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Effect of Catalyst and Polymerization Conditions on the Preparation of Low Molecular Weight Lactic Acid Polymers

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ABSTRACT: The synthesis of low molecular weight ($\bar{M}_n$(NMR) < 27 000 g/mol) lactic acid polymers by condensation polymerization of L-lactic acid was investigated. All polymerizations were carried out in the melt, using different catalysts and polymerization temperatures. The products were characterized by DSC, GPC, titrimetric methods, and ^{13}C-NMR. According to NMR, the resulting polymers contained less than 1 mol % of lactic acid monomer and less than 6.6 mol % of lactide. In ^{13}C-NMR studies, the molecular weights were calculated by using the previously identified end group peaks in the methine area. The calculated molecular weights were systematically smaller than the weight-average molecular weights determined by GPC and on the same order as the molecular weights determined by titrimetric methods. The weight-average molecular weights of prepared prepolymers determined by GPC varied from 3600 to 32 600 g/mol, depending on the catalyst and polycondensation conditions. In DSC studies the glass transition temperatures of the resulting polymers varied from 24 to 51 °C, and crystallinity varied from 0% to 52%. The annealing of the polymer samples had only a small effect on glass transition temperatures and crystallinity. According to our results, the best polycondensation catalyst was sulfuric acid, which produced the highest molecular weights and over 50% crystallinity. Sn(II) octoate produced quite a high molecular weight polymer which was totally amorphous (the proportion of D-lactic acid structures was about 48 mol %).

Introduction

Regarding lactic acid based polymers, the main interest has recently been in lactide polymerization. Many studies have been published where the effect of catalyst on the properties of the final polylactide has been investigated. Catalysts such as $SnCl_4$,[1] coordination catalyst (containing Zn and Al),[2] aluminum isopropoxide,[3] and Lewis acid catalysts[4,5] have been used in ring-opening polymerization of lactide. The common conclusion has been that different catalysts produce different kinds of poly(lactides). The main reason for different fine structures and molecular weights is ester interchange and racemization reactions during the polymerization. Tsuji *et al.*[6] studied the effects of annealing conditions on poly(L-lactide). They noticed that crystallinity and melting temperature increased with increasing annealing temperature and time.

In our previous studies,[7,8,9,10] we used Sn(II) octoate as the polycondensation catalyst. According to our studies, Sn(II) octoate produced prepolymers with molecular weights which were quite good, but the polymers were amorphous. Depending on the polymerization temperature, the proportion of D-lactic acid structures varied from 10 to 50 mol %. The proportion of D-lactic acid structures in the polymer chain leads to some crystallinity, but the molecular weight of this polymer is too low. Therefore, the effect of different catalysts on the properties of these prepolymers was studied. The low molecular weight lactic acid prepolymers are valuable raw materials in addition chemistry[9] and therefore it is essential to be able to control the molecular weights and crystallinity of these prepolymers. Our previous results indicated that there is some relation between the amount of D-lactic acid structures and crystallinity. In this work, we studied the effect of catalyst and polymerization conditions on the properties of the resulting low molecular weight lactic acid polymers and characterized the products by ^{13}C-NMR, DSC, GPC and titrimetric methods. Two different types of catalysts were studied. The catalyst types used were the proton acid catalysts (weak and strong) and Lewis acid catalysts (with various strength). The basic synthesis and characterization work of prepolymers was presented in our previous study.[10]

Experimental Section

Materials. L-Lactic acid (LA) from Fluka was a 90% aqueous solution of the monomer, 99% optically pure according to the manufacturer. The excess water was removed before use by distillation under reduced pressure at 100 °C. The following products were used without further treatment: phosphoric acid, zinc chloride, sulfuric acid, dibutyltin dilaurate, and chloroform from Fluka; antimony(III) oxide, titanium(IV) butylate, titanium(IV) isopropylate, and aluminium acetylacetonate from Aldrich Chemie; Sn(II) octoate from Sigma Chemical Co., and chloroform-d_1 with TMS (1%) (deuteration degree not less than 99.5%) from Merck.

Characterizations. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and polydispersity ($\bar{M}_w/\bar{M}_n$) were determined with respect to polystyrene standards by gel permeation chromatography. The Waters Associates system that was used was equipped with a Waters 700 Satellite wisp injector, a Waters 510 HPLC solvent pump, four linear PL gel columns (10^4, 10^5, 10^3, and 100 Å) connected in series, and a Waters 410 differential refractometer. All samples were analyzed at room temperature. Chloroform was used as eluent and was delivered at a flow rate of 1.0 mL/min. The samples were dissolved in chloroform at a concentration of 1.0% (w/v). The injection volume was 200 μL.

