# Use of Monocarboxylic Iron Derivatives in the Ring-Opening Polymerization of L-Lactide

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ABSTRACT: L-Lactide was ring-opening polymerized in the melt by using different organic monocarboxylic iron complexes. The complexes were those of iron and acetic acid, butyric acid, isobutyric acid, dichloroacetic acid, and trifluoroacetic acid. The polymerization temperature was in the range 170−210 °C, polymerization time between 0.5 and 25 h, and amount of catalyst added varied between 0.12 and 1.20 wt %. Iron butyrate and iron dichloroacetate complexes were low efficient catalysts in the ring-opening polymerization due to hydrolysis during the preparation. Iron acetate, iron trifluoroacetate, and iron isobutyrate complexes were efficient catalysts yielding a high molar mass poly(L-lactide) with a high monomer conversion. Under optimum conditions a poly(L-lactide) with a molar mass ($M_w$) of ca. 150 000 g/mol could be prepared. Monomer conversions over 85% were obtained in many experiments. High polymerization temperatures are required though with these kinds of iron catalysts, and some racemization of the polymerization products is evident. The polymerization experiments indicate that the oxidation state of the iron has an influence on the efficiency of the catalysts and that the iron is chemically bound to the polymer.

## Introduction

During the past decades an increasing attention has been paid to a number of aliphatic polyesters due to their biodegradability and biocompatibility. One of the most studied polyesters is polylactide, which is commonly prepared by ring-opening polymerization of lactide catalyzed by organometallic compounds. A number of different initiators and catalysts have been used in the ring-opening polymerization, including compounds of, for example, aluminum,[1−3] lead,[4] tin,[2,4−11] zinc,[12,13] and bismuth.[4] The catalytically active metal is, for instance in the use of stannous octoate, covalently bound to the polymer chains as a result of polymerization mechanisms and is in most cases difficult to remove completely from the polymer.[6] This may affect the degradation environment in a harmful way and possibly even result in accumulation. These effects are particularly undesired in medical applications, where both the polymer and the degradation products, including residues of the initiator, preferably should be nontoxic and resorbable. For this reason salts and complexes of metals such as Al, Bi, Cd, Pb, Y, and Sn compounds should be avoided.[14,15]

A number of iron compounds are, on the other hand, occurring in living organisms and in nature and can be regarded as less harmful than most other metal compounds.[16,17] The use of iron compounds in the ring-opening polymerization of lactide has, to our knowledge, been described only to some extent. Iron(III) oxide was used as catalyst in melt polymerizations of lactide.[4] These polymerization experiments were performed at various temperatures, but the catalyst proved to be useful only at the highest polymerization temperature (180 °C), where a yield of 91% could be obtained. However, the long reaction time caused a racemization of the polymerization product. In another study hematin and related porphyrin complexes were used in polymerizations under similar conditions.[18] The poly(L-lactide) (PLLA) prepared by using hematin showed yields up to 74%, and molar masses of 10 000 g/mol were obtained. Arvanitoyannis et al. prepared a polyester from L-lactide and sorbitol in the presence of $FeCl_3$.[19] The reaction was performed at 60 °C, and the polymer obtained was reported to be dark brown, which also was reported by Nakayama et al. when they prepared a poly($\beta$-methyl-$\delta$-valerolactone-*co*-L-lactide) by using $FeCl_3$.[20] In a recent study Kricheldorf and Damrau used iron lactate in the L-lactide polymerization.[14] Under optimum conditions viscosity average molar masses around 50 000 g/mol and yields above 90% were obtained. However, some degree of racemization was observed. In a previous study at our laboratory iron salts, and especially iron(II) acetate, were found to be potential catalysts in the ring-opening polymerization.[21] However, high polymerization temperatures are required in order to achieve high yields and molar masses of the resulting polymers, and some racemization is also evident. In this study the preparation and analysis of various organic iron complexes and the use of them in the polymerization of L-lactide are reported.

## Experimental Section

**Materials.** All solvents used were of analytical grade. The following products were used as received without any further treatment: acetic acid (Merck), butyric acid (Fluka), dichloroacetic acid (Aldrich), isobutyric acid (Fluka), trifluoroacetic acid (Aldrich), metallic iron powder (Aldrich, 99.9%), iron(II) oxide (Aldrich, 99%), iron(II) acetate (Aldrich, 95%), chloroform (Fluka), dioxane (Merck), ethyl acetate (Lab-Scan), methanol (Baker), and chloroform-*d* (Fluka) with a deuteration degree not less than 99.5%. Toluene (Baker) was dried and distilled from sodium under argon prior to use. The L-lactide (Purac) was recrystallized once from ethyl acetate and dried under vacuum at room temperature before use.

