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# Ring-Opening Homo- and Copolymerization of Cyclic Esters Catalyzed by Iron(III) Triflate

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**Abstract:** Biomass-based and biodegradable poly(L-lactide) (PLLA) is synthesized by ring-opening polymerization of L-lactide (LLA), for which tin(II) 2-ethylhexanoate is a major catalyst. However, the potential toxicity of tin can be a problem, especially in biomedical applications. In this study, we focused on iron, which is a non-toxic metal and an abundant resource. We investigated the ring-opening homo- and copolymerization of cyclic esters such as LLA and ε-caprolactone (CL) catalyzed by iron(III) triflate, $Fe(OTf)_3$, which is commercially available and known as a Lewis acid. In the polymerization of LLA in toluene at 110 °C, $Fe(OTf)_3$ showed relatively high activity and yielded PLLA with unimodal molecular weight distribution. The addition of 1,8-bis(dimethylamino)naphthalene (proton sponge: PS) to the $Fe(OTf)_3$ catalyst system increased the yield and molecular weight of the resulting polymer. In contrast, the polymerization of CL by $Fe(OTf)_3$ was decelerated by the presence of PS. The $Fe(OTf)_3$ system was found to have an exceptionally high preference for CL over LLA in the copolymerization of LLA and CL, with the reactivity ratio of $r_{LLA} = 0.51$ and $r_{CL} = 6.9$. In contrast, the $Fe(OTf)_3$–2PS system exhibited an LLA preference with $r_{LLA} = 15$ and $r_{CL} = 0.22$, indicating that the comonomer selectivity changed depending on the presence or absence of PS. While the LLA polymerization rate by the $Fe(OTf)_3$ system showed a second-order dependence on the $Fe(OTf)_3$ concentration, that of the $Fe(OTf)_3$–PS system showed a first-order dependence on the $Fe(OTf)_3$–PS concentration.

**Keywords:** ring-opening polymerization; L-lactide; ε-caprolactone; iron(III) triflate; copolymerization; comonomer reactivity ratio

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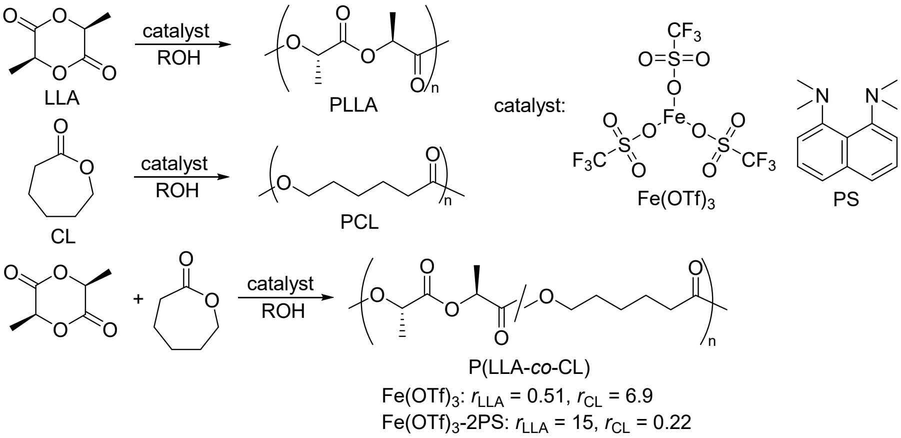
## 1. Introduction

As a result of recent environmental and resource problems, poly(L-lactic acid) (PLLA) is attracting attention due to its biodegradability and sustainability. PLLA is synthesized by the ring-opening polymerization (ROP) of L-lactide (LLA), a cyclic dimer of lactic acid. Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) is a major catalyst for the ROP of LLA [1–3]. $Sn(Oct)_2$ is easily available and handled, and the bulk polymerization of LLA can produce high molecular weight PLLA. However, tin compounds are known to have adverse effects on living organisms [4–6]. Therefore, the potential toxicity of Sn can be a problem, especially in biomedical applications. Many catalysts have been reported that contain elements other than tin at the active site [7–15].

Iron catalysts have attracted interest because the iron metal itself has low toxicity and is abundant [16]. In 1997, $Fe(OEt)_3$ was reported to catalyze the polymerization of LLA, although its structure was not clear [17]. In 2001, Tolman et al. reported on the synthesis and structures of a pentanuclear cluster of $Fe_5(O)(OEt)_{13}$ (**1**) and dinuclear iron complexes having bulky alkoxide ligands, $\{Fe(OR)_2\}_2(\mu\text{-}OR)_2$ (R = $CMe_2Ph$ (**2a**), $CHPh_2$ (**2b**)) [18]. The pentanuclear **1** was found to be highly active for the polymerization of LLA at 70 °C in toluene, yielding polymers with narrow molecular weight distribution. The dinuclear iron alkoxide **2a** also showed high activity for LLA polymerization, but the molecular weight distribution of the resulting polymer was rather broad. The diphenylmethoxy dinuclear complex **2b** yielded polymers with narrower molecular weight distribution (PDI~1.2) than **2a** [19]. A mononuclear iron complex with a benzamidinate supporting ligand catalyzed the ROP of LLA with lower activity [19]. Södergård and Stolt reported that some iron salts such as iron(II) acetate catalyzed the bulk polymerization of LLA at 210 °C [20] to give high molecular weight polymers. Iron(II) acetate–carboxamide systems were found to catalyze the controlled ROP of LLA at lower temperatures [21,22]. The iron complex, having three hydroxyl-functionalized dibenzoylmethane ligands, was found to act as both an initiator and a catalyst for the polymerization of lactide [23] and CL [24] to produce iron-centered three-arm star polymers. An iron–salen catalyst yielded polylactide with a narrow molecular weight distribution (PDI $\approx$ 1.1) even at 200 °C [25]. Iron chloride complexes that had bulky salen ligands activated with epoxide were reported to promote stereoselective ROP of *rac*-lactide [26]. Bis(imino)pyridine iron(II) alkoxide was active for lactide polymerization, while the corresponding iron(III) complex was inactive. Further, the lactide polymerization could be controlled by the redox of the iron catalyst [27,28]. A dialkyliron complex bearing a bis(imino)pyridine ligand was reported to promote syndioselective polymerization of *meso*-lactide in combination with an appropriate silanol [29]. A cyclopentadienyliron complex coordinated with an *N*-heterocyclic carbene ligand has high activity for the polymerization of LLA [30].

Another representative biodegradable polymer is poly(ε-caprolactone) (PCL), which is synthesized by the ROP of ε-caprolactone (CL). Iron complexes having three hydroxyl-functionalized dibenzoylmethane ligands [24] and Schiff-base macrocycle ligands [31] catalyzed the polymerization of CL and could be applied to the block copolymerization of CL and D,L-lactide. Some commercially available iron salts such as iron(III) perchlorate, iron(III) chloride, and iron(III) bromide were found to catalyze the ROP of CL [6]. Iron(II) complexes having *N*-(2-(diphenylphosphino)ethyl)-2-alkyl-5,6,7,8-tetrahydroquinolin-8-amine ligands were reported to polymerize CL to yield high molecular weight PCL [32].

In this study, we focused on iron(III) triflate, $Fe(OTf)_3$, because it was utilized as a Lewis acid catalyst in organic reactions [33] and the triflates of some other metals have been reported to catalyze the ROP of lactones and lactides [34–41]. Recently, Ling and coworkers reported the polymerization of CL by $Fe(OTf)_3$ in combination with $NaO^iPr$. This combination promoted "Janus polymerization", where concurrent cationic ring-opening copolymerization of tetrahydrofuran at one end and anionic ring-opening homopolymerization (AROP) of CL at the other end generated one growing chain at 40 °C or lower [42]. We have independently investigated the homo- and copolymerization of LLA and CL catalyzed by $Fe(OTf)_3$ without sodium alkoxide at higher temperatures, typically at 120 °C in bulk polymerization (Scheme 1). The effect of 1,8-bis(dimethylamino)naphthalene (proton sponge: PS) on the polymerization system was also investigated. We found that the commercially available $Fe(OTf)_3$ exhibited relatively high catalytic activity for the homo- and copolymerization of cyclic esters such as LLA and CL, and that its behavior could be significantly modulated by the addition of PS, especially in the copolymerization.



**Scheme 1.** Homo- and copolymerization of cyclic esters catalyzed by $Fe(OTf)_3$ with or without PS.

## 2. Results and Discussion

Solution polymerizations of LLA in toluene catalyzed by some iron compounds, $Fe(OTf)_3$, $FeCl_3$, and $Fe(OTf)_2$, were examined using 2-propanol as an initiator with a feed monomer–initiator–catalyst ratio of 100:1:1 at 65 °C or 110 °C (Table 1). Among these iron compounds, $Fe(OTf)_3$ was found to have significantly higher activity than those of $FeCl_3$ and $Fe(OTf)_2$, where the polymer yields reached >90% within 24 h at 65 °C (run 2) or within 6 h at 110 °C (run 4). The activity of $Fe(OTf)_3$ was comparable to that of $Sn(Oct)_2$ (runs 1 and 3 vs. runs 9 and 10, respectively). Although the molecular weight distributions of the PLLAs produced by $Fe(OTf)_3$ were broadened with time, their molecular weights increased with time and yield, indicating that polymerization proceeded in a somewhat controlled manner.

