

The Synthesis of Lactic-Acid-Based Telechelic Prepolymers

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ABSTRACT: We have studied how different catalysts and diols affect the properties of low-molecular-weight (M_w (GPC) < 49800 g/mol) lactic-acid-based telechelic prepolymers. The catalysts and diols were tested separately in our previous studies. In this study, we used the best previously tested diols and catalysts together in order to prepare different types of telechelic prepolymers (for example, crystalline or amorphous). All condensation polymerizations were carried out in the melt, using different diols and different catalysts. The prepolymers were characterized by differential scanning calorimetry, gel permeation chromatography, titrimetric methods, and ^{13}C nuclear magnetic resonance (^{13}C -NMR). According to NMR, the resulting polymers contained less than 1 mol % of lactic acid monomer and less than 5.1 mol % of lactide. Dibutyltin dilaurate, like tin(II) octoate, produced quite good molecular weights, but the resulting prepolymers contained exceptionally high amounts of *D*-lactic acid structures, and, therefore, these prepolymers were totally amorphous. Antimony(III) oxide produced a high-molecular-weight prepolymer when the diol used was aliphatic. Like DBTL, Sb_2O_3 produced amorphous prepolymers, which contained a lower amount of *D*-lactic acid structures than DBTL prepolymers. 1,8-dihydroxyanthraquinone produced a different kind of chain structure with Ti(IV)bu and Ti(IV)iso because one prepolymer had high crystallinity, and the other showed only a slight crystallinity. Sulphuric acid produced a very high-molecular-weight prepolymer with aliphatic 2-ethyl-1,3-hexanediol; and with aromatic diols, it produced quite good molecular weights, except with 1,8-dihydroxyanthraquinone. High-molecular-weight prepolymers produced with H_2SO_4 also showed high crystallinity; and, according to ^{13}C -NMR, they did not contain lactide and *D*-lactic acid structures. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1011–1016, 1998

INTRODUCTION

For several years we have studied the production of lactic acid based biodegradable polymers. Typically high molecular weight lactic acid polymers are prepared by the special condensation polymerization of lactic acid¹ or by the ring opening polymerization of lactide. In direct polycondensation the one problem for achieving high molecular weights is the depolymerization where the lactide is formed.²

In our process the lactic acid is first condensation polymerized to a low molecular weight prepolymer which contains one kind of end group. The molecular weight is then increased by joining prepolymer chains together using difunctional substances such as diisocyanates as the chain extenders. In our previous studies^{3,4,5,6,7} we have used 1,4-butanediol and tin(II) octoate in the synthesis of hydroxyl terminated prepolymers. With this diol/catalyst system it is possible to produce very good prepolymers for diisocyanate linking. The final poly(ester-urethanes) had a very good polymer characteristics and they all are amorphous. In order to use these new materials in a wider range of applications the crystallinity and

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glass transition temperature control is essential. In our latest studies we have tested the effect of different catalysts⁸ and different diols⁹ on the properties of the prepolymers. Based on these studies, we have selected the best catalysts and diols to be used together in lactic acid polymerization. In this article, we report how these catalyst/diol systems effect the properties of the final prepolymers. Our purpose was to develop different catalyst/diol systems for preparing prepolymers with different properties. We want to control the molecular weight, glass transition temperature and crystallinity of the prepared prepolymers. The basic synthesis and characterization work of prepolymers was presented in our previous study.⁷

EXPERIMENTAL

Materials

L-Lactic acid (LA) from Fluka (Switzerland, Buchs) 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: 2-ethyl-1,3-hexanediol, 1,5-dihydroxynaphthalene, 1,4- and 1,8-dihydroxyanthraquinone, 4,4-isopropylidenediphenol, 4-hydroxyphenyl sulphone, and 4,4'-dihydroxybiphenyl from Fluka. Sulphuric acid (H₂SO₄) and dibutyltindilaurate (DBTL) were from Fluka; antimony(III)oxide (Sb₂O₃), titan(IV)butylat [ti(IV)bu], titan(IV)isopropylat [Ti(IV)iso] were from Aldrich Chemie (Germany, Steinheim); and chloroform and chloroform-d₁, with the deuteration degree not less than 99.5%, were from Fluka.

