

# Telechelic Poly(L-lactic acid) for Dilactide Production and Prepolymer Applications

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**ABSTRACT:** The suitability of different types of telechelic poly(lactic acid) (PLA) copolymers for dilactide production and prepolymer products was evaluated. L-lactic acid (L-LA) was copolymerized with 1,4-butanediol, pentaerythritol, adipic acid, or 1,2,3,4-butanetetracarboxylic acid (1,2,3,4-BTCA). The influence of branching, the choice of catalyst, and the type of terminal groups on the properties and the thermal stability of the end product was determined. Carboxyl-termination of PLA was shown to lead to higher molar masses than hydroxyl-termination. The observed differences in the molar masses were explained by the lower thermal stability of the hydroxyl-terminated PLA, as evidenced by the faster depolymerization rate of the hydroxyl-terminated polymers and their higher tendency to undergo

racemization. Sn(Oct)<sub>2</sub> was found to be a more effective copolymerization catalyst than Fe(OAc)<sub>2</sub> in terms of the final molar masses obtained. It was additionally found that the amount of chains not attached to the comonomers decreased toward longer polymerization times and was typically higher for the hydroxyl-terminated copolymers. The results suggest that predominant carboxyl-termination would increase the thermal stability of PLA polymers, whereas hydroxyl-termination could be utilized to increase the production speed and efficiency of dilactide. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2602–2610, 2011

**Key words:** degradation; dilactide; poly(lactic acid); thermal properties; step-growth polymerization

## INTRODUCTION

Low molar mass poly(lactic acid) (PLA) produced by step-growth polymerization in the melt has two main end uses: (1) dilactide production and (2) prepolymer applications. High molar mass PLA is typically produced by the ring-opening polymerization (ROP) of dilactide,<sup>1</sup> even though it is possible to obtain higher molar masses also by step-growth polymerization in solvents or azeotropic conditions. In dilactide production, fast depolymerization of PLA or lactic acid (LA) oligomers into optically pure dilactide would be beneficial in terms of process time and economics. Faster and more complete depolymerization could thus also contribute to decreasing the production cost of high molar mass

PLA produced by the ROP route. In prepolymer applications, low molar mass PLA polymers can be used as modifiers, precursors,<sup>2,3</sup> or applications like hot melt adhesives,<sup>4–9</sup> as shown by our group previously. However, the typically poor thermal stability of low molar mass PLA, leading to dilactide formation, can cause problems in further reactions and processing of prepolymers. This will consequently affect the quality of the final product, since the polymer structure is often designed based on defined molar ratios.

In step-growth polymerization processes, the molar mass of the produced polymer is dependent on both reaction time and temperature. However, the chain growth of the polymer can be suppressed by the competing ring-formation<sup>10</sup> and hydration reactions due to the related thermodynamical equilibria. PLA also undergoes racemization or thermal degradation at high polymerization temperatures or after long reaction times.<sup>11–13</sup> Polymerization efficiency further depends on the catalyst system used.<sup>14–20</sup>

The PLA used for dilactide production typically has a relatively low molar mass. The reported optimal molecular weights used do, however, vary significantly. In some studies, efficient dilactide production is said to be feasible directly from LA or from low molecular weight oligomers,<sup>21</sup> whereas in others the preferred molar mass of the polymer has been up to 10,000 Da.<sup>22</sup> The molar masses of the

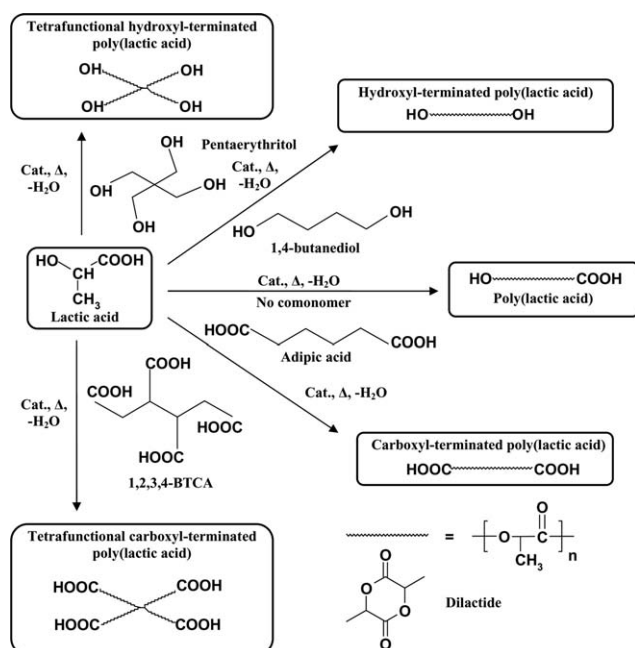
Additional Supporting Information may be found in the online version of this article

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**Scheme 1** Polymerization reactions involving LA and different comonomers. Also dilactide and chains not attached to the comonomers were formed in the polymerizations.

prepolymer products used for chain extension are also fairly low, typically a few thousand dalton, and thus in the same range as the ones used for dilactide production.

