



Environmentally benign process for bulk ring opening polymerization of lactones using iron and ruthenium chloride catalysts

Ravikumar R. Gowda, Debashis Chakraborty*

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600 036, Tamilnadu, India

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ABSTRACT

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ are found to be bulk polymerization catalysts for the ring opening polymerization of ϵ -caprolactone, δ -valerolactone and β -butyrolactone. These polymerizations can be significantly enhanced by conducting them in the presence of appropriate amounts of different alcohols. The major initiation pathway in the polymerization is found to proceed via the activated monomer mechanism and depending on the nature of the alcohol used, poly(lactones) with different end groups can be synthesized. Such polymerizations constitute an economical process, employing readily available inorganics as catalysts and do not necessitate solvents. The overall system is green and eco friendly.

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1. Introduction

In spite of the versatile applications of Lewis acids in organic synthesis [1–3], their use in polymer chemistry has been quite limited [4–7]. In the recent years, the increasing need to search alternative polymeric materials to those based on non-renewable petroleum resources, along with the desire to produce environmentally benign biodegradable plastics has provided active impetus towards the polymerization of cyclic esters [8–12]. Aliphatic polyesters have been implicated for biomedical applications such as delivery medium for the controlled release of drugs and biodegradable surgical sutures [13–15]. Polylactones have potential utility for such usage as a result of their permeability, biocompatibility and biodegradability [16–18]. One of the convenient strategies in synthesizing these polymers is the ring opening polymerization of the corresponding cyclic lactone monomers or functionally related compounds [19–21].

Although a multitude of initiators are known for such polymerizations [22–27], the major hurdle regarding the commercialization of such processes is the difficulty in removing catalyst residues and the cytotoxicity associated with such residues, which limit the use of these polymers in biomedical applications. An attractive process is envisioned to be engineered upon new catalysts that have environmentally benign metals that are constituents in the mammalian anatomy so that the residues are potentially harmless [28].

The coordination–insertion ring opening mode of polymerization is the most popular because of its capability in producing poly-

mers with narrow molecular weight distribution [9,21–23,29–38]. A large variety of metal complexes containing alkyl [39–43], alkoxide [29–38], carboxylates [44–46] and oxides [47] have been reported to possess good activity. Tin alkoxides being the most popular route often envisages initiators of the composition $\text{Sn}(\text{OR})_2$ [48–52]. Other metal alkoxides or aryloxides containing aluminum [53], lithium [54], titanium [55–57] and some lanthanides [58–61] have been reported. A plethora of bio-compatible metal based initiators have also been reported recently. These include examples from zinc [62], magnesium [63] and calcium [64]. In the 1980s, calcium ammoniate was popularly used for the ring opening polymerization of ϵ -caprolactone [65]. Extreme hydrolytic sensitivity and limited solubility in organic solvents restricted its use. Derivatives containing iron namely alkoxides [36,66], porphyrins [67] and acetates [68] have been used previously.

Interestingly, no detailed investigation has been reported using simple halides containing Group 8 metals. The feasibility of using metal halides as catalysts prompted us to investigate in details the ring opening polymerization characteristics using iron group chlorides towards ϵ -caprolactone, δ -valerolactone and β -butyrolactone. The extensive use of readily available and environmentally benign metal halides as catalysts has not been investigated extensively.

2. Experimental

2.1. Materials

ϵ -Caprolactone (CL), δ -valerolactone (VL) and β -butyrolactone (BL) were purchased from Aldrich, dried and distilled fresh

* Corresponding author. Tel.: +91 44 2257 4223; fax: +91 44 2257 4202.
E-mail address: dchakraborty@iitm.ac.in (D. Chakraborty).

prior to use. The alcohols mentioned in Tables 1–6 were used after drying using appropriate procedures [69]. Anhydrous FeCl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were purchased from Aldrich and used as received. ϵ -Hydroxycaproic acid (**1**) was purchased from Alfa Aesar and used after purification. Benzyl 6-hydroxyhexanoate (**2**) was prepared using the literature procedure [70].

2.2. Characterization

^1H NMR spectra in CDCl_3 were recorded on a Bruker Avance 400 MHz instrument. MALDI-TOF measurements were performed on a Bruker Daltonics instrument in dihydroxy benzoic acid matrix. Molecular weights and the polydispersity indices of the polymers were determined by GPC instrument with Waters 510 pump and Waters 410 differential refractometer as the detector. Three columns namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8 mm \times 300 mm) were connected in series. Measurements were done in THF at 27 °C. Number average molecular weights and polydispersity of polymers were measured relative to polystyrene standards. For CL, number average molecular weights were corrected according to Mark-Houwink corrections [71].

2.3. Typical procedure for bulk polymerization

The procedure described is for monomer and metal halide ratio of 200:1. For CL polymerization, 23.6 μmol of the metal halide alone or along with requisite amount of alcohol were taken in a flask under a nitrogen atmosphere. The contents were stirred and 0.5 mL CL (0.54 g, 4.71 mmol) was added neat. The mixture was rapidly stirred at the given temperature. A rise in viscosity was observed and finally the stirring ceased. For VL and BL polymerizations, 13.5 μmol and 15.3 μmol were used for 0.25 mL (0.27 g, 2.69 mmol of VL and 0.26 g, 3.06 mmol of BL) of monomer and a similar procedure was followed. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique [72]. The polymerizations were quenched by pouring the contents into cold heptane. The polymer was isolated by subsequent filtration and dried till a constant weight was attained.

2.4. Typical procedure for polymerization in toluene

For CL polymerization, 23.6 μmol of the metal halide alone or along with requisite amount of alcohol and 2 mL of dry toluene were taken in a flask under a nitrogen atmosphere. The contents were stirred and 0.5 mL CL (0.54 g, 4.71 mmol) was added. The mixture was rapidly stirred. For VL and BL polymerizations, 13.5 μmol and 15.3 μmol were used for 0.25 mL (0.27 g, 2.69 mmol of VL and 0.26 g, 3.06 mmol of BL) of monomer and a similar procedure was followed. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique [72]. The polymerizations were quenched by pouring the contents into

cold heptane. The polymer was isolated by subsequent filtration and dried till a constant weight was attained.

