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Controlled Ring-Opening Polymerization of ε-Caprolactone Catalyzed by Rare-Earth Perfluoroalkanesulfonates and Perfluoroalkanesulfonimides

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ABSTRACT: We examined ring-opening polymerizations (ROPs) of ε-caprolactone in toluene at 25−60 °C catalyzed by scandium perfluoroalkanesulfonates and perfluoroalkanesulfonimides. Using these scandium catalysts, which have strong electron-withdrawing ligands, the ROPs proceeded quickly. Under identical conditions, polymerizations were completed more rapidly for reactions catalyzed by scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$] and scandium nonafluorobutanesulfonimide [$Sc(NNf_2)_3$] than for those catalyzed by scandium trifluoromethanesulfonate [$Sc(OTf)_3$]. It was possible to synthesize poly(ε-caprolactone)s ($M_n = 2.6 \times 10^3 - 9.8 \times 10^3$) with low polydispersities ($M_w/M_n = 1.12 - 1.40$). After polymerization, the catalysts were easily recovered by simple filtration or by extraction with H_2O and could be reused. Other rare-earth nonafluorobutanesulfonimides [$M(NNf_2)_3$; M = Tm, Sm, and Nd] were also tested. Samarium nonafluorobutanesulfonimide [$Sm(NNf_2)_3$], as well as $Sc(NNf_2)_3$, catalyzed living polymerizations of ε-caprolactone. The reaction kinetics and activation thermodynamics of certain scandium catalysts and $Sm(NNf_2)_3$ were investigated. Increasing the perfluoroalkane chain length decreased the values of both the activation energy and the activation enthalpy. The ranked values of the activation free energies parallel those of the times required for completion of the polymerizations. ^{13}C NMR spectroscopy was used to characterize the relative Lewis acidities of certain catalysts. Our findings indicate that $Sc(NNf_2)_3$, which accelerated the ROP than $Sc(OTf)_3$ or $Sc(NTf_2)_3$, is an excellent catalyst for the ROP of ε-caprolactone.

Introduction

Polycaprolactone (PCL) is a well-known, commercially available, biodegradable polymer. Some important properties of PCL have received significant attention, and considerable effort has gone into the development of PCL synthesis. Especially, a PCL that has a narrow molecular-weight distribution would be useful for medical applications and polyurethane synthesis.[1] Compounds that have been assessed as catalysts for the ring-opening polymerization (ROP) of ε-caprolactone include metal complexes of tin,[2,3] aluminum,[4−7] iron,[8,9] neodymium,[10] yttrium,[11] zinc,[12,13] bismuth,[14] ruthenium,[15] and zirconocene,[16] enzymes,[17,18] organocatalysts,[19] and the Brönsted acids, sulfonic acid.[20] Commonly used catalysts for academic and industrial syntheses are tin(II) and tin(IV) alkoxides (or salts)[2,3] because it is possible to control of the molecular weight of the product when using these compounds, whereas conventional alkali-metal alkoxides, such as those of sodium, cause numerous inter- and intramolecular transesterifications. However, because tin compounds are very cytotoxic, more environmentally benign catalysts are needed.

Complexes incorporating rare-earth elements have been shown to be efficient catalysts for ROP reactions, especially for those involving lactones and lactides.[10,11] These catalysts are of particular interest for biomedical applications because rare-earth elements are nontoxic.[10] PCL has been synthesized via an ROP of ε-caprolactone catalyzed by $Sc(OTf)_3$, and the ROP proceeded in a quasi-living manner.[21−23] Recently, some Sc catalysts for the ROP of cyclic esters have been reported.[24−27] $Sc(OTf)_3$ is an attractive catalyst because it is a water-stable Lewis acid, is recyclable, does not promote transesterification during low-temperature polycondensations,[28−35] and has a low toxicity.[34,36]

We recently reported the ROP of ε-caprolactone using a polymer-supported catalyst (PS-Sc)[37] that consisted of $Sc(OTf)_3$ attached covalently to polystyrene beads. Using the PS-Sc system, the synthesized PCL had a narrow molecular weight distribution.[38,39] The use of PS-Sc simplified and hastened catalyst recovery because the polymer was recoverable upon filtration. Additionally, no loss of the catalyst was observed. However, the polymerization required a longer period of time than did a reaction catalyzed with $Sc(OTf)_3$ in solution and otherwise identical conditions. We calculated the reaction rate constants (k) for the PS-Sc and solution $Sc(OTf)_3$-catalyzed reactions and derived the activation energies (E_a) from the values of k using Arrhenius equation plots. The E_a values for the PS-Sc and $Sc(OTf)_3$ reactions were identical within experimental error. Therefore, that the polymerization proceeded more slowly for the PS−Sc-catalyzed reaction was probably caused by transport/diffusion limitations imposed by the solid nature of the catalyst [the value of the frequency factor (A) for PS-Sc was less than that for $Sc(OTf)_3$], even though all reaction conditions were the same, including the amounts of catalysts used.

It may also be possible to produce PCL in a benign fashion by using a smaller amount of a catalyst that is more active than is $Sc(OTf)_3$. Kobayashi[40] and Hanamoto[41] and their co-workers synthesized scandium nonafluorobutanesulfonate [$Sc(ONf)_3$] and scandium heptadecafluorooctanesulfonate [$Sc(OPf)_3$], which have stronger electron-withdrawing ligands than does $Sc(OTf)_3$, and used these Sc compounds as catalysts for aldol reactions[40] and hetero-Diels−Alder reactions,[41] respectively. Using $Sc(OPf)_3$, a hetero-Diels−Alder reaction of benzaldehyde with 2,3-dimethyl-1,3-butadiene proceeded quantitatively under mild conditions, whereas the reaction using $Sc(OTf)_3$ yielded only 35% of the theoretical amount of product. $Sc(ONf)_3$ and $Sc(OPf)_3$ have nonbranched ligands, whereas $Sc(NTf_2)_3$, synthesized by Ishihara and co-workers,[42] has branched ligands. $Sc(NTf_2)_3$ is a more effective