Characterizations

Molecular weights (\bar{M}_n and \bar{M}_w) and polydispersities (\bar{M}_w/\bar{M}_n) were determined with respect to polystyrene standards by gel permeation chromatography (GPC). The system from Waters Associates used was equipped with a Waters 700 Satellite wisp injector, a Waters 510 high-performance liquid chromatography (HPLC) solvent pump, four linear PL gel columns (10⁴, 10⁵, 10³, and 100 Å) connected in series, and a Waters 410 differential refractometer. All samples were analyzed at room temperature. Chloroform was used as the 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 nuclear magnetic resonance (NMR) measurements, the samples were dissolved in chloroform-d₁ in 5 mm NMR tubes at room temperature. The sample concentration was about 10% by weight. Proton-decoupled ¹³C-NMR spectra with nuclear Overhauser effect (NOE) were recorded on a Varian Unity 400 NMR spectrometer, working at 100.577 MHz for carbon-NOE-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 and at a cooling rate of 1°C/min. The glass transition temperatures and crystallinity 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),¹⁰ the relative crystallinity of the polymer was assessed. In this article, the relative degree of crystallinity is referred to as crystallinity, and T_m is the melting temperature.

Acid number was determined by a standard titrimetric method DIN 53 402. Every titration was repeated four times, and the reported result is an arithmetic average of these titres.

Synthesis of Lactic Acid Polymers

In preparing telechelic polymers with hydroxyl end groups, *L*-lactic acid was condensation-polymerized with 2 mol % of different diols and with 0.1 wt % of different catalysts. All polymerizations were carried out in the melt and under vacuum using a Büchi Rotavapor equipped with an oil bath. A continuous nitrogen gas flow was maintained under the surface of the melt. The rotation speed was approximately 100 r/min. Over a period of 8 h, the temperature of the oil bath was raised from 160 to 210°C, and the pressure was lowered from 500 to 30 mbar. After 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 analysed. The total polymerization time in every experiment was 24 h, and one sample was taken after 8 h of polymerization at the final polymerization temperature.

RESULTS AND DISCUSSION

A detailed description of the low-molecular-weight lactic acid polymer analysis was presented in our previous study,⁷ and the analysis results for the prepolymers prepared at 200°C are collected in Table I. 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. Table I lists the polymerizations, diols used, and characterization results for the prepolymers prepared at 200°C. The amount of lactic acid and lactide was calculated using the ¹³C-NMR spectra methine area peak integrals.

Polymerization Results

The polymerization results are collected in Table I. The results indicate that there are big differences in how different catalysts and diols work together in the polycondensation of lactic acid. For example, dibutyltindilaurate (DBTL) produced a high-molecular-weight prepolymer with 1,4-dihydroxyanthraquinone; but with 2,7-dihydroxynaphthalene, the resulting prepolymer had a very low molecular weight. As with molecular weight, there are very big differences in the amount of *D*-lactic acid structures and lactide formed during the polycondensation reactions. The amount of *D*-lactic acid structures formed varied from 0 to 66.3 mol %, depending on the diol and catalyst used. The amounts of lactide formed varied between 0 and 21.9 mol %. The high acid numbers indicate that the prepolymers were not completely hydroxyl-terminated. In some cases, the acid numbers were lower after 8 h of polymerization, indicating that the optimum polymerization times were between 8 and 24 h. In most cases, the acid numbers decreased when the polymerization was continued from 8 to 24 h; after 24 h, of polymerization the acid numbers were still quite high. This behavior indicates that the polymerization time should be longer since, according to our previous studies, the acid number should be close to or lower than unity. The results presented in Table I show that the glass transition temperatures and crystallinity of the prepolymer can be widely controlled.

DBTL produced high amounts of *D*-lactic acid structures with every diol tested. All prepolymers were amorphous, except the one that was prepared with 1,4-dihydroxyanthraquinone. This

prepolymer contained 46.3 mol % of *D*-lactic acid structures and still showed 2.6% crystallinity. It appears that DBTL and this diol produced a prepolymer that contains such uniform chains that some crystal structure could be formed. The low melting temperature shows that the chains contain a lot of defects (*D*-lactic acid structures). The molecular weight of the prepolymers decreased when the polymerization was carried out from 8 to 24 h. Logically, the acid number and glass transition temperature increased at the same time. It appears that the optimum polymerization time for DBTL and different diols is between 8 and 24 h. The amount of *D*-lactic acid structures increased when the polymerization was carried out from 8 to 24 h. This shows that the ester interchange reactions happen during polycondensation; and the longer the polymerization time, the higher the amount of *D*-lactic acid structures. The amount of lactide formed was less than 2.7 mol % for every prepolymer.