For NMR measurements, the samples were dissolved in chloroform-d_1 in 5 mm NMR tubes at room temperature. The sample concentration was about 10% by weight. Proton-decoupled ^{13}C-NMR spectra with NOE were recorded on a Varian Unity 400 NMR spectrometer, working at 100.577 MHz for carbon-13.

Differential scanning calorimetric (DSC) measurements were made on a PL Thermal Sciences DSC. The measurements were run from −50 to 200 °C at a heating rate of 10 °C/min. The glass transition temperatures and crystallinity

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Table 1. Polymerizations, Materials, and Characterization Results

polymer	catalyst	wt % catalyst	temp, °C	$\bar{M}_w$ (GPC), g/mol	PD (GPC)	$\bar{M}_n$ (^{13}C-NMR), g/mol	mol % D-lactic acid (^{13}C-NMR)	mol % lactide (^{13}C-NMR)	acid + hydroxyl number (titr)	$\bar{M}_n$ (titr), g/mol
11	H_3PO_3	0.1	180	3800	2.0	2400	12.7	4.4	50.9	2200
12	$ZnCl_2$	0.1	180	4700	2.2	5000	12.6	4.4	24.4	4600
13	Al(acac)	0.1	180	3600	2.0	3000	4.7	4.1	40.1	2800
14	Sn(II)oct	0.1	180	8000	2.6	6800	10.5	4.3	17.5	6400
15	no catalyst		180	3600	2.1	3500	9.5	3.8	37.4	3000
16	DBTL	0.1	180	6700	1.8	4800	4.0	1.3	25.5	4400
17	Sb_2O_3	0.1	180	10800	2.7	10000	6.3	3.5	12.2	9200
18	Ti(IV)bu	0.1	180	15000	2.1	14000	9.9	3.2	8.1	13900
19	Ti(IV)iso	0.1	180	12000	1.8	9000	7.1	0.6	13.7	8200
110	H_2SO_4	0.1	180	31000	1.7	28000	5.6		4.3	26000
21	H_3PO_3	0.1	200	6500	2.1	5800	12.9	5.4	21.6	5200
22	$ZnCl_2$	0.1	200	9100	2.5	9000	20.7	4.8	12.8	8800
23	Al(acac)	0.1	200	4900	2.0	4400	16.2	4.0	26.7	4200
24	Sn(II)oct	0.1	200	12900	2.5	8900	20.6	4.3	13.7	8200
25	no catalyst		200	6200	2.1	5800	12.4	5.2	20.8	5400
26	DBTL	0.1	200	14600	1.9	14400	10.1	4.4	7.9	14200
27	Sb_2O_3	0.1	200	17400	1.8	16600	10.7	3.9	6.9	16200
28	Ti(IV)bu	0.1	200	21600	1.9	21000	12.5	2.0	5.7	19600
29	Ti(IV)iso	0.1	200	19800	1.9	19600	12.9	1.6	6.2	18000
210	H_2SO_4	0.1	200	30600	1.8	29100	9.7		3.9	29000
31	H_3PO_3	0.1	220	7800	2.2	7700	27.1	5.7	16.0	7000
32	$ZnCl_2$	0.1	220	8100	2.2	7700	33.8	5.5	14.8	7600
33	Al(acac)	0.1	220	6500	2.2	5100	22.5	6.6	23.9	4700
34	Sn(II)oct	0.1	220	14000	2.9	9100	47.9	4.5	13.4	8400
35	no catalyst		220	7400	2.2	6800	17.6	5.9	16.7	6700
36	DBTL	0.1	220	25000	2.4	23000	16.3	2.6	5.3	21200
37	Sb_2O_3	0.1	220	16000	1.9	16600	17.3	0.7	7.4	15200
38	Ti(IV)bu	0.1	220	28200	1.8	26600	19.5	4.2	4.6	24500
39	Ti(IV)iso	0.1	220	23200	2.4	22000	20.7	1.9	5.5	20300
310	H_2SO_4	0.1	220	32600	1.8	29200	8.4		4.2	26800
41	H_3PO_3	0.5	200	10600	1.7	10400	18.0	3.7	11.2	10000
42	$ZnCl_2$	0.5	200	14800	1.7	9400	26.2	4.4	13.0	8600
43	Al(acac)	0.5	200	7100	1.6	6700	18.4	5.7	18.7	6000
44	Sn(II)oct	0.5	200	30800	1.7	28200	41.7	4.1	4.3	26000
45	no catalyst		200	6200	2.1	5800	12.4	5.2	20.8	5400
46	DBTL	0.5	200	25200	2.4	20600	6.1	3.8	5.8	19500
47	Sb_2O_3	0.5	200	26200	2.9	25100	12.3	2.4	4.7	23900
48	Ti(IV)bu	0.5	200	24700	1.8	18400	16.4	2.7	6.3	17700
49	Ti(IV)iso	0.5	200	22900	2.0	21500	17.9	2.8	5.4	20800
410	H_2SO_4	0.5	200	20400	1.9	18500	6.3		6.3	17800

data were determined from the second heating period. The crystallinity of different polymers was evaluated from the heat of fusion. By integrating the normalized area of the melting endotherm, determining the heat involved, and rating it to the reference 100% crystalline polymer (93.6 J/g),[11] the relative crystallinity of the polymer was assessed. In this paper the relative degree of crystallinity is referred to as crystallinity, and T_m is the melting temperature.