**Table 1.** Solution polymerization of LLA catalyzed by iron-based compounds [1].

| Run | Catalyst | Temp (°C) | Time (h) | Yield (%) | $M_n$(theo) [2] (kg/mol) | $M_n$(GPC) [3] (kg/mol) | $M_w/M_n$ [3] |
|---|---|---|---|---|---|---|---|
| 1 | $Fe(OTf)_3$ | 65 | 12 | 64 | 9.2 | 5.9 | 1.09 |
| 2 | | 65 | 24 | 93 | 13 | 11 | 1.20 |
| 3 | | 110 | 1.5 | 62 | 8.9 | 5.3 | 1.12 |
| 4 | | 110 | 6 | 93 | 13 | 9.5 | 1.53 |
| 5 | $FeCl_3$ | 65 | 24 | 0 | - | - | - |
| 6 | | 110 | 24 | 22 | 3.2 | 3.7 | 1.16 |
| 7 | $Fe(OTf)_2$ | 65 | 24 | 0 | - | - | - |
| 8 | | 110 | 24 | 9 | 1.3 | 4.2 | 1.08 |
| 9 | $Sn(Oct)_2$ | 65 | 12 | 95 | 14 | 15 | 1.09 |
| 10 | | 110 | 1.5 | 96 | 14 | 18 | 1.26 |

[1] Conditions: M (monomer) = LLA, I (initiator) = 2-propanol, C (catalyst), $[M]_0$:$[I]_0$:[C] = 100:1:1, $[M]_0$ = 1.0 mol/L, solvent = toluene. [2] $M_n$(theo) = 144.13 × $[M]_0/[I]$ × yield(%)/100. [3] Determined by GPC analysis in THF calibrated with standard polystyrenes.

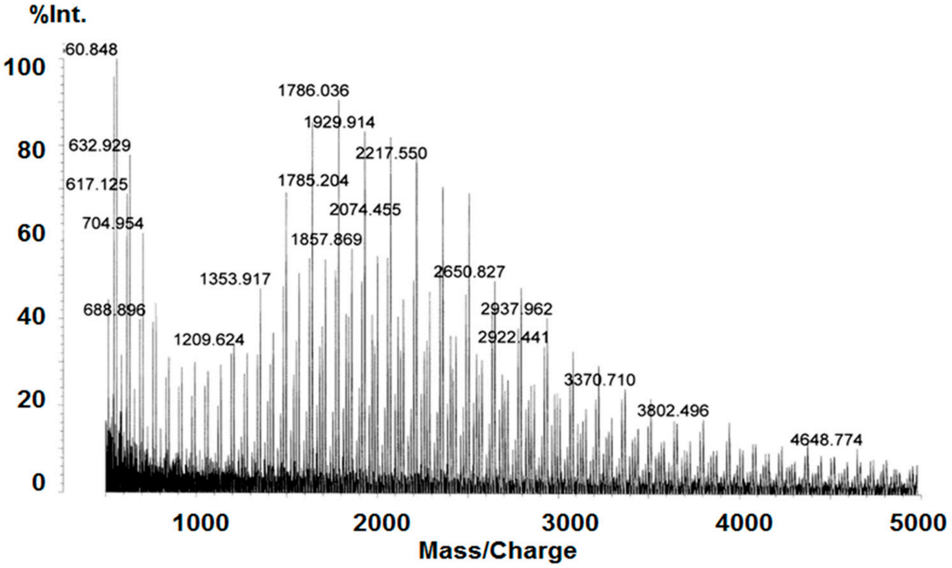
Bulk polymerizations of LLA catalyzed by $Fe(OTf)_3$ were carried out at a feed monomer–initiator–catalyst ratio of 1000:1:1 at 120 °C or 150 °C (Table 2). The bulk polymerization of LLA by $Fe(OTf)_3$ reached an 88% yield for 48 h at 120 °C and a 90% yield for 12 h at 150 °C. The molecular weights of the obtained polymers increased by increasing the polymer yields at 120 °C; however, the molecular weights were significantly lower than the theoretical values. Additionally, the molecular weight distributions became broader with time. The molecular weights of the polymers obtained at 150 °C were almost constant with time, indicating frequent chain transfer at 150 °C.

**Table 2.** Bulk polymerization of LLA catalyzed by $Fe(OTf)_3$ [1].

| Run | Temp (°C) | Time (h) | Yield (%) | $M_n$(theo) [2] (kg/mol) | $M_n$(GPC) [3] (kg/mol) | $M_w/M_n$ [3] |
|---|---|---|---|---|---|---|
| 11 | 120 | 3 | 16 | 23 | 6.3 | 1.11 |
| 12 | 120 | 6 | 24 | 35 | 12 | 1.22 |
| 13 | 120 | 12 | 49 | 71 | 24 | 1.41 |
| 14 | 120 | 24 | 58 | 84 | 24 | 1.42 |
| 15 | 120 | 48 | 88 | 130 | 33 | 1.57 |
| 16 | 150 | 3 | 32 | 46 | 9.0 | 1.31 |
| 17 | 150 | 6 | 89 | 130 | 11 | 1.39 |
| 18 | 150 | 12 | 90 | 130 | 11 | 1.52 |

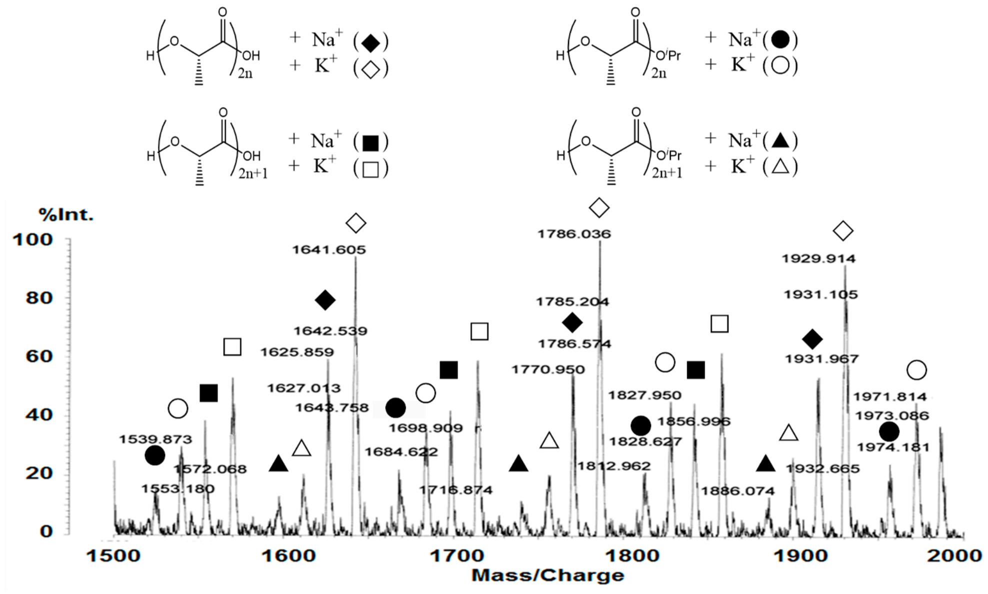
[1] Conditions: M (monomer) = LLA, I (initiator) = 2-propanol, C (catalyst) = $Fe(OTf)_3$, $[M]_0$:$[I]_0$:[C] = 1000:1:1. [2] $M_n$(theo) = 144.13 × $[M]_0/[I]$ × yield(%)/100. [3] Determined by GPC analysis in THF calibrated with standard polystyrenes.

The MALDI-TOF MS spectrum of the PLLA obtained in run 11 is shown in Figure 1. The spectrum showed several series of repeating peaks spaced by the molecular weight of the lactyl unit. The major four series can be assigned to the PLLAs by the combination of two initiators ($H_2O$ and $^i$PrOH) and two cations ($Na^+$ and $K^+$). The intensity of the signals for the PLLA initiated with $H_2O$ was higher than those initiated with $^i$PrOH, indicating the presence of residual $H_2O$ in the system. The residual $H_2O$ should also be the reason for the lower molecular weights of the obtained polymers compared with the theoretical molecular weight values. Since lactide is a cyclic dimer of lactyl units, the ROP of LLA should produce polymers composed of even numbers of lactyl units. However, the PLLA obtained by $Fe(OTf)_3$ that was composed of an odd number of lactyl units showed significant peaks, indicating transesterification.