**Catalyst Preparation.** The different organic iron derivatives were prepared by vaporizing the corresponding acid from A through B to the condenser C (Figure 1), condensing the

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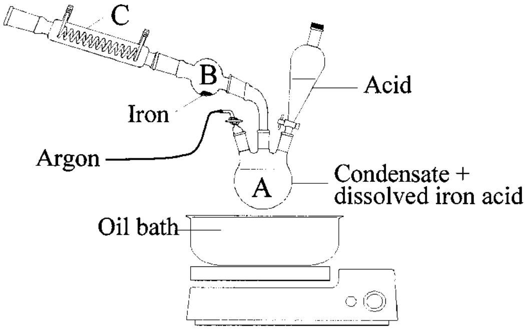


**Figure 1.** Schematic figure of the apparatus for preparing catalysts.

vapor as a hot condensate, passing through a bed of iron or iron(II) oxide powder, thereby forming some ferrous acid, and returning the condensate together with dissolved acid of the iron back to A.[22] The reaction was performed under an atmosphere of argon. After the desired reaction time the unreacted acid was removed, leaving a solid product, which was stored in an inert atmosphere in a desiccator until used in the polymerization experiments. No further purification was performed on the catalysts except for iron dichloroacetate, which was purified in dry toluene before use.

**Polymerization Procedure.** The catalyst was added to 2 g of monomer in 5 mL glass ampules before being sealed under a nitrogen atmosphere. Used amount of catalyst varied between 0.12 and 1.2 wt %, corresponding to molar ratios of approximately 100−1000. The polymerizations were performed in an oven at temperatures ranging from 170 to 210 °C. After the desired time (0.5−25 h) the polymerizations were discontinued by removing the ampules from the oven, and the polymerization products were removed from the ampules, examined, and stored in a desiccator before the characterization.

In some experiments the PLLA samples were purified by dissolving the polymer (5% w/v) and reprecipitating in a 5-fold of nonsolvent. For the iron content measurements one PLLA sample was extracted with a hydrochloric acid solution and washed in distilled water before the analysis.

**Measurements.** Molar mass ($M_W$) and molecular weight distribution (MWD) measurements were obtained by size exclusion chromatography (SEC). The system was based on a HPLC 2248 pump and RI detector from Pharmacia and a precolumn (AN Gel Guard Column) and a linear column (AN Gel Linear) from American Polymer Standards Corp. The mobile phase in the system was tetrahydrofuran (chromatography grade), and polystyrene standards were used for calibration (Perkin-Elmer). The operating conditions were the following: flow rate, 1 mL/min at 40 °C; sample concentration, 2 mg/mL. Injected sample volume was 100 $\mu$L, and the sample solution was filtered through a 0.2 $\mu$m filter before the injection.

The optical purity was determined from a hydrolyzed PLLA sample by separating the two enantiomers by using the liquid chromatography technique and calculating the relative amounts of D- and L-forms.[23]

Monomer conversion was determined using the NMR technique described by Eenink.[6] Polymer (1.5 wt %) was dissolved in chloroform-*d*, and $^1$H NMR spectra were collected with a 400 MHz JEOL spectrometer.

Calorimetric measurements were conducted on a Perkin-Elmer differential scanning calorimeter (system 7) calibrated with indium and zinc. 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 for a 100% crystalline PLLA.[24]

Iron content measurements were performed by using direct current plasma spectrometry (DCP) on a DCP Spectra Span III A. The samples were dissolved in nitric acid, and the measurements performed at 259.94 nm.

**Table 1. Reaction Conditions and Compounds Used in the Catalyst Preparation**

| no. | metal | acid | temp,[a] °C | time, h | appearance of the product |
|---|---|---|---|---|---|
| 1 | iron(II) oxide | acetic acid | 135 | 24 | red-brown powder |
| 2 | iron powder | acetic acid | 135 | 24 | white-greenish powder |
| 3 | iron powder | butyric acid | 165 | 24 | brown powder |
| 4 | iron powder | isobutyric acid | 175 | 24 | dark green powder |
| 5 | iron powder | dichloroacetic acid | 115 | 70 | brown clay[b] |
| 6 | iron powder | trifluoroacetic acid | 85 | 24 | white-brownish powder |

[a] Temperature of the oil bath. [b] Toluene added → brown-red powder.