3. Results and discussion

3.1. Polymerization activity and characteristics

Our impetus in this study began with the observation that anhydrous FeCl_3 alone can be used catalytically for the bulk polymerization of CL, VL and BL respectively producing appreciably high number average molecular weight (M_n) polymers. Since it is more practical to use hydrated FeCl_3 , taking into consideration the catalyst cost, anhydrous FeCl_3 was deliberately contaminated with a known stoichiometry of water and the polymerization reactions were reinvestigated. We observed that the M_n values in each case became almost double (Table 1) with a reduction in polymerization time to about half. The use of water as an initiator is known, although claimed to be ineffective towards the enhancement of rate of polymerization and molecular weights of the resulting polymers for catalyst bearing ligating initiating groups [73]. These polymerizations were conducted in a nitrogen atmosphere and the disappearance of the monomer was monitored using TLC analysis periodically and quenched when all the monomer was found consumed [72].

With the initial investigations producing commendable results, we decided to conduct in-depth investigations into the ring opening polymerization of the above mentioned lactone monomers using commercially available hydrated iron chlorides. To gain a substantial insight into the reaction pathway using NMR techniques, we decided to use ruthenium analogues as catalysts for similar reactions for CL and VL polymerizations.

Various polymerizations were performed using CL, VL and BL independently with commercially available $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ under different conditions of stoichiometry, temperature and in the presence of several alcohol initiators as indicated in Tables 2–4 respectively. These trials were performed under bulk conditions.

Analysis of the results for CL polymerization using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Table 2) reveals that there is an increase in the molecular weight (M_n) of the poly(caprolactone) with an increase in the ratio between monomer and catalyst ($[\text{CL}]_0/[\text{Cat}]_0$) along with an improvement in molecular weight distributions (MWDs) (Entries 1–5 of Table 2). In the presence of an alcohol, for a given ($[\text{CL}]_0/[\text{Cat}]_0$) ratio, reasonable degree of control was reflected in terms of lower MWDs (Entry 1 vs Entries 10–13 in Table 2) and enhanced molecular weights (M_n) of the resulting polymers. In such cases the polymerization was found to proceed to completion much faster as reflected by the time. At 80 °C, the polymerization proceeds rapidly where as at 0 °C and 15 °C, it is slower and the changes in M_n or MWDs are not significant when compared to the results obtained at 27 °C (Entry 1 vs Entries 6, 8 and 9). For $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ the trends were similar as compared to the reactions catalyzed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The variations of M_n with $[\text{CL}]_0/[\text{Cat}]_0$ ratio are depicted in Fig. 1. The

Table 1
Results of CL, VL and BL polymerization using anhydrous FeCl_3 at 27 °C.

Entry	Monomer (M)	Initiator (I)	$[\text{M}]_0/[\text{Fe}]_0/[\text{I}]_0$ ratio	t^a (min)	Yield (%)	$M_n^b/M_{th}^c \times 10^{-4}$	M_w/M_n
1	CL	None	200:1:0	60.0	100	1.94/2.28	1.87
2	CL	H_2O	200:1:5	26.4	100	3.89/0.46	2.06
3	VL	None	200:1:0	1.8	100	3.10/2.00	1.39
4	VL	H_2O	200:1:5	0.9	100	7.28/0.40	2.26
5	BL	None	200:1:0	0.6	100	1.22/1.72	1.78
6	BL	H_2O	200:1:5	0.3	100	2.48/0.35	1.76

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.

^b Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n in the case of CL polymerizations [71].

^c Calculated from $MW_{M_0}([\text{M}]_0/[\text{Fe}]_0)$ for cases where no water is used and $MW_{M_0}([\text{M}]_0/[\text{I}]_0) + MW_{\text{water}}$ for cases using water.

Table 2
Results of CL polymerization using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

Entry	Catalyst (Cat)	Initiator (I)	Temp. ($^{\circ}\text{C}$)	$[\text{CL}]_0/[\text{Cat}]_0$ ratio	t^a (min)	Yield (%)	$M_n^b/M_{th}^c \times 10^{-4}$	M_w/M_n
1	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	27	200:1:0	27.0	100	3.61/2.28	2.22
2	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	27	400:1:0	1.25 (h)	100	5.83/4.56	2.17
3	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	27	800:1:0	4.25 (h)	100	8.63/9.12	1.70
4	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	27	1000:1:0	10.25 (h)	100	10.41/11.40	1.49
5	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	27	1200:1:0	13.25 (h)	100	12.52/13.68	1.28
6	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	80	200:1:0	6.0	100	5.01/2.28	2.03
7	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	80	1000:1:0	15.0	100	3.88/11.40	2.06
8	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	15	200:1:0	1.25 (h)	100	5.72/2.28	2.08
9	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	None	0	200:1:0	3.25 (h)	100	6.33/2.28	2.03
10	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	BnOH	27	200:1:5	16.8	100	6.73/0.47	1.26
11	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	EtOH	27	200:1:5	22.8	100	5.98/0.46	1.54
12	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	<i>i</i> -PrOH	27	200:1:5	15.6	100	7.00/0.46	1.67
13	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Glycol	27	200:1:5	21.6	100	8.20/0.46	1.38
14	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	None	27	200:1:0	57.6	100	3.98/2.28	2.28
15	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	None	27	400:1:0	2.33 (h)	100	5.55/4.56	2.02
16	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	None	27	800:1:0	5.75 (h)	100	9.25/9.12	1.38
17	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	None	27	1000:1:0	7.50 (h)	100	10.81/11.40	1.24
18	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	None	27	1200:1:0	10.60 (h)	100	13.07/13.68	1.20
19	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	None	80	200:1:0	11.0	100	4.80/2.28	1.92
20	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	None	0	200:1:0	4.5 (h)	100	3.87/2.28	1.84
21	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	BnOH	27	200:1:5	42.0	100	8.41/0.47	1.14
22	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	EtOH	27	200:1:5	54.6	100	8.47/0.46	1.39
23	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	<i>i</i> -PrOH	27	200:1:5	39.6	100	6.60/0.46	1.21
24	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	Glycol	27	200:1:5	49.8	100	5.74/0.46	1.80
25	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	None	27	200:1:0	24.0 (h)	100	4.85/2.28	2.15
26	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	None	27	400:1:0	25.5 (h)	100	6.83/4.56	1.69
27	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	None	27	800:1:0	27.0 (h)	100	8.11/9.12	1.46
28	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	None	27	1000:1:0	29.0 (h)	100	8.92/11.40	1.40
29	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	None	27	1200:1:0	31.2 (h)	100	10.36/13.68	1.25
30	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	None	80	200:1:0	11.0 (h)	100	3.52/2.28	1.92
31	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	None	0	200:1:0	36.0 (h)	100	5.08/2.28	1.89
32	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	BnOH	27	200:1:5	14.0 (h)	100	8.21/0.47	1.43
33	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	EtOH	27	200:1:5	15.0 (h)	100	4.19/0.46	1.64
34	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	<i>i</i> -PrOH	27	200:1:5	14.5 (h)	100	5.23/0.46	1.56
35	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	Glycol	27	200:1:5	16.0 (h)	100	5.35/0.46	1.41