(**a**)

**Figure 1.** *Cont.*



(**b**)

**Figure 1.** MALDI-TOF MS spectra of PLLA synthesized by using $Fe(OTf)_3$ (run 11): (**a**) mass–charge range of 500 to 5000; (**b**) mass–charge range of 1500 to 2000.

In the reported polymerization of lactide catalyzed by $Sn(OTf)_2$, the addition of a base such as 1,8-bis(dimethylamino) naphthalene (proton sponge, PS) effectively enhanced the polymerization rate while keeping the polymerization control [43]. We also investigated the effect of several bases on the catalytic behavior of the $Fe(OTf)_3$ system for LLA polymerization and the results are summarized in Table 3. The addition of several tertiary amines such as PS, tributylamine (TBA), *N*,*N*-dimethylaniline (DMA), and $N,N,N',N'$-tetramethylethylenediamine (TMEDA) were examined (Table 3). As a result, the addition of diamines PS and TMEDA significantly improved polymer yields and molecular weights, while the addition of TBA or DMA decreased polymer yields. Among them, the use of two equivalents of PS (run 20) most effectively improved the polymer yield (from 49% to 86%) and the molecular weight ($M_n$ from 24 kg/mol to 99 kg/mol). While the addition of PS broadened the molecular weight, the molecular weight of PLLA obtained in the $Fe(OTf)_3$–2PS system (run 20) was closer to the theoretical value than it was in the system without PS (run 13).

**Table 3.** Bulk polymerization of LLA catalyzed by the $Fe(OTf)_3$–base systems [1].

| Run | Base | [Base]/[C] | Yield (%) | $M_n$(theo) [2] (kg/mol) | $M_n$(GPC) [3] (kg/mol) | $M_w/M_n$ [3] |
|---|---|---|---|---|---|---|
| 13 | - | 0 | 49 | 71 | 24 | 1.41 |
| 19 | PS | 1 | 59 | 85 | 56 | 1.51 |
| 20 | PS | 2 | 86 | 120 | 99 | 1.64 |
| 21 | TBA | 2 | 15 | 22 | 6 | 1.22 |
| 22 | DMA | 2 | 18 | 26 | 8 | 1.15 |
| 23 | TMEDA | 2 | 78 | 110 | 67 | 1.42 |

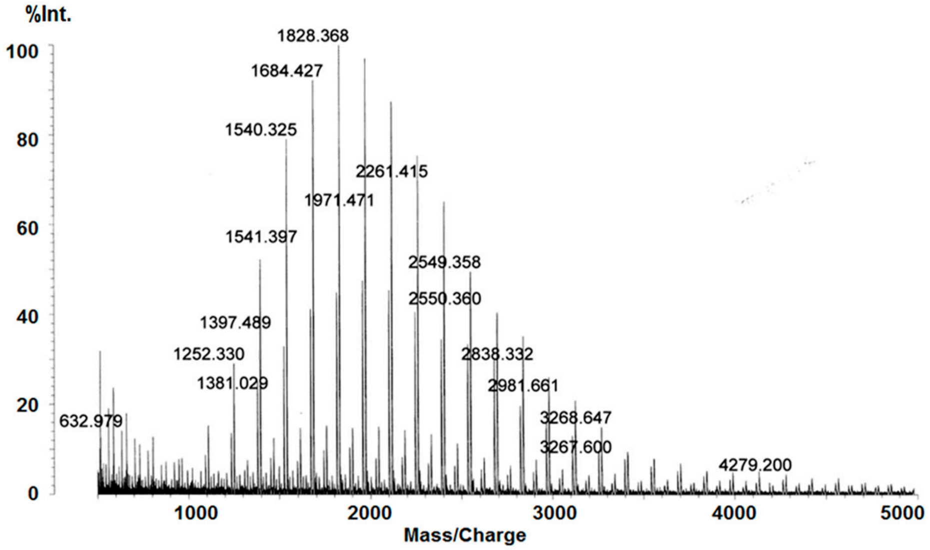
[1] Conditions: Temperature = 120 °C, Time = 12 h, M (monomer) = LLA, I (initiator) = 2-propanol, C (catalyst) = $Fe(OTf)_3$, $[M]_0:[I]_0:[C] = 1000:1:1$. [2] $M_n(\text{theo}) = 144.13 \times [M]_0/[I] \times \text{yield}(\%)/100$. [3] Determined by GPC analysis in THF calibrated with standard polystyrenes.

Bulk polymerizations of LLA were performed at various amounts of $^i$PrOH as an initiator (Table 4). In the $Fe(OTf)_3$ system without PS (runs 13, 24–26), the polymer yields gradually increased with increasing feed initiator, while the molecular weights remained almost constant around $M_n$ = 20 kg/mol, even at no addition of the initiator (run 24). In the $Fe(OTf)_3$–2PS system (runs 20, 27–29), the molecular weight of the resulting polymers tended to decrease with increasing initiator while keeping relatively high yields. This means that the molecular weight of the generated polymers can be controlled to some extent by the initiator concentration, although the molecular weight distributions were rather broad. When the polymerization was performed without an initiator, a polymer with $M_n$ of 150 kg/mol was formed. To analyze the PLLA obtained with the $Fe(OTf)_3$–2PS system by MALDI-TOF MS, a low molecular weight PLLA ($M_n$(GPC) = 4.6 kg/mol) was produced at $[M]_0/[I]_0$ = 1000/50 (run 30). The MALDI-TOF MS spectrum of the obtained PLLA in run 30 is shown in Figure 2. The spectrum showed a series of repeating peaks spaced by the molecular weight of lactyl units with the $^i$PrOH end group having a $Na^+$ or $K^+$ cation. Possibly due to the use of a large excess of $^i$PrOH against the catalyst and the effect of PS, the peaks for the $H_2O$-initiated PLLA were negligible. The peaks for the PLLA composed of even numbers of lactyl units were much stronger than those composed of odd numbers of lactyl units, indicating more suppressed transesterification in comparison with the $Fe(OTf)_3$ system without PS (Figure 1).

**Table 4.** Bulk polymerization of LLA catalyzed by the $Fe(OTf)_3$ systems [1].

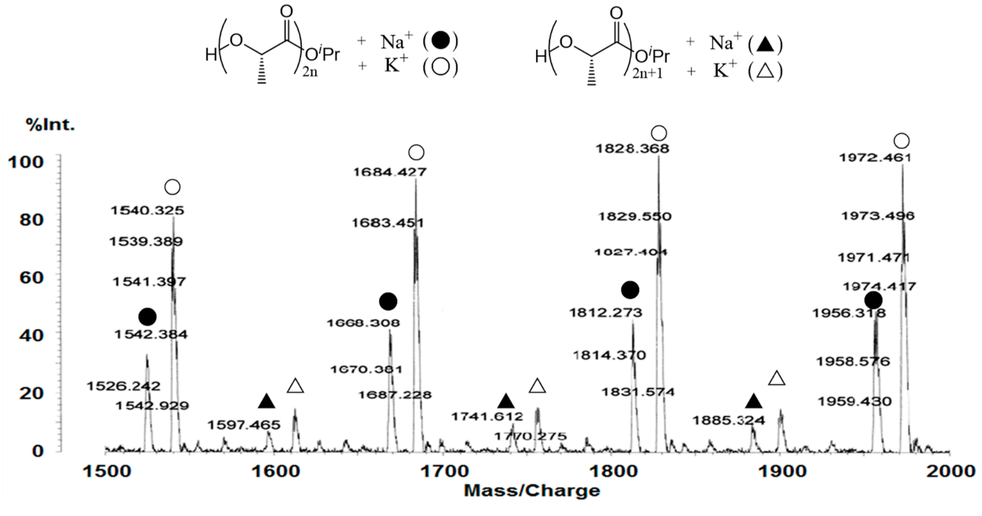
| Run | [PS]/[C] | $[M]_0/[I]_0$ | Yield (%) | $M_n$(theo) [2] (kg/mol) | $M_n$(GPC) [3] (kg/mol) | $M_w/M_n$ [3] |
|---|---|---|---|---|---|---|
| 24 | 0 | 1000/0 | 38 | - | 22 | 1.32 |
| 13 | 0 | 1000/1 | 58 | 83 | 24 | 1.42 |
| 25 | 0 | 1000/2 | 54 | 39 | 18 | 1.33 |
| 26 | 0 | 1000/4 | 75 | 27 | 23 | 1.24 |
| 27 | 2 | 1000/0 | 80 | - | 150 | 1.79 |
| 20 | 2 | 1000/1 | 86 | 120 | 99 | 1.64 |
| 28 | 2 | 1000/2 | 77 | 56 | 60 | 1.55 |
| 29 | 2 | 1000/4 | 93 | 34 | 58 | 1.60 |
| 30 | 2 | 1000/50 | 66 | 1.9 | 4.6 | 1.24 |

[1] Conditions: Temperature = 120 °C, Time = 12 h, M (monomer) = LLA, I (initiator) = 2-propanol, C (catalyst) = $Fe(OTf)_3$, $[M]_0:[C]_0$ = 1000:1. [2] $M_n$(theo) = 144.13 × $[M]_0/[I]_0$ × yield(%)/100. [3] Determined by GPC analysis in THF calibrated with standard polystyrenes.