Elemental analysis were performed on a Leco CHN-600 with infrared and thermal conductivity cell detectors. A weighed quantity of sample was burned in oxygen, and the carbon was measured as carbon dioxide and hydrogen as water vapor.

Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer Spectrum 1000. Powder formed compounds were compounded with KBr and pressed to pellets.

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 C 1s, O 1s, and Fe 2p regions were recorded for metallic iron and iron oxide samples before and after sputtering. The sample charging was noticed from the shift of C 1s by using 284.5 eV as reference value, and the binding energy of Fe 2p was corrected according to that.

## Results and Discussion

**Preparation of the Monocarboxylic Iron Derivatives.** Different iron compounds were reacted with various organic acids according to the conditions described in Table 1. Iron acetate complexes could be prepared from both iron(II) oxide and commercial metallic iron. However, XPS measurements proved that an oxidation of the metallic iron powder had occurred. Organic acids of different structures were also reacted with the iron compounds, but no specific trends could be noticed regarding their reactivity. The iron dichloroacetate reaction was made at 115 °C by using a simple system based upon a one-necked round-bottom flask equipped with a condenser instead of the system described in Figure 1. This because of the high boiling point of dichloroacetic acid (bp 194 °C) and the potential risk for degradation during the synthesis. The reaction time in this experiment was therefore prolonged from 24 to 70 h. The synthesis yielded a claylike product, and when purified with dry toluene, a brown-red powder precipitated from the solution mixture. Measurements performed by FTIR showed that this compound (**5**), as well as the iron butyrate (**3**) and the iron acetate prepared from iron(II) oxide (**1**), were hydrolyzed to some extent. The hydrolysis of these compounds probably occurred because the catalysts were in contact with air for some time during the evaporation and drying stages. Elemental analysis, FTIR measurements, and the color of the catalysts indicated that all the other iron compounds (**2**, **4**, and **6**) were not significantly oxidized or hydrolyzed but are indeed pure ferrous compounds. The color of the iron compounds is a good indicator of whether the compound has hydrolyzed. If hydrolyzed, even to some extent, the compound has a red to brown color which becomes darker during the aging in air. The ferrous compounds do not have this distinctive color. Also, the characteristic peak corresponding to −OH

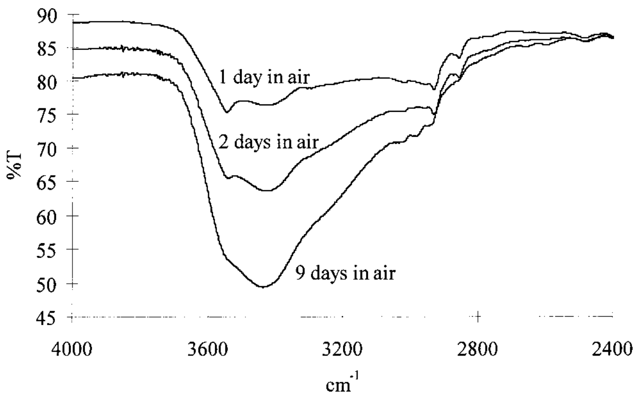


**Figure 2.** FTIR spectra of the −OH region for hydrolyzed iron acetate.

**Table 2. C and H Amounts in the Catalysts Determined by Elemental Analysis**

| catalyst | | amount of C, H (%) calcd | amount of C, H (%) measd |
|---|---|---|---|
| iron(II) acetate | C: | 27.6 | 28.3 |
| | H: | 3.5 | 3.5 |
| iron(II) trifluoroacetate | C: | 17.0 | 16.8 |
| | H: | 0.0 | 0.8 |
| iron(II) isobutyrate | C: | 41.8 | 44.3 |
| | H: | 6.1 | 6.4 |

stretching at 3300−3600 cm$^{-1}$ in the FTIR spectrum becomes more prominent upon hydrolysis as shown in Figure 2.

