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POLYLACTONES—18. POLYMERIZATION OF L,L-LACTIDE WITH Sn(II) AND Sn(IV) HALOGENIDES

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Abstract—Bulk polymerizations of L,L-lactide initiated with $SnCl_2$, $SnBr_2$, $SnCl_4$ or $SnBr_4$ were conducted at various temperatures. No racemization was found in the range 100–160° despite long reaction times (48 hr). At 180° the reaction time needs to be shortened to a few hours to avoid racemization. The absence of racemization at such high temperatures is a clear indication of a non-ionic insertion mechanism. The highest number-average molecular weights ($\bar{M}_n = 50,000$) were obtained with $SnBr_4$ and $SnCl_2$. The molecular weights were essentially independent of the monomer/initiator ratio, yet they increased with the purity of L,L-lactide. With intensively purified, reactants $\bar{M}_n$s up to 10^5 may be obtained. Lactic acid or its linear dimer, which were detected by ^{1}H-NMR spectroscopy as contaminants of L,L-lactide, obviously play the role of co-initiators. It is also demonstrated that traces of HBr or HCl do not initiate cationic polymerization of L,L-lactide.

INTRODUCTION

Tin(II) and tin(IV) salts, in particular Sn(II) octoate and $SnCl_4$, are well known as good catalysts of the polymerization of L,L-lactide [1–7]. Most authors seem to believe that these catalysts initiate a cationic polymerization, yet experimental evidence for such a mechanism has not been presented so far. In a previous paper [8] it was demonstrated that weak Lewis acids such as aluminium, tin or zinc alkoxides initiate a non-ionic insertion mechanism. In another part of this series [9], it was shown that strong Lewis acids (such as boron tribromide, aluminium tribromide, titanium and tin tetrabromide) react with δ-valerolactone or ϵ-caprolactone by ring-opening with bromine transfer. Further chain growth seems again to proceed according to an insertion mechanism involving the initially formed metal–oxygen bond. The present work was aimed at studying polymerizations of L,L-lactide initiated by Sn(II) or Sn(IV) halogenides. Both mechanistic and preparative aspects are considered.

EXPERIMENTAL PROCEDURES

Reagents: L,L-lactide was a gift of Boehringer (D-6507 Ingelheim). It was recrystallized from ethyl acetate (distilled over calcium hydride) and dried over P_4O_{10} *in vacuo*. $SnCl_2$, $SnBr_2$, $SnCl_4$ and $SnBr_4$ were purchased from Aldrich (St Louis, Mo., U.S.A.) and used without further purification. All reaction mixtures were prepared in a glove-box under N_2 dried with P_4O_{10}.

Polymerization (Tables 1–6, [8, 9])

All polymerizations were conducted in 50 ml Erlenmeyer flasks with ground glass-joints and glass-walls silanized with dimethyldichlorosilane. A sample (50 or 100 mmol) of L,L-lactide was weighed into the reaction vessel and the initiator was then added in the form of an 1 M solution in dry CH_2Cl_2. The reaction vessel was closed with a glass stopper and steel spring and completely immersed into a thermostated oil bath. The reaction product was dissolved in 100–150 ml CH_2Cl_2 and precipitated in 1.2 l. of cold methanol. The precipitated polylactide was isolated by filtration and dried at 40° *in vacuo*.

Polymerizations with methanol as co-initiator

A 2 M solution of dry methanol in dry CH_2Cl_2 was added to an 1 M solution of $SnBr_4$ or $SnCl_4$ in CH_2Cl_2, so that ratios of 1:5 or 1:10 (methanol/Sn) were obtained. The resulting reaction mixtures were immediately used as initiators.

Measurements

Inherent viscosities were measured in CH_2Cl_2 with an Ubbelohde viscometer at 25°. The intrinsic viscosities were measured in $CHCl_3$ at 30°.

GPC measurements were performed by means of a sequence of four different Ultrastyragel® columns. The molecular weights were calculated by means of a universal calibration curve based on polystyrene standards the intrinsic viscosities of which were determined in CH_2Cl_2 at 25°. The weight-average molecular weights ($\bar{M}_w$) were calculated from the maxima of the elution curses, thus slightly underestimating the true $\bar{M}_w$s.