(a)

**Figure 2.** *Cont.*



(**b**)

**Figure 2.** MALDI-TOF MS spectra of PLLA synthesized by using the Fe(OTf)$_3$–2PS system (run 30): (**a**) mass–charge range of 500 to 5000; (**b**) mass–charge range of 1500 to 2000.

The bulk polymerizations of CL catalyzed by Fe(OTf)$_3$ were also carried out at a feed monomer–initiator–catalyst ratio of 1000:1:1 at 120 °C (Table 5). The polymerization of CL by Fe(OTf)$_3$ rapidly proceeded to give PCL with $M_n$ of 14 kg/mol in an almost quantitative yield without PS (run 31). In contrast to the case of the LLA polymerization, the addition of PS into the CL polymerization system by Fe(OTf)$_3$ decreased the polymer yield, while the molecular weight of the resulting polymer increased.

**Table 5.** Bulk homopolymerization of CL catalyzed by the Fe(OTf)$_3$–PS systems [1].

| Run | [PS]/[C] | Time (h) | Yield (%) | $M_n$(theo) [2] (kg/mol) | $M_n$(GPC) [3] (kg/mol) | $M_w/M_n$ [3] |
|---|---|---|---|---|---|---|
| 31 | 0 | 3 | 93 | 106 | 14 | 1.56 |
| 32 | 2 | 6 | 55 | 63 | 31 | 1.53 |

[1] Conditions: Temperature = 120 °C, Time = 12 h, M (monomer) = CL, I (initiator) = 2-propanol, C (catalyst) = Fe(OTf)$_3$, $[M]_0:[I]_0:[C]$ = 1000:1:1. [2] $M_n$(theo) = 114.14 × $[M]_0/[I]_0$ × yield(%)/100. [3] Determined by GPC analysis in THF calibrated with standard polystyrenes.

Although many iron-based catalysts for the homopolymerization and block copolymerization of lactide and CL have been reported [16], investigations into their random copolymerizations have still been limited [22,44]. Since the Fe(OTf)$_3$ catalyst system was active for the polymerization of both LLA and CL, the random copolymerization of LLA and CL by this catalyst system was investigated. The bulk copolymerizations of LLA and CL by Fe(OTf)$_3$ at a $[LLA]_0$:$[CL]_0$:$[I]_0$:[C] feed ratio of 500:500:1:1 were examined in the presence or absence of PS (Table 6). The compositions of the obtained copolymers were determined from their $^1$H NMR spectra (Figures S1 and S2). In the absence of PS, the Fe(OTf)$_3$ system was found to incorporate CL preferentially to give a copolymer with low molar LLA content ($f_{LLA}$ = 17 mol%) at the initial stage (run 33). The polymer yield increased with polymerization time, while the molecular weight of the resulting polymer remained rather low at around $M_n$ = 12 kg/mol (runs 33–35), indicating accompanying chain transfer. This result was also supported by the significantly increasing signals for the CL–LLA and LLA–CL conjunctions in the $^1$H NMR spectra (Figure S1). In sharp contrast, LLA was preferentially incorporated in the presence of PS to give the LLA-rich copolymer ($f_{LLA}$ = 86 mol%) at the initial stage (run 36). The molecular weight as well as the yield of the copolymer increased with polymerization time; however, their PDI also increased with time, indicating some transesterification and/or slow initiation (runs 36–38).

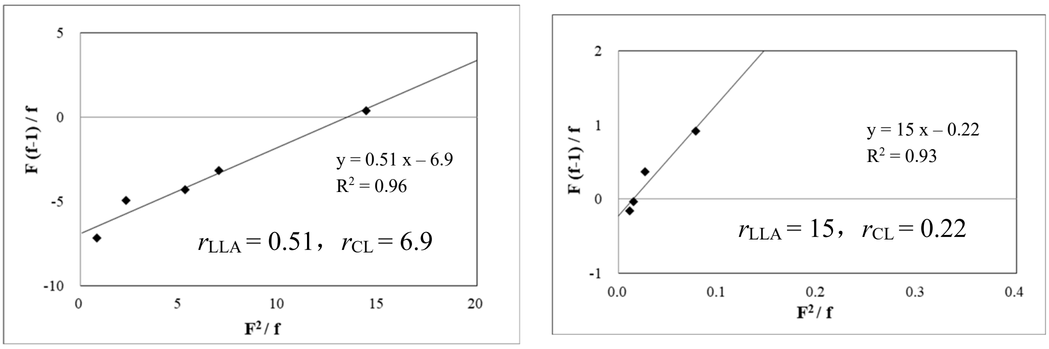
**Table 6.** Bulk copolymerization of LLA and CL using the Fe(OTf)$_3$ system [1].

| Run | [PS]/[C] | Time (h) | Yield [2] (%) | $f_{LLA}$ [3] (mol%) | $M_n$ [4] (kg/mol) | $M_w/M_n$ [4] | $T_g$ [5] (°C) | $T_m$ [6] (°C) | $\Delta H_m$ [6] (J/g) |
|---|---|---|---|---|---|---|---|---|---|
| 33 | 0 | 3 | 36 | 17 | 12 | 1.33 | −46.0 | 43.3 | 56.8 |
| 34 | 0 | 12 | 59 | 35 | 11 | 1.43 | −32.9 | n.d. [7] | n.d. [7] |
| 35 | 0 | 72 | 82 | 50 | 12 | 1.35 | −15.1 | n.d. [7] | n.d. [7] |
| 36 | 2 | 6 | 36 | 86 | 14 | 1.30 | 32.0 | 135.4 | 29.5 |
| 37 | 2 | 48 | 69 | 71 | 36 | 1.70 | 10.1 | 111.2 | 14.5 |
| 38 | 2 | 96 | 89 | 54 | 45 | 1.81 | −11.0 | n.d. [7] | n.d. [7] |

[1] Conditions: Temperature = 120 °C, M (monomer) = LLA and CL, I (initiator) = 2-propanol, C (catalyst) = Fe(OTf)$_3$, [LLA]$_0$:[ CL]$_0$:[I]$_0$:[C] = 500:500:1:1, [LLA]$_0$ = [CL]$_0$ = 3.5 mol/L. [2] Yield (%) = (Weight of the obtained copolymer)/(Sum of the weights of feed LLA and CL) × 100. [3] Molar LLA content in the copolymer determined by $^1$H NMR analysis. [4] Determined by GPC analysis in THF calibrated with standard polystyrenes. [5] Determined by DSC in the second heating scan. [6] Determined by DSC in the first heating scan. [7] Not detected.

The thermal properties of the obtained copolymers, as assessed from their DSC curves (Figures S3 and S4), are included in Table 6. The copolymer with a low $f_{LLA}$ of 17 mol% (run 33, high CL content of 83 mol%) obtained by the Fe(OTf)$_3$ catalyst system exhibited a melting transition at 43 °C for a long, continuous CL sequence (run 33). In contrast, the polymers with a high $f_{LLA}$ of 86 mol% (run 36) and 71 mol% (run 37) obtained by the Fe(OTf)$_3$–2PS system showed a melting transition for the PLLA segment at 135 and 111 °C, respectively. The glass transition temperature ($T_g$) of the copolymers increased with increasing $f_{LLA}$.