The hydroxyl and acid numbers were determined by standard titrimetric methods (DIN 53 240 and DIN 53 402). The molecular weights based on hydroxyl and acid numbers were calculated using the formula

$$\bar{M}_n(\text{titr}) = \frac{56.1 \times 2 \times 1000}{(\text{hydroxyl number} + \text{acid number})}$$

Every titration was repeated four times and the reported result is an arithmetic average of these titers.

For the annealing study, 1 g of polymer sample was placed on a small glass plate, and the plate placed in a reduced-pressure oven. The annealing temperature was 60 °C, and the annealing times were 12, 24, and 36 h. The annealing pressure was 10 mbars. After each annealing, the glass plate was removed from the oven and placed in a desiccator to cool down. After cooling, the sample was pulverized and analyzed.

Synthesis of Lactic Acid Polymers. All polymerizations were carried out in the melt, using 20 mL test tubes. For every polymerization, 7 g of L-lactic acid was accurately added to the test tube. An accurately weighed amount of catalyst was then added to the test tube, and the tube sealed with Glisseal laboratory grease. A continuous nitrogen gas flow was maintained under the surface of the polymerization mixture. The tube was placed in an oil bath and the temperature was raised from room temperature to 180 °C over a period of 4 h. Then, depending on the required polymerization temperature, the temperature was kept constant or raised over a period of 2 h. The total polymerization time in every experiment was 12 h. Table 1 lists the polymerizations, materials used, and some characterization results.

After 12 h polymerization, the molten polymer was poured into an aluminium pan and placed in a desiccator to cool down. After cooling, the resulting polymer was pulverized and analyzed.

Results and Discussion

A detailed description of the low molecular weight lactic acid polymer analysis is presented in our previous study,[10] and the analysis results are collected in Table 1. The GPC was calibrated with narrow polystyrene standards, and therefore GPC results were used only as a qualitative tool to check the peak shape and size distribution of the different polymers. The molecular weights determined by ^{13}C-NMR and titrimetric methods were then used as quantitative values. The number-average molecular weights determined by ^{13}C-NMR and titrimetric methods were very close to each other, but smaller than the molecular weights determined by GPC. Besides the end group analysis, ^{13}C-NMR was a useful tool in the quantitative analysis to determine remaining lactic acid, formed lactide, and different optical isomers. The amount of lactic acid and lactide was calculated using the methine area peak integrals.

Catalysis by hydrogen ions is the most common type of acid catalysis, but not the only type.[12] Metal ions other than hydrogen may function similarly. Metal ions act as catalysts by bonding to organic reactants and introducing charge into them, and often polarizing them and inducing the formation of carbenium ions. A metal ion (a Lewis acid) may be superior to a typical acid in several respects. It may introduce a multiple positive charge, whereas a proton can introduce only a single positive charge.[12]

When 0.1 wt % of catalyst was used in the polycondensation of lactic acid, the weight-average molecular weight of the resulting prepolymers typically increased when the polymerization temperature was raised. The polymerization with antimony oxide and zinc chloride reached highest molecular weights at 200 °C. The reason for this could be that at 220 °C the thermal degradation or ester interchange reactions are stronger than the reactions which increase the length of polyester chains. According to data analysis, racemization reactions increased when the polymerization temperature was increased. This can be seen from the increasing amount of D-lactic acid structures and the decreasing of crystallinity. When the amount of catalyst was increased to 0.5 wt % and the polymerization temperature was 200 °C, the weight-average molecular weight of the resulting polyester was clearly higher than the polyesters which were produced with a lower amount of catalyst. Only titanium(IV) butylate and sulfuric acid produced higher molecular weight polyester with a lower amount of catalyst.

Phosphoric acid (H_3PO_3) is a weak proton acid. It was quite a bad polycondensation catalyst in lactic acid polymerizations. Molecular weight of the resulting polyesters were quite low, except when 0.5 wt % of catalyst was used. The amount of D-lactic acid structures increased dramatically when polymerization temperature was raised to 220 °C. It seems like racemization reactions increased at higher temperatures. The amount of lactide formed was below 5.7 mol % in every polymerization.

