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Ring-opening polymerization of lactones by rare-earth metal triflates and by their reusable system in ionic liquids

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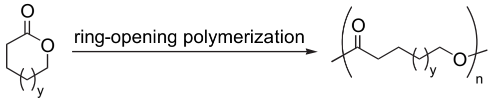
For the creativity, originality, and impact of his research on polymer chemistry as well as on organic chemistry, this paper is dedicated to Professor Hisashi Yamamoto with hearty respect

Abstract—The ring-opening polymerizations (ROPs) of lactones catalyzed by rare-earth metal trifluoromethanesulfonates (triflates) ($RE(OTf)_3$) were examined. Among various complexes, scandium triflate ($Sc(OTf)_3$) emerged as an effective catalyst in toluene. The ROP of lactones by $Sc(OTf)_3$ proceeded in a living fashion, and the number of polymer molecules was controlled by the amount of protic additives such as benzyl alcohol and H_2O. In other words, one molecule of $Sc(OTf)_3$ catalytically produced a number of polymer molecules (up to 40 molecules) depending on the amount of protic additives. The plausible mechanism was depicted as an activated monomer mechanism. The polylactones with a number-average molecular weight over 25,000 were successfully synthesized. Immobilization of $RE(OTf)_3$ was investigated in three ionic liquids, and cerium triflate ($Ce(OTf)_4$) showed relatively high catalytic activity in a biphasic system of 1-butyl-3-methylimidazolium hexafluoroantimonate and toluene in the ROP of ε-caprolactone (CL). The ionic liquid containing $Ce(OTf)_4$ was used, at least three times, in the ROP of CL without losing catalytic activity.

1. Introduction

Lewis acids are arguably one of the most versatile tools in organic synthesis.[1] Although a number of Lewis acids have been designed for any purpose, most of those designed and sophisticated Lewis acids do not tolerate moisture/water in general, so that rigorously anhydrous conditions are required in the reaction systems. Under such a situation, Kobayashi introduced $RE(OTf)_3$ in organic synthesis as extremely robust Lewis acids dealing with this problem.[2] One of their most fascinating features is the tolerance of a Lewis base such as water. In spite of their splendid success in organic synthesis,[1–3] their applications in the field of polymer synthesis are still limited.[4–7]



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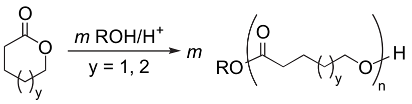
Aliphatic polyesters have received considerable attention due to their biocompatibility and biodegradability because we are recently concerned about our environment.[8] The controlled/living ROP of lactones[9] (Eq. 1) is the most practical method for synthesizing the polyesters with desired molecular weights in a narrow polydispersity range that is suitable for medical applications. Furthermore, it is an ideal process to synthesize the polyester from the standpoint of atom economy.[10] In the literature, most of the living ROP processes for lactones are reported via an anionic or coordination–insertion mechanism,[8,9,11] while there are only few of the cationic type because many of the cationic polymerizations easily cause side reactions, which terminate the propagation reaction. Even the most successful living cationic systems reported by Mukaiyama[12] are problematic for two reasons: (i) initiators/catalysts are extremely air and moisture sensitive; (ii) each molecule of the initiator produces only one molecule of the polymer at most, so that the process is a stoichiometric reaction in the sense of the number of molecules between the initiator and the polymer. A solution to these problems was found in the literature, in which Brønsted–Lowry acids catalyzed the ROPs of lactones[13,14] (Eq. 2). However, the number of these studies is small and their application is undeveloped.



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We investigated the ROP of lactones catalyzed by RE(OTf)$_3$ and found that Sc(OTf)$_3$ efficiently polymerized CL and δ-valerolactone (VL) in the controlled/living manner at ambient temperature. We also examined three ionic liquids[15] as immobilizing media for RE(OTf)$_3$ for the purpose of recycling the catalyst.