The optical rotations were measured at 25° on a Perkin–Elmer Md 241 polarimeter in 1 ml sample tubes of 10 cm length. The 100 MHz ^{1}H-NMR spectra were obtained on a Bruker AC-100 in 5 ml o.d. sample tubes. A sample (50 mg) of polylactide was measured in 1 ml $CDCl_3$ containing TMS as internal standard. The 360 MHz ^{1}H-NMR spectra were obtained similarly on a Bruker AM 360.

RESULTS AND DISCUSSION

Preparative aspects

All polymerizations of L,L-lactide were conducted in bulk, (i.e. without solvent) for the following reasons. First, under these conditions, high conversions are expected after short reaction times so that the risk of racemization is minimized. Second, a comparison of Sn(II) and Sn(IV) halogenides cannot be conducted in solution because Sn(II) halogenides are insoluble in all inert organic solvents. Third, polymerizations in the molten state are advantageous

Table 1. Bulk polymerizations of L,L-lactide with $SnBr_4$ or $SnCl_4$ with variation of the reaction temperature (48 hr, initial monomer/initiator ratio = 200:1)

No.	Initiator	Temp. (°C)	Yield (%)	$[\alpha]_{578}^{20}$ [a]	η_{inh} [b] (dl/g)	$\bar{M}_n$ [c] (visc.)	$\bar{M}_w$ [d] (GPC)
1	$SnBr_4$	100	96	−157	0.66	25,000	38,000
2	$SnBr_4$	120	98	−168	0.54	22,000	48,000
3	$SnBr_4$	140	95	−163	0.55	23,000	39,000
4	$SnBr_4$	160	91	−155	0.46	16,000	28,000
5	$SnBr_4$	180	61	—	0.10	2000	—
6	$SnCl_4$	100	93.5	−165	0.35	11,000	—
7	$SnCl_4$	120	96.5	166	0.34	14,000	42,000
8	$SnCl_4$	140	86	−160	0.54	16,000	66,800
9	$SnCl_4$	160	84.5	−156	0.40	13,000	43,000
10	$SnCl_4$	180	20	—	0.11	1800	<2000

[a] Measured with $c = 10$ g/l in dichloromethane at 25°.

[b] Measured with $c = 2$ g/l in dichloromethane at 25°.

[c] Calculated from the intrinsic viscosities in $CHCl_3$ at 30° and $[\eta] = 2.21 \cdot 10^{-4} \times M_n^{0.77}$ (Ref. [14]).

[d] Determined in CH_2Cl_2 at 25° with polystyrene standards and universal calibration.

Table 2. Bulk polymerizations of L,L-lactide with $SnCl_4$ or $SnCl_2$ with variation of the reaction temperature (48 hr, initial monomer/initiator ratio = 200:1)

No.	Initiator	Temp. (°C)	Yield (%)	$[\alpha]_{578}^{20}$ [a]	η_{inh} [a] (dl/g)	$\bar{M}_n$ [a] (visc.)	$\bar{M}_w$ [a] (GPC)
1	$SnBr_2$	100	94	−163	0.75	30,800	71,300
2	$SnBr_2$	120	95	−165	0.74	30,100	75,900
3	$SnBr_2$	140	97.5	−165	1.00	45,600	80,800
4	$SnBr_2$	160	90	−162	0.43	12,700	38,200
5	$SnBr_2$	180	76	−143	0.16	<4000	<3000
6	$SnCl_2$	100	81	−164	0.92	42,000	78,300
7	$SnCl_2$	120	94	−163	1.12	50,500	90,000
8	$SnCl_2$	140	96	−163	0.65	24,200	72,000
9	$SnCl_2$	160	89	−162	0.46	17,700	35,600
10	$SnCl_2$	180	46	−110	0.14	<2500	<3000

[a] Footnotes as for Table 1.

for copolymerizations of L,L-lactide and glycolide because blocks of the more reactive glycolide tend to precipitate from solution. Copolymers of lactide and glycolide are of interest for various pharmaceutical or medical purposes, and the reaction conditions optimized in this work for homopolymerizations should also be useful for copolymerizations.

A crucial point for a successful polymerization of L,L-lactide is the optical purity. A first series of polymerizations was designed to study the combined influence of initiator and temperature on optical purity. The results in Tables 1 and 2 show that all initiators allow racemization-free polymerizations of L,L-lactide at temperatures up to 160°. At 180° partial racemization was found along with a significant reduction of the molecular weights when a long reaction time (48 hr) was used (Tables 1 and 2). For the more acidic initiators $SnCl_4$ and $SnBr_4$, the resulting polylactide obtained at 180° had a dark colour so that the optical rotation could not be measured.