Zinc chloride ($ZnCl_2$) is a strong Lewis acid and an ester interchange catalyst. When it was used as catalyst in the polycondensation of lactic acid, the resulting polyesters had quite low molecular weights, except when 0.5 wt % of catalyst was used. A polymerization temperature of 220 °C produced a polyester with a molecular weight smaller than the polyester produced at 200 °C. The highest polymerization temperature (220 °C) produced 33.8 mol % of D-lactic acid structures in the polyester chain. The zinc chloride seems to be a stronger racemization catalyst than phosphoric acid. The amount of lactide formed varied from 4.4 to 5.5 mol %, depending on the polymerization conditions.

Aluminium acetylacetonate [Al(acac)] is a Lewis acid and a weak ester interchange catalyst. It worked quite badly as catalyst in the polycondensation of lactic acid. At 200 and 220 °C the polymerization without catalyst produced higher molecular weight polyester than the polymerizations with Al(acac) as catalyst. At higher polymerization temperatures the amount of D-lactic acid structures was quite high. Al(acac) seem to catalyzed the racemization reactions. The amount of lactide formed varied from 4.0 to 6.6 mol %, depending on the polymerization conditions.

Tin(II) octoate [Sn(II)oct] is a Lewis acid and a strong ester interchange catalyst. It produced quite high molecular weight polyesters in every polymerization temperature. However, when the polymerization temperature was raised, the amount of D-lactic acid structures increased dramatically. Tin(II) octoate seem to be the strongest racemization catalyst at higher temperatures and when higher amounts of catalyst were used in the polycondensation of lactic acid. The amount of lactide formed varied from 4.1 to 4.5 mol %, depending on the polymerization conditions.

When no catalyst was used in the polycondensation of lactic acid, the weight-average molecular weights of the resulting polyesters were quite low. When the polymerization temperature was raised, the amount of D-lactic acid structures increased quite smoothly. The amount of lactide formed varied from 3.8 to 5.9 mol %, depending on the polymerization conditions.

Dibutyltin dilaurate (DBTL) is a Lewis acid and an ester interchange catalyst. When it was used as catalyst in the polycondensation of lactic acid, the weight-average molecular weight of the resulting polyesters increased considerably when the temperature was raised from 180 to 220 °C. The highest temperature of 220 °C produced only 16.3 mol % of D-lactic acid structures in the polyester chain. This result shows that DBTL is a quite weak racemization catalyst. When the amount of catalyst was increased to 0.5 wt %, the weight-average molecular weight of the resulting polyester was clearly higher than the molecular weight achieved with a lower amount of catalyst. The proportion of D-lactic acid structures also increased slightly. The amount of lactide formed varied from 1.3 to 4.4 mol %, depending on the polymerization conditions.

Antimony(III) oxide (Sb_2O_3) is a Lewis acid and a weak ester interchange catalyst. When it was used as catalyst in the polycondensation of lactic acid, the weight-average molecular weight of the resulting polyesters was increased clearly when the temperature was raised from 180 to 200 °C. A polymerization temperature of 220 °C produced a polyester with a molecular weight about the same as the polyester produced at 200 °C. The small proportions of D-lactic acid structures show that only some racemization reactions happen when the temperature was increased. So reason for the low weight-average molecular weight for the polymer which was produced at 220 °C could be the thermal degradation reactions in the polymerization mixture. When the amount of catalyst was increased to 0.5 wt %, the weight-average molecular weight of the resulting polyester was increased by about 10000 g/mol when compared with the polymerization using a lower amount of catalyst. The proportion of D-lactic acid structures also increased slightly. This result shows again that antimony(II) oxide is a quite weak racemization catalyst. The amount of lactide formed varied from 0.7 to 3.9 mol %, depending on the polymerization conditions.

Titanium(IV) butylate [Ti(IV)bu] is a Lewis acid and a weak ester interchange catalyst. When it was used as catalyst in the polycondensation of lactic acid, the weight-average molecular weight of the resulting polyesters increased considerably when the temperature was raised from 180 to 220 °C. According to the low amounts of formed D-lactic acid structures, Ti(IV)bu seem to be a quite weak racemization catalyst. When the amount of catalyst was increased to 0.5 wt %, the weight-average molecular weight of the resulting polyester was lower than the molecular weight achieved with a lower amount of catalyst. The proportion of D-lactic acid structures also increased slightly. This result also shows that only some racemization reactions