2. Results and discussions

2.1. RE(OTf)$_3$-catalyzed ROPs of lactones

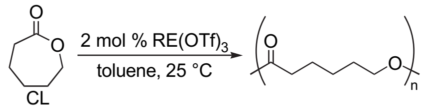
2.1.1. Various RE(OTf)$_3$-catalyzed ROPs of CL. At the outset of our study on the RE(OTf)$_3$-catalyzed ROP of lactones, we scouted effective catalysts among the various commercially available RE(OTf)$_3$ materials (Table 1). In the presence of 2 mol % of RE(OTf)$_3$ under a N_2 atmosphere, the ROP of CL in toluene was examined. The polymerization was traced by TLC analysis and quenched when CL was completely consumed or after 120 h. The poly(ε-caprolactone) (PCL) was successfully obtained by Sc(OTf)$_3$ in quantitative yield after 2 h, and the polydispersity index (PDI, M_w/M_n) was rather small (PDI 1.1_3, entry 1). By contrast, the ROP by congeneric Y(OTf)$_3$ was sluggish[16] and the number-average molecular weight (M_n) by size-exclusion chromatography (SEC) was small with a larger PDI (entry 2). La(OTf)$_3$ was more effective than Y(OTf)$_3$ but less than Sc(OTf)$_3$. The other lanthanide complexes were inferior to Sc(OTf)$_3$ and La(OTf)$_3$ (entries 4–9). As far as we examined, no clear tendency was found between the catalytic activity and the ionic radius of each metal. Although La is less expensive than Sc, we focused on Sc(OTf)$_3$ to investigate the ROP of lactones due to its high reactivity in the ROP of CL and its high versatility in various organic reactions.

2.1.2. Sc(OTf)$_3$-catalyzed ROP of lactones. It is notorious that lanthanide salts are difficult to obtain in an anhydrous state.[17] Because H_2O might have affected the polymerization somehow, we tried to dry Sc(OTf)$_3$. However, we faced a significantly reduced catalytic activity of Sc(OTf)$_3$ when it was simply heated in vacuo, so that we searched for an appropriate process to dry it. Although we do not have good reasons to explain it, we assume that tight aggregation of Sc(OTf)$_3$, which is not loosened by the addition of lactones, occurs by heating in vacuo. Lyophilized Sc(OTf)$_3$ in benzene prior to use was convenient and gave reproducible results, so that lyophilization was applied to all experiments from then on. The ROP of CL by 2 mol % of lyophilized Sc(OTf)$_3$ proceeded in toluene at 25 °C for 4 h under N_2, and PCL was obtained in quantitative yield (entry 1, Table 2). Although it needed a longer time than Sc(OTf)$_3$ used as purchased (entry 1, Table 1), the M_n value became twofold. The M_n value increased linearly with the conversion of CL, and the PDIs maintained between 1.1 and 1.2 throughout the polymerization. To investigate the effects of protic compounds on this polymerization, various amounts of benzyl alcohol (BnOH) were added. An excess amount of BnOH added to Sc(OTf)$_3$ did not terminate but rather accelerated the polymerization (entries 2–4). Meanwhile, M_n decreased as the amount of BnOH increased. Interestingly, VL, which has less ring-strain energy than CL,[18] was polymerized by Sc(OTf)$_3$ in a shorter time even at 0 °C, and the same effects of BnOH on M_n were observed (entries 5–8).

As shown in Table 2, the M_n of the polymer was dependent on the amount (mole percent) of BnOH. We suspected that lyophilized Sc(OTf)$_3$ still contained H_2O, which played the same role as BnOH. It was also suggested by the result of entry 1 of Table 1, in which Sc(OTf)$_3$ used as purchased gave the PCL with a smaller M_n value. We experimentally pursued the amount of H_2O in lyophilized Sc(OTf)$_3$ by analyzing the correlations among the amounts of Sc(OTf)$_3$, the M_ns, and the amounts of BnOH. The correlations of M_ns in Table 3 indicated that one molecule of Sc(OTf)$_3$ should have released one molecule of H_2O.

The high efficiency of this system and the less effects of H_2O in Sc(OTf)$_3$ on M_n values could be documented by reactions using excess amounts of protic compounds with Sc(OTf)$_3$ (Table 4). The polymerization of CL in the presence of 20 equiv of BnOH (2.0 mol %) with Sc(OTf)$_3$ (0.10 mol %) afforded quantitative PCL with a narrow PDI without difficulties (entry 1). The singlet methylene peak of benzylic protons (5.12 ppm) and the triplet methylene peak of RC*H*$_2$OH (3.62 ppm) were observed in the ^{1}H NMR spectrum. The average degree of polymerization