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.

^b Measured by GPC at 27 $^{\circ}\text{C}$ in THF relative to polystyrene standards with Mark-Houwink corrections for M_n [71].

^c Calculated from $MW_{CL}([\text{CL}]_0/[\text{Cat}]_0)$ for cases where no alcohol is used and $MW_{CL}([\text{CL}]_0/[\text{Cat}]_0) + MW_{ROH}$ for cases using alcohol.

plots are linear indicating that there is a continual rise in M_n with an increase in $[\text{CL}]_0/[\text{Cat}]_0$ ratio.

Having obtained encouraging results with CL, we proceeded towards investigating polymerizations using VL and BL employing the same metal salts under analogous conditions. These results using VL are summarized in Table 3.

VL has a greater tendency to undergo ring opening polymerisation reaction when compared to CL. At 27 $^{\circ}\text{C}$ (Table 3), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ yielded good results. Again the M_n val-

ues were found to increase with an increase in $[\text{VL}]_0/[\text{Cat}]_0$ (Entries 1–5, 11–15 and 21–25 of Table 3). In the presence of alcohols, better control of the polymerization reaction was reflected in terms of lower MWDs along with a reduction in the polymerization reaction time. The plot of M_n vs $[\text{VL}]_0/[\text{Cat}]_0$ ratio for $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Fig. 2) is linear for each case.

On a similar basis, polymerizations were conducted using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and BL and the results are enumerated in Table 4.

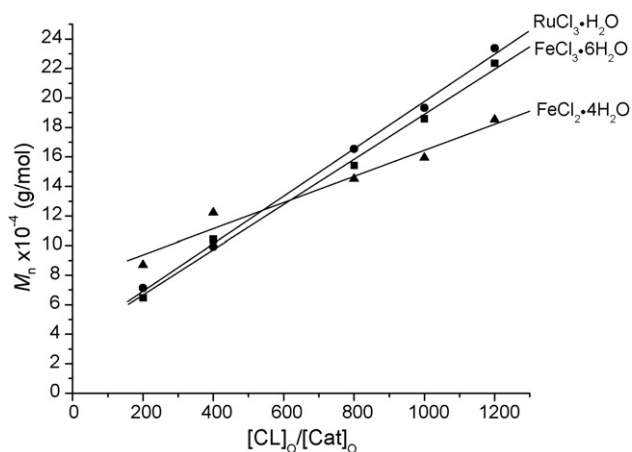


Fig. 1. Plot of M_n (vs polystyrene standards) vs $[\text{CL}]_0/[\text{Cat}]_0$ for CL polymerization at 27 $^{\circ}\text{C}$ using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

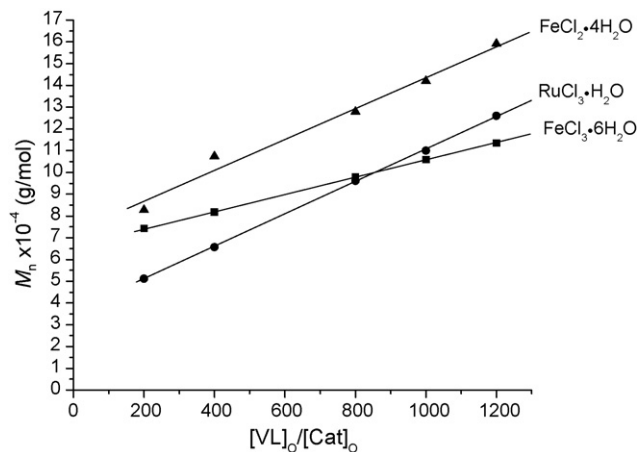


Fig. 2. Plot of M_n (vs polystyrene standards) vs $[\text{VL}]_0/[\text{Cat}]_0$ for VL polymerization at 27 $^{\circ}\text{C}$ using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

Table 3
Results of VL polymerization using FeCl₃·6H₂O, RuCl₃·H₂O and FeCl₂·4H₂O.