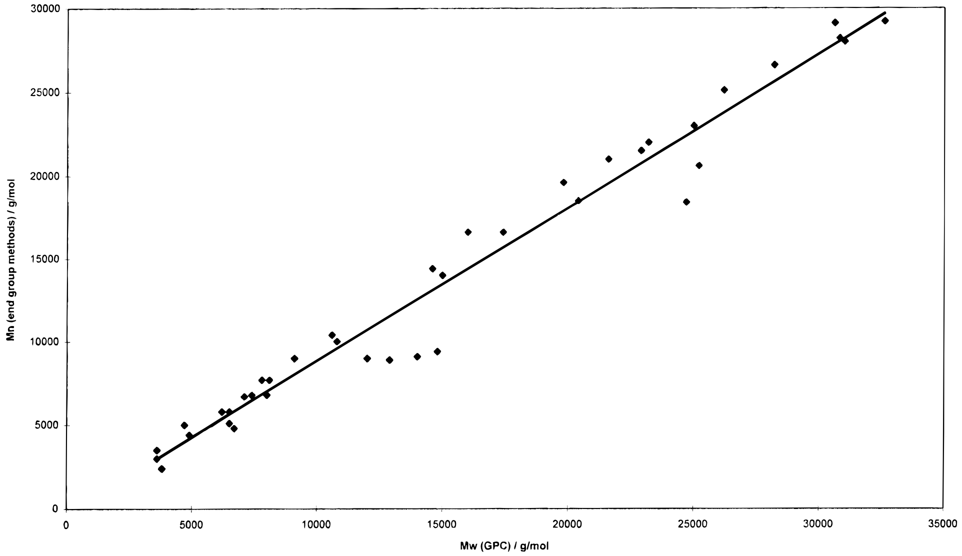


Figure 1. A plot of molecular weight determined by end group methods versus the molecular weight determined by GPC.

happen in the polymerization mixture. The amount of lactide formed varied from 2.0 to 4.2 mol %, depending on the polymerization conditions.

Titanium(IV) isopropylate [Ti(IV)iso] is also a Lewis acid and a weak ester interchange catalyst. The weight-average molecular weight of the resulting polyesters was increased when the polymerization temperature was raised from 180 to 220 °C, but not as significantly as in Ti(IV)bu polymerizations. The amounts of formed D-lactic acid structures were almost identical when compared with other titanium catalyst polymerizations. When the amount of catalyst was increased to 0.5 wt %, the weight-average molecular weight of the resulting polyester was about the same as the molecular weight achieved with a lower amount of catalyst. The proportion of D-lactic acid structures increased about 5 mol %. The amount of lactide formed varied from 0.6 to 2.8 mol %, depending on the polymerization conditions.

Sulfuric acid (H_2SO_4) is a very strong proton acid. When it was used as catalyst in the polycondensation of lactic acid, the polymerization temperature had only a small effect on the molecular weight of the resulting polyesters. Although the temperature was raised from 180 to 220 °C, the weight-average molecular weight of the resulting polyester was almost constant at about 29 000 g/mol. All polymerization temperatures produced less than 10 mol % of D-lactic acid structures in the polyester chains. When the amount of catalyst was increased to 0.5 wt %, and the polymerization temperature was 200 °C, the weight-average molecular weight of the resulting polyester was considerably lower than achieved with a lower amount of catalyst. The proportion of D-lactic acid structures also decreased from 9.7 to 6.3 mol %. The sulfuric acid produced lactide free polyesters. At this point, it looks as if strong proton acids prevent the formation of lactide.

Molecular Weight Characterizations. The molecular weights determined by ^{13}C-NMR and titrimetric methods were very close to each other. The number-average molecular weight determined by titrimetric methods was systematically a little smaller than the molecular weight determined by ^{13}C-NMR. In Figure 1 the number-average molecular weight determined by end group methods is shown against the weight-average molecular weight determined by GPC.

The data presented in Figure 1 show that weight-average molecular weights determined by GPC are systematically bigger than the molecular weights determined by end group methods. The plot in Figure 1 shows quite linear behavior. There are four points in Figure 1 where the plot is not on the same line. These four points are between 12 000 and 14 500 g/mol (GPC molecular weights). Figure 1 shows that the calibration of GPC can be carried out with the help of end-group based molecular weight determination. This kind of calibration needs more work to be precise, but if the data presented in this work is used in the calibration of GPC, the equation would be M_n(end group methods) = $0.9201M_w$(GPC) − 324.86, with an R^2 value of 0.9699. This equation is only trend setting and a more precise equation will be reported later.

Thermal Characterization. The results of thermal characterization are shown in Table 2. The first values for T_g, T_m, and crystallinity denote the properties of polyesters just after the polymerization. The next values are the characterization results for annealed polyester samples. The samples were annealed for 12, 24, and 36 h at 60 °C. There was no change detected in molecular weights during the annealing of polymer samples.

The glass transition temperatures of polymers after polymerization varied from 34 to 52 °C. The polymers which had over 40% crystallinity did not show glass transition temperatures after a polymerization, but every annealed sample which had over 40% crystallinity showed a glass transition temperature. The relation between molecular weight and glass transition temperature can be clearly seen for every polymer tested. The rule "the higher the molecular weight, the higher the glass transition temperature" is followed quite closely. Annealing had only a small effect on the glass transition temperatures. Typically, the glass transition temperature stays constant or is increased by a couple of degrees during the annealing.