The iron acetate prepared from oxidized metallic iron powder (**2**) had a melting point of ca. 191 °C. However, the compound degraded at this temperature. The color, melting point, and the fact that the iron acetate catalyst prepared from metallic iron degraded during the melting process are consistent with the data given for iron(II) acetate in the literature.[25,26] Elemental and FTIR analysis gave further indications that the compound is an anhydrous ferrous acetate. A melting point for iron isobutyrate and iron trifluoroacetate could not be determined, probably due to degradation during the thermal treatment, but no data regarding these compounds have been found in the literature. No melting point measurements were performed on the other catalysts because the −OH region in the FTIR spectra indicated that the catalysts were not pure. This is also the reason that elemental analysis only was performed on iron isobutyrate, iron trifluoroacetate, and the iron acetate prepared from iron powder (Table 2).

The iron acetate prepared from iron(II) oxide was hydrolyzed during the synthesis and is most likely a basic iron acetate. The hydrolysis is, however, not dependent on whether iron(II) oxide or metallic iron is used in the synthesis. The most probable reason for the hydrolysis is the absence of inert atmosphere during the evaporation step. This might also be the reason for the hydrolysis of the iron butyrate and iron dichloroacetate catalysts.

## Polymerizations Performed by Using the Iron Complexes

**The Color of the PLLA.** The color of the polymers varied from light yellow to brown, depending on the polymerization conditions, regardless of catalyst used. Polymerization time, catalyst concentration, and temperature affected the appearance of the PLLA. The discoloring of the polymers might be related to oxidized iron or to side- and transesterification reactions of the PLLA. The discoloring decreased as a function of storage time of the PLLA, which indicated that the brown color originates from organic compounds undergoing reactions rather than from the iron oxides.

**Table 3. Polymer Characteristics for the PLLA Catalyzed with Anhydrous Iron Acetate at 170 °C**

| added amt of catalyst (wt %) | polym time (h) | $M_w$ (g/mol) | MWD | $T_m$ (°C) | $X_c$ (%) |
|---|---|---|---|---|---|
| 0.24 | 1 | 17 800 | 1.65 | 101 | *a* |
| | 2 | 30 400 | 1.54 | 126 | 14 |
| | 3 | 43 200 | 2.99 | 133 | 8 |
| | 4 | 24 500 | 3.55 | 152 | 11 |
| | 5 | 42 400 | 5.15 | 150 | 7 |
| | 7 | 31 200 | 5.44 | 157 | 29 |
| | 10 | 65 900 | 5.25 | 155 | 21 |
| | 25 | 15 800 | 2.99 | 153 | 28 |
| 1.20 | 1 | 16 700 | 1.46 | 102 | *a* |
| | 2 | 46 100 | 4.24 | 101 | *a* |
| | 3 | 68 900 | 5.29 | 134 | 11 |
| | 4 | 59 000 | 4.06 | 145 | 9 |
| | 5 | 53 100 | 4.19 | 134 | 18 |
| | 7 | 28 400 | 4.68 | 146 | 9 |
| | 10 | 25 400 | 3.35 | 159 | 15 |
| | 25 | 14 400 | 2.66 | 157 | 25 |

[a] $X_c$ is related to the L-lactide.

**Basic and Anhydrous Iron Acetate as Catalysts.** The iron complexes prepared were used as catalysts in the polymerization of L-lactide. By using the basic iron acetate (**1**) the molar mass ($M_w$) of the poly(L-lactide) increased rapidly, after an activation phase, to ca. 40 000 g/mol before remaining almost constant during all the reaction time at 210 °C (0.12 wt % catalyst). The molecular weight distribution varied between 1.9 and 2.8, but no specific trend could be noticed. The conversion increased in 4 h to about 90%, before leveling out. The racemic purity of the polymer decreased continuously with time, and the amount of D-form reached a value of 10.6% in 8 h. No melting peaks could be determined for any of the polymers.

Anhydrous iron acetate (**2**)-catalyzed polymerizations of L-lactide were performed at various temperatures (170−190−210 °C), and the amount of catalyst used varied between 0.12 and 1.20 wt %. The polymer characteristics for the PLLA catalyzed with this iron compound at 170 °C are shown in Table 3.