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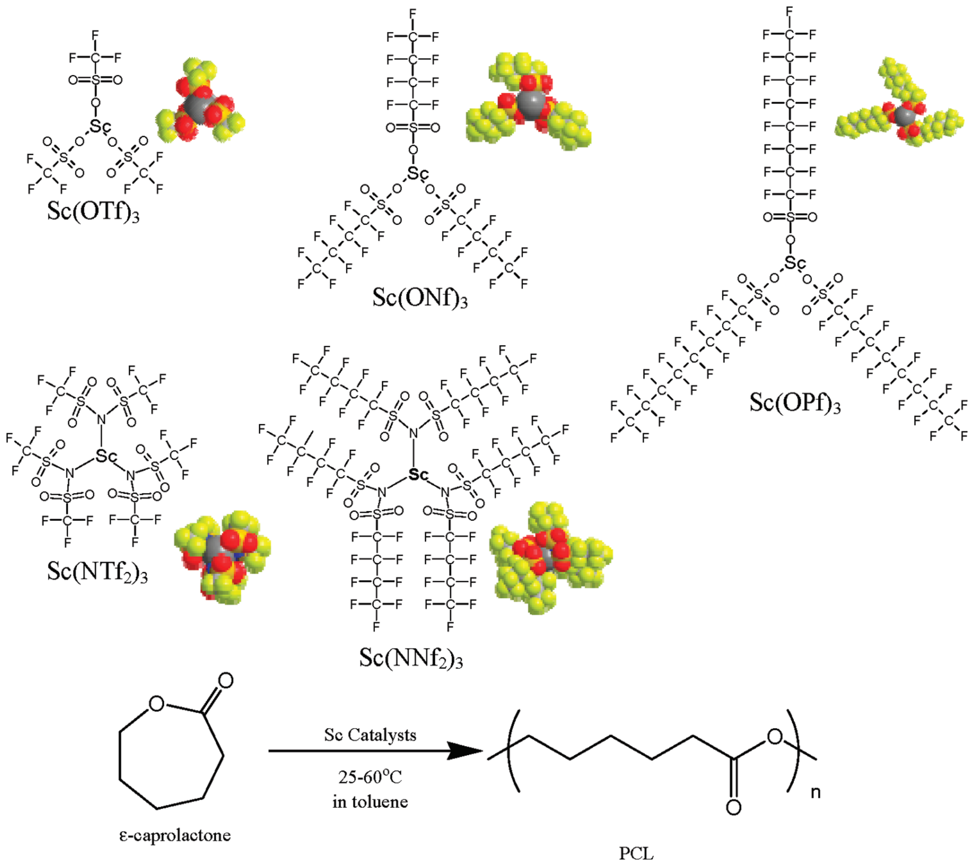
Scheme 1. Ring-Opening Polymerization of ε-Caprolactone[a]



[a] Formulas and space-filling models of the scandium catalysts Sc(OTf)$_3$, Sc(ONf)$_3$, Sc(OPf)$_3$, Sc(NTf$_2$)$_3$, and Sc(NNf$_2$)$_3$ that were used for this report are shown.

catalyst for acylations than is Sc(OTf)$_3$.[42] These Sc catalysts are easy to synthesize. Using these catalysts, we have recently reported the dehydration polycondensations of dicarboxylic acids and diols.[43] Furthermore, other rare-earth metal perfluoroalkanesulfonimides [M(NNf$_2$)$_3$; M = Tm, Sm, and Nd] were also found to be effective catalysts for the polycondensations. Polymerization proceeded with smaller amounts of the catalysts (0.01−0.5 mol %), and higher molecular weight polyesters ($M_n = 14.8 \times 10^3 - 23.5 \times 10^3$) were synthesized, in which Tm(NNf$_2$)$_3$ showed the highest catalytic activity.[43]

In this paper, we report the characteristics for ROPs of ε-caprolactone catalyzed by the scandium compounds Sc(ONf)$_3$, Sc(OPf)$_3$, Sc(NTf$_2$)$_3$, and Sc(NNf$_2$)$_3$. These compounds contain electron-withdrawing groups that are stronger than OTf. The polymerization time courses catalyzed by these scandium compounds were compared with that catalyzed by Sc(OTf)$_3$. Furthermore, other rare-earth metal catalysts (incorporating Tm, Sm, or Nd) were also tested. To investigate the reaction kinetics and the ROP mechanism, temperature studies were performed and Arrhenius and Eyring plots were analyzed. To characterize the relative Lewis acidities of certain of the rare-earth metal catalysts, ^{13}C NMR spectra of ethyl acetate in the presence of a catalyst (equimolar mixtures) in acetone-d_6 were acquired.

Experimental Section

Materials. ε-Caprolactone, ethanol (EtOH), petroleum ether, chloroform, and toluene were purchased from Nacalai Tesque (Kyoto, Japan) and were distilled before use. Sc(OTf)$_3$ was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Tm(OTf)$_3$ was purchased from Wako Pure Chemical (Osaka, Japan). Sm(OTf)$_3$ was purchased from Strem Chemicals, Inc. (Newburyport, MA). Nd(OTf)$_3$, Gd(OTf)$_3$, Dy(OTf)$_3$, and Er(OTf)$_3$ were purchased from Aldrich Co., Ltd. (Milwaukee, WI). Sc(ONf)$_3$,[40] Sc(OPf)$_3$,[41] Sc(NTf$_2$)$_3$,[42] Sc(NNf$_2$)$_3$,[43] Tm(NTf$_2$)$_3$,[43] Tm(NNf$_2$)$_3$,[43] Sm(NNf$_2$)$_3$,[43] and Nd(NNf$_2$)$_3$[43] were prepared according to literature reports. The rare-earth metal catalysts were dried under reduced pressure overnight before use.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded at 27 °C using a Bruker Analytik DPX200 spectrometer (200 MHz for ^{1}H) and a Bruker Analytik DRX600 spectrometer (600 MHz for ^{13}C). The number-average molecular weights (M_n) and the polydispersity indexes (M_w/M_n) of the polymers were estimated using a size exclusion chromatography (SEC) system that was calibrated with polystyrene standards. The chromatographic system included a Tosoh DP8020 pump system, an RI detector (Tosoh RI-8020), and a TSKgel SuperMultiporeHZ-M column. Chromatographies were performed with chloroform as the eluent, at a flow rate of 0.35 mL/min, and at 40 °C. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Kratos PCAxima CFRplus V2.4.0 mass spectrometer, with dithranol as the matrix reagent. To generate sodium-cationized ions of the PCLs ([M + Na]$^+$), NaI was used.

Ring-Opening Polymerizations of ε-Caprolactone in Toluene Catalyzed by Rare-Earth Metal Compounds. A typical polymerization procedure was performed as follows. In a 10 mL round-bottom flask, under reduced pressure in a freeze-dryer, a rare-earth metal catalyst was dried to remove adsorbed water. Toluene, ε-caprolactone, and EtOH were then added to the flask that had been placed in a controlled-temperature water or oil bath under a nitrogen atmosphere, and the mixture was stirred. The polymerization was monitored using the ^{1}H NMR signal at 4.06 ppm (t, $-$CO$-$O$-$CH_2-, 6.4 Hz).

^{13}C NMR Spectroscopy of Ethyl Acetate in the Presence of a Scandium or a Samarium Catalyst. Ethyl acetate (0.08 mmol) and a scandium [Sc(OTf)$_3$, Sc(NTf$_2$)$_3$, or Sc(NNf$_2$)$_3$; 0.08 mmol] or a samarium catalyst [$Sm(OTf)_3$ or $Sc(NNf_2)_3$; 0.08 mmol] were dissolved in acetone-d_6 (0.5 mL). NMR spectra (600 MHz) of these samples were recorded.

Recovery of $Sc(OPf)_3$, $Sc(NTf_2)_3$, and $Sc(NNf_2)_3$. After a reaction was completed, the reaction mixture was diluted with toluene (ca. 20 mL). $Sc(OPf)_3$ was recovered by simple filtration (80% yield). $Sc(NTf_2)_3$ and $Sc(NNf_2)_3$ were both recovered by extraction with H_2O. The aqueous layer was evaporated to recover the catalysts. The toluene layer was evaporated, and the PCL, which was a white powder, was dried under vacuum.