Every polymer prepared at 180 °C showed crystallinity. When the polymerization temperature was increased to 200 °C, the crystallinity of the prepared polymers decreased, except for the polymers which were prepared using DBTL (polymer 26), Sb_2O_3 (polymer 27), or sulfuric acid (polymer 210) as catalyst. The only polymers which showed crystallinity at 220 °C were polymers where DBTL (polymer 36) and sulfuric acid (polymer 310) were used as catalyst. When the amount of catalyst was 0.5 wt %, $ZnCl_2$, Al(acac), Sn(II)oct, and

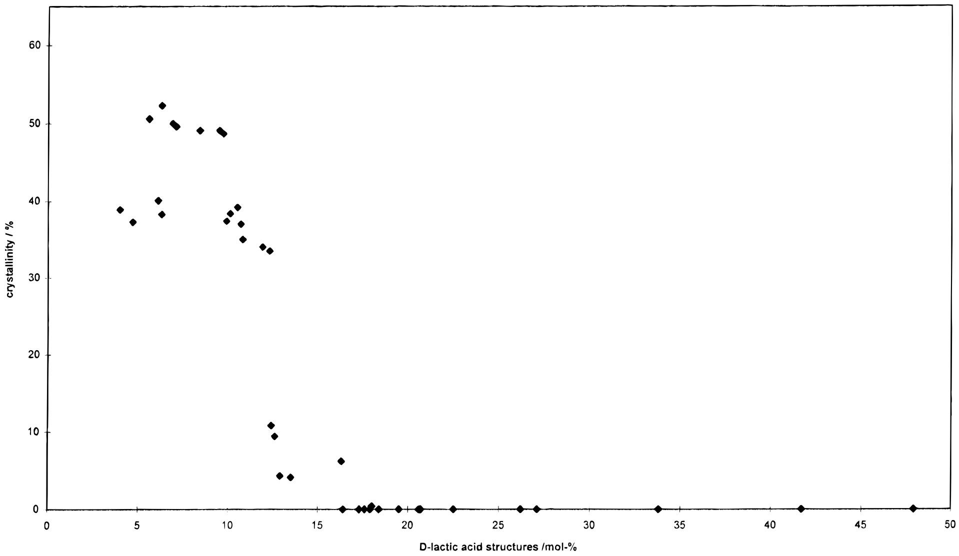


Figure 2. A plot of crystallinity determined by DSC versus the amount of D-lactic acid structures determined by ^{13}C-NMR.

Table 2. Thermal Characterization Results

	after polymerization			after 12 h of annealing			after 24 h of annealing			after 36 h of annealing		
polymer	T_g, °C	T_m, °C	% crystallinity	T_g, °C	T_m, °C	% crystallinity	T_g, °C	T_m, °C	% crystallinity	T_g, °C	T_m, °C	% crystallinity
11	34	136	5.4	37	137	5.4	34	138	5.4	37	137	5.6
12	40	139	9.1	40	139	9.6	39	140	13.3	40	139	14.2
13	35	127	37.3	35	133	1.6	34	130	0.9	35	134	2.2
14	43	148	39.2	46	148	46.6	30	147	45.6	35	148	44.2
15	35	136	49.1	36	136	49.5	35	136	50.2	36	136	51,1
16	42	143	38.9	32	146	38.5	44	144	39.1	45	145	41.8
17	41	142	38.3	43	142	38.5	43	144	41.2	45	145	44.7
18	48	150	37.4	42	155	37.0	49	150	39.3	50	151	37.3
19		151	49.6	52	155	39.6	51	151	38.4	51	151	38.6
110		164	50.6	48	165	53.0	41	161	57.3	57	158	58.4
21	41	141	5.3	42	140	5.3	42	140	5.5	42	141	5.6
22	44			45	134	1.2	38	134	1.8	44	135	2.3
23	38	136	0.4	38	135	1.1	49	136	2.5	38	136	1.8
24	47			47	133	0.3	40	130	0.4	46	127	0.6
25	40	137	10.8	40	139	9.5	40	141	9.8	41	141	11.9
26	45	143	38.4	43	144	29.7	45	146	28.0	46	147	28.4
27	44	144	37.1	45	154	37.8	49	150	39.9	51	151	40.9
28		150	24.2	48	156	24.0	53	147	21.3	54	148	21.1
29	51	144	4.3	50	157	14.7	54	149	18.8	55	149	20.2
210		154	48.7	55	161	41.3	56	153	35.4	57	154	35.5
31	39			41			39			41		
32	41			43			41			44		
33	41			41			40			42		
34	44			45			46			46		
35	39			40			37			41		
36	49	143	6.2	51	144	5.7	52	144	5.0	53	144	4.1
37	52			53			53			54		
38	49			49			50			53		
39	49			50			51			52		
310		163	49.1	50	163	49.3	54	166	49.8	58	158	49.4
41	41	134	0.4	43	133	1.7	42	136	1.2	44	131	1.2
42	45			47			46			46		
43	39			39	133	2.2	36	137	2.1	38	137	2.2
44	49			47			48			47		
45	41	138	10.8	42	138	11.1	41	142	11.5	42	142	11.6
46		160	40.1	53	158	40.5	53	158	39.6	50	161	38.7
47	49	148	33.5	55	147	31.2	49	153	29.6	55	153	30.3
48	49			52			52			52		
49	48			51			51			53		
410		163	52.3	50.3	164	53.9	55	154	52.1	56	154	53.0