In a second series of polymerizations initiated by $SnBr_2$ and $SnBr_4$, the time-dependence of the optical purity was investigated. The results summarized in Table 3 demonstrate that even at 180° racemization-

Table 3. Bulk polymerizations of L,L-lactide with $SnBr_2$, $SnBr_4$ with variation of the reaction time (180°, initial monomer/initiator ratio = 200:1)

No.	Initiation	Time (hr)	Yield (%)	η_{inh} [a] (dl/g)	$[\alpha]_{578}^{20}$ [b]
1	$SnBr_2$	1	98	0.88	−159.2
2	$SnBr_2$	2	93	0.53	−162.0
3	$SnBr_2$	4	92	0.54	−160.7
4	$SnBr_2$	8	92	0.33	−160.3
5	$SnBr_2$	24	90	0.25	−152.8
6	$SnBr_2$	48	76	0.16	−143.0
7	$SnBr_4$	1	79	0.78	−159.1
8	$SnBr_4$	2	91	0.78	−161.0
9	$SnBr_4$	4	92	0.54	−159.0
10	$SnBr_4$	8	94	0.54	−160.6
11	$SnBr_4$	24	88	0.22	= 155.8
12	$SnBr_4$	48	61	0.11	Not measurable

[a] Measured with $c = 2$ g/l in CH_2Cl_2 at 25°.

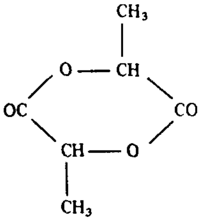
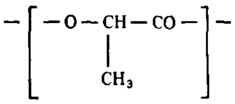
[b] Measured with $c = 10$ g/l in CH_2Cl_2 at 25°.

Table 4. Bulk polymerization of L,L-lactide with $SnBr_4$ at 150° with variation of the initial monomer/initiator ratio (M/I)

No.	M/I	Time (hr)	Yield (%)	$[\alpha]_{578}^{20}$ [a]	η_{inh} [a] (dl/g)	$\bar{M}_n$ [a] (visc.)	$\bar{M}_w$ [a] (GPC)
1	100:1	48	98	−156.5	0.60	21,000	57,000
2	150:1	48	98	−163.5	0.66	24,000	67,000
3	200:1	48	97	−165.5	0.65	24,000	63,000
4	400:1	48	95	−166.5	0.58	20,000	56,000
5	100:1	96	93	−160.5	0.67	23,000	65,000
6	150:1	96	93	−162.5	0.63	21,000	62,000
7	200:1	96	98	−162.0	0.64	21,000	59,000
8	400:1	96	93	−160.0	0.58	19,000	51,000

[a] Footnotes as for Table 1.

Table 5. ^1H-NMR chemical shifts δ (ppm, relative to internal TMS) of lactic acid and its derivatives measured in $CDCl_3$

	Chemical shift C_α	 C_β
$H_3C-CH(OH)\,CO_2H$	4.478 4.408 4.339 4.269	1.515 1.445
$H_3C-CH(OH)\,CO_2C_2$	4.341 4.269 4.198 4.127	1.449 1.380
$H_3C-CHCl-CO_2C_2H_5$	4.354 4.275 4.204 4.133	1.724 1.655
$H_3C-CH\cdot Br-CO_2C_2H_5$	4.335 4.267 4.196 4.125	1.857 1.788
	5.197 5.130 5.063 4.997	1.693 1.627
 $-\left[-O-\underset{CH_3}{CH}-CO-\right]-$	5.261 5.207 5.136 5.067	1.616 1.545

free polymerizations can be performed, provided the reaction time is reduced to a few hours. Because such short reaction times suffice to bring about yields >95% and $\bar{M}_n$s up to 50×10^3, the long reaction time used for polymerizations of Tables 1 and 2 are not required for preparative purposes at 180°. In contrast the data of Table 3 prove that long reaction times reduce not only the optical purity but also the molecular weight. At 160° and lower reaction temperatures, degradation by "back-biting" does not take place. The GPC measurements of the reaction mixtures do not reveal any cyclic oligomer (Fig. 1). What kind of degradation takes place at 180° and how the degradation depends on structure and concentration of the initiator will be reported in a later paper.

