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Ring-Opening Polymerization of L-lactide by Means of Different Iron Compounds

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SUMMARY: L-lactide was bulk-polymerized in the presence of various commercially available iron compounds. The polymerization temperature was in the range of 140 and 230 °C, the monomer to initiator/catalyst ratio varied between 100 and 10 000, and the polymerization time between 30 minutes and 24 hours.

Iron oxides, iron chlorides and sulfuric iron compounds were low efficient and are not suitable for melt polymerization of lactide. The oxidation state was noticed not to affect the efficiency. Ferrocene required long polymerization times and a high concentration of the compound before a high molar mass polymer was received. Organic iron salts were also found to be efficient initiators/catalysts, except for the hydrated iron(III)citrate. Especially iron(II)acetate caused a rapid polymerization with a high conversion and molar mass.

Introduction

Lactic acid based plastics are hydrolyzable, and have been proposed as a potential candidate as a future packaging material due to regulations favoring recycling and/or composting. The ring-opening route, commonly used in the preparation of polylactide, is mostly initiated/catalyzed by organometallic compounds, of which residues also are found in the polymerization product. The metallic residues are often difficult to remove completely which may result in accumulation in the compost. The harmful effects may be suppressed or avoided by using catalytically active compounds degrading into bioacceptable compounds, for example iron compounds. Most of the commercially available iron compounds have been regarded as low-toxic(1) and iron compounds are furthermore substances frequently occurring in the nature. The use of

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iron compounds for catalyzing polymerizations of lactides have, to our knowledge, been described only to some extent. Iron(III)oxide was used as catalyst in ring-opening melt-polymerizations of lactide$^{2)}$. These polymerization experiments were performed at various temperatures, but the iron(III)oxide proved to be useful only at the highest polymerization temperature (180 °C). In another study hematin and related portphyrin complexes were used in polymerizations under similar conditions. The PLLA prepared by using hematin showed yields up to 74% and molar masses up to 10 000 were found$^{3)}$. Arvanitoyannis *et al.* prepared a polyester from L-lactide and sorbitol in presence of several different metal compounds, among others $FeCl_3$. However, this reaction was performed at 60 °C and the polymer obtained was reported to be dark brown$^{4)}$.

This paper reports the results of a study where melt-polymerizations of L-lactide were performed by using various commercially available iron compounds as initiators. The molar mass, its distribution, the monomer conversion and thermal properties were studied as a function of polymerization time and temperature.

Experimental

Polymerization procedure

L-lactide (Purac) was recrystallized once from ethyl acetate (Aldrich). The iron compounds (Aldrich) were stored in a desiccator and used without further purification before they, together with the monomer, were put into 5 ml glass ampoules, which were sealed in a glove-box. The monomer to initiator (M/I) ratio varied between 100 and 10 000 and the polymerization temperatures between 140 and 230 °C. The ampoules were kept in an oven at given temperature until the polymerizations were interrupted after desired time by removing the ampoules from the oven. The polymerization products were removed from the ampoules, examined, and stored in ambient conditions for further characterization, which in general was performed the following day.

Measurements

Molar mass measurements were obtained by Size Exclusion Chromatography (SEC). The system was based on a HPLC 2248 pump and RI detector from Pharmacia, and a pre-column (AN Gel Guard Column) and a linear column (AN Gel

Linear) from American Polymer Standards Corporation. The mobile phase in the system was tetrahydrofuran (chromatography grade) and the operating conditions in the system were: flow rate 1 ml/min at 40 °C; sample concentration 2 mg/ml. Polystyrene standards were used for calibration (Perkin-Elmer). The injected sample volume was 100 µl and the sample solution was filtered through a 0.2 µm filter before the injection. The optical purity was determined from a hydrolyzed PLLA sample by separating the two enantiomers using liquid chromatography with a special method developed for this purpose[5)].