Entry	Catalyst (Cat)	Initiator (I)	Temp. (°C)	[VL] ₀ : [Cat] ₀ : [I] ₀ ratio	t ^a (min)	Yield (%)	M _n ^b /M _{th} ^c × 10 ⁻⁴	M _w /M _n
1	FeCl ₃ ·6H ₂ O	None	27	200:1:0	0.96	100	7.43/2.00	2.07
2	FeCl ₃ ·6H ₂ O	None	27	400:1:0	1.56	100	8.17/4.00	1.96
3	FeCl ₃ ·6H ₂ O	None	27	800:1:0	3.00	100	9.78/8.00	1.73
4	FeCl ₃ ·6H ₂ O	None	27	1000:1:0	3.48	100	10.59/10.00	1.63
5	FeCl ₃ ·6H ₂ O	None	27	1200:1:0	3.90	100	11.34/12.00	1.56
6	FeCl ₃ ·6H ₂ O	None	0	200:1:0	13.98	100	6.49/2.00	1.99
7	FeCl ₃ ·6H ₂ O	BnOH	27	200:1:5	0.78	100	6.17/0.41	1.78
8	FeCl ₃ ·6H ₂ O	EtOH	27	200:1:5	1.08	100	5.77/0.40	1.53
9	FeCl ₃ ·6H ₂ O	<i>i</i> -PrOH	27	200:1:5	0.72	100	5.62/0.41	1.49
10	FeCl ₃ ·6H ₂ O	Glycol	27	200:1:5	0.90	100	7.10/0.41	1.47
11	RuCl ₃ ·H ₂ O	None	27	200:1:0	1.92	100	5.12/2.00	2.37
12	RuCl ₃ ·H ₂ O	None	27	400:1:0	3.60	100	6.56/4.00	2.09
13	RuCl ₃ ·H ₂ O	None	27	800:1:0	6.00	100	9.61/8.00	1.61
14	RuCl ₃ ·H ₂ O	None	27	1000:1:0	7.20	100	11.00/10.00	1.47
15	RuCl ₃ ·H ₂ O	None	27	1200:1:0	8.28	100	12.60/12.00	1.32
16	RuCl ₃ ·H ₂ O	None	0	200:1:0	15.60	100	2.17/2.00	1.30
17	RuCl ₃ ·H ₂ O	BnOH	27	200:1:5	1.56	100	5.50/0.41	1.83
18	RuCl ₃ ·H ₂ O	EtOH	27	200:1:5	1.80	100	3.67/0.40	1.41
19	RuCl ₃ ·H ₂ O	<i>i</i> -PrOH	27	200:1:5	1.69	100	5.61/0.41	1.22
20	RuCl ₃ ·H ₂ O	Glycol	27	200:1:5	1.74	100	2.18/0.41	1.19
21	FeCl ₂ ·4H ₂ O	None	27	200:1:0	2.33 (h)	100	8.27/2.00	2.06
22	FeCl ₂ ·4H ₂ O	None	27	400:1:0	3.00 (h)	100	10.73/4.00	1.70
23	FeCl ₂ ·4H ₂ O	None	27	800:1:0	4.00 (h)	100	12.79/8.00	1.51
24	FeCl ₂ ·4H ₂ O	None	27	1000:1:0	4.50 (h)	100	14.20/10.00	1.41
25	FeCl ₂ ·4H ₂ O	None	27	1200:1:0	5.10 (h)	100	15.91/12.00	1.33
26	FeCl ₂ ·4H ₂ O	None	80	200:1:0	1.50 (h)	100	5.89/2.00	2.12
27	FeCl ₂ ·4H ₂ O	None	0	200:1:0	6.00 (h)	100	10.18/2.00	1.53
28	FeCl ₂ ·4H ₂ O	BnOH	27	200:1:5	1.66 (h)	100	14.44/0.41	1.37
29	FeCl ₂ ·4H ₂ O	EtOH	27	200:1:5	1.90 (h)	100	7.76/0.40	1.39
30	FeCl ₂ ·4H ₂ O	<i>i</i> -PrOH	27	200:1:5	1.69 (h)	100	5.86/0.41	1.77
31	FeCl ₂ ·4H ₂ O	Glycol	27	200:1:5	1.70 (h)	100	8.85/0.41	1.27

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.^b Measured by GPC at 27 °C in THF relative to polystyrene standards.^c Calculated from MW_{VL}([VL]₀/[Cat]₀) for cases where no alcohol is used and MW_{VL}([VL]₀/[I]₀) + MW_{ROH} for cases using alcohol.

The results follow the general trends discussed for the other polymerizations using FeCl₃·6H₂O. Again the plot of M_n vs [BL]₀/[Fe]₀ is found to be linear (see [supplementary material](#)).

The results using anhydrous FeCl₃ and H₂O as an initiator are similar to those using FeCl₃·6H₂O, RuCl₃·H₂O and FeCl₂·4H₂O for CL, VL and BL polymerizations (Entries 2, 4 and 6 of Table 1 vs Entry 1 of Tables 2–4). This indicates that such polymerizations can be mediated using H₂O. Similarly, other stronger nucleophiles such as alcohols may be used. We have studied the effect of various alcohols (Tables 2–4) and found that the polymerizations proceed much faster in their presence. Moreover, some degree of control in terms of improvements in the MWDs was noticed but living polymerization was never observed. There was no general trend observed to explain the relative behaviour of the different

alcohols in the different lactone polymerizations discussed using FeCl₃·6H₂O, RuCl₃·H₂O and FeCl₂·4H₂O [74]. In the presence of different alcohols (Tables 2–4), the observed molecular weights of the polymers were found to be much higher in magnitude than those calculated. Hence it is reasonable to conclude that the rates of initiation and propagation are much more rapid than that of chain transfer. As a consequence, a better control over M_n is observed. For polymerizations where there is slow initiation or rapid transesterification, the observed M_n is lower in magnitude than those calculated [75–77].

The dependence of molecular weight (M_n) upon varying the feed ratio of CL (Fig. 3) and VL (Fig. 4) to benzyl alcohol (BnOH) as an initiator was examined using FeCl₃·6H₂O and RuCl₃·H₂O. The molecular weight (M_n) increased almost linearly with increasing

Table 4
Results of BL polymerization using FeCl₃·6H₂O.