The monomer reactivity ratio of LLA and CL in the bulk copolymerization by Fe(OTf)$_3$ was investigated using the Fineman–Ross method. The detailed data are included in the Supporting Information and the Fineman–Ross plots are shown in Figure 3. For the Fe(OTf)$_3$ system without PS, the reactivity ratio was estimated as $r_{LLA}$ = 0.51 and $r_{CL}$ = 6.9 (Figure 3a). The high CL preference of the Fe(OTf)$_3$ system in the LLA–CL copolymerization is exceptional among the reported systems, where most lactide–CL copolymerizations showed lactide preferences over CL [45–48]. In the cationic copolymerization of CL and LLA by using CF$_3$SO$_3$H and $^i$PrOH, LLA was preferentially consumed [49]. The iron(III) guanidine complex [44] and the iron(II) acetate–carboxamide system [22] also polymerize LLA preferentially in the LLA–CL copolymerization. Strictly random copolymerization of lactide and CL was catalyzed by aluminum complexes bearing a bulky salen ligand [50] or pyrrolylpyridylamido [51]. Aluminum complexes of non-chiral-salalen ligands were reported to promote lactide–CL copolymerization with CL preference ($r_{lactide}$ = 0.85 and $r_{CL}$ = 2.95) [52]. To the best of our knowledge, the CL preference of Fe(OTf)$_3$ is the highest among the reported catalysts for lactide–CL copolymerization, although the molecular weights were not controlled. Although the Fe(OTf)$_3$ has a CL preference, the LLA–CL copolymerization by Fe(OTf)$_3$ is accompanied by chain transfer as indicated by the constant $M_n$ vs. yield, suggesting that the copolymers of a wide range of compositions should be produced at high conversion. In sharp contrast, the Fe(OTf)$_3$–2PS system favored LLA incorporation in the LLA–CL copolymerization with $r_{LLA}$ = 15 and $r_{CL}$ = 0.22 (Figure 3b). This tendency is influenced by the homopolymerization of each monomer, where the LLA polymerization was accelerated and the CL polymerization was decelerated by the addition of PS (vide supra). Considering the continuous increase in $M_n$ with increasing yield, the LLA–CL copolymerization by Fe(OTf)$_3$–2PS should produce a gradient copolymer. Thus, the comonomer preference in the LLA-CL copolymerization by the Fe(OTf)$_3$ catalyst system was switched by the addition of PS. We speculate that the polymerization mechanism should be different depending on the presence or absence of PS (vide infra).



(**a**) (**b**)

**Figure 3.** Plots for the Fineman–Ross method of the copolymerization of LLA and CL catalyzed by $Fe(OTf)_3$ with or without PS. (**a**) $[PS]/[Fe(OTf)_3] = 0$; (**b**) $[PS]/[Fe(OTf)_3] = 2$.

To obtain information on active species, the dependence of the polymerization rate on the $Fe(OTf)_3$ concentration was investigated (Figure 4). The detailed data are included in the Supporting Information. The $\ln([LLA]_0/[LLA])$ values were proportional to the polymerization time, indicating that the reaction rate was first order with respect to monomer concentration. The dependence of the polymerization rate on the concentration of the catalyst (Figure 4 left) as shown by the slope of the plots (2.1) indicates that the polymerization rate constant of LLA had a second-order dependence on the concentration of $Fe(OTf)_3$. From the LLA polymerization experiments under the constant $[LLA]_0$:$[^i PrOH]_0$:[PS] ratio and different $[Fe(OTf)_3]$:[PS] ratio, the highest rate constant was observed at a $[Fe(OTf)_3]$:[PS] ratio of 1:4 (Figure S7). The slope of the apparent rate constants (1.1) in the LLA polymerization by the $Fe(OTf)_3$–4PS system indicated first-order dependence (Figure 4 right). Thus, the LLA polymerization mechanisms should be significantly different between the $Fe(OTf)_3$ and the $Fe(OTf)_3$–PS systems.

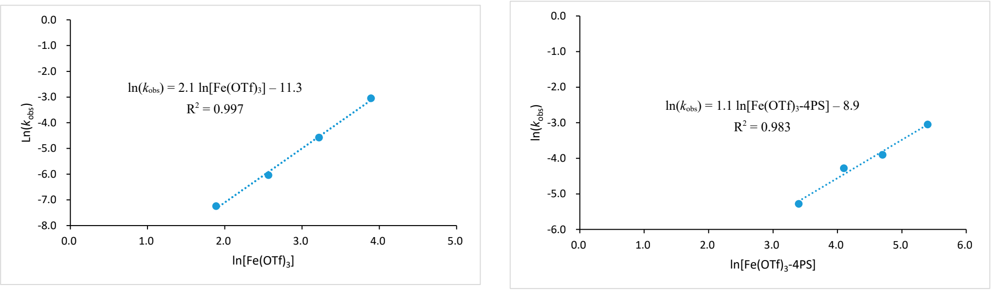
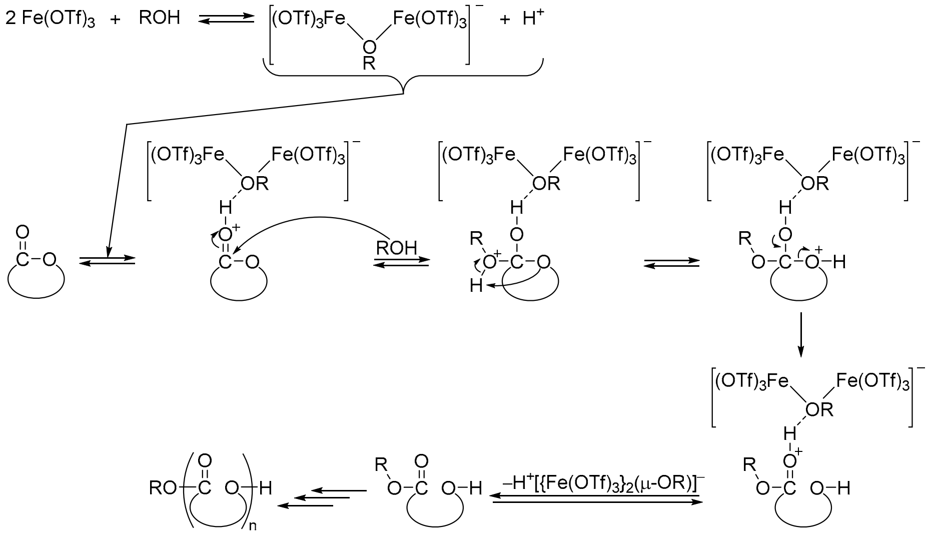
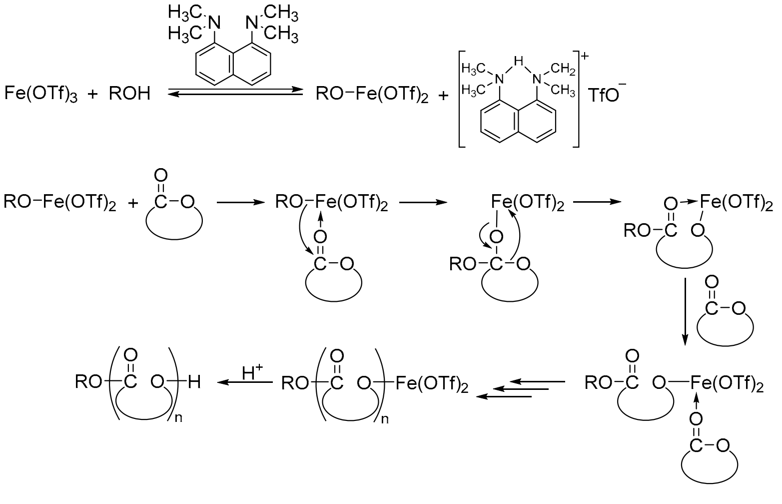


**Figure 4.** Dependence of the LLA polymerization rate on $Fe(OTf)_3$ (**left**) and $Fe(OTf)_3$–4PS (**right**) concentration.

Considering these results, we speculated about the mechanism of the ROP of cyclic esters by the $Fe(OTf)_3$ and $Fe(OTf)_3$–PS systems. In the $Fe(OTf)_3$ system without PS, we speculate that cationic polymerization by an activated monomer mechanism could occur (Scheme 2). From the second-order dependence of LLA polymerization rate on $Fe(OTf)_3$, two molecules of $Fe(OTf)_3$ could react with an alcohol to produce $H^+$ and $[\{Fe(OTf)_3\}_2(\mu\text{-}OR)]^-$. The generated $H^+$ could promote the ROP of cyclic esters as reported for the TfOH system [49]. In the copolymerization of LLA and CL by $Fe(OTf)_3$, the much bulkier counter anion $[\{Fe(OTf)_3\}_2(\mu\text{-}OR)]^-$, rather than $OTf^-$, should be present in the vicinity of the activated monomers, $[H\text{-}LLA]^+$ and $[H\text{-}CL]^+$. Further, the more crowded $[H\text{-}LLA]^+[\{Fe(OTf)_3\}_2(\mu\text{-}OR)]^-$ ion pair should be prevented to a larger extent from reacting with the -OH end group rather than $[H\text{-}CL]^+[\{Fe(OTf)_3\}_2(\mu\text{-}OR)]^-$ to polymerize CL preferentially. In the system without PS, the generated $H^+$ could also cause acid-catalyzed transesterification [53] associated with the ring-opening polymerization. In the presence of PS, the generated $H^+$ should be trapped with PS to form a $[H\text{-}PS]^+$ cation. $OTf^-$ should be eliminated as a counter anion to generate neutral $Fe(OTf)_2(OR)$ species, which should be monomeric, as speculated from the first-order dependence of the LLA polymerization rate on the $Fe(OTf)_3$–4PS system. The generated $Fe(OTf)_2(OR)$ could promote the coordinated polymerization of cyclic esters (Scheme 3). In the copolymerization of LLA and CL by the $Fe(OTf)_3$–PS system, more electron-rich LLA could coordinate to the iron center preferentially over CL. The addition of PS should also suppress the acid-catalyzed transesterification.