The results obtained at 100–160° (Tables 1 and 2) show that the molecular weights depend on the nature of the catalyst. The best results were obtained with $SnCl_2$ and $SnBr_4$ and the worst with $SnCl_4$. In order to study the influence of the initiator concentration on the molecular weight, a third series of polymerizations was conducted a 150° with $SnBr_4$. The results in Table 4 demonstrate that the molecular weights are almost independent of the monomer to initiator ratio (M/I). A mechanistic explanation of this result is discussed below. It is worth noting that Sn(II) halogenides of commercial purity and a once-recrystallized L,L-lactide enable the synthesis of poly(L-lactide) with $\bar{M}_n$ up to 50×10^3 and $\bar{M}_w$ in the range $80–100 \times 10^3$. In the opinion of the authors, the

Table 6. Bulk polymerizations of L,L-lactide conducted at 120° (24 hr) with $SnBr_4$ or $SnCl_4$ under variation of the monomer/initiator (M/I) ratio

No.	Initiator	M/I	Yield (%)	$[\alpha]^{20}_{578}$ [a]	η_{inh} [b] (dl/g)	$\bar{M}_n$ [c] (visc.)
1	$SnBr_4$	1:1	98	−146.0	0.45	14,500
2	$SnBr_4$	2:1	99	−152.0	0.50	17,000
3	$SnBr_4$	5:1	99	−158.0	0.56	19,000
4	$SnBr_4$	10:1	97	−163.0	0.56	20,000
5	$SnBr_4$	50:1	98	−159.5	0.57	19,000
6	$SnCl_4$	1:1	46	—	0.08	—
7	$SnCl_4$	2:1	55	—	0.07	—
8	$SnCl_4$	5:1	67	—	0.09	—
9	$SnCl_4$	10:1	89	—	0.16	—
10	$SnCl_4$	50:1	95	−160.5	0.34	—

[a] Measured with $c = 10$ g/l in dichloromethane at 25°.
[b] Measured with $c = 2$ g/l in dichloromethane at 25°.
[c] Calculated from the intrinsic viscosities in $CHCl_3$ at 30° and $[\eta] = 2.21 \cdot 10^{-4} \times \bar{M}_n^{0.77}$ (Ref. [14]).

Table 7. Bulk polymerizations of L,L-lactide at 120°/48 hr (M/I = 100:1)

No.	Initiator	Purity of L,L-lactide	Yield (%)	η_{inh} [a] (dl/g)	Retention time [b] (min)
1	$SnBr_4$	crude	99.0	0.48	23.85
2	$SnBr_4$	1 × recrystallized	95.0	0.85	22.57
3	$SnBr_4$	3 × recrystallized	96.0	1.40 [c]	22.22
4	$SnCl_4$	crude	96.5	0.47	23.72
5	$SnCl_4$	1 × recrystallized	96.5	0.49	23.70
6	$SnCl_4$	3 × recrystallized	97.0	0.55	23.50
7	$SnBr_2$	crude	95.5	0.32	24.30
8	$SnBr_2$	1 × recrystallized	96.0	0.41	23.90
9	$SnBr_2$	3 × recrystallized	95.5	0.56	22.70
10	$SnCl_2$	crude	97.0	0.34	24.30
11	$SnCl_2$	1 × recrystallized	96.5	0.68	22.90
12	$SnCl_2$	3 × recrystallized	97.0	0.87	22.60

Influence of monomer purity on the molecular weight.
[a] Measured with $c = 2$ g/l in dichloromethane at 25°.
[b] Measured in dichloromethane at 25°.
[c] $\bar{M}_n = 90{,}000$ calculated from the intrinsic viscosity in $CHCl_3$ at 30° and $[\eta] = 2.21 \cdot 10^{-4} \times \bar{M}_n^{0.77}$ (Ref. [14]).

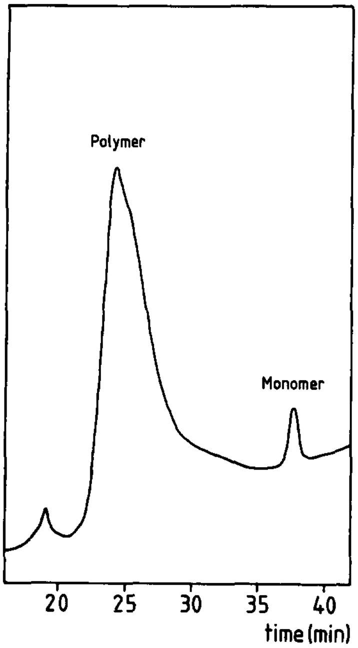


Fig. 1. GPC elution curve of the reaction mixture obtained from L,L-lactide and $SnBr_4$ (M/I = 200:1) after 96 hr at 160°.