Results and Discussion

We performed ROPs of ε-caprolactone catalyzed by the scandium catalysts $Sc(ONf)_3$ and $Sc(OPf)_3$, which have linear, strong electron-withdrawing ligands, and $Sc(OTf)_3$ (each at 0.5 mol %; Table 1) and compared their reaction properties. EtOH and toluene were used as the initiator and the solvent, respectively, and the initial monomer concentration ($[M]_0$) was 3 M. The ROPs proceeded at 25 °C under mild conditions (runs 1, 4, and 7). The ROPs proceeded more rapidly at 50−60 °C without broadening the polydispersities of the PCLs (runs 2, 3, 5, 6, 8, and 9). The time courses for completion of the $Sc(ONf)_3$-catalyzed polymerizations were similar to those catalyzed by $Sc(OTf)_3$. Although $Sc(OPf)_3$ contains longer perfluoroalkane chains, when it was used as a catalyst, the reaction time at 25 °C needed for complete polymerization was longer than were those of $Sc(OTf)_3$ and $Sc(ONf)_3$, probably because $Sc(OPf)_3$ was not fully soluble. At 60 °C, the polymerization time course catalyzed by $Sc(OPf)_3$ was the same as those catalyzed by $Sc(OTf)_3$ and $Sc(ONf)_3$ because, at 60 °C, $Sc(OPf)_3$ was soluble in the reaction mixture.

Table 1. Ring-Opening Polymerizations of ε-Caprolactone Catalyzed by Scandium Perfluoroalkanesulfonates[a]

run	catalyst	temp (°C)	time (h)	conv[b] (%)	$M_n{}^c \times 10^{-3}$	$M_w/M_n{}^c$
1	$Sc(OTf)_3$	25	24	96	4.3	1.20
2	$Sc(OTf)_3$	50	8	98	3.7	1.17
3	$Sc(OTf)_3$	60	8	>99	3.6	1.23
4	$Sc(ONf)_3$	25	24	>99	5.4	1.21
5	$Sc(ONf)_3$	50	12	>99	4.8	1.18
6	$Sc(ONf)_3$	60	8	>99	3.7	1.36
7	$Sc(OPf)_3$	25	36	>99	4.2	1.17
8	$Sc(OPf)_3$	50	24	>99	5.2	1.21
9	$Sc(OPf)_3$	60	8	99	3.2	1.31

[a] Conditions: 0.5 g (3 M) monomer; $[M]_0/[I]_0 = 40$; catalyst, 0.5 mol %; initiator, EtOH. [b] Monomer conversion ($\{[M]_0 - [M]\}/[M]_0$) determined using the ^1H NMR the intensity ratio of the signals at 4.06 ppm (t, $-CO-O-CH_2-$, 6.4 Hz) and 4.15−4.30 ppm (m, $-CO-O-CH_2-$, ε-caprolactone) with $CDCl_3$ as the solvent. [c] Determined using size exclusion chromatograms with $CHCl_3$ as the solvent. The column was calibrated using poly(styrene) standards.

Next, we carried out ROPs of ε-caprolactone catalyzed by the scandium perfluoroalkanesulfonimides, $Sc(NTf_2)_3$ (Table 2, runs 1−8) and $Sc(NNf_2)_3$ (Table 2, runs 9−16). The ligands of these compounds are branched and are strongly electron withdrawing. Using $Sc(NTf_2)_3$ and $Sc(NNf_2)_3$ (each at 0.5 mol %), the ROPs proceeded quickly at 25 °C (runs 1 and 9, respectively). The ROPs catalyzed by 0.1 mol % $Sc(NTf_2)_3$ and $Sc(NNf_2)_3$ were complete within 32 and 12 h, respectively, at 25 °C (runs 5 and 13), and the synthesized PCLs had narrow polydispersities ($M_n = 6.7 \times 10^3$ and 4.4×10^3, $M_w/M_n = 1.15$ and 1.18, respectively). At 35 °C, the $Sc(NNf_2)_3$-catalyzed ROP (run 15) completed faster than $Sc(NTf_2)_3$-catalyzed ROP (run 7), indicating that the catalytic activity of $Sc(NNf_2)_3$ is higher than that of $Sc(NTf_2)_3$. At the higher temperature of 50 °C, the time required for a nearly complete polymerization was further shortened, and the increased temperature did not substantially affect the molecular weight distributions (runs 8 and 16). For all reactions, a plot of the polymer M_ns as a function of the amount of product (conversion) was linear, indicating that neither transesterification nor termination occurred during the ROP reactions (data not shown).

Next, we carried out a two-addition polymerization of ε-caprolactone with $Sc(NTf_2)_3$ as the catalyst to investigate its controlled polymerization. Additional monomer was added to the sample 1.5 h after the start of the reaction (Table 2, run 2, $M_n = 2.6 \times 10^3$, $M_w/M_n = 1.29$) and then reacted for an additional 3 h. The molecular weight of PCL increased ($M_n = 5.5 \times 10^3$) without increasing the molecular weight distribution ($M_w/M_n = 1.34$; Figure 1). Therefore, the ROP was a living polymerization.

To attempt to increase the molecular weight of the product, the $[M]_0/[I]_0$ ratio was increased from 40 to 240. Consequently, we could synthesize larger molecular weight PCLs catalyzed by $Sc(NTf_2)_3$ and $Sc(NNf_2)_3$ in < 24 h (Table 2, run 4, $M_n = 9.8 \times 10^3$, $M_w/M_n = 1.28$; run 12, $M_n = 8.0 \times 10^3$, $M_w/M_n = 1.40$).

After polymerization, taking advantage of its low solubility at room temperature, $Sc(OPf)_3$ was easily recovered by filtration (80% yield). To recover $Sc(NTf_2)_3$ and $Sc(NNf_2)_3$, they were extracted with H_2O from the toluene solution and isolated upon evaporation (84% yield for both catalysts). The FT-IR spectra of recovered $Sc(OPf)_3$, $Sc(NTf_2)_3$, and $Sc(NNf_2)_3$ were the same as those of the corresponding virgin compounds. Therefore, the recovered catalysts could be used again. When the recovered catalysts were used, the polymerization times, PCL molecular weights, and the polydispersities were the same as those found when virgin catalysts were used (runs 5 and 6, 13 and 14).