**Scheme 2.** Speculated mechanism for the ring-opening polymerization of a cyclic ester catalyzed by the $Fe(OTf)_3$ system in the absence of PS.



**Scheme 3.** Speculated mechanism for the ring-opening polymerization of a cyclic ester catalyzed by the $Fe(OTf)_3$ system in the presence of PS.

## 3. Experimental Section

### 3.1. Materials

All manipulations were carried out under an $N_2$ atmosphere using standard Schlenk techniques. Iron(III) chloride (97%), iron(II) trifluoromethanesulfonate (85%), and 1,8-bis(dimethylamino)naphthalene (99%) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Iron(III) trifluoromethanesulfonate (98%) was purchased from Santa Cruz Biotechnology (Dallas, TX, USA). Tin(II) 2-ethylhexanoate was purchased from Kishida Chemicals Co., Ltd. (Osaka, Japan). All these reagents were used without further purification. Toluene was purified by distillation from sodium–benzophenone under nitrogen and stored over sodium. L-Lactide (LLA) and ε-caprolactone (CL) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). LLA was sublimed before use. 2-propanol was distilled and diluted with toluene to prepare 0.0386 mol/L and 0.129 mol/L stock solutions before being used as an initiator. 1,8-bis(dimethylamino)naphthalene (PS) and tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) were diluted with toluene to prepare 0.347 mol/L and 0.0772 mol/L stock solutions before use, respectively.

### 3.2. Measurements

$^1$H NMR spectra were recorded on a Varian (Palo Alto, CA, USA) system 500 spectrometer (500 MHz for $^1$H nucleus). Chemical shifts of $^1$H NMR spectra were calibrated by using residual chloroform (δ = 7.26 ppm) in $CDCl_3$. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) measurements on a Tosoh (Tokyo, Japan) GPC system (SC-8010) equipped with an RI detector connected to a series of TSK gel columns, namely, G2000, G3000, G4000, and G5000. THF was used as an eluent at a flow rate of 1.0 mL/min at 40 °C. The GPC curves were calibrated using standard polystyrenes. MALDI-TOF MS experiments were carried out on a SHIMADZU (Tokyo, Japan) AXIMA-CFR plus equipped with a pulsed $N_2$ laser (337nm, 3 ns pulse width) using 2,5-dihydroxybenzoic acid (DHBA) as a matrix at the Natural Science Center for Basic Research and Development (N-BRAD), Hiroshima University. Spectra were recorded in a positive-ion linear mode. Polymer samples were dissolved in chloroform (1 mg/mL). DHBA was dissolved in a 1:1 mixture of aqueous 0.1% trifluoroacetic acid solution and ethanol as a matrix solution. The polymer solution was deposited on a sample slide with the matrix solution, and the solvents were evaporated before measuring. The melting point ($T_m$), heat of fusion ($\Delta H_m$), and glass transition temperature ($T_g$) of the polymers were measured using differential scanning calorimetry (DSC) on a Seiko (Chiba, Japan) DSC 6220 apparatus. The heating rate was 10 °C/min or 20 °C/min in a nitrogen stream.

### 3.3. Solution Polymerization of LLA in Toluene Without PS

A typical procedure (Table 1, run 1): $Fe(OTf)_3$ (0.0175 g, $3.47 \times 10^{-2}$ mmol), L-lactide (0.5 g, 3.47 mmol), and 0.0386 mol/L isopropanol solution in toluene (0.90 mL, $3.47 \times 10^{-2}$ mmol) were charged into a 10 mL Schlenk tube. Then, toluene (2.1 mL) was added so that the initial concentration of L-lactide was set at 1.0 mol/L. The resulting solution was stirred at 65 °C for 12 h. The reaction was quenched by the addition of methanol (ca. 20 mL). The precipitated polymers were collected and dried in vacuo.

### 3.4. Bulk Polymerization of LLA Without PS

A typical procedure (Table 5, run 11): $Fe(OTf)_3$ (0.0017 g, $3.47 \times 10^{-3}$ mmol), L-lactide (0.5 g, 3.47 mmol), and 0.129 mol/L isopropanol solution in toluene (0.027 mL, $3.47 \times 10^{-3}$ mmol) were charged into a 10 mL Schlenk tube. The resulting mixture was stirred at 120 °C for 3 h. Then, toluene (0.063 mL) was added so that the initial concentration of L-lactide was set at 6.8 mol/L. The reaction was quenched by the addition of methanol (ca. 20 mL). The precipitated polymers were collected and dried in vacuo.

### 3.5. Bulk Polymerization of LLA with PS

A typical procedure (Table 3, run 19): $Fe(OTf)_3$ (0.0017 g, $3.47 \times 10^{-3}$ mmol), L-lactide (0.5 g, 3.47 mmol), 0.347 mol/L PS solution (0.010 mL, $3.47 \times 10^{-3}$ mmol), and 0.129 mol/L isopropanol solution (0.027 mL, $3.47 \times 10^{-3}$ mmol) were charged into a 10 mL Schlenk tube. Then, toluene (0.053 mL) was added so that the initial concentration of L-lactide was set at 6.8 mol/L. The resulting mixture was stirred at 120 °C for 12 h. The reaction was quenched by the addition of methanol (ca. 20 mL). The precipitated polymers were collected and dried in vacuo.

### *3.6. Bulk Polymerization of CL Without PS*

A typical procedure (Table 5, run 31): $Fe(OTf)_3$ (0.0022 g, 4.37 × $10^{-3}$ mmol), CL (0.485 mL, 4.38 mmol), and 0.129 mol/L isopropanol solution (0.034 mL, 4.37 × $10^{-3}$ mmol) were charged into a 10 mL Schlenk tube. Then, toluene (0.079 mL) was added so that the initial concentration of CL was set at 7.3 mol/L. The resulting mixture was stirred at 120 °C for 3 h. The reaction was quenched by the addition of methanol (ca. 20 mL). The precipitated polymers were collected and dried in vacuo.

### *3.7. Bulk Polymerization of CL with PS*

A typical procedure (Table 5, run 32): $Fe(OTf)_3$ (0.0022 g, 4.37 × $10^{-3}$ mmol), CL (0.485 mL, 4.38 mmol), 0.347 mol/L PS solution in toluene (0.025 mL, 8.7 × $10^{-3}$ mmol), and 0.129 mol/L isopropanol solution (0.034 mL, 4.37 × $10^{-3}$ mmol) were charged into a 10 mL Schlenk tube. Then, toluene (0.054 mL) was added so that the initial concentration of CL was set at 7.3 mol/L. The resulting mixture was stirred at 120 °C for 12 h. The reaction was quenched by the addition of methanol (ca. 20 mL). The precipitated polymers were collected and dried in vacuo.

### *3.8. Bulk Copolymerization of LLA with CL in the Absence of PS*

A typical procedure (Table 6, run 33): $Fe(OTf)_3$ (0.0034 g, 6.94 × $10^{-3}$ mmol), L-lactide (0.5 g, 3.47 mmol), CL (0.384 mL, 3.47 mmol), and 0.129 mol/L isopropanol solution in toluene (0.054 mL, 6.94 × $10^{-3}$ mmol) were charged into a 10 mL Schlenk tube. Then, toluene (0.128 mL) was added so that the initial concentration of the monomer (LLA+CL) was set at 7.0 mol/L. The resulting mixture was stirred at 120 °C for 3 h. The reaction was quenched by the addition of methanol (ca. 20 mL). The precipitated polymers were collected and dried in vacuo.

### *3.9. Bulk Copolymerization of LLA with CL in the Presence of PS*

A typical procedure (Table 6, run 36): $Fe(OTf)_3$ (0.0034 g, 6.94 × $10^{-3}$ mmol), L-lactide (0.5 g, 3.47 mmol), CL (0.384 mL, 3.47 mmol), 0.347 mol/L PS solution in toluene (0.040 mL, 1.39 × $10^{-2}$ mmol), and 0.129 mol/L isopropanol solution (0.054 mL, 6.94 × $10^{-3}$ mmol) were charged into a 10 mL Schlenk tube. Then, toluene (0.088 mL) was added so that the initial concentration of the monomer (LLA+CL) was set at 7.0 mol/L. The resulting mixture was stirred at 120 °C for 6 h. The reaction was quenched by the addition of methanol (ca. 20 mL). The precipitated polymers were collected and dried in vacuo.