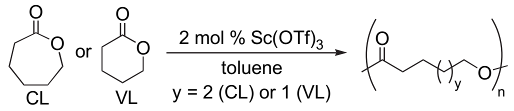
Table 1. RE(OTf)$_3$-catalyzed ROP of CL[a]



Entry	RE(OTf)$_3$	Time, h	Yield, %	M_n[b]	M_w/M_n[b]
1	Sc	2	100	3500	1.1_3
2	Y	120	100	1700	1.2_9
3	La	3	100	2900	1.1_6
4	Ce[c]	8.5	100	1800	1.2_1
5	Nd	120	70	900	1.1_9
6	Eu	114	100	1700	1.2_2
7	Gd	120	74	1600	1.1_7
8	Yb	30	100	1700	1.2_3
9	Lu	91	99	2200	1.3_0

[a] Polymerization conditions: CL, 0.110 mL (0.99 mmol); catalyst, 0.020 mmol (2 mol %); BnOH, 0.020 mmol; toluene, 1 mL; temp, 25 °C.
[b] Estimated by SEC (polystyrene standards, $CHCl_3$).
[c] Ce(OTf)$_4$.

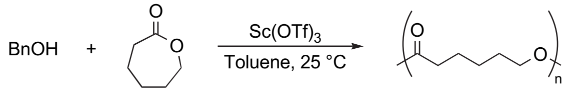
Table 2. Sc(OTf)$_3$-catalyzed ROP of CL in the presence of various amounts of BnOH[a]



Entry	Monomer	BnOH, mol %	Time, h	Yield, %	M_n[b]	M_w/M_n[b]
1	CL	0	4	>99	6900	1.1_3
2		2	2.3	>99	3500	1.1_3
3		5	2	>99	2400	1.1_7
4		10	2	>99	1600	1.1_8
5	VL	0	1.5	96	4300	1.1_5
6		2	1	95	2900	1.1_7
7		5	1	97	1900	1.1_8
8		10	1	95	1400	1.1_7

[a] Sc(OTf)$_3$, 2 mol % (0.02 mmol); CL or VL, 1.0 mmol; toluene, 1.0 mL; temp, 25 °C (CL) or 0 °C (VL).
[b] Estimated by SEC ($CHCl_3$, polystyrene standards).

Table 3. Estimation of the amount of H_2O in $Sc(OTf)_3$[a]



BnOH, mol %	1 mol % of Sc M_n		2 mol % of Sc M_n
0	(13,400)[b]	← x 2	6,900
	↑ x 3	↖ x 4	↑ x 2
2	4,400	← x 4/3	3,500

[a] The M_n values were obtained at a nearly quantitative conversion of CL ($\geq$98%), unless otherwise noted. All PDI values were between 1.0_9 and 1.1_4.

[b] The M_n value was calculated from the linear relationship between the conversion of CL and M_n (14%–2000; 44%–6100; 54%–7900; 73%–9500) using a least-squares method.

Table 4. Catalytic approach to the ROP of lactones using $Sc(OTf)_3$ in the presence of ROH[a]

Entry	Monomer	$Sc(OTf)_3$, mol %	ROH (mol %)	Time, h	Yield, %	M_n[b]	M_w/M_n[b]
1	CL	0.10	BnOH (2.0)	120	>99	7500	1.1_2
2	CL	0.10	H_2O (2.0)	120	>99	7700	1.1_0
3	VL	0.10	BnOH (2.0)	16	>99	7500	1.1_5
4	VL	0.05[c]	BnOH (2.0)	36	>99	7200	1.1_5

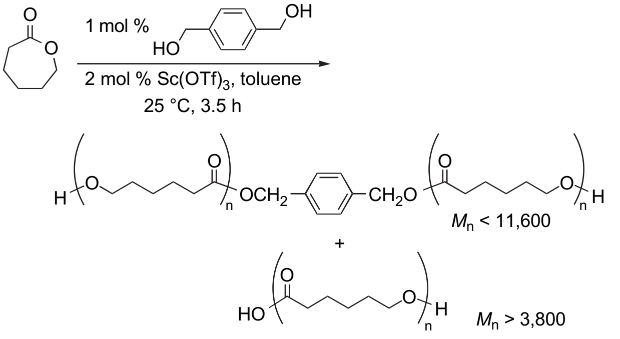
[a] Polymerization conditions: $Sc(OTf)_3$, 0.020 mmol; CL or VL, 20 mmol; toluene, 20 mL; temp, 25 °C (CL) or 0–25 °C (VL).