Table 2. Ring-Opening Polymerizations of ε-Caprolactone Catalyzed by Scandium Perfluoroalkanesulfonimides[a]

run	catalyst	ratio (mol %)	$[M]_0$ (M)	$[M]_0/[I]_0$	temp (°C)	time (h)	conv[b] (%)	$M_n{}^c \times 10^{-3}$	$M_w/M_n{}^c$
1	$Sc(NTf_2)_3$	0.5	3	40	25	<2	>99	3.2	1.23
2	$Sc(NTf_2)_3$	0.5	1	40	50	1.5	>99	2.6	1.29
3	$Sc(NTf_2)_3$	0.2	3	40	25	8	>99	5.3	1.18
4	$Sc(NTf_2)_3$	0.2	3	240	25	<24	>99	9.8	1.28
5	$Sc(NTf_2)_3$	0.1	3	40	25	32	>99	6.7	1.15
6	recovered $Sc(NTf_2)_3$	0.1	3	40	25	24	>99	6.5	1.19
7	$Sc(NTf_2)_3$	0.1	3	40	35	20	>99	5.4	1.23
8	$Sc(NTf_2)_3$	0.1	3	40	50	6	96	6.2	1.18
9	$Sc(NNf_2)_3$	0.5	3	40	25	<2	>99	3.3	1.24
10	$Sc(NNf_2)_3$	0.5	1	40	50	1.5	>99	2.9	1.20
11	$Sc(NNf_2)_3$	0.2	3	40	25	5	>99	4.7	1.20
12	$Sc(NNf_2)_3$	0.2	3	240	25	<24	>99	8.0	1.40
13	$Sc(NNf_2)_3$	0.1	3	40	25	12	>99	4.4	1.18
14	recovered $Sc(NNf_2)_3$	0.1	3	40	25	24	>99	7.5	1.12
15	$Sc(NNf_2)_3$	0.1	3	40	35	8	>99	5.3	1.16
16	$Sc(NNf_2)_3$	0.1	3	40	50	4	98	4.9	1.25

[a] Conditions: monomer: 0.5 g; initiator, EtOH. [b] Monomer conversion determined by ^1H NMR spectroscopy as described in footnote b of Table 1. [c] Determined as described in footnote c of Table 1.

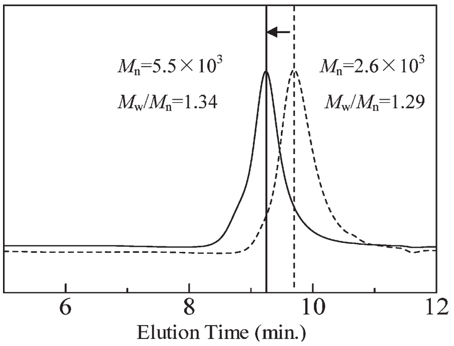


Figure 1. Size exclusion chromatograms for PCL produced using Sc$(NTf_2)_3$ as the catalyst. Before (Table 2 run 2, dash line) and after (solid line) the second addition of ε-caprolactone. Flow rate: 0.35 mL/min. Eluent: $CHCl_3$.

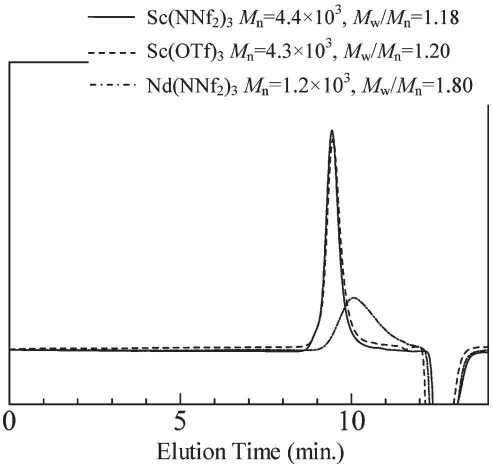


Figure 2. Size exclusion chromatograms for PCLs produced using $Sc(NNf_2)_3$ (Table 2 run 13, solid line), $Sc(OTf)_3$ (Table 1 run 1, dashed line), and $Nd(NNf_2)_3$ (Table 3 run 7, long−short-dashed line) as the catalysts. Flow rate: 0.35 mL/min. Eluent: $CHCl_3$.

We also surveyed catalysts containing other rare-earth metals [$M_1(OTf)_3$, M_1 = Tm, Sm, Nd, Gd, Dy, and Er; $M_2(NNf_2)_3$, M_2 = Tm, Sm, and Nd]. The $M_1(OTf)_3$ compounds tended to be less effective catalysts (Table 3, runs 1, 4, 6, and 8−10) than was $Sc(OTf)_3$ (Table 1, run 2). Although polymerizations were completed in shorter periods of time when $Tm(NTf_2)_3$, $Tm(NNf_2)_3$, and $Nd(NNf_2)_3$ were the catalysts (runs 2, 3, and 7), the PCL molecular weight distributions were broader than when $Sc(NNf_2)_3$ was used. In Figure 2, SEC runs are shown for the PCLs produced using $Sc(NNf_2)_3$, $Sc(OTf)_3$, and $Nd(NNf_2)_3$. The widths of the peaks indicate that the use of $Sc(NNf_2)_3$ and $Sc(OTf)_3$ did not broaden the molecular-weight distributions, although the use of $Nd(NNf_2)_3$ did. Given the results, $Sc(NNf_2)_3$ appears to be an excellent catalyst for the ROP of ε-caprolactone.

$Sm(NNf_2)_3$ also catalyzed the ROP effectively without broadening the molecular weight distribution (run 5). Additionally, the polymerization occurred more rapidly when $Sm(NNf_2)_3$ was used instead of $Sm(OTf)_3$ (run 4) without broadening of the M_w/M_n but occurred more slowly than when $Sc(NNf_2)_3$ was used.

MALDI-TOF mass spectra of the PCLs produced by $Sc(NNf_2)_3$, $Sm(NNf_2)_3$, and $Nd(NNf_2)_3$ catalysts were used to determine the absolute molecular weights and the structures of the products (Figure 3). In the spectra, there are two or three sets of peaks, with two of the three sets having a peak repeat of 114 *m*/*z*, which corresponds to the molecular weight of the ε-caprolactone unit. There is a second pattern for which peaks are offset by 28 *m*/*z*. The 28 *m*/*z* difference corresponds to the molecular weight difference between EtOH (46 Da) and H_2O (18 Da), suggesting that the ROPs were initiated both by EtOH and by H_2O *in situ*. The relative peak intensities in the mass spectrum of the PCL produced using $Nd(NNf_2)_3$ indicated that the polymerization initiator was mainly H_2O, rather than EtOH. Moreover, a third set of peaks ascribed to cyclic polyesters were remarkably detected in the spectra of PCL produced using $Nd(NNf_2)_3$. Such peaks were absent in the spectrum of PCL produced using $Sc(NNf_2)_3$. Probably, initiation by H_2O followed by intermolecular condensation of the α-hydroxyl and ω-carboxyl termini is the reason that the ROP catalyzed by $Nd(NNf_2)_3$ did not proceed in a living manner.

Table 3. Ring-Opening Polymerizations of ε-Caprolactone Catalyzed by Rare-Earth Perfluoroalkanesulfonates or Perfluoroalkanesulfonimides[a]

run	catalyst	$[M]_0/[I]_0$	temp (°C)	time (h)	conv[b] (%)	M_n[c] × 10^{-3}	M_w/M_n[c]
1	$Tm(OTf)_3$	40	50	72	>99	4.5	1.41
2	$Tm(NTf_2)_3$	40	50	36	>99	3.5	1.53
3	$Tm(NNf_2)_3$	40	50	24	>99	3.9	1.77
4	$Sm(OTf)_3$	40	50	72	73	3.4	1.16
5	$Sm(NNf_2)_3$	40	50	2.5	>99	4.9	1.25
6	$Nd(OTf)_3$	40	50	24	4		
7	$Nd(NNf_2)_3$	40	50	8	>99	1.2	1.80
8	$Gd(OTf)_3$	40	50	48	17	0.8	1.15
9	$Dy(OTf)_3$	40	50	48	26	1.2	1.25
10	$Er(OTf)_3$	40	50	48	35	1.6	1.26

[a] Conditions: monomer, 0.5 g; $[M]_0$ = 3 mol/L; catalyst, 0.5 mol %; initiator, EtOH. [b] Monomer conversion determined as described in footnote b of Table 1. [c] Determined as described in footnote c of Table 1.