Entry	Initiator (I)	Temp. (°C)	[BL] ₀ : [Fe] ₀ : [I] ₀ ratio	t ^a (min)	Yield (%)	M _n ^b /M _{th} ^c × 10 ⁻⁴	M _w /M _n
1	None	27	200:1:0	0.24	100	2.42/1.72	1.95
2	None	27	400:1:0	0.54	100	3.02/3.44	1.60
3	None	27	800:1:0	1.14	100	3.19/6.88	1.37
4	None	27	1000:1:0	1.50	100	4.54/8.60	1.40
5	None	27	1200:1:0	2.10	100	5.03/10.32	1.32
6	None	0	200:1:0	12.00	100	1.31/1.72	1.76
7	BnOH	27	200:1:5	0.18	100	4.49/0.35	1.25
8	EtOH	27	200:1:5	0.27	100	1.84/0.35	1.56
9	<i>i</i> -PrOH	27	200:1:5	0.19	100	3.37/0.35	1.63
10	Glycol	27	200:1:5	0.24	100	2.99/0.35	1.62

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.^b Measured by GPC at 27 °C in THF relative to polystyrene standards.^c Calculated from MW_{BL}([BL]₀/[Fe]₀) for cases where no alcohol is used and MW_{BL}([BL]₀/[I]₀) + MW_{ROH} for cases using alcohol.

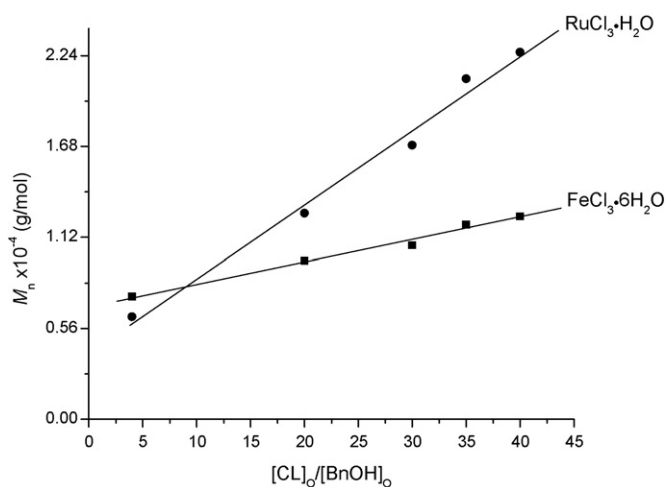


Fig. 3. Plot of M_n vs feed ratio of CL to BnOH at 27 °C.

feed ratio of CL or VL to BnOH. Similar studies were done using BL (see supplementary material).

3.2. Kinetics of polymerization

The kinetic studies for the polymerization of CL and VL using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ in ratio $[\text{M}]_0/[\text{Cat}]_0 = 200$ were performed (see supplementary material). The results are depicted in Fig. 5 and Fig. 6 respectively. Since BL polymerizations are extremely rapid, such a study could not be done with accuracy.

The plots suggest that at first there is an induction period followed by a first-order dependence of rate of polymerization on monomer concentration. Such an induction period for CL polymerizations with non-living characteristics have been reported previously [36,74,78–79]. It has been sufficiently illustrated that the structure of the initiator may influence the strength of the catalyst/initiator interaction [51,80]. These interactions at the early stages of the reaction are responsible for the formation of the “true” initiating species followed by subsequent ring opening [80]. The catalysts used in these studies are hydrated metal salts. As a result such interactions are feasible. Induction periods using water as an initiator is well documented [73].

The $\ln([\text{M}]_0/[\text{M}]_t)$ versus time plots (Figs. 7 and 8) exhibit linear variation. From the slope of the plots, the values of the

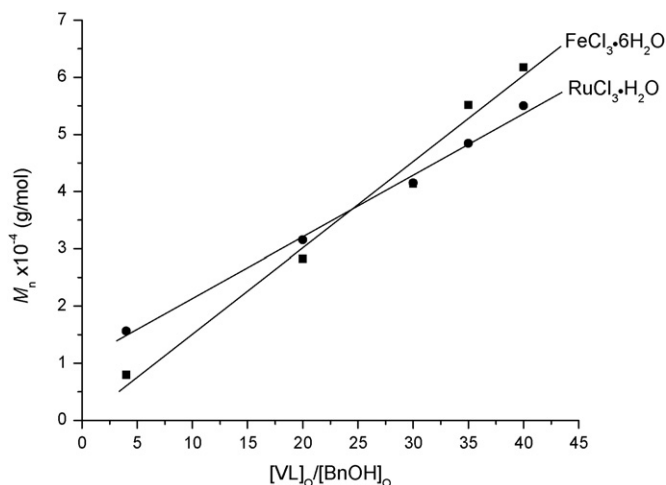


Fig. 4. Plot of M_n vs feed ratio of VL to BnOH at 27 °C.

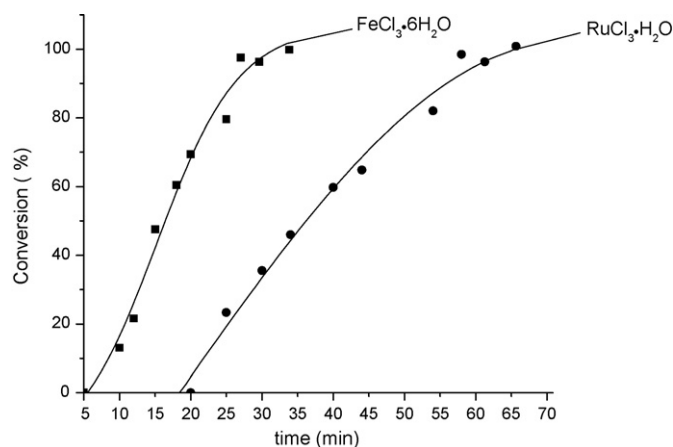


Fig. 5. CL conversion vs time plot using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$: $[\text{M}]_0/[\text{Cat}]_0 = 200$ at 27 °C.