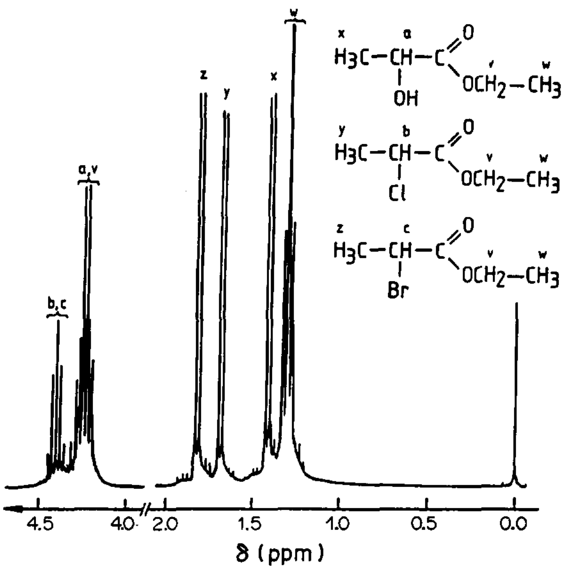
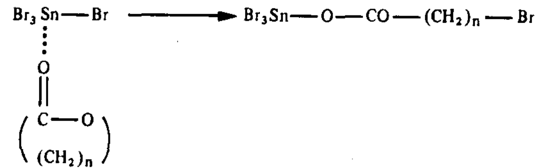


Fig. 2. 360 MHz ^{1}H-NMR spectrum of a mixture of ethyl lactate, ethyl-α-bromopropionate and ethyl-α-chloropropionate measured in $CDCl_3$.

methods used here for the calculation of $\bar{M}_n$ and $\bar{M}_w$ are not accurate enough to allow detailed discussion of the molecular weight distribution and its relation to the polymerization mechanism. Nonetheless, it is satisfactory to find $\bar{M}_w/\bar{M}_n$ ratios of the order of 2–3 under conditions allowing transesterification processes. Similar $\bar{M}_w/\bar{M}_n$ ratios were reported for tetraphenyltin initiated bulk polymerizations of D,L-lactide [10].

Endgroup analyses

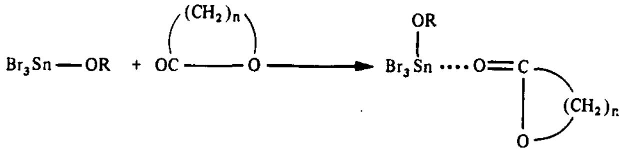
As reported previously, δ-valerolactone and ε-caprolactone react with acidic metal bromides (e.g. BBr_3, $AlBr_3$, $TiBr_4$, $SnBr_4$) in such a way that the ring cleavage involves transfer of a bromine atom (equation 1). The ring scission is then followed by a non-ionic insertion mechanism, which consists of at least two steps: (1) complexation of the lactone via its carbonyl oxygen (equation 2); (2) ring-opening of the lactone by the highly reactive metal–oxygen bond (equation 3). It is characteristic for this reaction sequence that oligoesters or polyesters are formed containing —CH_2—Br endgroups in addition to —CH_2—OH and —CO_2H endgroups [9].



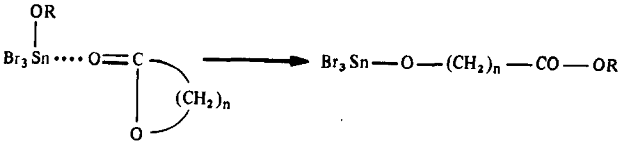
$$Br_3Sn{-}Br\cdots O{=}\overset{\displaystyle (\,C{-}O\,)}{\underset{\displaystyle (CH_2)_n}{}} \longrightarrow Br_3Sn{-}O{-}CO{-}(CH_2)_n{-}Br$$

(1)

These results demonstrate that a successful elucidation of the polymerization mechanism requires unambiguous identification of endgroups. For oligolactides, elemental analyses may allow detection of CH—Cl or CH—Br endgroups, yet this method is not suited for higher molecular weights. As described for other polylactones [8, 9, 11], high resolution ^{1}H-NMR spectroscopy may yield satisfactory results even for higher molecular weights, provided that suitable model compounds are available. For the present work ethyl lactate, ethyl 2-chloropropionate and ethyl 2-bromopropionate served as models of endgroups. Their chemical shifts along with those of L,L-lactide and poly(L-lactide) are listed in Table 5.