Monomer conversion determinations and end group detection studies were performed by using NMR technique. The polymer was dissolved in chloroform-d_1 (1.5 wt%) and ^{1}H-NMR spectra were collected with a 500 MHz JEOL spectrometer. The monomer conversion determination method has been described elsewhere[6)]. Calorimetric measurements were conducted with a Perkin-Elmer Differential Scanning Calorimeter (System 7). The heating rate was 10 °C/min and after rapid cooling a second run was performed. The degree of crystallinity was calculated from the melt enthalpy by using 93.1 J/g as the value of the melt enthalpy for a 100% crystalline poly(L-lactide) (PLLA)[7)]. XPS spectra were obtained by using a Perkin-Elmer 5400 ESCA spectrometer employing Mg Kα X-rays. A survey scan spectrum and narrow scans in the C1s, O1s and Fe2p regions were recorded for metallic iron and iron oxide samples before and after sputtering. The sample charging was noticed from the shift of C1s by using 284.5 eV as reference value and the binding energy of Fe2p was corrected according to that. In order to observe differences in the oxidation state between the surface and the bulk the samples were eroded in situ by using argon ion bombardment between measurements.

Results and discussion

Iron oxides

Polymerizations of L-lactide were performed by using iron of different oxidation states as initiators. The differences in oxidation states between the surface and the bulk of the iron compounds were measured by using XPS-technique. Tab. 1 describes the experiments and provides experimental conditions and general comments on the different polymerizations. The polymerization time is in general given as the longest reaction time in the series of several experiments performed. The two columns to the right contain comments on the reaction products and molar mass values. The reaction temperature was 210 °C in all the experiments in Tab. 1. Commercially available metallic iron powder was also used as initiator/catalyst in the polymerizations, but the results are left out as the XPS measurements proved that an oxidation of the iron had occurred. Further XPS measurements showed no differences in the oxidation state of bulk and surface for the different iron oxides used. In general the iron oxides seemed not to be efficient in the polymerization of lactide. Iron(II)oxide required long reaction times, which could be reduced by increasing the temperature. The polymer had a molar mass of ca. 16 000 after 24 hours at 210 °C, which proved that the molar mass increased slowly during the polymerization. DSC measurements showed that the poly(L-lactide) had a low melting point (130 °C) and a low degree of crystallinity of 19%. However, the presence of a melting peak suggests that the degree of racemization was low[8]. Of all the iron oxides the hydrated iron(III)oxide initiated the polymerization best, but required fairly long polymerization times. After a reaction time of 22 hours, the monomer conversion was about 65%, when using hydrated iron oxide as initiator.

Tab.1. Reaction conditions and product characteristics in the L-lactide polymerizations at 210 °C using iron of different oxidation states

Iron compound	M/I mol/mol	Reaction time h	Appearance of the product	M_W g/mol
Iron(II)oxide	100	24	Yellowbrown polymer	16 000
	1 000	20	Yellow polymer	7 000
Iron (II,III)oxide	100	24	Lightbrown polymer	15 000
	1 000	22	Yellow oligomeric solid	5 000
Iron(III)oxide	100	10	Grey oligomeric solid	5 000
	1 000	22	Monomeric solid	-
Iron(III)oxide, hydrated	100	6	Yellowbrown polymer	20 000
	1 000	22	Brown polymer	26 000

Iron chlorides

Both iron(II)chloride and iron(III)chloride were used as initiators in the melt-polymerizations of L-lactide. At 180 °C no difference could be noticed between the efficiency of the compounds. The molar mass increased continuously, but slowly, with time and the highest molar mass (M_w) was 17 000, which was reached after 21 hours. The value of the dispersion index was also increasing with time, being 2.3 after 21 hours of polymerization. The conversion increased more rapidly than the molar mass and conversions above 80% were obtained after eight hours. Almost complete monomer conversion was reached after 21 hours of polymerization. At 210 °C the polymerization reaction was much more rapid than at 180 °C, resulting in a maximum molar mass (M_w) of 18 000 (when $FeCl_2$ was used) after three hours. The monomer conversion exceeded 90% after three hours of polymerization for both iron chlorides and they were equally efficient.