The molar mass of the polymer reached a maximum of ca. 60 000−70 000 g/mol in most experiments, regardless of the polymerization temperature. An activation phase could also be noticed in these polymerizations, as well as in all experiments regardless of the type of catalyst used. The time for reaching the maximum molar mass decreased with increasing temperature, but a decrease in the molar mass could be noticed at 210 °C, which can be related to degradation reactions and transesterification. The molar mass of the PLLA decreased, for example, from 78 000 g/mol (2 h) to 16 000 g/mol (5 h) when 0.12 wt % catalyst was used at 210 °C. The same trend was evident at all polymerization temperatures and catalyst amounts tested. However, the trend was not that evident at lower temperatures (170 and 190 °C), and the polymerization seemed more controlled than at 210 °C. Also, the MWD showed a maximum before starting to decrease (Figure 3). This trend was evident at all polymerization temperatures, regardless of amount of catalyst added. As the polymerization proceeded, the MWD value usually decreased to 2.5−3.

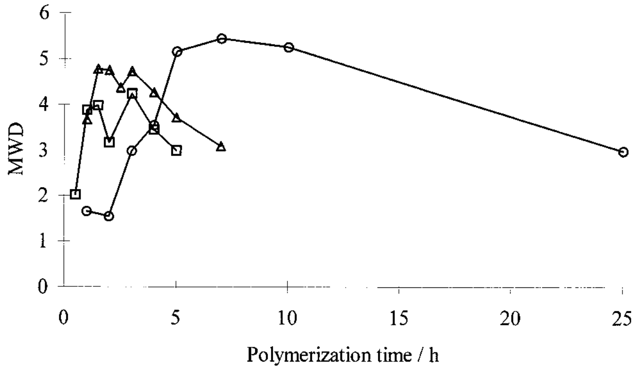


**Figure 3.** Molecular weight distribution for the PLLA at 170 (○), 190 (△), and 210 °C (□) by using 0.24 wt % anhydrous iron acetate catalyst.

**Table 4. Monomer Conversion for the PLLA as a Function of Polymerization Time at 170, 190, and 210 °C[a]**

| polym time (h) | monomer conversion (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | iron acetate | | | iron isobutyrate | | | iron trifluoroacetate | | |
| | 170 °C | 190 °C | 210 °C | 170 °C | 190 °C | 210 °C | 170 °C | 190 °C | 210 °C |
| 1 | | 29.7 | 44.7 | 12.0 | 4.2 | 36.0 | 3.1 | 4.0 | 15.8 |
| 1.5 | | 57.7 | 64.7 | | 18.4 | | | | 49.5 |
| 2 | 7.4 | 71.1 | 73.3 | | | 80.4 | | 37.4 | 71.7 |
| 3 | | 79.0 | 90.2 | 37.9 | 53.5 | | 13.3 | | 88.9 |
| 5 | | 90.8 | 91.5 | 52.6 | 72.6 | 84.5 | | | 96.4 |
| 7 | | 94.8 | | 65.3 | 79.6 | | | 85.7 | |
| 10 | 50.6 | | | 72.5 | | | 31.5 | | |
| 25 | | | | | | | 87.6 | | |

[a] 0.24 wt % catalyst used.

The conversion for the anhydrous iron acetate-catalyzed polymerizations increased rapidly at 190 and 210 °C, but 170 °C seemed to be too low a temperature for the ring-opening polymerization with this kind of catalyst (Table 4). At 170 °C only a 50% monomer conversion could be obtained after 10 h of polymerization when 0.24 wt % catalyst was used. When 1.2 wt % catalyst was used, the monomer conversion reached a value of 85% in 10 h. At a polymerization temperature of 190 °C (0.12 wt % catalyst) the conversion exceeded 95% in 7 h and 85% in 5 h at 210 °C.

Most of the polymers prepared with anhydrous iron acetate showed a crystalline melting point, suggesting an optical purity of at least 90%.[27] However, the endothermal melt enthalpy is small, which probably is due to some extent of racemization. Typical melting points were in the range 153−159 °C for the polymers with a high molar mass. The degree of crystallinity was about 5% at the early stages (1.5−2.5 h) of the polymerization but increased later on to about 25% (5−7 h). This trend is more evident at higher polymerization temperatures (190−210 °C) than at 170 °C.

The maximum molar mass for the PLLA prepared by using the basic iron acetate (**1**) was considerably lower than for the PLLA prepared with a pure ferrous acetate (**2**). However, the monomer conversion did increase to 90%, even though the molar mass remained constant. Also, the hydrolyzed iron butyrate catalyst showed the same trend in the polymerization.

