.14	–
7	150	24	66	0.31	3.3	77	0.13	1.5
8	150	48	59	0.26	–	75	0.13	–

[a] Initial molar monomer/initiator ratio.

[b] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2.

[c] Average lengths of the isotactic blocks as determined by NMR spectroscopy.

TABLE 3. Bulk Polymerizations Conducted with Sb(III) 2-Ethylhexanoate Initiator (M/I = 100:1)[a]

			racemic-D,L-Lactide			*meso*-D,L-Lactide		
No.	Temperature, °C	Time, h	Yield, %	η_{inh},[b] dL/g	L_i[c]	Yield, %	η_{inh},[b] dL/g	L_i[c]
1	120	4	1	–	–	4	–	1.3
2	120	8	5	–	3.2	11	–	–
3	120	16	45	0.19	–	30	0.10	–
4	120	24	61	0.20	–	56	0.14	–
5	120	48	59	0.18	2.9	76	0.26	1.4

[a] For footnotes, see Table 2.

lactide do not show any indication of transesterification. Thus, the Bi-initiated polymerizations of *rac.*-D,L-lactide seemingly involve a considerable degree of stereospecificity favoring a syndiotactic combination of D,D- and L,L-lactide. A mechanistic explanation for this observation cannot be offered at the current state of research. However, it may be said in summary that no catalyst has been found so far which enables a stereospecific polymerization of *rac.*-D,L-lactide favoring the formation of isotactic blocks.

TABLE 4. Polymerizations Conducted in Xylylene or Bulk at 120°C with Bi(III) 2-Ethylhexanoate as Initiator (M/I = 100:1)[a]

			racemic-D,L-Lactide			*meso*-D,L-Lactide		
No.	Reaction medium	Time, h	Yield, %	η_{inh},[b] dL/g	L_i	Yield, %	η_{inh},[b] dL/g	L_i[c]
1	Xylene	4	53	0.26	2.6	48	0.15	1.4
2	Xylene	8	74	0.23	–	64	0.38	–
3	Xylene	16	87	0.20	–	66	0.17	–
4	Xylene	24	91	0.20	–	68	0.14	–
5	Xylene	48	88	0.18	2.6	70	0.13	1.4
6	–	2	41	0.17	2.6	62	0.09	1.4
7	–	4	60	0.27	–	63	0.11	–
8	–	8	80	0.34	–	75	0.16	–
9	–	16	90	0.34	–	89	0.19	–
10	–	24	88	0.38	2.6	56	0.06	1.4

[a] For footnotes, see Table 2.

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