(2)



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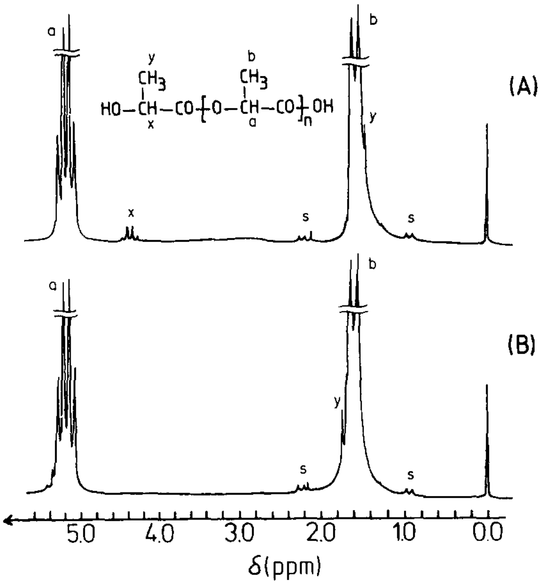


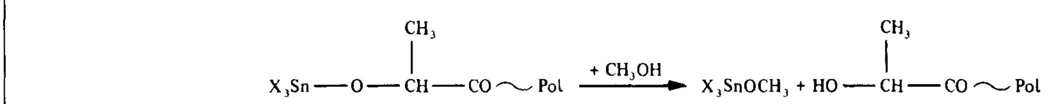
Fig. 3. 100 MHz ^{1}H-NMR spectrum of a $SnBr_4$-initiated poly(L-lactide), (Table 6, No. 4) measured in $CDCl_3$ after precipitate from methanol (A), and the same solution after addition of trifluoroacetic anhydride (B).

These shift data and the ^{1}H-NMR spectrum of Fig. 2 demonstrate that all three kinds of endgroups can be distinguished from each other and from the monomeric units of the polymer chain.

In order to achieve more reliable differentiation between OH and halogen endgroups, the spectroscopic effect of addition of phenylisocyanate or trifluoroacetic anhydride was studied. Figure 3A displays the typical ^{1}H-NMR signal pattern of a polylactide with OH endgroup. Addition of phenylisocyanate or other acylating reagents causes acylation of the OH endgroup with the consequence that their ^{1}H-NMR signals shift downfield and overlap with the signals of the backbone units (Fig. 3B) [10, 11]. This shift effect is, of course, not observable for Br or Cl endgroups.

Mechanistic aspects

In order to elucidate the first step of Sn halogenide initiated polymerizations of lactide, several polymerizations were conducted with extremely low M/I ratios (Table 6). These polymerizations were designed to yield oligomers which would allow easy characterization of endgroups. When $SnCl_4$ was used as initiator, low molecular weight polylactide could indeed be isolated (Table 6, Nos 6–9), yet chloride-containing endgroups were not detected either by elemental analyses or by ^{1}H-NMR spectroscopy. With $SnBr_4$ as initiator, relatively high molecular weights were obtained in all experiments (Table 6, Nos 1–5). It is of particular interest that the molecular weights are nearly independent of the initiator concentration, in good agreement with the results listed in Table 6. Another important result of these polymerizations is the identification of OH endgroups in all polylactides isolated from the experiments of Table 6 (Fig. 3A, B). Bromine-containing endgroups were never found. These findings allow two important conclusions. First, the initiation step is not identical with that found for δ-valero or ε-caprolactone (equation 1). Second, the propagation step is identical; it involves a Sn–oxygen bond which after hydrolysis (or methanolysis) yields the OH endgroups (equation 4).



$$X_3Sn—O—\overset{CH_3}{\overset{|}{CH}}—CO\sim Pol \xrightarrow{+\,CH_3OH} X_3SnOCH_3 + HO—\overset{CH_3}{\overset{|}{CH}}—CO\sim Pol \qquad (4)$$