One explanation can be that the efficiency of the catalyst is dependent on the oxidation state of the iron. The earlier statement that the oxidation state not affecting the effectivity of the catalyst seemed to be valid for inorganic compounds[21] but not for organometallic iron compounds. In the earlier study the iron compounds used were iron oxides, iron chlorides, and iron sulfates, which are not very efficient catalysts due to the absence of organic ligands. The polymerization rate was because of that not affected in any significant way. In this study, the catalysts used are more effective, and a difference in the effectivity could therefore be noticed.

**Table 5. Polymer Characteristics for the PLLA Catalyzed with Iron Isobutyrate at 190 °C**

| added amt of catalyst (wt %) | polym time (h) | $M_w$ (g/mol) | MWD | $T_m$ (°C) | $X_c$ (%) |
|---|---|---|---|---|---|
| 0.12 | 1 | 115 800 | 1.54 | 93 | *a* |
| | 1.5 | 138 600 | 1.63 | 131 | 9 |
| | 2 | 148 000 | 1.60 | 126 | 13 |
| | 2.5 | 136 300 | 2.01 | 130 | 9 |
| | 3 | 144 400 | 1.76 | *b* | |
| | 4 | 142 600 | 1.76 | 145 | 4 |
| | 5 | 117 200 | 2.22 | 146 | 6 |
| | 7 | 109 900 | 2.02 | 150 | 1 |
| 0.24 | 1 | 103 000 | 2.81 | 89 | *a* |
| | 1.5 | 124 800 | 1.82 | 124 | 10 |
| | 2 | 122 800 | 1.95 | 128 | 13 |
| | 2.5 | 123 600 | 2.02 | *b* | |
| | 3 | 114 800 | 1.82 | 139 | 1 |
| | 4 | 110 100 | 2.07 | *b* | |
| | 5 | 112 100 | 1.73 | 147 | 2 |
| | 7 | 88 600 | 1.97 | 149 | 5 |

[a] $X_c$ is related to the L-lactide. [b] No melting peak could be detected.

Another explanation is that the hydroxyl group in the basic iron acetate may have a retarding effect on the efficiency. In, for example, sodium acetate-catalyzed ring-opening polymerizations, where the monomer becomes the initiator due to deprotonation,[4] the sodium forms such a strong base that the propagation phase is terminated, and a low molar mass polymer is obtained even though the conversion increases. Iron, on the other hand, does not form a strong base and is able to react with the growing chains, and therefore a relatively high molar mass polymer is achieved.

**Iron Butyrate and Iron Isobutyrate as Catalysts.** Experiments were also performed in order to study how the flexibility of the ligands affected the polymerization results. One catalyst containing flexible linear butyrate ligands (**3**) was prepared and another one containing branched isobutyrate ligands with a more forced configuration (**4**). In the polymerizations where iron butyrate was used the molar mass ($M_w$) of the PLLA reached a maximum of ca. 36 000 g/mol after 2 h (210 °C, 0.12 wt % catalyst), after which the molar mass did not change. The conversion increased slowly, from 6% in 1 h to 75% in 5 h. No melting points could be determined for any of the polymers due to racemization. Polymerization experiments with iron butyrate were only performed at 210 °C, as the polymerization rate at this temperature indicated too slow a rate at lower temperatures.

Iron isobutyrate-catalyzed polymerizations were performed at 170, 190, and 210 °C with catalyst amounts of 0.12−1.2 wt %. The polymer characteristics for the PLLA catalyzed with iron isobutyrate at 190 °C are shown in Table 5. The molar mass of the PLLA increased rapidly at 190 and 210 °C, exceeding 100 000 g/mol in 1 h. Under optimum conditions a PLLA with a $M_w$ of ca. 150 000 g/mol could be prepared. The monomer conversion at this point was 30%. At 170 °C the molar mass of the polymer reached a maximum of 90 000 g/mol after 4 h of polymerization, regardless of amount of catalyst used. Degradation reactions were not