Antimony(III)oxide (Sb₂O₃) and 2-ethyl-1,3-hexanediol, and 2,7-dihydroxynaphthalene and 1,8-dihydroxyanthraquinone produced prepolymers with a raised weight-average molecular weight when polymerization was continued from 8 to 24 h. However, the high acid numbers indicate that the polymerization time should be longer than 24 h. The polymerization with 2-ethyl-1,3-hexanediol produced a prepolymer with a fairly low acid number. The molecular weights of these prepolymers were reasonably high. Only 1,4-dihydroxyanthraquinone and 4-hydroxybiphenyl sulphone produced prepolymers with molecular weights higher after 8 h of polymerization than after 24 h of polymerization. After 24 h of polymerization, the weight-average molecular weight of these prepolymers had decreased, and the acid number had increased. This shows that these prepolymers had reached their highest molecular weights before 24 h of polymerization. All prepolymers prepared with Sb₂O₃ were amorphous, and they contained about 30 mol % of *D*-lactic acid structures. It appears that Sb₂O₃ produced prepolymer chains where the *D*-lactic acid structures were randomly distributed. The glass transition temperatures of the prepolymers were about 45°C. The amount of lactide was less than 3.3 mol % for every prepolymer.

Titan(IV)butylat [Ti(IV)bu] produced a high-molecular-weight prepolymer with every diol except 2,7-dihydroxynaphthalene. The molecular weight of every prepolymer increased dramatically when the polymerization was carried out

Table I Results after 24 Hours of Polymerization at 200°C and with 2 mol % of Diol and 0.1 wt % of Catalyst

Polymer	Diol	Catalyst	\bar{M}_w (GPC)	PD (GPC)	<i>D</i> -lactic Acid Struc (¹³ C-NMR) (mol %)	Lactide (¹³ C-NMR) (mol %)	Acid Number (Titr)	T_g (°C)	T_m (°C)	Crystallinity (%)
1	2-ethyl-1,3-hexanediol	DBTL	6800	1.7	51.3	1.9	6.6	32	nd ^a	0
2	2-ethyl-1,3-hexanediol	Sb ₂ O ₃	21,100	1.7	27.6	3.4	4.6	46	nd	0
3	2-ethyl-1,3-hexanediol	Ti(IV)bu	24,700	1.6	27.7	3.6	1.6	45	nd	0
4	2-ethyl-1,3-hexanediol	Ti(IV)iso	19,400	1.6	23.1	2.5	3.5	44	nd	0
5	2-ethyl-1,3-hexanediol	H ₂ SO ₄	49,800	6.3	0	0.3	8.9	50	161	46.2
6	2,7-dihydroxynaphthalene	DBTL	3700	1.6	66.3	2.1	32.4	36	nd	0
7	2,7-dihydroxynaphthalene	Sb ₂ O ₃	16,800	2.2	33.4	3.3	8.7	45	nd	0
8	2,7-dihydroxynaphthalene	Ti(IV)bu	10,000	2.1	21.4	5.1	11.7	42	nd	0
9	2,7-dihydroxynaphthalene	Ti(IV)iso	9800	2.0	21.9	2.9	12.1	27	nd	0
10	2,7-dihydroxynaphthalene	H ₂ SO ₄	18,400	2.0	0	0	8.0	60	164	33.3
11	1,4-dihydroxyanthraquinone	DBTL	23,200	1.5	46.3	2.7	5.9	40	135	2.6
12	1,4-dihydroxyanthraquinone	Sb ₂ O ₃	11,100	1.4	36.9	3.0	20.1	44	nd	0
13	1,4-dihydroxyanthraquinone	Ti(IV)bu	16,000	1.5	31.8	2.4	10.9	41	120	4.6
14	1,4-dihydroxyanthraquinone	Ti(IV)iso	17,800	1.6	26.7	2.3	13.1	42	125	3.5
15	1,4-dihydroxyanthraquinone	H ₂ SO ₄	21,700	1.6	0	0	8.8	50	167	54.1
16	1,8-dihydroxyanthraquinone	DBTL	20,200	1.6	47.3	2.5	11.4	41	nd	0
17	1,8-dihydroxyanthraquinone	Sb ₂ O ₃	13,800	1.5	34.6	3.1	18.3	47	nd	0
18	1,8-dihydroxyanthraquinone	Ti(IV)bu	18,400	1.6	8.2	2.8	18.5	53	156	38.8
19	1,8-dihydroxyanthraquinone	Ti(IV)iso	18,000	1.6	21.4	2.1	11.2	45	140	9.4
20	1,8-dihydroxyanthraquinone	H ₂ SO ₄	2900	1.3	0	0	57.6	21	nd	0
21	4-hydroxybiphenyl sulfone	DBTL	13,200	2.1	48.2	2.9	31.6	44	nd	0
22	4-hydroxybiphenyl sulfone	Sb ₂ O ₃	9000	1.9	32.1	2.8	37.9	46	nd	0
23	4-hydroxybiphenyl sulfone	Ti(IV)bu	21,300	2.1	28.1	4.2	27.8	47	nd	0
24	4-hydroxybiphenyl sulfone	Ti(IV)iso	20,800	2.0	25.6	3.3	30.8	47	nd	0
25	4-hydroxybiphenyl sulfone	H ₂ SO ₄	19,600	2.4	0	0	30.7	53	157	36.5