both Ti catalysts produced amorphous polymers, while all other catalysts produced crystalline polymers. The only catalyst which produced high crystallinity polymers (about 50%) was sulfuric acid, and furthermore, these polymers had the highest molecular weights.

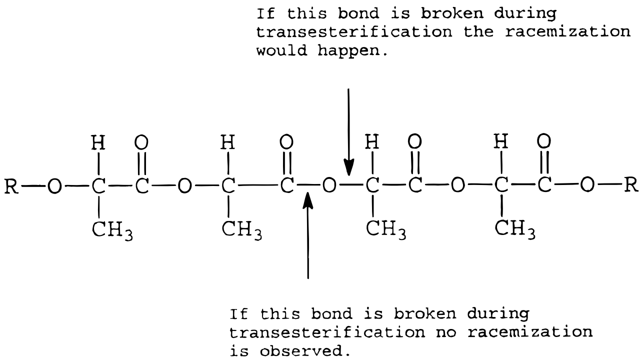
Annealing had only a small effect on crystallinity. The amorphous polymers did not crystallize during the annealing and for the crystalline polymers the crystallinity increased slightly.

As shown in Figure 2, the effect of D-lactic acid structures on the crystallinity of the polymer samples was clear. Crystallinity decreased rapidly with increased D-lactic acid structures in the polymer, and when the proportion of D-lactic acid structures was over

17 mol %, the polymers were all amorphous. Figure 2 also shows that when the proportion of D-lactic acid exceeded 10 mol %, the crystallinity of the polymers decreased considerably. The polymers containing about 5 mol % of D-lactic acid structures show a lower degree of crystallinity than the polymers which contain about 8 mol % of D-lactic acid structures. The explanation could be that the lower amounts of D-lactic acid units are randomly divided in the polymer chains, while others show some kind of block structure. If the melting temperature is high, then the polymer should have very uniform chains. The lower the melting temperature, the more defects, such as D-lactic acid structures, the polymer chains contain. At 180 °C, all catalysts except H_3PO_4 and $ZnCl_2$ produced high crystallinity polymers. The polymer which was produced with sulfuric acid had the highest melting temperature (164 °C) and the highest crystallinity (50.6 °C). The other polymers had over 37% crystallinity and a melting temperature below 151 °C. According to the melting temperature, sulfuric acid seemed to produce a polymer which had very few structural defects in the polymer chain. For the other catalysts, the low melting temperature and high crystallinity seem to result from some kind of block structure, because randomly placed D-lactic acid units cannot form crystals. When the polymerization temperature was increased, the crystallinity of the polymers decreased and the molecular weights increased for every catalyst except sulfuric acid. The explanation for lower crystallinity could be that longer polymer chains contain more D-lactic acid structures, and the order of these structures seems to be random. Sulfuric acid seems to produce polymer chains which contain very few D-lactic acid defects.

The Connection between Racemization and Ester Interchange Reactions. Polymerization without a catalyst produced a highly crystalline polymer at 180 °C, but when the polymerization temperature was raised to 200 °C the crystallinity of the polymer decreased from 49.1 to 10.8 mol %, and at 220 °C, the resulting polymer was amorphous. This kind of temperature dependence can be seen for every catalyst except H_2SO_4, which produced highly crystalline polymers whatever conditions were used. The strong ester interchange catalysts $ZnCl_2$ and Sn(II)oct already produced totally amorphous polymers at 200 °C. When the amount of catalyst was increased, the crystallinity of the polymers decreased for every catalyst except DBTL, Sb_2O_3, and H_2SO_4. For Sn(II)oct, the amount of D-lactic acid structures increased from 20.6 to 41.7 mol % when the amount of catalyst was increased from 0.1 to 0.5 wt %. This kind of increase in D-lactic acid structures when the amount of catalyst is increased could be caused by ester interchange reactions since when the amount of catalyst is increased the number of points where the reaction can take place also increases. For Sn(II)oct, which is itself an ester, the ester interchange reactions with polyester chains should be very probable. The results for Sn(II)oct strongly support this presumption about ester interchange reactions.