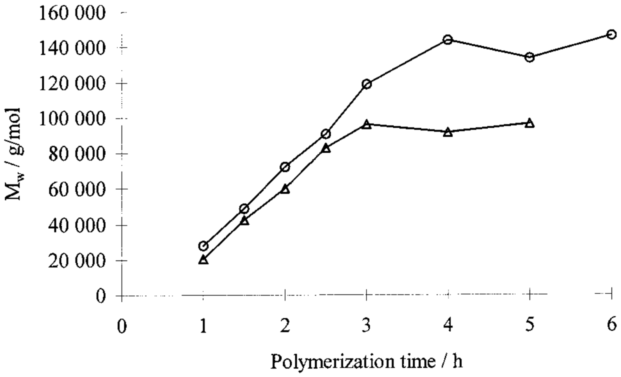


**Figure 4.** Molar mass for the PLLA prepared at 190 °C by using 0.12 (○) and 0.24 wt % (△) iron trifluoroacetate.

as evident in the iron isobutyrate-catalyzed polymerization as for the PLLA polymerized with iron acetate. At high polymerization temperatures, and especially at 210 °C, the monomer conversion increased rapidly as a function of the polymerization time (Table 4). In 2 h a 80% conversion could be achieved. At 170 °C the conversion increased more slowly, and a 65% conversion was obtained after 7 h of polymerization. The melting point and the crystallinity of the polymers were in general low.

**Iron Dichloroacetate and Iron Trifluoroacetate as Catalysts.** Further experiments were performed in order to study the influence of the electronegativity on the polymerization rate. In the polymerizations performed by using iron dichloroacetate (**5**), the molar mass of the PLLA reached a value of ca. 25 000 g/mol after 3 h of polymerization (210 °C, 0.12 wt % catalyst). Typical values of the dispersion index varied between 2 and 2.5 for polymerization times exceeding 2 h. No melting peak could be determined for the PLLA prepared with iron dichloroacetate.

Iron trifluoroacetate (**6**)-catalyzed polymerizations were performed at 170, 190, and 210 °C with catalyst amounts of 0.12−1.2 wt %. The molar mass for the PLLA catalyzed with iron trifluoroacetate at 190 °C is shown in Figure 4. The amount catalyst added had a significant influence on the molar mass of the polymer in the iron trifluoroacetate-catalyzed polymerizations. A maximum molar mass of ca. 140 000 g/mol was achieved at 190 °C. At 170 and 210 °C the highest molar mass obtained was in the range of 100 000−110 000 g/mol. At 210 °C degradation reactions seemed not to be as strong in the iron trifluoroacetate-catalyzed polymerizations as in the iron acetate-catalyzed polymerizations. Also, the monomer conversion increased rapidly at both 190 and 210 °C but more modestly at 170 °C. A conversion exceeding 95% was obtained in 5 h of polymerization at 210 °C (Table 4). The polymers obtained by using iron trifluoroacetate showed a low degree of crystallinity, usually about 5%.

**Speculations on Polymerization Mechanisms.** To find out more about the polymerization mechanism, an attempt was made to purify a PLLA sample by dissolving and precipitating it six times in chloroform/methanol. The PLLA sample was prepared at 180 °C by using commercial iron(II) acetate with a molar monomer-to-initiator ratio of 13. The crude polymer had a molar mass ($M_w$) of 50 000 g/mol and a monomer conversion of 52%. DSC measurements showed that the melt enthalpy increased from 1 to 24 J/g (second heating) from the crude polymer to the six times purified PLLA. It has been shown that iron compounds cause racemization during thermal treatment and thus decrease the crystallinity of the polymer.[14] The increase in melt enthalpy could therefore be related to a decrease in the iron content in the polymer as a function of repeated purification. Direct current plasma spectrometry measurements did, however, show that all iron could not be washed away by this method. On the contrary, the measurements showed an increase in the iron content from the crude polymer to the once precipitated one. When changing the solvents from chloroform/methanol to dioxane/water, similar results were obtained. Only by extraction with a hydrochloric acid solution could all the iron be removed from a three times purified polymer sample. This procedure did, however, lower the molar mass of the PLLA from 94 000 to 59 000 g/mol, which indicates that the iron is chemically bound to the polymer chains. Additionally, $^1$H NMR studies on the PLLA showed a singlett at ca. 2.1 ppm relative to TMS which can be related to the methyl in acetate end groups.[28] To confirm the NMR results, several PLLA samples were made by using high catalyst concentrations, and the spectrum from a purified PLLA sample prepared at 180 °C (M/I = 5) is shown in Figure 5.