The step-growth polymerization of LA and properties of different LA-based copolymers produced by this method are relatively vastly reported in scientific literature in general.<sup>23–26</sup> However, the effects of the type of chain end-termination on the polymerization processes of LA-based low molar mass compounds or the production efficiency of dilactide has not been sufficiently reported in the literature. It was anticipated that the dilactide production efficiency and speed could be optimized by using low molar mass PLA having a defined structure and chain termination as the raw material instead of the typically used linear PLA homopolymer. On the other hand, low molar mass PLA having an improved thermal stability would be ideal for prepolymer applications. L-LA was thus polymerized in the presence of small amounts of different comonomers (1,4-butanediol, pentaerythritol, adipic acid, or 1,2,3,4-BTCA). The use of these comonomers was intended to provide the polymer with a certain molecular structure (linear or 4-arm branched backbone) and terminal groups, i.e., predominant carboxyl (–COOH) or hydroxyl (OH) termination. The molar mass of the polymers was designed to be in a suitable range for both dilactide production and prepolymer applications. The main reactions involved in the polymerizations are schematically presented

in Scheme 1. The influence of branching, the choice of catalyst, and the type of terminal groups on the polymerization reaction and the thermal stability of the end product was evaluated.

## MATERIALS

The L-LA used was an 88 or 92% aqueous solution (Purac, The Netherlands). The free water in the L-LA was removed at ca. 100°C prior to polymerization (referred to as dry LA). The comonomers used were pentaerythritol (Aldrich, St. Luis, US-MO), 1,2,3,4-butanetetracarboxylic acid (1,2,3,4-BTCA) (Aldrich, St. Luis, US-MO), adipic acid (Riedel-de Haën, Seelze, Germany), and 1,4-butanediol (Fluka, Buchs, Germany). The solvents used included chloroform (CHCl<sub>3</sub>) (Merck, Darmstadt, Germany or Rathburn, Walkerburn, Scotland), tetrahydrofuran (THF) (Merck, Darmstadt, Germany or Rathburn, Walkerburn, Scotland), methanol (Riedel-de Haën, Seelze, Germany or Fluka, Buchs, Germany), chloroform-*d* (CDCl<sub>3</sub>) (Aldrich, St. Luis, US-MO), and acetone-*d*<sub>6</sub> (Aldrich, St. Luis, US-MO). The catalysts used were iron(II) acetate (Fe(OAc)<sub>2</sub>) (Aldrich, St. Luis, US-MO) and tin(II) octoate (Sn(Oct)<sub>2</sub>) (Sigma, St. Luis, US-MO). The reagents were used as received.

## METHODS

### Polymerization procedure

Dried L-LA (typically 25 g), the comonomer, and the catalyst (0.1 wt % of dry L-LA) were added to a 250 mL round-bottomed flask. The theoretical degree of polymerization (DP) of the PLA branches was set to 50, independent of the initiator type. The polymerizations were conducted in a rotary evaporator under vacuum as described previously.<sup>17</sup> Briefly, the temperature was raised to 180°C in ca. 1 h and to higher reaction temperatures in 1.5 h under nitrogen purge. The reaction mixture was heated for 2 h after reaching the desired temperature. After this, the nitrogen gas flow was stopped and vacuum applied, and a final pressure of 7 ± 5 mbar was reached in ~ 3 h. Purification of the polymers used for the depolymerization study was conducted by precipitation of the product from CHCl<sub>3</sub> into a fivefold amount of methanol.

### Characterization

The proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR) measurements were conducted with a JEOL L400 spectrometer. The samples were dissolved in CDCl<sub>3</sub> and tetramethylsilane (TMS) was used as an internal standard. The acid number (AN, in mg KOH/g of sample) was determined in

**TABLE I**  
Gravimetric Yields of the Produced Polymers After a Polymerization Time of 23 h

Comonomer	Catalyst	Gravimetric yield (%)
–	Sn(Oct) <sub>2</sub>	67
	Fe(OAc) <sub>2</sub>	71
1,4-Butanediol	Sn(Oct) <sub>2</sub>	64
	Fe(OAc) <sub>2</sub>	nm
Pentaerythritol	Sn(Oct) <sub>2</sub>	61
	Fe(OAc) <sub>2</sub>	78
Adipic acid	Sn(Oct) <sub>2</sub>	77
	Fe(OAc) <sub>2</sub>	69
1,2,3,4-BTCA	Sn(Oct) <sub>2</sub>	74
	Fe(OAc) <sub>2</sub>	71

nm, not measured.