Organic iron salts

Three different commercially available iron salts were tested in polymerization experiments. The iron compounds used and the general trends in the polymerization are listed in Tab. 2.

Tab.2. Polymerization conditions and examples of the product characteristics for the PLLA initiated by using different iron salts at 210 °C

Iron salt	M/I mol/mol	Reaction time h	Appearance of the product	Molar mass[a)]	Monomer conversion[b)]
Iron citrate, hydrated	100	0 - 16	Transparent solid	Low	Low
	1 000	0 - 24	Monomeric solid	-	-
D-gluconic acid iron salt	100	0 - 10	Black solid	-	-
	1 000	1 - 20	Brown glassy polymer	Middle	High
	5 000	4 - 24	Lightbrown polymer	Middle	High
	10 000	4 - 16	Brown polymer	Middle	Low
Iron acetate	100	1 - 2	Brown glassy polymer	Middle	Middle
	500	1 - 2	Lightbrown polymer	Middle	Middle
	1 000	1 - 3	Yellow polymer	High	High
	10 000	1 - 20	Yellow polymer	Middle	Low

[a)] Low $M_w < 10\ 000$; Middle = 10 000 - 50 000; High > 50 000.
[b)] Low conversion < 20%; Middle = 20 - 70%; High > 70%.

Polymerizations performed by using hydrated iron(III)citrate at a monomer to initiator ratio (M/I) of 1 000 were not successful. No polymerization was initiated even after 20 hours. At M/I = 100 the highest molar mass was 5 000 (M_w), which was obtained after 16 hours of reaction.

The iron salt of D-gluconic acid proved to initiate the L-lactide polymerization. The reaction was rapid at higher amounts of the initiator (i.e. M/I = 100), causing a black solid residue after as short a reaction time as 40 minutes. At monomer to initiator ratios (M/I) of 1 000, 5 000 and 10 000 a high molar mass polymer was obtained (Fig. 1).

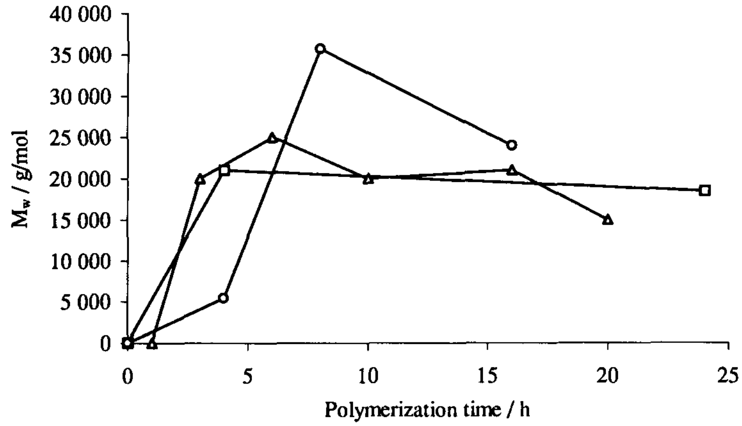

Fig. 1. The molar mass for the PLLA prepared at 210 °C by using the iron salt of D-gluconic acid as initiator at M/I = 1 000 (Δ), 5 000 (□), and 10 000 (O) as a function of the polymerization time

The molar mass seemed to be independent of the monomer to initiator ratio in the range of 1 000 to 10 000. After an initial propagation during 5 - 10 hours a degradation phase seemed to start. Typical values of the dispersion index were 1.7 - 1.9 regardless of the polymerization time. The monomer conversion measured for the PLLA prepared at M/I ratios of 1 000 and 5 000 showed the same trend with no monomer conversion during the first six hours, but with a fast increase in the conversion after that. All the measured conversions were higher than 55% and in most polymerizations exceeding eight hours above 77%.