[b] By SEC ($CHCl_3$, polystyrene standards).

[c] $Sc(OTf)_3$, 0.010 mmol.

(DP) by ^1H NMR was estimated to be 50. This result was consistent with the calculation based on 2 mol % of ROH (DP=50), not on 0.10 mol % of $Sc(OTf)_3$ (DP=1000). H_2O instead of BnOH also functioned as an additive and the DP by ^1H NMR was 47 (entry 2). The obtained polymer was an attractive telechelic α-carboxylic-ω-hydroxy functional PCL. It should be noted that excess carboxylic acid in the reaction system did not affect the catalytic activity of $Sc(OTf)_3$. Because VL was more reactive in this system, an even lesser amount (0.05 mol %) of $Sc(OTf)_3$ in the presence of 2 mol % of BnOH was sufficient (entry 4). This catalytic approach can minimize the effects of contamination of H_2O from lyophilized $Sc(OTf)_3$, and the molecular weights of PCLs are highly controlled. In the most successful living cationic polymerization of lactones before, one molecule of the reactive metal complex produced, at most, one polymer molecule.[12] On the contrary, one molecule of $Sc(OTf)_3$ produced a large number of polymer molecules, up to 40 molecules (entry 4), which was controlled by the amount of inert ROH, and the present polymerization system appeared to be catalytic in the sense of the number of molecules between polymer and reactive $Sc(OTf)_3$.

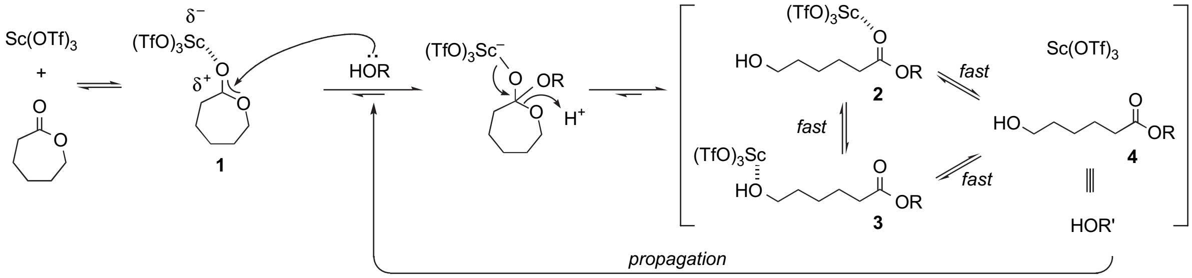
We also examined other protic additives. The polymerization using 2 mol % of benzylamine ($BnNH_2$) sluggishly proceeded, while the oligomer (M_n=800, PDI=1.2_4) was afforded after 5 days. On the other hand, the quantitative conversion of CL was observed after 21 h in the presence of 2 mol % of diphenylamine (Ph_2NH), although the molecular weight was not controlled (M_n=1500, M_w/M_n=1.1_8). Due to the strong coordination of the amide group to $Sc(OTf)_3$, the Lewis acidity of $Sc(OTf)_3$ might have been diminished. A diol, *p*-xylylene glycol, appeared to be an efficient additive (Eq. 3). The ROP of CL occurred from both the hydroxy groups of *p*-xylylene glycol (1 mol %), which was confirmed by ^1H NMR. The SEC trace of the crude polymer was bimodal. Probably, the α-(carboxylic acid)-ω-hydroxyl PCL also formed by H_2O of lyophilized $Sc(OTf)_3$. The two reaction sites of *p*-xylylene glycol lead to a PCL with a twofold M_n value relative to the PCL afforded by H_2O. The approximate M_n values by SEC suggested that our assumption should be reasonable.