duplicates by applying a standard method (DIN 53402) and using THF or CHCl<sub>3</sub> : ethanol (2 : 1) as solvents. The size exclusion chromatography (SEC) measurements were conducted using a system based on a Pharmacia LKB-HPLC Pump 2248, TSK-gel G3000, G2500 and G1500HXL columns, and an LKB 2142 RI detector. THF was used as the sample solvent and the mobile phase in the SEC measurements, and monodisperse polystyrene standards used for calibration. The TGA instrument used was a Mettler Toledo TGA851e attached to Pfeiffer Vacuum ThermoStar model GSD 301 T3 mass spectrometer. The depolymerization rates were calculated from the weight loss curves by dividing the nondepolymerized sample amount (calculated by subtracting the residual weight from the initial sample amount) by the time it took for the sample to reach a constant weight. The reported depolymerization rates therefore represent the overall mass loss of the samples and they have been normalized to a sample weight of 10 mg. The amount of residual catalyst was determined using Perkin Elmer Optima 5300 DV inductively coupled plasma-optical emission spectrometer (ICP-OES). The D/L stereoisomer ratio of LA was determined by high-performance liquid chromatography (HPLC) in duplicates. Phenomenex Chirex D-Penicillamine 4 × 30 mm<sup>2</sup> and 4 × 150 mm<sup>2</sup> columns were used as the guard column and the analytical column, respectively. The mobile phase used was an aqueous 3 mM CuSO<sub>4</sub> solution. The HPLC samples were prepared by hydrolyzing them in 1M NaOH at 60–100°C until no solids were visible. After this, the samples were neutralized with 1M HCl and diluted with the mobile phase to 0.5% or less.

## RESULTS AND DISCUSSION

The polymerization reactions of the PLA homopolymers and the different copolymers were followed by determining the gravimetric yields after a polymer-

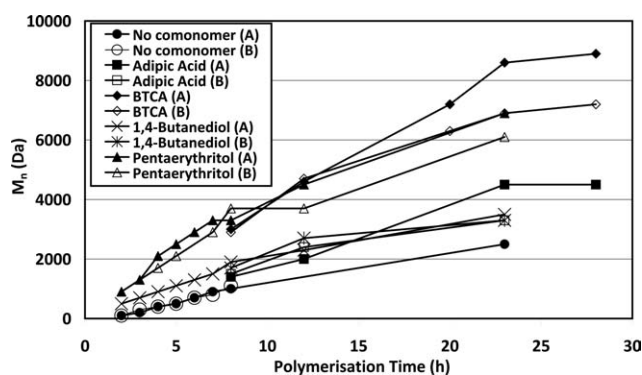
ization time of 23 h and by following changes in their molar masses by AN titrations and <sup>1</sup>H-NMR after specific reaction times throughout the polymerizations. The AN and <sup>1</sup>H-NMR results were also utilized in the estimation of the relative amounts of free chains not attached to the comonomers. The thermal stability of the polymers was evaluated by TGA. The racemization occurred during the drying of the lactic acid and the polymerization of the tetrafunctional copolymers was additionally quantified by determining the relative amounts of the D- and L-isomers of lactic acid by HPLC.

### Gravimetric yield

The gravimetric yields of the polymers were ~60–80% after a polymerization time of 23 h (Table I), which is in the range of values typically obtained in step-growth polymerization of LA.<sup>26</sup> The relatively low yield values obtained suggested dilactide formation and consequent evaporation from the reaction mixture during the polymerization. Trapped dilactide was in fact detected in all of the copolymers by <sup>1</sup>H-NMR. However, since both LA and dilactide are distilled off from the polymer melt with the condensing water, the gravimetric yields could not be directly used to quantify the amount of evaporated dilactide.

### Polymer structure and molar mass

End-group titrations and <sup>1</sup>H-NMR were used in the determination of the structures and the molar masses of the polymers. The polymerizations were conducted at 180°C and the samples analyzed were as-polymerized. A summary of the calculation methods used to estimate the DPs, molar masses, and the relative amounts of free chains in the polymers can be found in the Supporting Information.



**Figure 1** Molar masses of the carboxyl- and hydroxyl-terminated copolymers and the PLA without a comonomer as a function of polymerization time. The molar masses were determined by AN-titrations (PLA homopolymers and carboxyl-terminated copolymers) or <sup>1</sup>H-NMR (hydroxyl-terminated copolymers). Catalysts: A = Sn(Oct)<sub>2</sub>, B = Fe(OAc)<sub>2</sub>.