^a nd = not detectable.

from 8 to 24 h. The acid number of the prepolymer that was produced with 2-ethyl-1,3-hexanediol, was 1.6, which is a very good value. The acid numbers of the other prepolymers indicate that the polymerization time was not long enough. Only 1,4- and 1,8-dihydroxyanthraquinone produced prepolymers that show crystallinity. The prepolymer that was produced with 1,4-dihydroxyanthraquinone showed only a slight crystallinity, while the 1,8-dihydroxyanthraquinone prepolymer showed over 38% crystallinity. Low crystallinity and melting temperature indicate that the 1,4-dihydroxyanthraquinone prepolymer chains are not uniform and contain a lot of defects. According to ^{13}C -NMR, these defects must be *D*-lactic acid units. However, these *D*-lactic acid units must be quite well organized because the amount of *D*-lactic acid units are as high as 31.8 mol %, and the prepolymer still shows crystallinity. The amount of lactide was less than 5.1 mol % for every prepolymer.

Titan(IV)isopropylat [Ti(IV)iso] produced quite similar prepolymers to those produced with Ti(IV)bu. Both catalysts produced almost equal molecular weights, and the molecular weight of every prepolymer increased dramatically when the polymerization was carried out from 8 to 24 h. Ti(IV)iso produced slightly crystalline prepolymers with 1,4- and 1,8-dihydroxyanthraquinone. Both of these prepolymers had low crystallinity and melting temperatures, and they contained over 20 mol % of *D*-lactic acid structures. High acid numbers (except with 2-ethyl-1,3-hexanediol) indicate that the polymerization time should be longer than 24 h. The amounts of lactide formed were smaller than for the prepolymers prepared with Ti(IV)bu.

Sulphuric acid (H_2SO_4) produced high molecular weight and crystalline prepolymers with every diol except 1,8-dihydroxyanthraquinone, which produced a very low molecular weight and amorphous lactic acid oligomer. With all the other diols, the molecular weight of the prepolymer increased dramatically when polymerization was carried out from 8 to 24 h. In addition, the crystallinity of the prepolymers did not decrease during 24 h of polycondensation. The acid numbers indicate that the polymerization time should be a little bit longer; and, in particular, the 4-hydroxybiphenyl sulphone polymerization should be much longer. The highest weight-average molecular weight (49800 g/mol) was achieved with 2-ethyl-1,3-hexanediol, and the highest crystallinity with 1,4-dihydroxyanthraquinone. According to

^{13}C -NMR results, the resulting prepolymers did not contain *D*-lactic acid structures and lactide. It appears that sulphuric acid prevents the formation of lactide and catalyzes the ester interchange reactions through the breaking of the carbonyl-oxygen bond. The glass transition temperatures of the high-molecular-weight prepolymers prepared with H_2SO_4 were clearly higher than those of the prepolymers prepared with other catalysts.