(3)

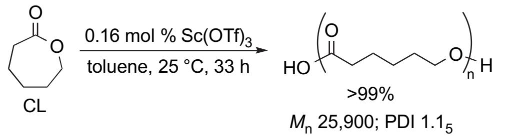
The formation of benzyl ester at the early stage of polymerization was confirmed by the consumption of BnOH by TLC and the ^1H NMR spectrum of the reaction mixture. A plausible activated monomer mechanism[13,14] is presented in Scheme 1. Coordination of CL to $Sc(OTf)_3$ affords the cationic complex **1**, which is attacked by ROH to produce the corresponding linear ester. The rapid equilibria among **2**, **3**, and **4** played a crucial role in promoting the polymerization. $Sc(OTf)_3$ is preferentially coordinated by CL under a rapid equilibria to form **1**. The free hydroxy ester **4** can serve as an alcohol (R′OH) and attacks electrophilic **1**. There are three keys to this polymerization: the equilibria among **2**, **3**, **4**, and reactive **1** should be rapid; monomer CL is more Lewis basic than the linear (poly)ester; the Lewis acid should discriminate the slight difference in Lewis basicity. If the linear (poly)esters are more Lewis basic, the propagation reaction will be sluggish, and a controlled PDI will not be expected due to the side reaction of ester exchanges between polymers. One of the suggestions to support this mechanism is the fact that VL polymerizes much faster than CL does. In the conventional ROPs of lactones in a coordination–insertion mechanism, CL is polymerized faster than VL due to the larger ring-strain.[18] However, the Lewis basicity is more important in the ROP of lactones via an activated monomer mechanism.[13a,19]

Some compounds such as $Et_3O^+\cdot PF_6^-$ and $Et_3O^+\cdot SbF_6^-$ were known as catalysts that promote the ROP of lactones in the presence of ROH via an activated monomer mechanism, although they were limited only in the synthesis of polymers with relatively small M_n values ($M_n\leq3500$). The ROPs of CL and VL to synthesize the polyesters with higher M_n values were carried out. Taking the mechanism into consideration, maintaining higher concentrations of $Sc(OTf)_3$ and ROH by slow addition of CL or VL in toluene should be



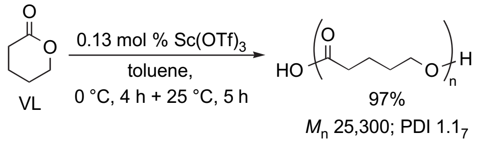
Scheme 1. A plausible mechanism of the ROP of CL by $Sc(OTf)_3$ via an activated monomer mechanism.

effective to complete the polymerization in a short time. The ROPs of CL and VL were carried out by multi-additions of monomer CL/VL by tracing the consumption of CL/VL by TLC, and corresponding polyesters with higher M_n values were obtained as shown in Eqs. 4 and 5. When the ROP of CL was conducted under the final conditions in Eq. 4 from the beginning, it took 4 days to obtain a similar PCL. Assuming that the polymerization proceeded via a coordination–insertion mechanism by formation of Sc–OR bonds, the procedure in Eq. 4 should not be effective.



(4)

Conditions: $Sc(OTf)_3$, 10 mg (20 μmol); CL/toluene (time), 330 μL/1 mL (3 h) + 330 μL/1 mL (6 h) + 660 μL/2 mL (24 h).



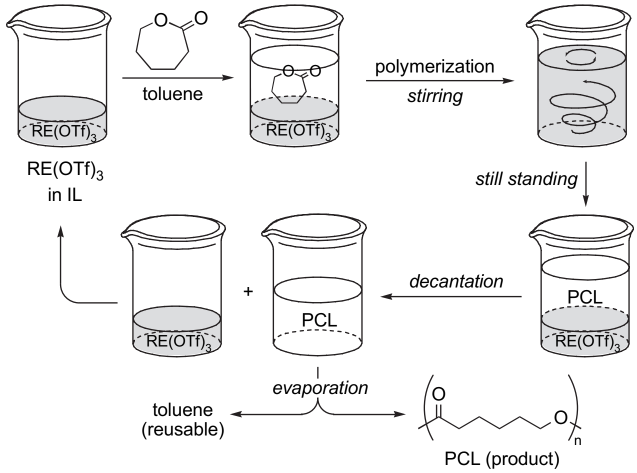
(5)

Conditions: $Sc(OTf)_3$, 10 mg (20 μmol); VL/toluene (temp., time), 280 μL/1 mL (0 °C, 2 h) + 280 μL/1 mL (0 °C, 2 h; 25 °C, 1 h) + 280 μL/1 mL (1 h) + 280 μL (25 °C, 8 h).