**TABLE II**  
<sup>1</sup>H-NMR and GPC Results for the Fe(OAc)<sub>2</sub>- and Sn(Oct)<sub>2</sub>-Catalyzed PLA Homopolymers

Catalyst	Polym. time (h)	<sup>1</sup> H-NMR	GPC	
		<i>M<sub>n</sub></i> (Da)	<i>M<sub>n</sub></i> (Da)	<i>M<sub>w</sub></i> (Da)
Fe(OAc) <sub>2</sub>	2	200	–	–
	3	300	–	–
	4	300	–	–
	5	500	–	–
	6	800	–	–
	7	900	–	–
	8	1200	900	2500
	23	2600	2700	7300
Sn(Oct) <sub>2</sub>	2	200	–	–
	3	300	–	–
	4	300	–	–
	5	500	–	–
	6	500	–	–
	7	1000	–	–
	8	1100	–	–
	23	2600	2700	7300

Linear PLA homopolymer chains theoretically contain both a hydroxyl and a carboxyl end-group. The molar masses of the PLA homopolymers were therefore determined both by AN-titrations (Fig. 1) and <sup>1</sup>H-NMR spectra (Table II). The molar mass determination based on <sup>1</sup>H-NMR was conducted by relating the signals typically appearing at 4.3–4.4 ppm in the <sup>1</sup>H-NMR spectra to the methine protons of the PLA chain (5.1–5.3 ppm). The molar masses of the PLA homopolymers were additionally determined by GPC (Table II). The number average molar masses obtained for the PLA homopolymer using different methods (AN titrations, <sup>1</sup>H-NMR, and GPC) correlated well with each other.

The AN and <sup>1</sup>H-NMR analysis conducted on the copolymers confirmed the formation of the di- or tetrafunctional molecules presented in Scheme 1. However, in addition to telechelic PLA polymers having the desired end functionality, also dilactide and free PLA chains not attached to the comonomers were detected in all of the samples, as discussed in more detail in the following paragraphs. These polymer products were thus essentially blends of copolymers and linear chains of PLA homopolymers.

Predominantly, hydroxyl-terminated copolymers were obtained using 1,4-butanediol or pentaerythritol as comonomers, and the molar masses of these copolymers were thus estimated by <sup>1</sup>H-NMR. The use of adipic acid or 1,2,3,4-BTCA, on the contrary, resulted in predominantly carboxyl-terminated copolymers, and the molar masses of these copolymers were determined by AN-titrations. The molar masses of the homopolymers and the hydroxyl and carboxyl-terminated copolymers are graphically summarized in Figure 1 as a function of polymerization time.

The theoretical molar masses of the copolymers of 1,4-butanediol and pentaerythritol were 7300 Da and 14,500 Da, respectively, and those of the copolymers of adipic acid and 1,2,3,4-BTCA 7400 and 14,600 Da, respectively. The actual molar masses of the copolymers were in general lower than the theoretical values calculated based on the reagent ratio at the end of the polymerizations. This was probably related to the presence of PLA homopolymer chains as well as to the formation of dilactide by the back-biting mechanism and its consequent evaporation from the polymer melt during polymerization. Theoretically, if some of the LA is removed from the reaction mixture as dilactide, a lower LA to comonomer ratio and consequently also lower molar mass of the polymer would be obtained.

The tetrafunctional copolymers reached approximately double the molar masses of the difunctional ones, which, in turn, typically had higher molar masses than the PLA homopolymer. This was probably related to the lower number of functionality of these comonomers, affecting the relative number of chain ends available for depolymerization. It was additionally noted that the Sn(Oct)<sub>2</sub>-catalyzed carboxyl-terminated copolymers typically had higher molar masses than the Fe(OAc)<sub>2</sub>-catalyzed ones after longer polymerization times. No significant differences between the molar masses of the Fe(OAc)<sub>2</sub> or Sn(Oct)<sub>2</sub>-catalyzed PLA homopolymer were, however, detected within the first 8 h. The growth rate of a single chain was approximately the same for the PLA homopolymer and the copolymers of pentaerythritol during the initial phase of the polymerization (<10 h), suggesting that the type of chain end-termination only starts to play a more important role after longer polymerization times.