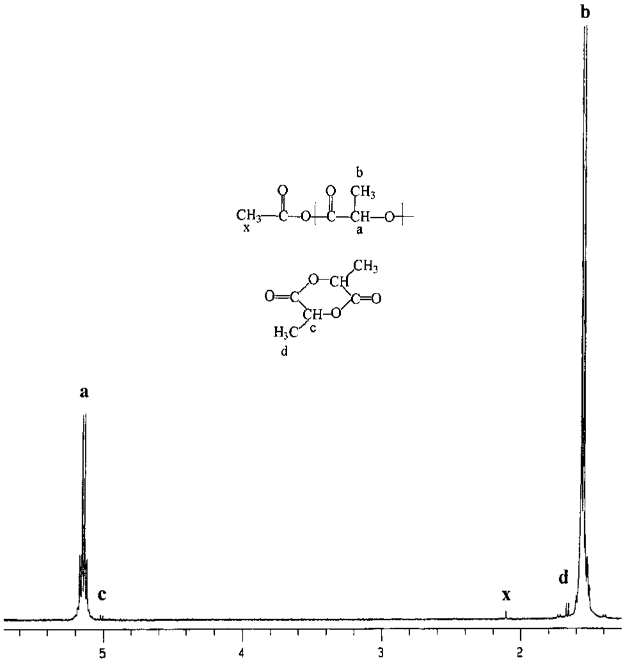
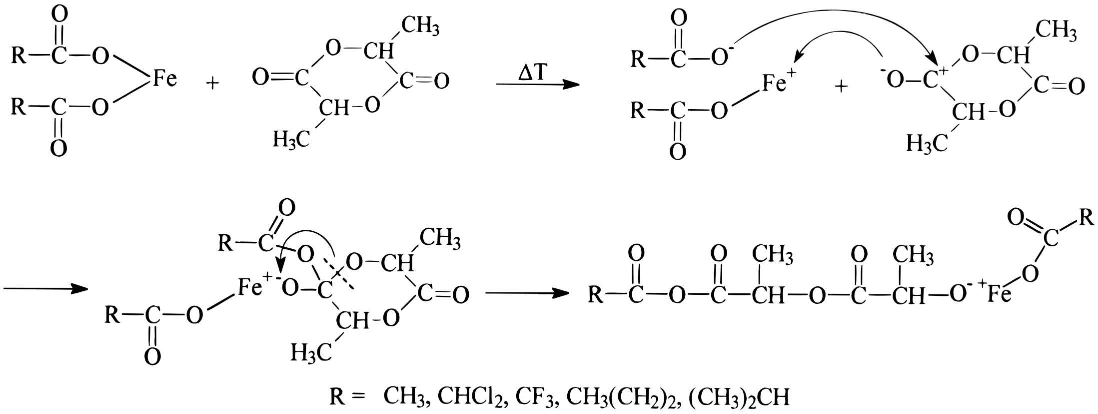


**Figure 5.** $^1$H NMR spectrum of purified PLLA prepared at 180 °C (M/I = 5).

Iron acetate degrades at about 190 °C and was found to be quite inactive when used in polymerizations below that temperature. The same trend was also noticed for the other iron catalysts used in this study. This indicated that the catalyst has to be thermally activated in the beginning of the polymerization in order to be effective (Scheme 1). This activation could result in an anion of the acetate, which is able to initiate the polymerization in a purely anionic manner. This might also explain the racemization. However, experiments indicate that part of the iron can be removed by dissolving/precipitation, but some of it is chemically bound, which cannot be explained with a pure anionic mechanism, as no iron is supposed to be attached to the polymers in anionic polymerization. A pure anionic mechanism would furthermore not yield methyl end

**Scheme 1**



groups, which were found for the PLLA prepared by using iron acetate. Our studies indicated that the acetate anion, as well as the iron partly, is chemically attached to the polymer chain, and the proposed polymerization mechanism is an anionic type of coordination insertion as described in Scheme 1.

## Conclusions

Polymerizations of L-lactide in the melt have been performed by using different monocarboxylic iron compounds as catalysts. The complexes of iron acetate, iron trifluoroacetate, and iron isobutyrate can be regarded as efficient catalysts, and a high molar mass PLLA can readily be achieved with these kinds of catalysts. The crystallinities of the polymers were in general low, and especially for the PLLA prepared with iron trifluoroacetate, which indicates that electronegative substituents on the catalyst have an effect on the thermal properties of the polymer. The experiments show that high temperatures are required to obtain a high molar mass polymer with high monomer conversion. The experiments also demonstrate an activation phase in the beginning of the polymerization, after which the polymerization is rapid. The iron complexes of butyrate and dichloroacetate, as well as the basic iron acetate, were not as efficient as the others of the catalysts tested in the polymerization of L-lactide, probably due to the fact that these catalysts were, at least partly, hydrolyzed.

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