$\ln[M]_0/[M]$ is plotted as a function of time to determine the rate constant (k_p) for the ROPs catalyzed by $Sc(OTf)_3$, $Sc(ONf)_3$, $Sc(NTf_2)_3$, $Sc(NNf_2)_3$, and $Sm(NNf_2)_3$ (Figure 4). The rate constant for the $Sc(OPf)_3$-catalyzed ROP was not determined because the catalyst is insoluble at 25 °C. Linear dependences were found for $\ln([M]_0/[M])$ vs time at several temperatures for all polymerizations. Using the values of the slopes and eq 2, we calculated the k_p. Du and colleagues calculated the k_p using eq 2 for ROP of lactide using $Sn(oct)_2$ initiated by PEG.[44] The activation energies (E_a) were calculated using the values of the slopes of Arrhenius plots (Figure 5, top) and the Arrhenius equation (eq 3). For the plots, the values of the correlation coefficients (R) are all >0.99. The activation parameters are summarized in Table 4.

$$\mathrm{M} + \mathrm{C} \underset{k_{c-}}{\overset{k_{c+}}{\rightleftarrows}} \mathrm{MC}^{\ddagger} \qquad \mathrm{I} + \mathrm{MC}^{\ddagger} \xrightarrow{k_x} \mathrm{P}$$

$$k_{c+}[\mathrm{M}][\mathrm{C}] = k_{c-}[\mathrm{MC}^{\ddagger}] \qquad \frac{d[\mathrm{P}]}{dt} = -\frac{d[\mathrm{M}]}{dt} = \sum_{x=0} k_x[\mathrm{MC}^{\ddagger}][\mathrm{I}] = \sum_{x=0} \frac{k_{c+}k_x}{k_{c-}}[\mathrm{M}][\mathrm{C}][\mathrm{I}] = k_p[\mathrm{M}][\mathrm{C}][\mathrm{I}] \quad (1)$$

$$k_p = \frac{k_{app}}{3600[\mathrm{I}][\mathrm{C}]} = \frac{(\ln[\mathrm{M}]_0/[\mathrm{M}])/t}{3600[\mathrm{I}][\mathrm{C}]} \quad (2)$$

$$k = A e^{(-E_a/RT)} \qquad \log k = -\frac{E_a}{RT} + \log A \quad (3)$$

The E_a values for the $Sc(ONf)_3$- and $Sc(OTf)_3$-catalyzed reactions are comparable. We expected that catalysis by $Sc(NTf_2)_3$ and $Sc(NNf_2)_3$ would cause the values of E_a to be smaller than those of the other Sc catalysts because the perfluoroalkanesulfonimides are more strongly electron-withdrawing groups;[45] however, their values are greater than those of $Sc(OTf)_3$ and $Sc(ONf)_3$, possibly because the electrostatic interaction of N atom in the imide ligand with δ+ carbonyl carbon inhibits

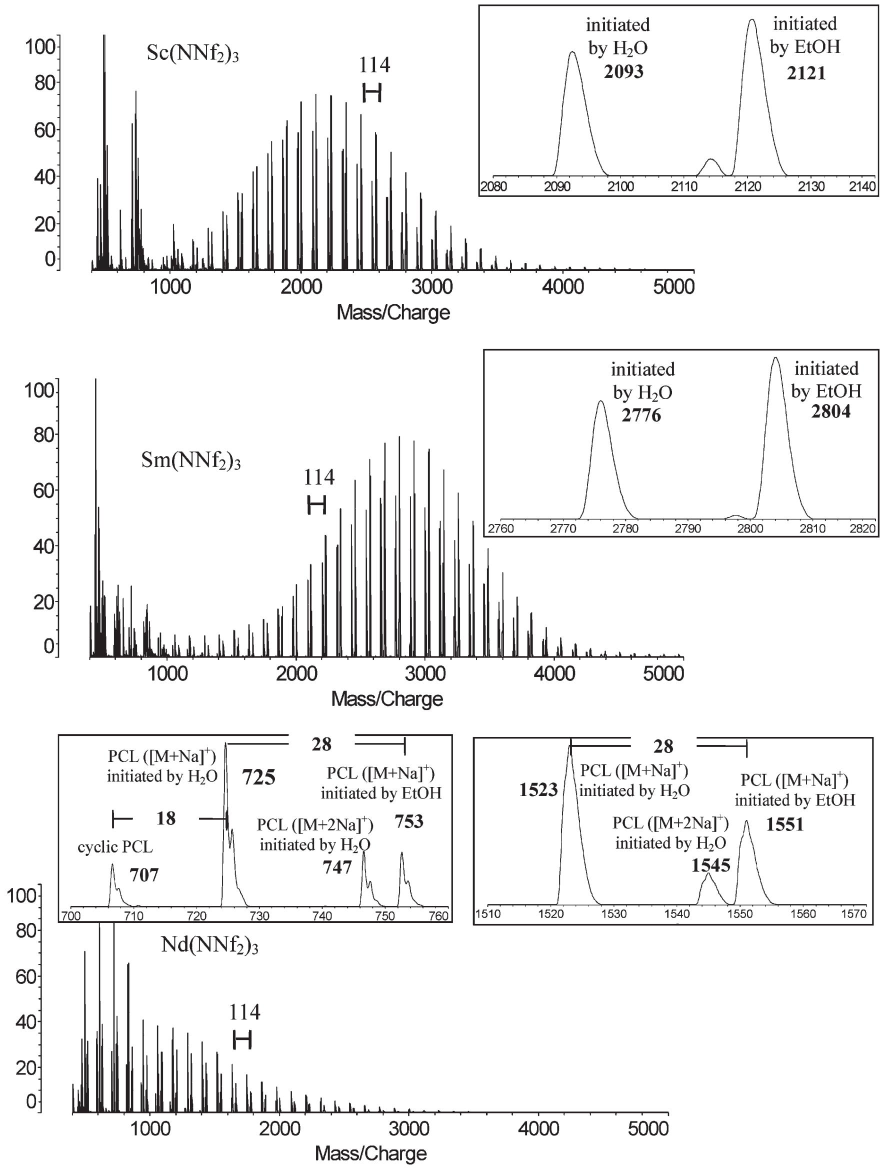


Figure 3. MALDI-TOF mass spectra of PCL produced using $Sc(NNf_2)_3$ (top), $Sm(NNf_2)_3$ (middle), and $Nd(NNf_2)_3$ (bottom) as the catalysts ($[M]_0 = 3.0$ M, [catalyst] = 0.5 mol %, 50 °C). Each inset shows an expanded *m*/*z* range.