The hydroxyl-terminated copolymers typically reached slightly lower molar masses than the carboxyl-terminated ones having the same number of functionality and using the same catalyst, especially after longer polymerization times (Fig. 1). The molar masses determined after a polymerization time of 23 h in the copolymerization of LA and 1,4-butanediol were 3300–3500 Da. The molar masses of the copolymers of pentaerythritol were 6100–6900 Da after the same polymerization time. The copolymers of adipic acid and 1,2,3,4-BTCA reached molar masses of 3300–4500 and 7200–8900 Da, respectively. The typically higher molar masses reached for the carboxyl-terminated polymers were probably related to back-biting reactions resulting in dilactide formation, since blocking of the hydroxyl end-group by for example acetylation<sup>27,28</sup> is known to improve the thermal stability of PLA in the presence of residual catalyst.

AN-titrations and <sup>1</sup>H-NMR were used in estimating the relative amount of chains not attached to the

**TABLE III**  
AN and <sup>1</sup>H-NMR Results of the Hydroxyl-Terminated Copolymers Produced at 180°C

Comonomer	Catalyst	Polym. time (h)	AN (mg [KOH]/g [sample])	<sup>1</sup> H-NMR		
				<i>F</i> <sub>NMR</sub>	<i>F</i> <sub>AN</sub>	
1,4-Butanediol	Fe(OAc) <sub>2</sub>	8	58	0.76	0.90	
		12	27	0.54	0.63	
		23	24	0.43	0.70	
	Sn(Oct) <sub>2</sub>	2	294	0.96	1.60	
		3	164	0.91	1.06	
		4	112	0.88	0.98	
		5	95	0.86	0.98	
		6	80	0.82	0.91	
		7	57	0.76	0.82	
		8	43	0.65	0.76	
		12	31	0.58	0.67	
		23	16	0.29	0.49	
		Pentaerythritol	Fe(OAc) <sub>2</sub>	2	273	0.98
3	165			0.94	1.19	
4	127			0.91	1.15	
5	93			0.80	0.99	
7	53			0.70	0.77	
8	41			0.63	0.68	
12	30			0.59	0.49	
23	8			0.40	0.22	
Sn(Oct) <sub>2</sub>	2			279	0.90	1.51
	3			144	0.90	1.12
	4		103	0.85	1.04	
			5	77	0.75	0.92
			6	62	0.71	0.88
		7	49	0.63	0.77	
		8	42	0.59	0.67	
		12	33	0.53	0.67	
		23	14	0.20	0.44	

The AN values are presented to illustrate the fact that also chains not attached to the comonomers were present.

comonomer (*F*<sub>AN</sub>) for the batches containing predominantly hydroxyl-functional comonomers (1,4-butanediol or pentaerythritol, Table III). The AN of the hydroxyl-terminated copolymers are shown in Table III to illustrate how the amount of carboxyl-terminated chains, i.e., free chains not attached to the comonomers, decreased as a function of polymerization time. The relative amount of chains not attached to the hydroxyl-functional comonomers was also estimated by <sup>1</sup>H-NMR alone (*F*<sub>NMR</sub>). Both of the values (*F*<sub>AN</sub> and *F*<sub>NMR</sub>) decreased as a function of polymerization time.

The hydroxyl groups detected by <sup>1</sup>H-NMR were utilized, together with the AN of the copolymer, in the estimation of the *F*<sub>AN</sub> of the batches containing carboxyl-functional comonomers (adipic acid or 1,2,3,4-BTCA, Table IV). The relative amount of chains not attached to adipic acid was also calculated based on <sup>1</sup>H-NMR only (*F*<sub>NMR</sub>). The *F*<sub>AN</sub> values of the carboxyl-terminated copolymers decreased with polymerization time (Table IV). The *F*<sub>NMR</sub> and *F*<sub>AN</sub> values obtained for the copolymers of adipic acid correlated relatively well with each other.

The differences in the molar masses observed for the polymers having different types of chain termination could be partly related to the fact that the relative

**TABLE IV**  
*F*<sub>NMR</sub> and *F*<sub>AN</sub> of the Carboxyl-Terminated Copolymers Produced at 180°C

Comonomer	Catalyst	Polym. time (h)	<i>F</i> <sub>NMR</sub>	<i>F</i> <sub>AN</sub>
Adipic acid	Fe(OAc) <sub>2</sub>	8	0.76	0.78
		12	0.49	0.43
		23	0.24	0.20
Adipic acid	Sn(Oct) <sub>2</sub>	8	0.81	0.87
		12	0.64	0.66
		23	0.24	0.28
		28	0.10	0.10
1,2,3,4-BTCA	Fe(OAc) <sub>2</sub>	8	–	0.67
		12	–	0.72
		20	–	0.41
		23	–	0.44
1,2,3,4-BTCA	Sn(Oct) <sub>2</sub>	28	–	0.23
		8	–	0.69
		12	–	0.70
		20	–	0.58
		23	–	0.26
		28	–	0.23