When the results for polymerization without a catalyst and with different types of catalyst are compared, the theory that ester interchange reactions are causing the racemization gains more evidence. The L-lactic acid which was used as raw material was 99% optically pure, and the probability that L-lactic acid undergoes the reaction which turns it to D-lactic acid is very small. When the ester interchange reaction happens, the ester bond in the polymer chain is first broken, and then a new ester bond is formed. During this reaction, there are two points where the ester bond can break. If the carbonyl−oxygen bond is broken there are no racemization expected, but if the alkyl−oxygen bond is broken, the racemization is observed. In Figure 3 are shown the two points where the ester bond can break.


If this bond is broken during transesterification the racemization would happen.

If this bond is broken during transesterification no racemization is observed.

Figure 3. Two points where the ester bond can break.

At lower temperatures the ester interchange reactions happen probably through the breaking of carbonyl−oxygen bond, and when the temperature is raised, the breaking of alkyl−oxygen bond increased. The catalysts like Sn(II)oct seem to catalyze the breaking of alkyl−oxygen bonds, which is seen as higher amounts of D-lactic acid structures. For the other Lewis acid catalysts, the ester interchange effect through the breaking of alkyl−oxygen bonds could be detected, but the magnitude of this effect was not as great as for Sn(II)oct. The strong proton acid, sulfuric acid, did not catalyze the ester interchange reactions through the breaking of alkyl−oxygen bonds, while the weak proton acid phosphoric acid seemed to catalyze these reactions. The reason for this could be that when the strong proton acids are present the ester bond breaking happens only through typical carbonyl−oxygen bond breaking. For some Lewis acid catalysts, the molecular weight of the resulting polymers was high, even though ester interchange reactions happened in the polymerization mixture.

Conclusions

The properties of low molecular weight lactic acid polyesters can be widely controlled by the use of different catalysts and polymerization temperatures. Results have shown that the weight-average molecular weight can be as high as 32 000 g/mol, and at the same time the resulting polyester can have 49.1% crystallinity. By choosing the catalyst and polymerization conditions, the crystalline behaviour of the resulting polyesters can be varied from totally amorphous to highly crystalline. The weight-average molecular weight can be controlled from 3600 g/mol to 32000 g/mol, and the glass transition temperatures from 34 to over 50 °C. The amount of D-lactic acid structures in the polyester chain determined by ^{13}C-NMR correlated very well with the crystallinity behaviour determined by DSC. The number-average molecular weights determined by ^{13}C-NMR were similar to the molecular weights determined by titrimetric methods. Both of these methods are based on end group analysis of the polymer chains, and therefore, it was expected that results would be very close to each other. The molecular weights determined by GPC were systematically bigger than those determined by ^{13}C-NMR and titrimetric methods.

According to our results, sulfuric acid was the best catalyst at every temperature, if high molecular weight and crystallinity are desired. Both titanium compounds, antimony(II) oxide, and DBTL catalyst also produced high molecular weights and varying amounts of crystallinity. At 220 °C, these catalysts produced high molecular weights and amorphous polyesters. Only Al(acac) produced lower molecular weights than the polymerization without a catalyst. Phosphoric acid, $ZnCl_2$, and Sn(II) octoate produced quite high molecular weight polyesters, with low crystallinity at higher polymerization temperatures.

References and Notes

(1) Lillie, E.; Schulz, R. C. *Makromol. Chem.* **1975**, *176*, 1901.
(2) Bero, M.; Kasperczyk, J.; Jedlinski, Z. *J. Makromol. Chem.* **1990**, *191*, 2287.
(3) Dubois, C.; Jacobs, C.; Jerome, R.; Teyssie, P. *Macromolecules* **1991**, *24*, 2266.
(4) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419.
(5) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Polym. Bulletin* **1991**, *26*, 71.
(6) Tsuji, H.; Ikada, Y. *Polymer* **1995**, *36*, 2709.
(7) Hiltunen, K.; Seppälä, J. V.; Härkönen, M. *J. Appl. Polym. Sci.*, in press.
(8) Hiltunen, K., Seppälä, J. V.; Itävaara, M.; Härkönen, M. *J. Environ. Polym. Deg.*, in press.
(9) Hiltunen, K.; Seppälä, J. V.; Härkönen, M. *J. Appl. Polym. Sci.*, in press.
(10) Hiltunen, K.; Seppälä, J. V.; Härkönen, M.; Väänänen, T. *Macromolecules*, in press.
(11) Leenslag, J. W.; Gogolewski, S.; Pennings, A. J. *J. Appl. Polym. Sci.* **1984**, *29*, 2829.
(12) Gates, B. C. *Catalytic Chemistry*; John Wiley & Sons, Inc.: New York, 1992; p 40.

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