## 4. Conclusions

Commercially available $Fe(OTf)_3$ was found to promote the ROP of lactide and lactones even in the absence of cocatalysts. The addition of a bulky base, typically PS, increased the LLA polymerization rate while suppressing transesterification to give a high molecular weight PLLA. In contrast, the addition of PS into the CL polymerization system catalyzed by $Fe(OTf)_3$ decelerated the CL polymerization. The copolymerization of LLA and CL by using $Fe(OTf)_3$ without PS showed exceptionally high CL preference. In contrast, the $Fe(OTf)_3$–PS system showed LLA preference. Although the molecular weights of the resulting polymers were not well controlled, the comonomer preference in the copolymerization of LLA and CL by the $Fe(OTf)_3$ catalyst system was found to be switched by the addition of PS. The reaction mechanism of the polymerization of cyclic esters should be different based on the presence or absence of PS.

**Supplementary Materials:** The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/catal14120945/s1, Figure S1: $^1H$ NMR spectra of poly(LLA-*co*-CL) obtained by $Fe(OTf)_3$ (runs 33–35); Figure S2: $^1H$ NMR spectra of poly(LLA-*co*-CL) obtained by $Fe(OTf)_3$–2PS (runs 36–38); Figure S3: DSC carves of poly(LLA-*co*-CL) obtained by $Fe(OTf)_3$ (runs 33–35); Figure S4: DSC carves of poly(LLA-*co*-CL) obtained by $Fe(OTf)_3$–2PS (runs 36–38); Table S1: Bulk copolymerization of LLA and CL using the $Fe(OTf)_3$ system for the Fineman–Ross method; Table S2: Bulk polymerization of LLA catalyzed by $Fe(OTf)_3$; Figure S5: The relation of $\ln([LLA]_0/[LLA])$ versus time for the bulk polymerization of LLA by $Fe(OTf)_3$; Table S3: Dependence of reaction rate of LLA polymerization on $Fe(OTf)_3$ concentration; Table S4: Polymerization of LLA catalyzed by $xFe(OTf)_3$–16PS; Figure S6: The relation of $\ln([LLA]_0/[LLA])$ versus time in bulk polymerization of LLA by $Fe(OTf)_3$–PS; Table S5: Dependency of reaction rate by $xFe(OTf)_3$–16PS on $Fe(OTf)_3$ concentration; Figure S7: Dependence of reaction rate on the $[PS]/[Fe(OTf)_3]$ ratio; Table S6: Bulk polymerization of LLA catalyzed by $Fe(OTf)_3$–4PS; Figure S8: The relation of $\ln([LLA]_0/[LLA])$ versus time in bulk polymerization of LLA by $Fe(OTf)_3$–4PS; Table S7: The dependence of LLA polymerization reaction rates on the $[Fe(OTf)_3\text{–}4PS]$ concentration.

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## References

1. Penczek, S.; Duda, A.; Kowalski, A.; Libiszowski, J.; Majerska, K.; Biela, T. On the mechanism of polymerization of cyclic esters induced by tin(II) octoate. *Macromol. Symp.* **2000**, *157*, 61–70. [CrossRef]
2. Kowalski, A.; Duda, A.; Penczek, S. Mechanism of Cyclic Ester Polymerization Initiated with Tin(II) Octoate. 2.† Macromolecules Fitted with Tin(II) Alkoxide Species Observed Directly in MALDI−TOF Spectra. *Macromolecules* **2000**, *33*, 689–695. [CrossRef]
3. Sosnowski, S.; Lewinski, P. L-Lactide polymerization catalysed by tin(II) 2-ethyl-hexanoate. A deeper look at chain transfer reactions. *Polym. Chem.* **2015**, *6*, 6292–6296. [CrossRef]
4. Tanzi, M.C.; Verderio, P.; Lampugnani, M.G.; Resnati, M.; Dejana, E.; Sturani, E. Cytotoxicity of some catalysts commonly used in the synthesis of copolymers for biomedical use. *J. Mater. Sci. Mater. Med.* **1994**, *5*, 393–396. [CrossRef]
5. Yamada, T.; Jung, D.-Y.; Sawada, R.; Tsuchiya, T. Intracerebral microinjection of stannous 2-ethylhexanoate affects dopamine turnover in cerebral cortex and locomotor activity in rats. *J. Biomed. Mater. Res. Part B Appl. Biomater.* **2008**, *87B*, 381–386. [CrossRef]
6. Hege, C.S.; Schiller, S.M. Non-toxic catalysts for ring-opening polymerizations of biodegradable polymers at room temperature for biohybrid materials. *Green Chem.* **2014**, *16*, 1410–1416. [CrossRef]
7. O'Keefe, B.J.; Hillmyer, M.A.; Tolman, W.B. Polymerization of lactide and related cyclic esters by discrete metal complex. *J. Chem. Soc. Dalton Trans.* **2001**, 2215–2224. [CrossRef]
8. Kamber, N.E.; Jeong, W.; Waymouth, R.M.; Pratt, R.C.; Lohmeijer, B.G.G.; Hedrick, J.L. Organocatalytic Ring-Opening Polymerization. *Chem. Rev.* **2007**, *107*, 5813–5840. [CrossRef]
9. Dubois, P.; Coulembier, O.; Raquez, J.-M. (Eds.) *Handbook of Ring-Opening Polymerization*; Wiley: Weinheim, Germany, 2009.
10. Arbaouia, A.; Redshaw, C. Metal catalysts for ε-caprolactone polymerisation. *Polym. Chem.* **2010**, *1*, 801–826. [CrossRef]
11. Li, X.; Chen, C.; Wu, J. Lewis Pair Catalysts in the Polymerization of Lactide and Related Cyclic Esters. *Molecules* **2018**, *23*, 189. [CrossRef] [PubMed]
12. Walsh, D.J.; Hyatt, M.G.; Miller, S.A.; Guironnet, D. Recent Trends in Catalytic Polymerizations. *ACS Catal.* **2019**, *9*, 11153–11188. [CrossRef]
13. McGraw, M.L.; Chen, E.Y.-X. Lewis Pair Polymerization: Perspective on a Ten-Year Journey. *Macromolecules* **2020**, *53*, 6102–6122. [CrossRef]
14. Li, H.; Shakaroun, R.M.; Guillaume, S.M.; Carpentier, J.-F. Recent Advances in Metal-Mediated Stereoselective Ring-Opening Polymerization of Functional Cyclic Esters towards Well-Defined Poly(hydroxy acid)s: From Stereoselectivity to Sequence-Control. *Chem. Eur. J.* **2020**, *26*, 128–138. [CrossRef]
15. Dong, X.; Robinson, J.R. The versatile roles of neutral donor ligands in tuning catalyst performance for the ring-opening polymerization of cyclic esters. *New J. Chem.* **2022**, *46*, 444–453. [CrossRef]
16. Wang, Y.; Wang, X.; Zhang, W.; Sun, W.-H. Progress of Ring-Opening Polymerization of Cyclic Esters Catalyzed by Iron Compounds. *Organometallics* **2023**, *42*, 1680–1692. [CrossRef]
17. Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. Quantitative comparison of selectivities in the polymerization of cyclic esters. *Macromol. Symp.* **1997**, *123*, 93–101. [CrossRef]