**TABLE V**  
**Results from the TGA Heating Ramp Experiment**  
**(Heating from 35 to 500°C at 10°C/min)**

Comonomer	Degradation onset (°C)	Depolymerization rate (mg/min)	Residue (wt %)
–	299	0.7	0.2
Adipic acid	312	0.5	1.0
1,2,3,4-BTCA	298	0.6	1.0
1,4-Butanediol	262	0.8	0.3
Pentaerythritol	270	0.7	0.4

The polymers had been prepared with Sn(Oct)<sub>2</sub> as the catalyst.

amount of chains not attached to the comonomer ( $F_{AN}$  or  $F_{NMR}$ ) was in general higher for hydroxyl-terminated copolymers than for carboxyl-terminated ones. The chains not attached to comonomers theoretically decrease the number average molar mass of the copolymers, assuming that both the free and the attached PLA chains have the same length. However, the lengths of the PLA chains are not uniform in practice, and the  $F_{AN}$  values must therefore only be considered as indicative. Minor differences may also arise from the fact that the  $F$  values of the hydroxyl- and carboxyl-terminated copolymers were determined using slightly different methods, as specified in the Supporting Information.

The presence of chains not attached to comonomers has been recognized also in previous studies on telechelic PLA.<sup>29,30</sup> However, the available information about the dependence of their amount on the polymerization time or the type of chain termination has been scarce. The  $F$  values determined in this study decreased with polymerization time. It was additionally noted that it took longer to reach low  $F$  values in the polymerizations than for the growth of the molar mass to slow down. The molar masses of the polymers had typically reached a relatively constant level after a polymerization time of ca. 20 h, but the  $F$  values still kept decreasing at this stage. Therefore, to make the polymerization process as economical and efficient as possible, an optimum between reaction time, final molar mass and the quality of the telechelic polymer in terms of chain end functionality should be found specifically for the chosen application. The concept of  $F_{AN}$  or  $F_{NMR}$  could thus be utilized as a supporting tool for other quality control methods for example in the evaluation of LA-based polymers. A high  $F$  value can have crucial effects on the polymer properties, especially if the polymer is used as a telechelic prepolymer.

### Depolymerization

Knowledge of the depolymerization characteristics of different types of PLA is crucial to be able to optimize their polymerization processes. Similarly, fast

and complete depolymerization of PLA, leading to dilactide formation, would be desirable in the ROP route. In addition to increasing the yield of the desired end-product, an optimized process will reduce the operating time and result in cost savings. The thermal degradation of the Sn(Oct)<sub>2</sub>-catalyzed polymers purified by precipitation was thus studied by TGA. Residual catalyst has been reported to decrease the melt stability of PLA, and the precipitation process reported only to remove the nonbonded Sn-catalyst (ca. 70% of catalyst remaining in the polymer after a similar purification step in another study).<sup>28</sup> This is in agreement with the results obtained for the PLA in this study. The amount of catalytic metal, as determined by ICP-OES, typically decreased to ca. 70% in the precipitation process. Dilactide was the only depolymerization product, as confirmed by mass spectroscopy. This is typical for PLA containing Sn, since Sn-catalyzed pyrolysis has been reported to start through a random degradation and mainly involve zero-order weight loss with dilactide as the main product after this.<sup>31</sup> However, for the sample containing pentaerythritol, a very small amount of LA was observed at the beginning of the measurement.

The TGA studies were commenced by conducting a heating ramp experiment. The samples were heated from 35 to 500°C at 10°C/min. The hydroxyl-terminated copolymers showed lower depolymerization onsets, higher depolymerization rates and lower weight residues than the carboxyl-terminated ones (Table V).

In the second series of TGA experiments the copolymers were heated from 35°C to 300°C at 50°C/min and isothermally kept at 300°C until a constant weight had been reached (Table VI). The hydroxyl-terminated samples had significantly lower weight residues and higher depolymerization rates than the carboxyl-terminated ones, indicating faster and more complete depolymerization.