Because the ROP of CL and VL proceeded in a controlled manner, the block polymer synthesis of PCL and PVL was examined. The SEC traces of both the PCL-*block*-PVL and PVL-*block*-PCL were bimodal. We have assumed that the heterogeneous $Sc(OTf)_3$ in toluene had something to do with this. Addition of the same monomer maintains the polarity of the reaction mixture, which does not cause the problems (see Eqs. 4 and 5), while addition of another monomer changes the polarity in the polymerization system. Probably, some insoluble $Sc(OTf)_3$ gets soluble by change of polarity and releases H_2O that can be the initiation terminus of the homopolymerization of the second monomer.

2.2. ROP of CL by $RE(OTf)_3$ in ionic liquids

2.2.1. Screening of $RE(OTf)_3$-ILs. Ionic liquids (ILs) are liquid salts at low temperature (<100 °C).[15b] Some ILs are insoluble both in H_2O and in many conventional organic solvents. However, ILs dissolve various inorganic compounds. Due to their characteristics, ILs, especially room-temperature ones, have been applied to many organic reactions as environmentally friendly reaction media.[20,21] In polymer chemistry, there are reports of polymer syntheses by using IL,[20,22,23] although they are still under development. We investigated the immobilization of $RE(OTf)_3$ in ionic liquids for the repeated use of metal complexes (Scheme 2). To $RE(OTf)_3$ in an IL is added CL in toluene, and the two-phase mixture is vigorously stirred to polymerize CL. When CL is completely converted into PCL, the reaction mixture is left at rest and the PCL in toluene is collected by decantation. The ROP of CL in the biphasic reaction ideally affords the product PCL without any waste products, so that no purification is required. If the $RE(OTf)_3$ is completely immobilized in the IL, evaporation of toluene of the organic phase affords pure PCL. The evaporated toluene can also be reused as a solvent.



Scheme 2. A schematic ROP of CL using reusable $RE(OTf)_3$ in an ionic liquid.

To see how Scheme 2 works, we focused on 1-butyl-3-methylimidazolium (BMIM) salts due to their easy access and stability when exposed to air and moisture. All polymerizations were traced by TLC analysis at 25 °C. Using three ionic liquids, [BMIM][BF_4], [BMIM][PF_6], and [BMIM][SbF_6], various $RE(OTf)_3$s were screened (Table 5). When the counter anion of BMIM was BF_4^-, all polymerization reactions were very slow to afford only oligomers ($M_n \leq 600$) (entries 1–9). To our surprise, $Sc(OTf)_3$ and $Eu(OTf)_3$ did not polymerize CL in [BMIM][BF_4] (entries 1

Table 5. The ROP of CL by RE(OTf)$_3$ in ILs[a]

Entry	RE	X$^-$	Time, h	Yield, %	M_n	M_w/M_n
1	Sc	BF_4^-	2 d	0	—	—
2	Y		7 d	29	500	1.1_5
3	La		2 d	29	300	1.1_6
4	Ce[b]		6 d	32	600	1.2_0
5	Nd		6 d	30	500	1.2_0
6	Eu		2 d	0	—	—
7	Gd		5 d	30	600	1.2_1
8	Yb		4 d	27	500	1.2_1
9	Lu		3 d	26	500	1.1_7
10	Sc	PF_6^-	42	80	2500	1.4_4
11	Y		53	83	2800	1.4_2
12	La		46	100	3700	1.5_3
13	Ce[b]		47	100	3500	1.5_6
14	Nd		35	100	2700	1.4_1
15	Eu		49	100	2400	1.4_5
16	Gd		48	100	3400	1.5_0
17	Yb		48	43	1600	1.5_3
18	Lu		47	100	4400	1.4_9
19	Sc	SbF_6^-	30	87	900	1.3_1
20	Y		48	99	1800	1.2_4
21	La		42	100	1800	1.2_1
22	Ce[b]		29	100	1700	1.2_2
23	Nd		43	100	1700	1.2_7
24	Eu		48	44	1500	1.1_3
25	Gd		29	100	2500	1.2_5
26	Yb		48	82	1400	1.2_1
27	Lu		48	80	1100	1.1_8

[a] Polymerization conditions: RE(OTf)$_3$, 20 μmol; ionic liquid ([BMIM]X), 0.50 mL; CL, 0.11 mL (0.99 mmol); toluene, 1.0 mL; temp, 25 °C; N_2.
[b] Ce(OTf)$_4$.