The Effect of Diol

In our earlier work,³⁻⁷ we have used 1,4-butanediol as a functionalizing substance. In these studies, we noticed that it is possible to produce hydroxyl-terminated prepolymer and that the molecular weight of the prepolymer can be controlled by the amount of diol. Even in earlier studies, we noticed that the polycondensation of lactic acid proceeds differently when the diol is added to the polymerization mixture. With Sn(II)Oct, the collected results are as follows (at 200°C): no diol $\bar{M}_w = 12900$ g/mol; with 2 mol % of 1,4-butanediol, $\bar{M}_w = 12000$ g/mol; with 2 mol % of 1,4-dihydroxyanthraquinone, $\bar{M}_w = 26800$ g/mol; and even as high as 71800 g/mol, molecular weights can be achieved. In our recent studies, we have investigated how different catalysts work in the polycondensation of pure *L*-lactic acid⁸ and the effect if the catalyst is Sn(II)Oct and the diol is changed.⁹ In this study, we examined the production of lactic-acid-based telechelic prepolymers with different catalysts and diols. According to our results, the diol, catalyst, and, perhaps, lactic acid formed some kind of active center, which polymerized lactic acid faster and more efficiently than if just catalyst and lactic acid were used. The structure of this possible center is not yet clear and requires further investigation. What is clear is that very high molecular weights (71800 g/mol) can be achieved with different catalyst-diol-lactic acid systems. If the structure of this possible active center is optimized, the production of high-molecular-weight poly(lactic acid) by condensation polymerization may be achievable.

CONCLUSIONS

In this study, we used 2 mol % of different diols and 0.1 wt % of different catalysts in order to prepare hydroxyl-terminated prepolymers. In our latest studies, we have tested different catalysts⁸ and different diols with Sn(II)Oct.⁹ In this study,

we tested the best previously tested catalysts and diols in order to produce different kinds of hydroxyl-terminated prepolymers. Dibutyltin-dilaurate, like tin(II)octoate, produced quite good molecular weights; but the resulting prepolymers contained exceptionally large amounts of *D*-lactic acid structures, and, therefore, these prepolymers were totally amorphous. Antimony(III)oxide produced a high-molecular-weight prepolymer when the diol used was aliphatic. All the aromatic diols with antimony(III)oxide produced prepolymers with clearly lower molecular weights. Like DBTL, Sb₂O₃ produced amorphous prepolymers, which contained lower amounts of *D*-lactic acid structures than DBTL prepolymers. Both titanium compounds produced almost equal molecular weight prepolymers with every diol tested. Only 1,8-dihydroxyanthraquinone produced a different kind of chain structure with Ti(IV)bu and Ti(IV)iso because the one prepolymer had a high crystallinity and the other showed only a slight crystallinity. Sulphuric acid produced a very high-molecular-weight prepolymer with aliphatic 2-ethyl-1,3-hexanediol; with aromatic diols, it produced quite good molecular weights, except with 1,8-dihydroxyanthraquinone. High-molecular-weight prepolymers also showed high crystallinity; and, according to ¹³C-NMR, they did not contain lactide and *D*-lactic acid structures.

Sulphuric acid and all diols tested except 1,8-dihydroxyanthraquinone and Ti(IV)bu and 1,8-dihydroxyanthraquinone produced an ester interchange mechanism where the possible ester interchange reactions happen mainly through the breaking of the oxygen-carbonyl bond. This mechanism leads to optically pure polyester chains. All other catalyst-diols systems seem to catalyze ester interchange reactions through the breaking of the alkyl-oxygen bond. The catalyst,

diol, and, perhaps, lactic acid seemed to form some kind of active center, which polymerized the lactic acid monomer more efficiently than the system without diol or catalyst. Some of these possible centers produced amorphous, and the other, crystalline prepolymers. 2-ethyl-1,3-hexanediol formed the most efficient center if the molecular weight was observed with sulphuric acid, with antimony(III)oxide, and with Ti(IV)bu. DBTL, on the other hand, formed its most active center with 1,4-dihydroxyanthraquinone, and Ti(IV)iso with 4-hydroxybiphenyl sulphone. If the crystallinity was observed, Ti(IV)bu formed the most efficient center with 1,8-dihydroxyanthraquinone, and sulphuric acid with 1,4-dihydroxyanthraquinone. In other words, the structure of the diol and catalyst had a big effect on the properties of the final prepolymers.

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