The copolymers were also analyzed by isothermal TGA at their individual depolymerization onset temperatures determined in the heating ramp experiment described above (Table VII). The samples were

**TABLE VI**  
**Results from the Isothermal TGA Runs Conducted at**  
**300°C (heating from 35°C to 300°C at 50°C/min) the**  
**Polymers Had Been Prepared with Sn(Oct)<sub>2</sub> as the**  
**Catalyst**

Comonomer	Depolymerization rate (mg/min)	Residue (wt %)
–	0.3	0.3
Adipic acid	0.2	1.7
1,2,3,4-BTCA	0.2	2.3
1,4-Butanediol	1.5	0.2
Pentaerythritol	1.2	0.5

**TABLE VII**  
**Results from the Isothermal TGA Runs Conducted at the Individual Depolymerization Onset Temperatures of the Polymers (Heating from 35°C to the Chosen Temperature at 50°C/min)**

Comonomer	T (°C)	Depolymerization rate (mg/min)	Residue (wt %)
–	300	0.3	0.6
Adipic acid	315	0.7	1.5
1,2,3,4-BTCA	300	0.2	2.2
1,4-Butanediol	265	1.1	0.9
Pentaerythritol	270	0.8	1.0

The polymers had been prepared with Sn(Oct)<sub>2</sub> as the catalyst.

heated from 35°C to the onset temperature at 50°C/min and kept at this temperature until reaching a constant weight. The linear copolymers showed in general higher degradation rates and lower weight residues than the tetrafunctional ones. The hydroxyl-terminated polymers showed higher degradation rates and lower weight residues than the carboxyl-terminated ones also in this experiment.

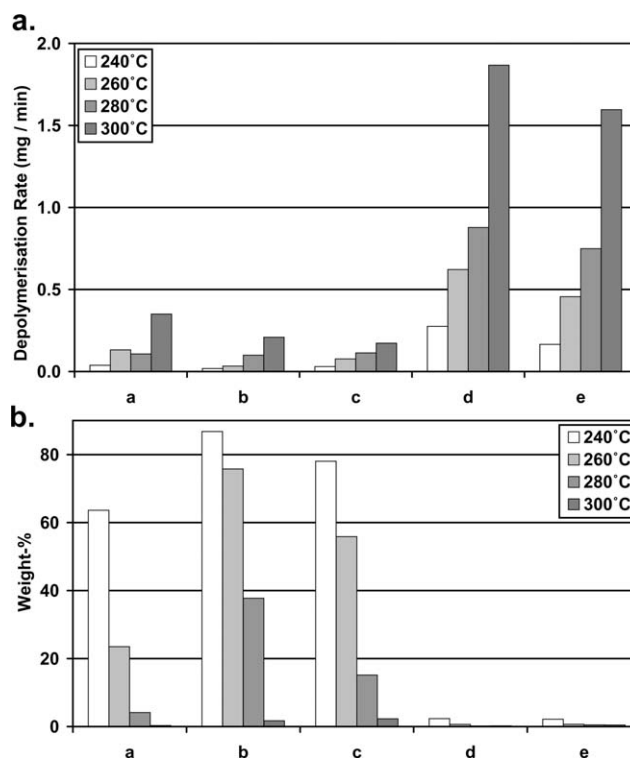
In the last part of the TGA studies, the copolymers were heated from 35 to 240, 260, 280, or 300°C at 50°C/min and isothermally heated for 60 min. The degradation rates of the samples increased as a function of temperature of the isothermal step [Fig. 2(a)]. The degradation rate of the PLA homopolymer was in general slightly higher than those of the carboxyl-terminated polymers. The hydroxyl-terminated samples showed remarkably faster depolymerization rates than the other polymers at the four different temperatures used. The relationship between the type of copolymer chain termination and its depolymerization characteristics was also demonstrated by the weight residues determined after the 60 min isothermal heating interval [Fig. 2(b)]. The residual weights of the different polymers decreased as a function of temperature. The hydroxyl-terminated copolymers had the lowest weight residues of the studied polymers at the end of the TGA runs, the difference being especially significant below 300°C. At 240°C, for example, almost 90% of the sample weight was left for the linear carboxyl-terminated polymer (copolymer of adipic acid), compared with approximately 2 wt % for the hydroxyl-terminated polymers. Only the hydroxyl-terminated polymers had reached a constant weight after the 60 min heating period at 240 and 260°C. At 300°C, all of the studied polymers had reached constant, low weight residues (2.2 wt % or less).

In summary, apparent differences in the thermal stabilities of the Sn(Oct)<sub>2</sub>-catalyzed polymers having predominant hydroxyl or carboxyl-termination were detected. Hydroxyl-terminated copolymers were

found to depolymerize into dilactide at a faster rate and more completely in terms of their residual weights, compared with the carboxyl-terminated copolymers. This probably caused also the observed differences in the molar masses of the copolymers having different functionalities. Hydroxyl-terminated star-shaped PLA copolymers have also previously been found to be slightly less thermally stable compared with carboxyl-terminated ones,<sup>27,32</sup> but the results have not been directly related to their polymerizability of lactide production efficiency previously.