nucleophilic attack of hydroxyl propagating center. The E_a values for the $Sc(NNf_2)_3$-catalyzed reaction are smaller than those of the $Sc(NTf_2)_3$-catalyzed reaction. Koppel and colleagues evaluated various ligands chosen according to their abilities to withdraw electrons.[45] They concluded that bis(nonafluorobutanesulfonyl)imide [$(NNf_2)_3$] had even a better election-withdrawing ability than did trifluoromethanesulfonimide [$(NTf_2)_3$].[45]

$$k = \frac{k_B T}{h} e^{(-\Delta H^{\ddagger}/RT)} e^{(\Delta S^{\ddagger}/R)}$$

$$log \frac{k}{T} = -\frac{\Delta H^{\ddagger}}{RT} + log \frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \qquad (4)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (5)$$

$$k = \frac{k_B T}{h} e^{(-\Delta H^{\ddagger} + RT - RT)/RT} e^{(\Delta S^{\ddagger}/R)} = \frac{e k_B T}{h} e^{(-\Delta H^{\ddagger} - RT)/RT} e^{(\Delta S^{\ddagger}/R)}$$

$$A = \frac{e k_B T}{h} e^{(\Delta S^{\ddagger}/R)}, \quad E_a = \Delta H^{\ddagger} + RT$$

$$E_a \neq \Delta G^{\ddagger} \qquad (6)$$

As a result, we could not explain the ROP results in this study using semiempirical Arrhenius equation. Therefore, the activation enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) were calculated using the values obtained for the rate constants, Eyring plots (Figure 5, bottom) and the Eyring equation (eq 4).[46] The Eyring equation was used to calculate the kinetic parameters for the ROP of cyclic ester.[47-50] The free energy of activation ($\Delta G^{\ddagger}$) is more theoretical factor and not equal to E_a (eq 6). $\Delta G^{\ddagger}$ was calculated using eq 5. Furthermore, to fully understand how the chemical nature of the catalysts determines their activities, the entropic effects ($\Delta S^{\ddagger}$) must also be examined. The negative values for $\Delta S^{\ddagger}$ indicate that the ring-opening mechanism of ε-caprolactone is a sterically hindered one, which agrees with that found by Dubois and colleagues[47] for the ROP of ε-caprolactone initiated with functional aluminum alkoxides. These parameters are consistent with a reaction pathway involving the attack of a nucleophilic center (polymer chain end) to a metal-bound ε-caprolactone (Scheme 2).[49] As the result, the ranked values of the $\Delta G^{\ddagger}$s for these scandium-catalyzed reactions well-parallel those of the rate constants. The values of $\Delta G^{\ddagger}$ for $Sc(NNf_2)_3$ indicate that it is the most effective

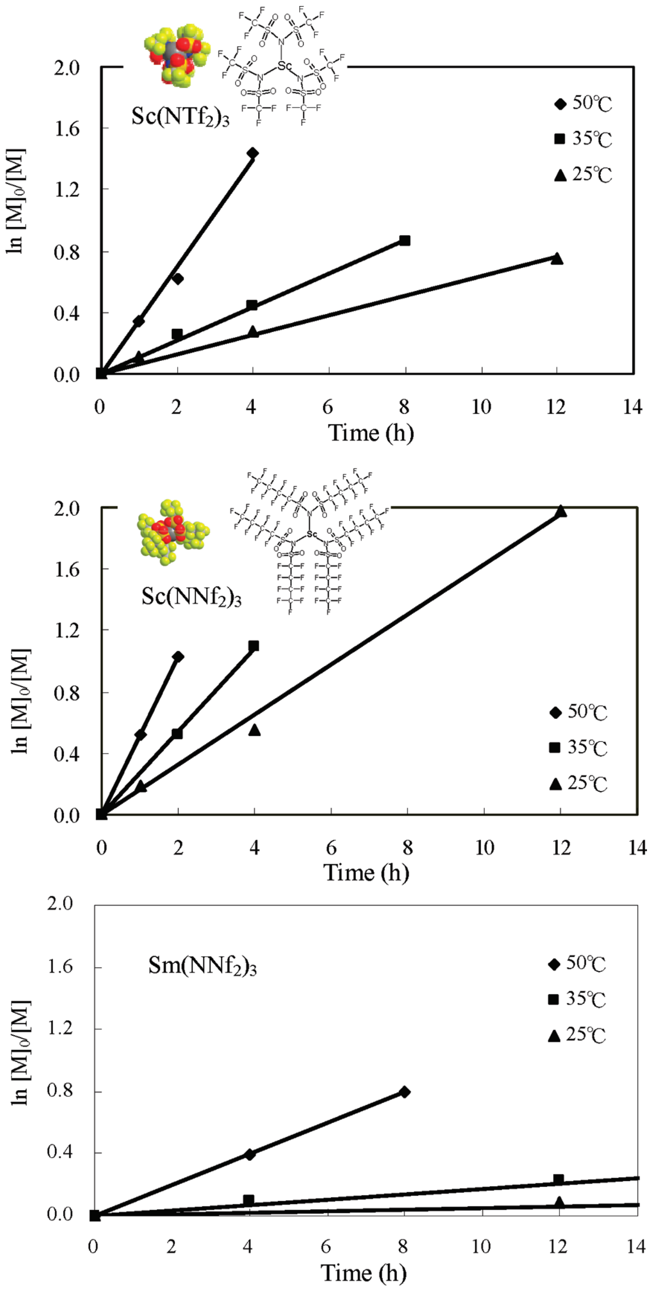


Figure 4. Plots of $\ln[M]_0/[M]$ vs time for ROPs of ε-caprolactone catalyzed by $Sc(NTf_2)_3$ (top), $Sc(NNf_2)_3$ (middle), and $Sm(NNf_2)_3$ (bottom) (initiator: EtOH, $[M]_0 = 3.0$ M, [catalyst] = 0.1 mol %).

catalyst at all temperatures for the ROP of ε-caprolactone when the reaction is thermodynamically controlled.

To determine the relative Lewis acidities of the scandium and samarium catalysts, ^{13}C NMR spectra were recorded. Ethyl acetate was used as a model for ε-caprolactone. Figure 6 shows the ^{13}C NMR spectra of ethyl acetate in acetone-d_6 with an equimolar amount of a scandium or samarium catalyst present. The ethyl acetate carbonyl carbon chemical shifts are found between 170.9 ppm (uncomplexed ethyl acetate) and 171.4 ppm ($Sc(NNf_2)_3$, $\Delta\nu = 0.54$ ppm). The downfield-shifted signals can be attributed to coordination of the carbonyl carbon to the metal. The $\Delta\nu$ value found when $Sc(NNf_2)_3$ ($\Delta\nu = 0.54$) was present is larger than those found when $Sc(OTf)_3$ ($\Delta\nu = 0.32$) or $Sc(NTf_2)_3$ ($\Delta\nu = 0.37$) were present. Therefore, $Sc(NNf_2)_3$ is the strongest scandium-containing Lewis acid. The $\Delta\nu$ value (0.57) for the carbonyl carbon of ethyl acetate when $Sm(NNf_2)_3$ was present was also greater than that found ($\Delta\nu = 0.35$) when $Sm(OTf)_3$ was present, which suggests that, in general and at least for the ROP of ε-caprolactone, a rare-earth metal ligated with $(NNf_2)_3$ provides the strongest possible Lewis acid. The ranked values of the chemical shift differences parallel those of the polymerization rate constants and the $\Delta G^{\ddagger}$ values. Although $Sm(NNf_2)_3$ also indicated higher $\Delta G^{\ddagger}$ values, it was difficult for us to compare Sm catalyst with Sc catalysts because these catalysts have another catalytic center.