18. O'Keefe, B.J.; Monnier, S.M.; Hillmyer, M.A.; Tolman, W.B. Rapid and Controlled Polymerization of Lactide by Structurally Characterized Ferric Alkoxides. *J. Am. Chem. Soc.* **2001**, *123*, 339–340. [CrossRef] [PubMed]
19. O'Keefe, B.J.; Breyfogle, L.E.; Hillmyer, M.A.; Tolman, W.B. Mechanistic Comparison of Cycllic Ester Polymerizations by Novel Iron(III)-Alkoxide Complexes: Single vs. Multiple Site Catalysis. *J. Am. Chem. Soc.* **2002**, *124*, 4384–4393. [CrossRef]
20. Södergård, A.; Stolt, M. Ring-opening polymerization of L-lactide by means of different iron compounds. *Macromol. Symp.* **1998**, *130*, 393–402. [CrossRef]
21. Naolou, T.; Lendlein, A.; Neffe, A.T. Amides as Non-polymerizable Catalytic Adjuncts Enable the Ring-Opening Polymerization of Lactide With Ferrous Acetate Under Mild Conditions. *Front. Chem.* **2019**, *7*, 346. [CrossRef] [PubMed]
22. Kirchhecker, S.; Nguyen, N.; Reichert, S.; Lützow, K.; Bungu, P.S.E.; Wangelin, A.J.v.; Sandl, S.; Neffe, A.T. Iron(II) carboxylates and simple carboxamides: An inexpensive and modular catalyst system for the synthesis of PLLA and PLLA-PCL block copolymers. *RSC Adv.* **2023**, *13*, 17102–17113. [CrossRef]
23. Gorczynski, J.L.; Chen, J.; Fraser, C.L. Iron Tris(dibenzoylmethane)-Centered Polylactide Stars: Multiple Roles for the Metal Complex in Lactide Ring-Opening Polymerization. *J. Am. Chem. Soc.* **2005**, *127*, 14956–14957. [CrossRef] [PubMed]
24. Chen, J.; Gorczynski, J.L.; Fraser, C.L. Iron Tris(dibenzoylmethane) Centered PCL and PCL-b-PLA Stars from Dual Functional Catalyst-Initiators. *Macromol. Chem. Phys.* **2010**, *211*, 1272–1279. [CrossRef]
25. Idage, B.B.; Idage, S.B.; Kasegaonkar, A.S.; Jadhav, R.V. Ring opening polymerization of dilactide using salen complex as catalyst. *Mater. Sci. Eng. B* **2010**, *168*, 193–198. [CrossRef]
26. Duan, R.; Hu, C.; Li, X.; Pang, X.; Sun, Z.; Chen, X.; Wang, X. Air-Stable Salen–Iron Complexes: Stereoselective Catalysts for Lactide and ε-Caprolactone Polymerization through in Situ Initiation. *Macromolecules* **2017**, *50*, 9188–9195. [CrossRef]
27. Biernesser, A.B.; Li, B.; Byers, J.A. Redox-Controlled Polymerization of Lactide Catalyzed by Bis(imino)pyridine Iron Bis(alkoxide) Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 16553–16560. [CrossRef]
28. Biernesser, A.B.; Chiaie, K.R.D.; Curley, J.B.; Byers, J.A. Block Copolymerization of Lactide and an Epoxide Facilitated by a Redox Switchable Iron-Based Catalyst. *Angew. Chem. Int. Ed.* **2016**, *55*, 5251–5254. [CrossRef] [PubMed]
29. Manna, C.M.; Kaur, A.; Yablon, L.M.; Haeffner, F.; Li, B.; Byers, J.A. Stereoselective Catalysis Achieved through in Situ Desymmetrization of an Achiral Iron Catalyst Precursor. *J. Am. Chem. Soc.* **2015**, *137*, 14232–14235. [CrossRef]
30. Nylund, P.V.S.; Monney, B.; Weder, C.; Albrecht, M. N-Heterocyclic carbene iron complexes catalyze the ring-opening polymerization of lactide. *Polym. Chem.* **2022**, *12*, 996–1004. [CrossRef] [PubMed]
31. Wang, K.; Prior, T.J.; Hughes, D.L.; Arbaoui, A.; Redshaw, C. Coordination chemistry of [2 + 2] Schiff-base macrocycles derived from the dianilines [(2-$NH_2C_6H_4)_2X$] (X = $CH_2CH_2$, O): Structural studies and ROP capability towards cyclic esters. *Dalton Trans.* **2021**, *50*, 8057–8069. [CrossRef] [PubMed]
32. Wang, Y.; Zhang, W.; Wang, X.; Zuo, W.; Xue, X.; Ma, Y.; Sun, W.-H. N-(2-(Diphenylphosphino)ethyl)-2-alkyl-5,6,7,8-tetrahydroquinolin-8-amines iron(II) complexes: Structural diversity and the ring opening polymerization of ε-caprolactone. *RSC Adv.* **2023**, *13*, 29866–29878. [CrossRef] [PubMed]
33. Adibi, H.; Samimi, H.A.; Beygzadeh, M. Iron(III) trifluoroacetate and trifluoromethanesulfonate: Recyclable Lewis acid catalysts for one-pot synthesis of 3,4-dihydropyrimidinones or their sulfur analogues and 1,4-dihydropyridines via solvent-free Biginelli and Hantzsch condensation protocols. *Catal. Commun.* **2007**, *8*, 2119–2124. [CrossRef]
34. Möller, M.; Kånge, R.; Hedrick, J.L. $Sn(OTf)_2$ and $Sc(OTf)_3$: Efficient and versatile catalysts for the controlled polymerization of lactones. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 2067–2074. [CrossRef]
35. Nomura, N.; Taira, A.; Tomioka, T.; Okada, M. A Catalytic Approach for Cationic Living Polymerization: $Sc(OTf)_3$-Catalyzed Ring-Opening Polymerization of Lactones. *Macromolecules* **2000**, *33*, 1497–1499. [CrossRef]
36. Kunioka, M.; Wang, Y.; Onozawa, S.-y. Polymerization of Poly(ε-caprolactone) Using Yttrium Triflate. *Polym. J.* **2003**, *35*, 422–429. [CrossRef]
37. Wang, Y.; Onozawa, S.-y.; Kunioka, M. Ring-opening polymerization of ε-caprolactone with yttrium triflate. *Green Chem.* **2003**, *5*, 571–574. [CrossRef]
38. Wang, Y.; Kunioka, M. Ring-opening polymerization of cyclic monomers with aluminum triflate. *Macromol. Symp.* **2005**, *224*, 193–205. [CrossRef]
39. Kunioka, M.; Wang, Y.; Onozawa, S.-y. Poly(lactic acid) polymerized by aluminum triflate. *Macromol. Symp.* **2005**, *224*, 167–179. [CrossRef]
40. Nomura, N.; Taira, A.; Nakase, A.; Tomioka, T.; Okada, M. Ring-opening polymerization of lactones by rare-earth metal triflates and by their reusable system in ionic liquids. *Tetrahedron* **2007**, *63*, 8478–8484. [CrossRef]
41. Lahcini, M.; Qayouh, H.; Yashiro, T.; Weidner, S.M.; Kricheldorf, H.R. Bismuth-Triflate-Catalyzed Polymerizations of ε-Caprolactone. *Macromol. Chem. Phys.* **2011**, *212*, 583–591. [CrossRef]
42. Zhang, K.; Bai, T.; Ling, J. Iron(III) Triflate as a Green Catalyst for Janus Polymerization to Prepare Block Polyesters. *Macromolecules* **2023**, *56*, 7389–7395. [CrossRef]
43. Möller, M.; Nederberg, F.; Lim, L.S.; Kånge, R.; Hawker, C.J.; Hedrick, J.L.; Gu, Y.; Shah, R.; Abbott, N.L. Stannous(II) trifluoromethane sulfonate: A versatile catalyst for the controlled ring-opening polymerization of lactides: Formation of stereoregular surfaces from polylactide "brushes". *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39*, 3529–3538. [CrossRef]
44. Rittinghaus, R.D.; Zenner, J.; Pich, A.; Kol, M.; Herres-Pawlis, S. Master of Chaos and Order: Opposite Microstructures of PCL-co-PGA-co-PLA Accessible by a Single Catalyst. *Angew. Chem. Int. Ed.* **2022**, *61*, e202112853. [CrossRef]

45. Vion, J.M.; Jerome, R.; Teyssie, P.; Aubin, M.; Prudhomme, R.E. Synthesis, characterization, and miscibility of caprolactone random copolymers. *Macromolecules* **1986**, *19*, 1828–1838. [CrossRef]
46. Vanhoorne, P.; Dubois, P.; Jerome, R.; Teyssie, P. Macromolecular engineering of polylactones and polylactides. 7. Structural analysis of copolyesters of iε-caprolactone and L- or D,L-lactide initiated by triisopropoxyaluminum. *Macromolecules* **1992**, *25*, 37–44. [CrossRef]
47. Darensbourg, D.J.; Karroonnirun, O. Ring-Opening Polymerization of l-Lactide and ε-Caprolactone Utilizing Biocompatible Zinc Catalysts. Random Copolymerization of l-Lactide and ε-Caprolactone. *Macromolecules* **2010**, *43*, 8880–8886. [CrossRef]
48. Stirling, E.; Champouret, Y.; Visseaux, M. Catalytic metal-based systems for controlled statistical copolymerisation of lactide with a lactone. *Polym. Chem.* **2018**, *9*, 2517–2531. [CrossRef]
49. Baśko, M.; Kubisa, P. Cationic copolymerization of ε-caprolactone and L,L-lactide by an activated monomer mechanism. *J. Polym. Sci. Part A Polym. Chem.* **2006**, *44*, 7071–7081. [CrossRef]
50. Nomura, N.; Akita, A.; Ishii, R.; Mizuno, M. Random Copolymerization of ε-Caprolactone with Lactide Using a Homosalen—Al Complex. *J. Am. Chem. Soc.* **2010**, *132*, 1750–1751. [CrossRef] [PubMed]
51. Li, G.; Lamberti, M.; Pappalardo, D.; Pellecchia, C. Random Copolymerization of ε-Caprolactone and Lactides Promoted by Pyrrolylpyridylamido Aluminum Complexes. *Macromolecules* **2012**, *45*, 8614–8620. [CrossRef]
52. Pilone, A.; Maio, N.D.; Press, K.; Venditto, V.; Pappalardo, D.; Mazzeo, M.; Pellecchia, C.; Kol, M.; Lamberti, M. Ring-opening homo- and co-polymerization of lactides and ε-caprolactone by salalen aluminum complexes. *Dalton Trans.* **2015**, *44*, 2157–2165. [CrossRef]
53. Otera, J. Transesterification. *Chem. Rev.* **1993**, *93*, 1449–1470. [CrossRef]