Iron acetate proved to be an efficient initiator for the ring-opening melt-polymerization of L-lactide. The reaction temperature affected the polymerizations and, unlike the polymerizations where the iron salt of D-gluconic acid was used, the M/I ratio strongly affected the molar mass of the obtained poly(L-lactide) (Fig. 2).

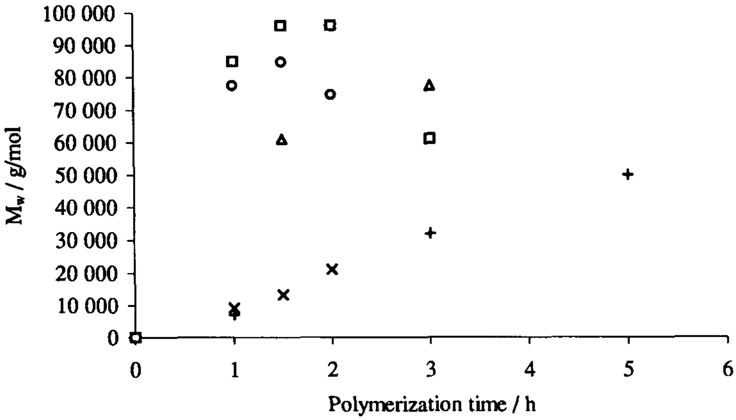

Fig.2. The molar mass for the PLLA prepared at 210 °C by using iron(II)acetate as initiator at M/I ratios: 500 (×), 750 (O), 1 000 (□), 2 000 (Δ), and 10 000(+)

The optimal M/I ratio was found to be in the region of 750 - 2 000, resulting in molar masses above 60 000 (M_w) after 1 - 2 hours of polymerization. After this time a decrease in the molar mass could be noticed (for the PLLA:s prepared at M/I = 750 and 1 000), which can be explained by termination followed by degradation of the polymer. Both the M/I ratios 100 and 10 000 resulted in significantly lower molar masses. At higher initiator concentrations the amount of growing chains apparently increased, which in general resulted in lower molar masses but higher conversions. The degradation started at an earlier stage when higher initiator/catalyst concentrations were used. At lower concentrations the propagation stage continued even after five hours of reaction. This may be a consequence of the difficulties of the monomer units to find initiator species, resulting in a slow polymerization rate. The molar mass, as well as the polymerization rate, was affected by the temperature. The molar mass increased continuously at 210 °C but at 190 °C this behaviour could not be observed for polymerization times exceeding 1.5 hours. At 170 °C the temperature seemed to be too low for initiating any reaction at all. This suggests that iron(II)acetate can be used for bulk-polymerization of L-lactide only at high temperatures. The molar mass distribution for a PLLA polymerized in an iron(II)acetate initiated route at temperatures above 190 °C is broad and typical values of the dispersion index varied between 2.7 - 3.5 for reaction times exceeding one hour. For shorter reaction times (below one hour) the dispersion index was about 2.0 at temperatures between 190 and 220 °C. The monomer conversion in the polymerization was determined for some of the iron(II)acetate initiated/catalyzed samples by using ^{1}H-NMR technique. The conversion was a function of both time and temperature. At 210 °C the conversion started to increase after a sort of activation time and increased rapidly with time, reaching a maximum conversion of 96% after 2 hours (Fig. 3).

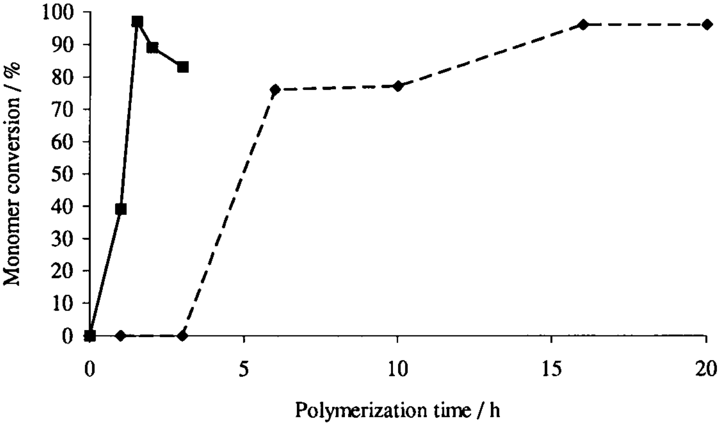

Fig.3. The monomer conversion for the PLLA prepared at 190 °C (broken line) and 210 °C (unbroken line) by using iron(II)acetate as initiator (M/I = 2 000)