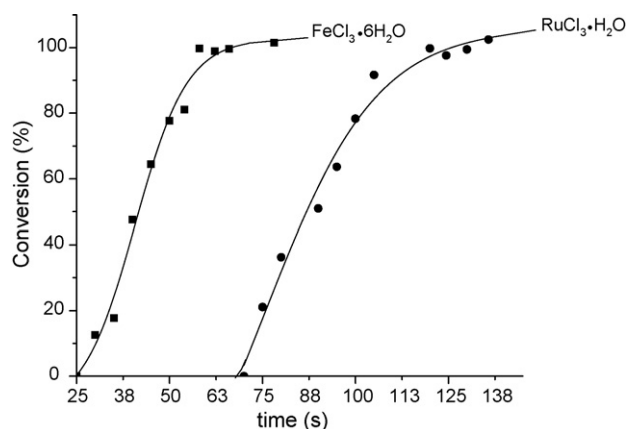


Fig. 6. VL conversion vs time plot using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$: $[\text{M}]_0/[\text{Cat}]_0 = 200$ at 27 °C.

apparent rate constant (k_{app}) for CL polymerizations initiated by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ were found to be $7.38 \times 10^{-2} \text{ min}^{-1}$ and $4.80 \times 10^{-2} \text{ min}^{-1}$ and k_{app} for VL polymerizations were estimated to be $5.43 \times 10^{-2} \text{ s}^{-1}$ and $4.48 \times 10^{-2} \text{ s}^{-1}$. The orders of magnitude of k_{app} for CL polymerization indicate that these are much faster than the results known for iron alkoxides [36] and ruthenium phosphine derivatives [74].

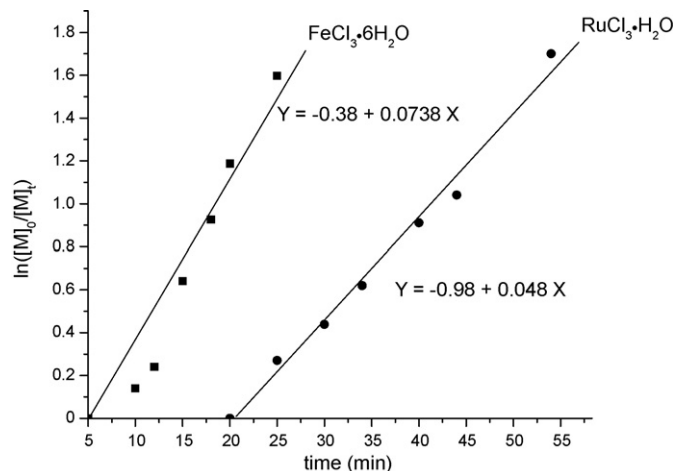
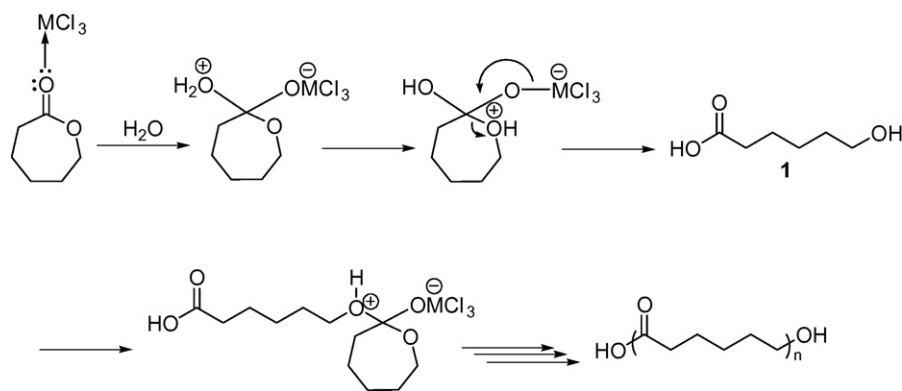


Fig. 7. Semilogarithmic plots of CL conversion in time initiated by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$: $[\text{M}]_0/[\text{Cat}]_0 = 200$ at 27 °C.



Scheme 1. Reaction pathway for CL polymerization.

3.3. Mechanism of polymerization

To gain insight into the polymerization characteristics and final composition of the product, it was decided to investigate the polymerization using CL and VL more closely. Low molecular weight oligomers of poly(caprolactone) and poly(valerolactone) were synthesized by stirring these monomers with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ in 15:1 molar ratio under neat conditions at 27°C . The product was extracted with heptane. In all the cases the residue (after removal of heptane) were analyzed thoroughly using MALDI-TOF. In case of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$, the product was analyzed using ^1H NMR spectroscopy. Using CL as the substrate for such studies, MALDI-TOF results reveals the major product of the composition $\text{HO}[\text{CO}(\text{CH}_2)_5\text{O}]_n\text{H}$ which is further supported by ^1H NMR spectroscopy (see [supporting material](#)).

These observations can be rationalized by considering the reaction pathway depicted in [Scheme 1](#).

If ϵ -hydroxycaproic acid (**1**) is assumed as a polymerization intermediate, it must act as an initiator and possess the capability of initiating polymerization when used along with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{RuCl}_3 \cdot \text{H}_2\text{O}$. Low molecular weight oligomers of poly(caprolactone) were synthesized by stirring CL with $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ in the presence of **1** as the initiator in 15:1:2 molar ratio under neat conditions at 27°C . The work up was done in a similar manner. The ^1H NMR spectrum of the crude product had the same characteristics when $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ was used alone. Polymerizations using CL, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{RuCl}_3 \cdot \text{H}_2\text{O}$, and **1** in the ratio 200/1/5 were conducted inde-

pendently at 27°C . For $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, the polymerization time is 6.6 min ($M_n = 7.84 \times 10^{-4}$ g/mol, $M_w/M_n = 1.39$) and for $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ the polymerization time is 10.8 min ($M_n = 8.01 \times 10^{-4}$ g/mol, $M_w/M_n = 1.42$). The polymerization is much faster (Entries 1 and 14 of [Table 2](#)), providing sufficient credence to **1** being considered as a true intermediate. Hence, **1** is a suitable initiator towards the synthesis of poly(caprolactone) with $-\text{OH}$ end terminal groups.