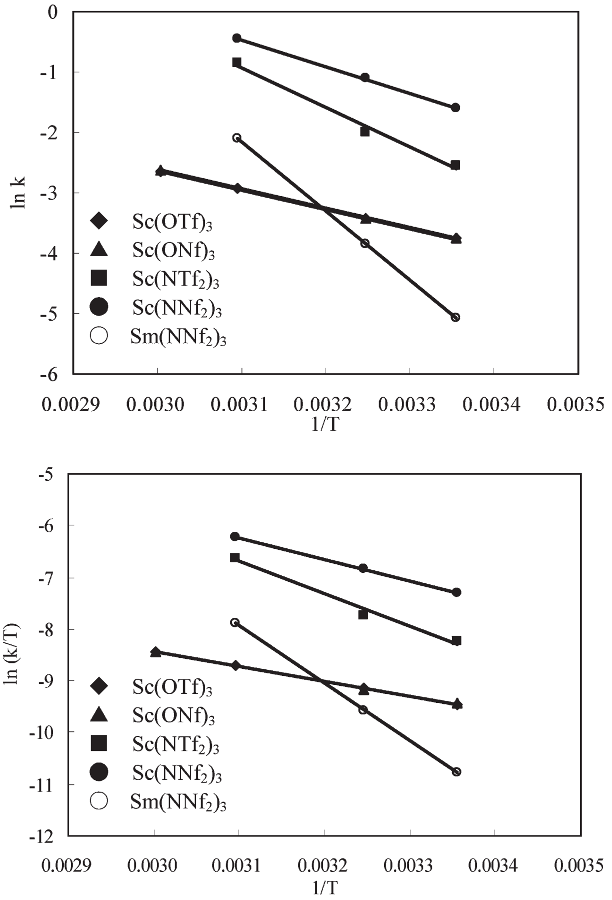


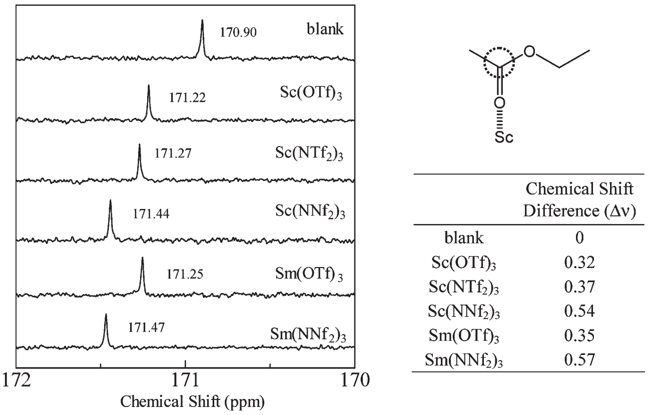
Figure 5. Arrhenius plots (top) and Eyring plots (bottom) of the ROPs of ε-caprolactone catalyzed by rare-earth catalysts (initiator: EtOH; solvent: toluene).

In this article, we described ROPs of ε-caprolactone catalyzed by the scandium catalysts $Sc(ONf)_3$, $Sc(OPf)_3$, $Sc(NTf_2)_3$, and $Sc(NNf_2)_3$ which have stronger electron-withdrawing ligands than does $Sc(OTf)_3$. Polymerization proceeded more rapidly when the catalyst was $Sc(NTf_2)_3$ or $Sc(NNf_2)_3$ than it did when $Sc(OTf)_3$ was the catalyst. Using the scandium catalysts, PCLs with M_ns (between 2.6×10^3 and 9.8×10^3) and low polydispersities ($M_w/M_n = 1.12-1.40$) were synthesized. Furthermore, for the two-addition polymerization, the M_n increased with the second addition, but the molecular weight distribution did not. A plot of the PCL molecular weights versus the extent of polymerization (conversion) is linear; therefore, the PCL molecular weight is directly proportional to the extent of the polymerization. These results indicate that the scandium-catalyzed reactions were living polymerizations of ε-caprolactone. After polymerization, the Sc catalysts were easily recovered by simple filtration or extraction with H_2O from the toluene solutions and could be reused. Other rare-earth metal catalysts (M = Tm, Sm, and Nd) were also tested. We demonstrated that $Sm(NNf_2)_3$ is the most effective catalyst of the non-scandium catalysts. The Arrhenius equation and the Eyring equation were used to

Table 4. Reaction Rate Constants, Activation Energies, and Activation Enthalpy, Entropy, and Free Energy for the ROPs of ε-Caprolactone

	$k_p \times 10^{2a}$ (L^2 mol^{-2} s^{-1})							$\Delta G^{\ddagger d}$ (kJ mol^{-1})		
	298 K	308 K	323 K	333 K	$E_a{}^b$ (kJ mol^{-1})	$\Delta H^{\ddagger c}$ (kJ mol^{-1})	$\Delta S^{\ddagger c}$ (J K^{-1} mol^{-1})	298 K	308 K	323 K
$Sc(OTf)_3$	2.33	3.25	5.38	7.08	26.5	23.8	−196.2	82.3	84.3	87.2
$Sc(ONf)_3$	2.36	3.23		7.22	26.6	23.9	−195.8	82.3	84.3	87.2
$Sc(NTf_2)_3$	7.81	13.6	42.9		55.0	52.5	−90.6	79.5	80.4	81.7
$Sc(NNf_2)_3$	20.1	33.5	63.7		36.8	34.3	−143.2	76.9	78.4	80.5
$Sm(NNf_2)_3$	0.63	2.11	12.3		95.2	92.6	23.6	85.6	85.3	85.0

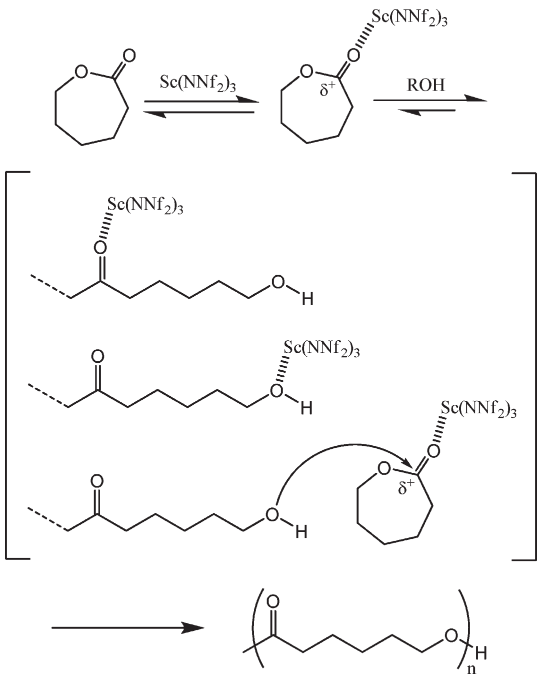
[a] k_p were calculated using the values of the slopes for $\ln([M]_0/[M])$ vs time and eq 2. [b] E_a were calculated using the values of the slopes of Arrhenius plots and eq 3. [c] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated using the values obtained for the Eyring plots and eq 4. [d] $\Delta G^\ddagger$ were calculated using eq 5.