### Racemization

The properties of PLA depend strongly on its optical purity. Even though the stereoisomer contents of polymer grade LA solutions are typically well defined, racemization occurred during the polymerization or processing of PLA can have drastic effects on the final properties of the product. For example, D-lactoyl units in PLLA increase the biodegradation rate of the polymer in soil.<sup>33</sup> Enantiomeric impurities also affect the mechanical properties of the material due to changes in crystallization behavior.<sup>34</sup> In dilactide production, the yield and the quality of the desired end-product, e.g., LL-dilactide, decreases, if



**Figure 2** (a) Depolymerization rates and (b) weight residues determined by TGA after a 60 min isothermal heating period at different temperatures (shown in the legend). Sample identification: (a) PLA homopolymer, (b) copolymer of adipic acid, (c) copolymer of 1,2,3,4-BTCA, (d) copolymer of 1,4-butanediol, and (e) copolymer of pentaerythritol. Sn(Oct)<sub>2</sub> was used as a catalyst.

**TABLE VIII**  
**Relative D- and L-stereoisomer Contents of the LA Used as a Reagent and the Tetrafunctional Copolymers Produced at 180 and 200°C for 24 h, as Determined by HPLC**

Sample type	L-LA (%)	D-LA (%)
LA	98.9	1.2
Dried LA	98.6	1.5
4-Arm COOH term. 180°C	97.3	2.7
4-Arm COOH term. 200°C	95.2	4.9
4-Arm OH-term. 180°C	97.4	2.6
4-Arm OH-term. 200°C	93.3	6.8

also other stereoisomers (i.e. DD- or DL-dilactide) are formed due to the presence of D-lactoyl units in the low molar mass polymer that is thermally degraded.

The depolymerization studies conducted by TGA showed that the type of chain termination plays an important role in the thermal stability of low molar mass PLA. The L-LA used as a reagent and the Sn(Oct)<sub>2</sub>-catalyzed copolymers of pentaerythritol or 1,2,3,4-BTCA were included in this study to find out if the type of chain termination also affects the extent of racemization occurring during polymerization. The LA was analyzed by HPLC both before and after the removal of the free water contained in it to evaluate the effect of the drying procedure on its quality. The polymerization temperatures used were 180 and 200°C were used as reaction temperatures, and the total reaction time was 24 h.

Racemization of LA due to the drying procedure was found to be negligible (Table VIII). The D-LA contents of the copolymers were slightly higher than for the dried L-LA after polymerization at 180°C, but both of the copolymers had undergone significant racemization at 200°C (Table VIII). The hydroxyl-terminated tetrafunctional polymer had a higher D-LA content (6.8%) than the carboxyl-terminated one (4.9%) at 200°C. Since hydroxyl-terminated copolymers depolymerized more easily into dilactide than the carboxyl-terminated ones, this can have been partially caused by racemization of the dilactide present in the melt. Dilactide has been reported to be more sensitive to racemization than PLA, because it is more easily deprotonated due to favorable entropy changes.<sup>35</sup> Analysis of racemization of the dilactide evaporated from the polymer melt would provide more data related to this theory and will be considered in the future studies. The extent of racemization occurred for the tetrafunctional copolymers can be considered significant with regard to its effect on polymer properties especially at a polymerization temperature of 200°C, independent of whether the poly-

mers would be used for chain extending or dilactide production.

## CONCLUSIONS

Copolymers of L-LA and 1,4-butanediol, pentaerythritol, adipic acid or 1,2,3,4-butanetetracarboxylic acid (1,2,3,4-BTCA) were successfully prepared. Sn(Oct)<sub>2</sub> was found to be a slightly more efficient catalyst than Fe(OAc)<sub>2</sub> in the polymerization of the di- and tetrafunctional PLA copolymers. The amount of chains not attached to the comonomer (*F*) decreased as a function of polymerization time and was typically higher for the hydroxyl-terminated copolymers. It also seemed that longer reaction times were required to reach low *F* values than for the molar mass to stabilize to a constant level. The carboxyl-terminated copolymers reached slightly higher molar masses after longer polymerization times and they were also found to be more stable in terms of depolymerization and racemization. Carboxyl-termination of PLA could therefore be beneficial, if dilactide or telechelic polymers of high optical purity are desired. Hydroxyl-termination, on the other hand, should be preferred, if rapid unzipping depolymerization resulting in dilactide formation is considered an advantage. Faster depolymerization caused by hydroxyl-termination could also shorten the overall production time of poly(lactide) produced by ROP, and result in cost savings. The polymer type and the reaction parameters should thus be chosen case-specifically, depending on the end-use application of the PLA polymer.

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