For VL, MALDI-TOF results reveals the major product of the composition $\text{HO}[\text{CO}(\text{CH}_2)_4\text{O}]_n\text{H}$ which is further supported by ^1H NMR spectroscopy (see [supporting material](#)).

The attributes of such a working hypothesis suggests the formation of poly(caprolactone) with $-\text{OH}$ end terminal groups if water is used as an initiator.

To understand the effect of BnOH, CL or VL along with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and BnOH in the ratio 15:1:2. On a similar basis the reaction mixtures were analyzed using MALDI-TOF and ^1H NMR spectroscopy for reactions using $\text{RuCl}_3 \cdot \text{H}_2\text{O}$. MALDI-TOF results reveal the major product of the composition $\text{PhCH}_2\text{O}[\text{CO}(\text{CH}_2)_5\text{O}]_n\text{H}$. This is further substantiated by ^1H NMR spectroscopy in the case where $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ was used. These results are shown in [Figs. 9 and 10](#) respectively.

Analysis of [Fig. 9](#) reveals the presence of $\text{HO}[\text{CO}(\text{CH}_2)_5\text{O}]_n\text{H}$ ($m/z = 611.5, 725.6, 839.7, 953.8, \dots$) in addition to the peaks indicating the required product. Since we are using hydrated salts as initiators, the presence of peaks indicating the role of H_2O is obvious. On the basis of [Scheme 1](#), one may consider $\text{BnO}-\text{C}(\text{O})(\text{CH}_2)_5\text{O}-\text{H}$ (**2**) as the possible intermediate. For understanding the authenticity of this pathway, bench scale polymerization of CL using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ in the presence of requisite amounts **2** in the ratio 200/1/5 were performed at 27°C . For $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, the polymerization time is 15 min ($M_n = 9.22 \times 10^{-4}$ g/mol, $M_w/M_n = 1.40$) and for $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ the polymerization time is 27 min ($M_n = 6.83 \times 10^{-4}$ g/mol, $M_w/M_n = 1.37$). Similar studies with VL indicated a polymer of composition $\text{PhCH}_2\text{O}[\text{CO}(\text{CH}_2)_4\text{O}]_n\text{H}$ as the major product (see [supporting material](#)).

The results presented here indicate the ring opening polymerizations to proceed by an activated monomer mechanism [81–82]. An intuition to support this is that the polymerization of BL is the fastest followed by VL and then CL. This is against the conventional coordination–insertion mechanism wherein the trend would be the reverse with the polymerization of CL being the fastest due to largest ring strain [83].

3.4. Comparison of polymerization results

In order to compare our results with those known for iron [36] and ruthenium [74] based catalysts we present here results for poly-

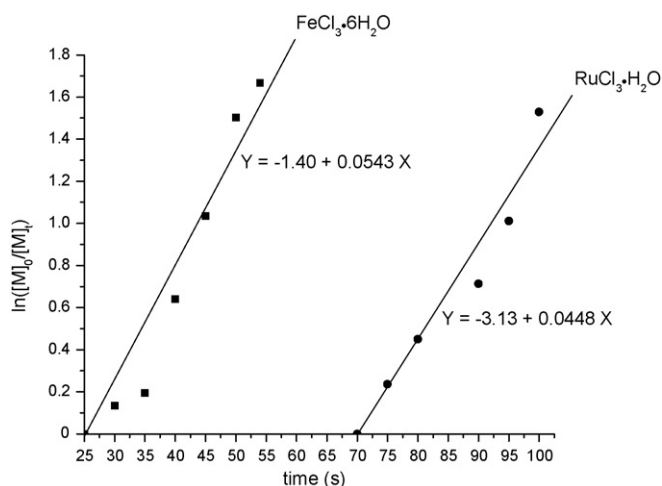


Fig. 8. Semilogarithmic plots of VL conversion in time initiated by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$: $[M]_0/[Cat]_0 = 200$ at 27°C .