and 6). In sharp contrast, all complexes in [BMIM][PF$_6$] were effective in affording PCL (entries 10–18). The La, Ce, Gd, and Lu complexes produced PCL with relatively higher M_n values (entries 12, 13, 16, and 18). Sb is a congener of P, and results similar to those of the [BMIM][PF$_6$] system were obtained (entries 19–27). The organic and IL phases became inseparable emulsions when Sc(OTf)$_3$, Eu(OTf)$_3$, Gd(OTf)$_3$, and Lu(OTf)$_3$ were used (entries 19, 24, 25, and 27). These results suggested that interactions between rare-earth metals and the counter anions of ILs should effect polymerization reactions. Although drastic improvements were not observed by changing the counter anions of ILs, the ROP of CL occurred in the biphasic system of organic solvent and IL.

2.2.2. Recyclable system using Ce(OTf)$_4$–[BMIM][SbF$_6$]. The ROP of CL using Ce(OTf)$_4$–[BMIM][SbF$_6$] was relatively efficient from the view point of the reaction time and yield, and the recyclable catalysis according to Scheme 2 was examined. After the first ROP of CL, the organic phase was separated from the ionic liquid, which contained Ce(OTf)$_4$. The toluene solution was concentrated in vacuo to afford analytically pure PCL. The remaining Ce(OTf)$_4$–[BMIM][SbF$_6$] was repeatedly used (Table 6). The first cycle was slightly slower than others (cycles 2 and 3) to reach quantitative conversion. The reused Ce(OTf)$_4$–[BMIM]-[SbF$_6$] polymerized CL without losing the catalytic activity, and the obtained PCLs were consistent. We expected that the afforded PCL would be a higher polymer as Ce(OTf)$_4$–[BMIM][SbF$_6$] was repeatedly used, because H_2O of Ce(OTf)$_4$ would be consumed by the initiation reactions of the first cycle. However, our expectation did not observed. ^{1}H NMR clearly indicated the existence of terminal CH_2OH, while the initiation terminus was not detectable. Although the initiation reaction is unknown yet, we documented that the ionic liquids were suitable for immobilizing RE(OTf)$_3$.

Table 6. The ROP of CL using recyclable Ce(OTf)$_4$–[BMIM][SbF$_6$][a]

Cycle	Time, h	Yield, %	M_n	M_w/M_n
1	29	100	2000	1.3_2
2	23	100	2100	1.4_2
3	23	100	2000	1.4_9

[a] Polymerization conditions, see footnotes of Table 5.

3. Conclusions

Here we reported a living cationic ROP of lactones in toluene using Sc(OTf)$_3$ via an activated monomer mechanism and the ROP of CL by recyclable Ce(OTf)$_4$–[BMIM][SbF$_6$]. Among various rare-earth metal triflates, Sc(OTf)$_3$ emerged as an efficient catalyst in toluene under mild conditions and did not lose the catalytic activity in the presence of ROH/H_2O. However, ROH/H_2O controlled the number of polymer molecules, which consequently controlled the molecular weight of the polymer at a certain conversion of the monomer. That is, this polymerization was a catalytic version of the living cationic ROP in the sense of the number of polymer molecules. In our experiments, up to 20 molecules of PCL or 40 molecules of PVL were synthesized from one molecule of Sc(OTf)$_3$ using BnOH as an additive. In addition, PCL and PVL over M_n 25,000 were synthesized in this polymerization system. Immobilization of RE(OTf)$_3$ in ionic liquids to establish a recyclable ROP system was successful. Although the initiation reaction was not clear and M_n was not controllable yet, Ce(OTf)$_4$–[BMIM][SbF$_6$] was a recyclable catalyst for the ROP of CL.