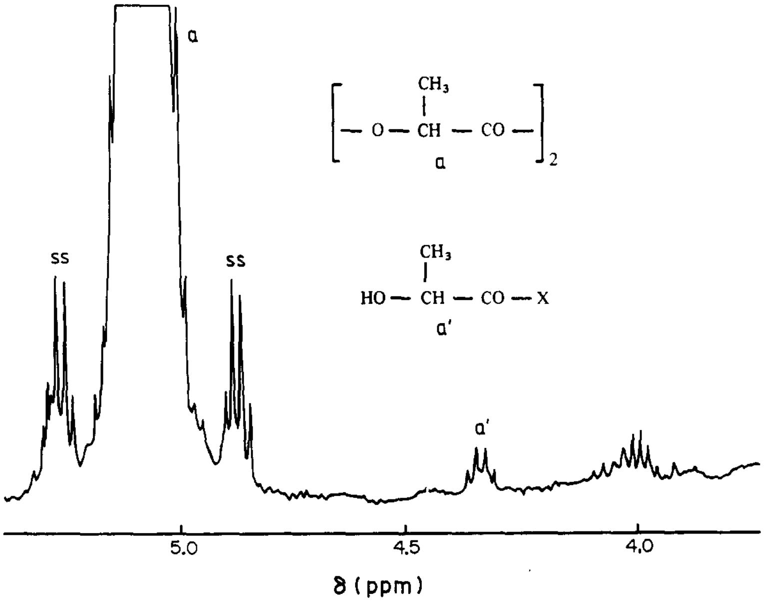
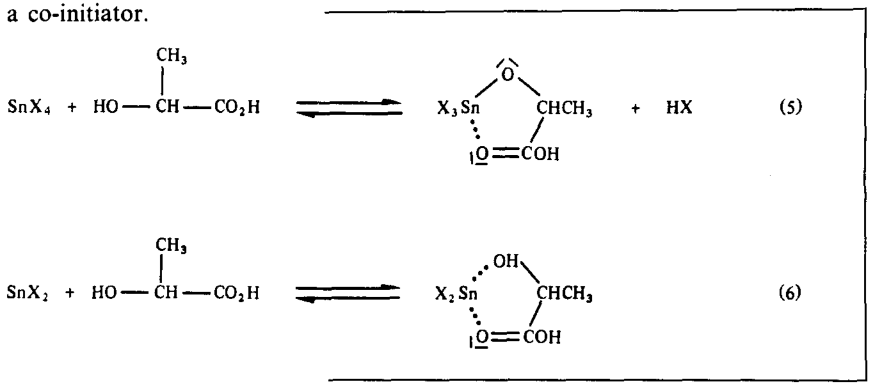


Fig. 4. 360 MHz ^{1}H-NMR spectrum of crude L,L-lactide measured in $CDCl_3$.

The absence of an initiation step according to equation 1 not only agrees with the absence of halogen-containing endgroups, it also fits in with the independence of the molecular weights of the M/I ratio. Obviously the secondary carbon of the lactidyl unit is less sensitive to nucleophilic attack of a bromide than the primary carbon of a lactone. At this point the question arises which reaction is responsible for the initiation. The most obvious explanation was to assume that an OH-containing contaminant of the monomer reacts as co-initiator. However, 360 MHz ^{1}H-NMR spectra with high signal-to-noise ratio exclusively revealed lactidyl units with OH and CO_2H endgroups. The only contaminants that might be present in L,L-lactide and fit in with all observations are water, lactic acid and its linear dimer, lactidyl lactic acid.

In order to check the above hypothesis, the following steps were taken. L,L-lactide samples with three degrees of purity were prepared and investigated: (A) crude monomer, (B) once recrystallized monomer and (C) three times recrystallized L,L-lactide. 360 MHz ^{1}H-NMR spectra of the crude monomer revealed weak signals of lactidyl units that agree with the signals of lactic acid (Fig. 4 and Table 7). Additional signals (1.2 and 4.0 ppm) of an unidentified lactic acid derivative were also found. However, these impurities could not be detected in recrystallized lactide. Furthermore, numerous polymerizations were conducted with L,L-lactide samples of various purities (Table 7). The molecular weights of the resulting polylactides were characterized by inherent viscosities and retention times obtained by GPC measurements. Both methods agree in that the molecular weights increase with increasing purity of the monomer. These results suggest the following initiation mechanism. Lactic acid or its linear dimer form a complex with a tin halogenide which entails the formation of a Sn–oxygen bond. In the case of Sn(IV) halogenides, formation of a Sn—O covalence replacing at least one halogen is most likely (equation 5) whereas, in the case of Sn(II) halogenides, formation of a true complex is more probable (equation 6). Sn–oxygen bond is then the active species which initiates the insertion mechanism outlined in equation (3). Although, the L,L-lactide used in this work was dried over P_4O_{10} *in vacuo*, traces of water might also act as a co-initiator.