At 190 °C the conversion increased more slowly, and the activation phase was also extended. However, the conversion reached values close to 100% for longer polymerization times. DSC measurements of the PLLA from the iron acetate initiated polymerizations were performed. Only the melting peak (endothermal) could be noticed (melting point at ca. 145 °C). However, the presence of the melting peak confirmed that racemization did not occur to any great extent. The low melting point can be explained by the high content of low molar mass polymers/oligomers in the sample or/and some degree of racemization. The endothermal melting enthalpy was reduced in the second run of the sample (e.g. from 20.5 to 4.6 J/g), which may be caused by a racemization during the thermal treatment. The racemic purity of the PLLA polymerized at 210 °C by using iron(II)acetate as initiator ($M/I = 1\ 000$, $t = 2$ h) was furthermore measured by using HPLC and the amount of D-form found was 2.1%.

Other iron compounds

Ferrocene (dicyclopentadienyliron) was used as initiator/catalyst in the polymerization of L-lactide at temperatures between 140 and 230 °C. At polymerization temperatures between 140 and 180 °C no reaction could be detected at any M/I ratios between 100 and 1 000 even after 24 hours of reaction time. The ferrocene required long polymerization times (24 h) and low monomer to initiator ratio (100) before a high viscous product was received at 210 °C (M_W ca. 40 000, MWD = 1.7). An attempt to increase the polymerization rate was made by increasing the reaction temperature to 230 °C. By this manner a PLLA ($M_w = 30\ 000$) was obtained after eight hours of polymerization. In prolonging the reaction time degradation became dominating. In the DSC curve no melting peak could be observed, which indicates racemization.

Polymerizations initiated/catalyzed by iron sulfide proceeded slowly and resulted in a maximum molar mass of 15 000 and 92% conversion after 9 hours. The conversion, determined with ^{1}H-NMR, increased more slowly than that with other iron compounds used as initiators. The NMR measurements showed furthermore an additional quartet, which was increasing with time. This quartet can be related to the methine group next to the carboxylic end group$^{9)}$. This proved that, compared to other iron compounds, using iron sulfide resulted in a larger amount of low molar mass poly(lactic acid). Both iron(II)sulfate ($FeSO_4 \cdot 7\ H_2O$) and iron(III)sulfate ($Fe_2(SO_4)_3 \cdot 5\ H_2O$)were used as initiators/catalysts in the polymerization of L-lactide. Neither of the iron sulfates could be regarded efficient. The highest molar masses (M_w) in the range of 8 000 - 9 000 were obtained after polymerization times exceeding 24 hours at 210 °C. The conversion increased slowly, but reached a level above 90% after 24 hours of polymerization.

Conclusions

L-lactide was bulk-polymerized by using several different types of iron compounds. All iron compounds required fairly high polymerization temperatures. The iron oxides, iron chlorides and sulfuric iron compounds were equally efficient. These compounds can be considered as low efficient and are not suitable if a high molar mass product is desired. Furthermore, a high monomer to initiator ratio was required before any adequate polymerization occurred. The oxidation state was noticed not to affect the efficiency. Iron salts were found to be potential initiators/catalysts, except for the hydrated iron(III)citrate. Especially iron(II)acetate proved to be efficient. In general the iron compounds caused a rapid and high conversion of the monomer into polymer. However, most of the efficient iron compounds were not activated before an activation phase, after which the reaction was rapid.

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