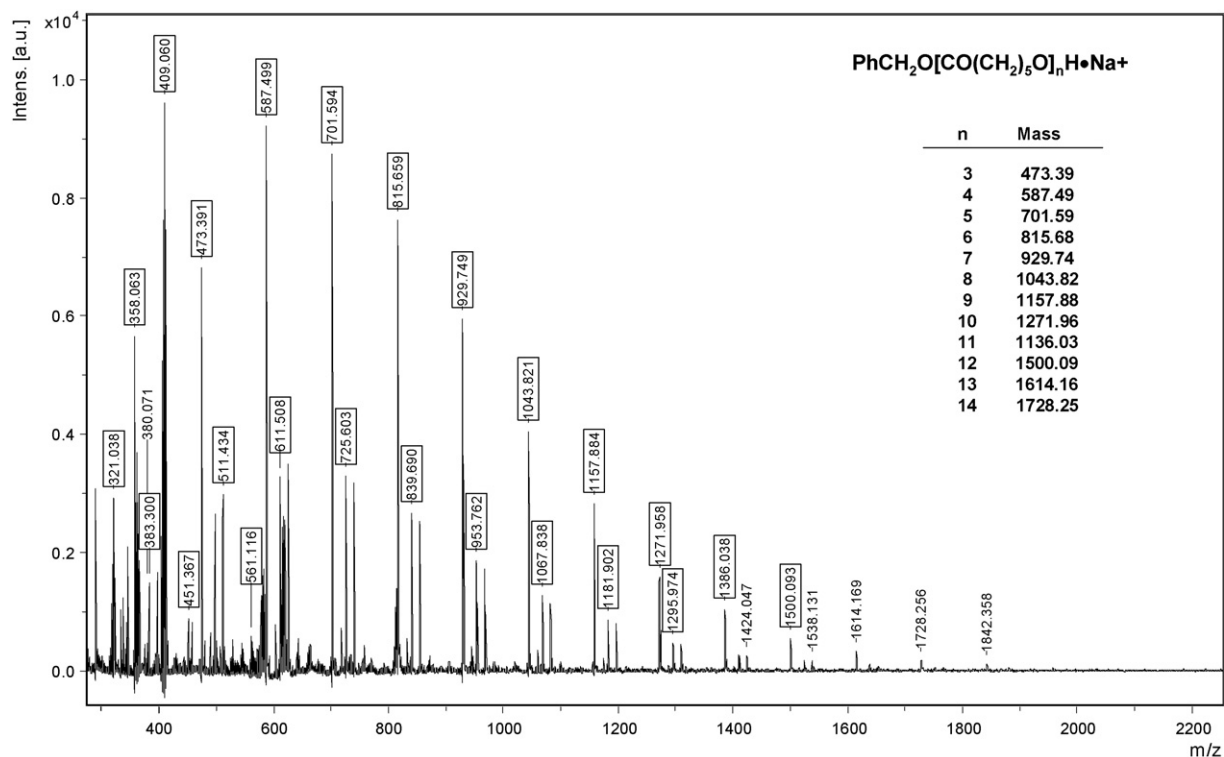


Fig. 9. MALDI-MS of the crude product obtained from a reaction between CL and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ along with BnOH in 15:1:2 ratio.

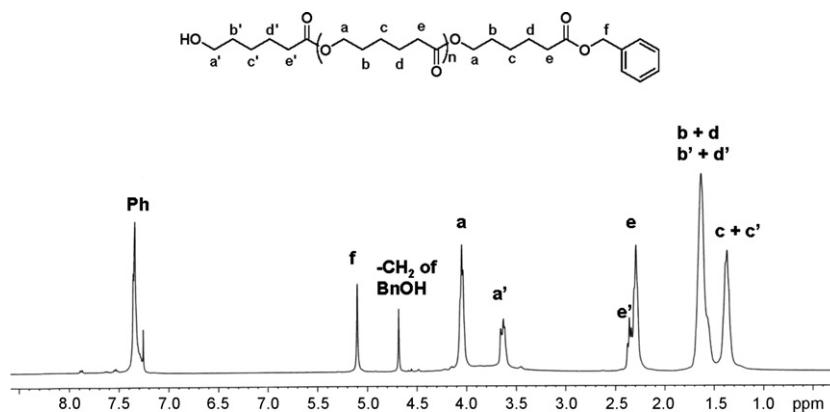


Fig. 10. ^1H NMR spectrum of the crude product obtained from a reaction between CL and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ along with BnOH in 15:1:2 ratio.

merizations conducted in the presence of toluene (Tables 5 and 6 respectively).

In the case of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, our results for CL polymerizations (Tables 5 and 6) are superior or comparable to the ones reported using alkoxide based ligand environments around iron [36] in terms of control of M_n and MWDs, polymerization time and much larger k_{app} . Using $\text{RuCl}_3 \cdot \text{H}_2\text{O}$, our results prove better in terms of larger k_{app} and narrower MWDs in comparison to the results reported for complexes having phosphine ligand environment around ruthenium [74]. Such observations are also seen for the bulk polymerizations conducted in the absence of solvents.

We have noticed that polymerizations in the absence of nitrogen atmosphere or using undistilled solvent or monomers led to extensive transesterification reaction leading to the formation of low molecular weight oligomers.

Table 5

Results of CL, VL and BL polymerization using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ in 200:1 ratio at 27 °C in toluene.

Entry	Monomer (M)	Catalyst (Cat)	t^a (min)	Yield (%)	$M_n^b/M_{th}^c \times 10^{-4}$	M_w/M_n
1	CL	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	1.0 (h)	100	3.12/2.28	1.27
2	CL	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	1.5 (h)	100	2.26/2.28	1.26
3	VL	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	9.6	100	8.22/2.00	1.19
4	VL	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	12.6	100	8.02/2.00	1.13
5	BL	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	6.0	100	2.97/1.72	1.21

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.

^b Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n in the case of CL polymerizations [71].

^c Calculated from $MW_{M_0}([M]_0/[Cat]_0)$.

Table 6

Results of CL, VL and BL polymerization using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ in the presence of BnOH in 200:1:5 ratio at 27 °C in toluene.

Entry	Monomer (M)	Catalyst (Cat)	t^a (min)	Yield (%)	$M_n^b/M_{th}^c \times 10^{-4}$	M_w/M_n
1	CL	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	30.0	100	1.82/0.47	1.25
2	CL	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	50.0	100	1.26/0.47	1.28
3	VL	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	6.0	100	5.45/0.41	1.18
4	VL	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	8.4	100	2.73/0.41	1.23
5	BL	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	3.0	100	1.92/0.35	1.20

^a Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.

^b Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n in the case of CL polymerizations [71].

^c Calculated from $MW_{M_0}([M]_0/[I]_0) + MW_{\text{BnOH}}$.

4. Conclusion

In summary, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ are potent towards the ring opening polymerization of lactones. Alcohol initiators enhance the tendency of polymerization and produce an alkoxy end terminal functionalized product. The major initiation pathway in the polymerization is understood to be the activated monomer mechanism and can be used towards the synthesis of telechelic polymers with tunable properties. This polymerization contributes to an economical process employing readily available commercial inorganics as catalysts and does not necessitate solvents. The overall system is green, eco friendly and environmentally benign since iron is a natural human constituent and these polymers being biodegradable. The achievement of obtaining good molecular weights without having to resort to elaborate ligands is a noted feature for our system.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.11.010.

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