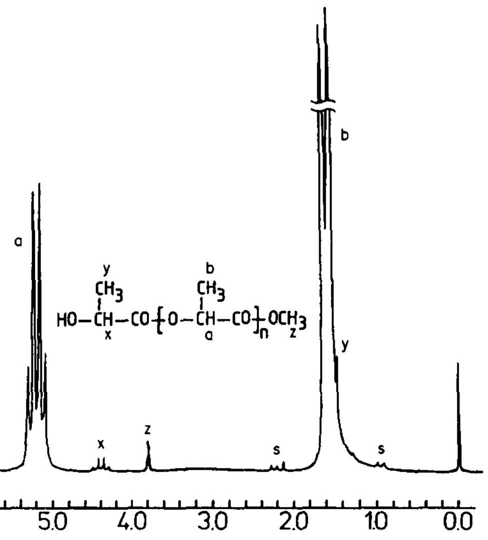
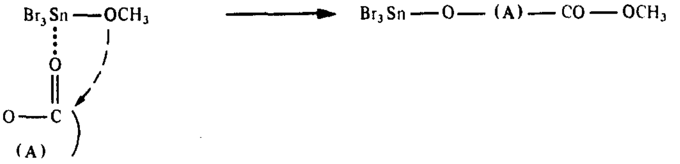


Fig. 5. 100 MHz ^{1}H-NMR spectrum of a poly(L-lactide) initiated with $SnBr_4$/MeOH (10:1 molar mixture).

Two aspects of this mechanism were separately investigated. First the effect of an OH group containing co-initiator, and second, the role of HBr or HCl liberated according to equation (5). In order to study the role of an OH-co-initiator, 1:5 and 1:10 mixtures of methanol and $SnBr_4$ or $SnCl_4$ were prepared and used as initiators *in situ*. Bulk polymerizations were conducted at 120°/48 hr with molar monomer/methanol ratios of 50:1 and 100:1 (monomer/Sn ratio = 10:1). The ^{1}H-NMR spectra of the polylactide samples after reprecipitation display the signals of methyl ester endgroups and OH endgroups (Fig. 5). The intensity ratio of the endgroup signals suggests that most polylactide chains possess one methyl ester and one HO endgroup. These results fit in with the initiation mechanism of equations (7) and (8) followed by the propagation and alcoholysis outlined in equations (3) and (4).

Finally, two series of bulk polymerizations were conducted with variation of the temperature (100, 120, 140, 160 and 180°C). In the first series a 40% by weight solution of HBr in acetic acid was used as initiator with an M/I ratio of 200:1 for the second series, a saturated solution of HCl in dry nitrobenzene was used. However, regardless of initiator and temperature, polylactide was never obtained. GPC analyses of the reaction mixtures proved the presence of unreacted monomer. These negative

$$\mathrm{Br_4Sn + HO{-}CH_3 \rightleftharpoons Br_3SnOCH_3 + HBr} \quad (7)$$



(8)

results perfectly agree with previous studies of cationic polymerizations of L,L-lactide [12]. Triflc acid and methyl triflate are the only cationic initiators reported so far, active enough to polymerize L,L-lactide. Therefore, the assumption of Kohn *et al.* [5] that HBr (or HCl) might react as cationic initiator is not acceptable in the case of lactide.

In a future paper, kinetic studies of solution polymerizations of ϵ-caprolactone initiated with various tributyltin derivatives will be reported. These kinetic studies demonstrate that the Sn—alkoxide bond is by a factor 10^3–10^4 more reactive than SnBr, Sn—Cl and Sn—S—bonds.

CONCLUSIONS

The results suggest the following mechanistic concept for tin halogenide initiated polymerizations of L,L-lactide. The tin halogenide forms a complex with lactic acid or another OH group containing impurity of monomer or reaction medium. The initially formed tin–oxygen bond is the active species and polymerizes lactide by an non-ionic insertion mechanism. Hydrolytic or methanolytic cleavage of the tin alkoxide bond yields polylactide with one carboxyl group and one CH—OH chain end.

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