4. Experiments

4.1. General

All manipulations were carried out using standard Schlenk-line techniques, and all reactions were performed in oven-dried glassware under a N_2 atmosphere. ^{1}H NMR spectra were recorded on Varian Gemini-300 in $CDCl_3$. Molecular weights of the polymers were estimated by size-exclusion chromatography (SEC), a Tosoh SD8020 system using polystyrene standards ($CHCl_3$, Tosoh TSKgel G5000H$_{xL}$, G3000H$_{xL}$, and G2000H$_{xL}$ columns). The spectral data of PCLs and PVLs obtained using Sc(OTf)$_3$ in the presence of BnOH in this paper were consistent with those in the literature.[11e,g]

4.2. Materials

Toluene (1 L) was first treated with concd H_2SO_4 (80 mL) for a few days at room temperature and then washed with H_2O (100 mL×2), 2 N NaOH (100 mL), and H_2O (100 mL×2) again. After being dried over $MgSO_4$, toluene was heated to reflux under N_2 in the presence of Na–benzophenone for a few days and distilled prior to use. Purification of benzene followed the procedure for toluene. Sc(OTf)$_3$ was purchased from Strem and other commercially available

$RE(OTf)_3$ materials from Aldrich. BnOH, CL, and VL were distilled from CaH_2 and stored under N_2. Deionized water was used as an additive in entry 2 of Table 4. Ionic liquids were prepared according to the literature. Other chemicals were used as purchased.

4.3. Polymerization procedures

Preparation of $Sc(OTf)_3$: in a dry box under N_2, $Sc(OTf)_3$ (10 mg, 20 mmol) was introduced into a dried Schlenk flask equipped with a magnetic stirrer bar. After the flask was equipped with a rubber septum, it was taken out of the dry box. Benzene (1.0 mL) was added to the flask and the suspension was stirred for a minute. The suspension was lyophilized using dry ice/MeOH and a vacuum pump.

Typical procedure 1 (entry 2, Table 2): to lyophilized $Sc(OTf)_3$ in a Schlenk flask, toluene (1.0 mL) and BnOH (20 μL, 20 mmol) were added under N_2. The mixture was stirred for 5 min and then CL (110 μL, 0.99 mmol) was added to the mixture to start the polymerization at 25 °C. The polymerization was traced by TLC, and the mixture was diluted with toluene (~10 mL) when CL was completely consumed. The organic layer was washed with H_2O (~10 mL) to remove $Sc(OTf)_3$, dried over Na_2SO_4, and filtered. The filtrate was concentrated in vacuo to afford analytically pure PCL (116 mg, 100% yield).

Typical procedure 2 (entry 1, Table 4): to lyophilized $Sc(OTf)_3$ in a Schlenk flask, toluene (20 mL) and BnOH (41 μL, 0.40 mmol) were added to start the polymerization under N_2. The mixture was stirred for 5 min and then CL (2.3 mL, 20 mmol) was added to the mixture to start the polymerization at 25 °C. The polymerization was traced by TLC, and the mixture was diluted with toluene (300 mL) when CL was completely consumed after 120 h. The organic layer was washed with H_2O (100 mL) to remove $Sc(OTf)_3$, dried over Na_2SO_4, and filtered. The filtrate was concentrated in vacuo to afford analytically pure PCL (2.4 g, 100% yield).

Typical procedure 3 (Eq. 3): to lyophilized $Sc(OTf)_3$ in a Schlenk flask, toluene (1.0 mL) and CL (330 μL, 3.0 mmol) were added to start the polymerization. The polymerization was traced by TLC. After 3 h, additional toluene (1.0 mL) and CL (330 μL, 3.0 mmol) were added to the mixture. Stirring was continued for an additional 6 h, followed by additional toluene (1.0 mL) and CL (660 μL, 6.0 mmol). Stirring was continued for an additional 24 h (totally 33 h), and the polymerization was quenched as usual to afford the PCL (1.4 g, 100%).

Typical procedure 4 (entry 22, Tables 5 and 6): to lyophilized $Ce(OTf)_4$ in a Schlenk flask, [BMIM][SbF_6] (0.50 mL) was added under N_2. The mixture was stirred for 5 min, and toluene (1.0 mL) and CL (110 μL, 0.99 mmol) were added to start the polymerization. The mixture was stirred vigorously. The polymerization was quenched after 29 h by addition of toluene (~10 mL). The organic layer was separated by decantation, and the ionic liquid was washed with toluene (5.0 mL×3) under N_2. The combined organic layer was concentrated in vacuo. ^1H NMR indicated that analytically pure PCL formed (117 mg, 100%). To the remaining ionic liquid, toluene (1.0 mL) and CL (110 μL, 0.99 mmol) were added under N_2, and the same procedure was repeated to reuse $Ce(OTf)_4$–[BMIM][SbF_6].

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