	Chemical Shift Difference (Δv)
blank	0
$Sc(OTf)_3$	0.32
$Sc(NTf_2)_3$	0.37
$Sc(NNf_2)_3$	0.54
$Sm(OTf)_3$	0.35
$Sm(NNf_2)_3$	0.57

Figure 6. ^{13}C NMR spectra of ethyl acetate acquired in the absence (top spectrum) or the presence of a rare-earth metal catalyst in acetone-d_6. Top spectra are expanded regions showing the carbonyl carbon regions.

Scheme 2. A Plausible Mechanism of the ROP of ε-Caprolactone Using Scandium Catalyst via an Activated Monomer Mechanism



investigate the reaction kinetics of the scandium catalysts and $Sm(NNf_2)_3$. The values of $\Delta G^\ddagger$ for the polymerizations catalyzed by the scandium compounds and the Lewis acidities evaluated by ^{13}C NMR spectra for equimolar mixtures of ethyl acetate and the catalysts are both consistent with the times required to complete the polymerizations, showing that $Sc(NNf_2)_3$ is an excellent candidate for ROP of ε-caprolactone. Our work now makes it possible to synthesize PCL of $M_n = 2.6 \times 10^3 - 9.8 \times 10^3$ with low polydispersities ($M_w/M_n = 1.12 - 1.40$) at a moderate temperature (25−50 °C), within a shorter period of time using a smaller amount of catalyst, compared with $Sc(OTf)_3$. These fundamental results are important and useful for environmentally friendly procedures when designing functional polymers or frontier materials.

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References and Notes

(1) Boiteux, G.; Cuve, L.; Pascault, J. P. *Polymer* **1994**, *35*, 173–178.
(2) Kricheldorf, H. R.; Lee, S.-R. *Macromolecules* **1996**, *29*, 8689–8695.
(3) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 689–695.
(4) Stridsberg, K. M.; Ryner, M.; Albertsson, A.-C. *Adv. Polym. Sci.* **2002**, *157*, 41–46.
(5) Kageyama, K.; Ogino, S.-I.; Aida, T. *Macromolecules* **1998**, *31*, 4069–4073.
(6) Boffa, L. S.; Novak, B. M. *Macromolecules* **1997**, *30*, 3494–3506.
(7) Ko, B.-T.; Lin, C.-C. *Macromolecules* **1999**, *32*, 8296–8300.
(8) Kadokawa, J.; Iwasaki, Y.; Tagaya, H. *Green Chem.* **2002**, *4*, 14–16.
(9) Hillmyer, M. A.; Tolman, W. B.; O'Keefe, B. J. *Dalton Trans.* **2001**, *15*, 2215–2224.
(10) Tortosa, K.; Hamaide, T.; Boisson, C.; Spitz, R. *Macromol. Chem. Phys.* **2001**, *202*, 1156–1160.
(11) Martin, E.; Dubois, P.; Jerome, R. *Macromolecules* **2003**, *36*, 7094–7099.
(12) Kricheldorf, H. R.; Kreiser-Saundress, I. *Macromol. Chem. Phys.* **1998**, *199*, 1081–1087.
(13) Duda, A.; Kowalski, A.; Penczek, S.; Uyama, H.; Kobayashi, S. *Macromolecules* **2002**, *35*, 4266–4270.
(14) Kricheldorf, H. R.; Behnken, G.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3175–3183.
(15) Mata-Mata, J. L.; Gutiérrez, J. A.; Paz-Sandoval, M. A.; Madrigal, A. R.; Martínez-Richa, A. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6926–6942.
(16) Kostakis, K.; Mourmouris, S.; Karanikolopoulos, G.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3524–3537.
(17) MacDonald, R. T.; Pulapura, S. K.; Svirkin, Y. Y.; Gross, R. A.; Kaplan, D. L.; Akkara, J.; Swift, G.; Wolk, S. *Macromolecules* **1995**, *28*, 73–78.
(18) Bankova, M.; Kumar, A.; Impallomeni, G.; Ballistreri, A.; Gross, R. A. *Macromolecules* **2002**, *35*, 6858–6866.
(19) Kamber, N. E.; Jeong, W.; Gonzalez, S.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2009**, *42*, 1634–1639.
(20) Gazeau-Bureau, S.; Delcroix, D.; Martín-Vaca, B.; Bourissou, D.; Navarro, C.; Magnet, S. *Macromolecules* **2008**, *41*, 3782–3784.

(21) Nomura, N.; Taira, A.; Tomioka, T.; Okada, M. *Macromolecules* **2000**, *33*, 1497–1499.

(22) Nomura, N.; Taira, A.; Nakase, A.; Tomioka, T.; Okada, M. *Tetrahedron* **2007**, *63*, 8478–8484.

(23) Möller, M.; Kange, R.; Hedrick, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2067–2074.

(24) Gao, W.; Cui, D.; Liu, X.; Zhang, Y.; Mu, Y. *Organometallics* **2008**, *27*, 5889–5893.

(25) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Lara-Sánchez, A.; Martínez-Caballero, E.; Tejeda, J.; Sánchez-Barba, L. F.; Alonso-Moreno, C.; López-Solera, I. *Organometallics* **2008**, *27*, 976–983.

(26) Massa, W.; Agarwal, S.; Grabe, N.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1910–1914.

(27) Ling, J.; Shen, J.; Hogen-Esch, T. E. *Polymer* **2009**, *50*, 3575–3581.

(28) Takasu, A.; Oishi, Y.; Iio, Y.; Inai, Y.; Hirabayashi, T. *Macromolecules* **2003**, *36*, 1772–1774.

(29) Takasu, A.; Iio, Y.; Oishi, Y.; Narukawa, Y.; Hirabayashi, T. *Macromolecules* **2005**, *38*, 1048–1050.

(30) Takasu, A.; Iio, Y.; Mimura, T.; Hirabayashi, T. *Polym. J.* **2005**, *37*, 946–953.

(31) Takasu, A.; Takemoto, A.; Hirabayashi, T. *Biomacromolecules* **2006**, *7*, 6–9.

(32) Takasu, A.; Narukawa, Y.; Hirabayashi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5247–5253.

(33) Takasu, A.; Shibata, Y.; Narukawa, Y.; Hirabayashi, T. *Macromolecules* **2007**, *40*, 151–153.

(34) Shibata, Y.; Takasu, A. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5747–5759.

(35) Takasu, A.; Tsuruta, H.; Narukawa, Y.; Shibata, Y.; Oshimura, M.; Hirabayashi, T. *Macromolecules* **2008**, *41*, 4688–4693.

(36) Hirano, S.; Suzuki, K. T. *Environ. Health Perspect.* **1996**, *104*, 85–95.

(37) Nagayama, S.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 567–569.

(38) Takasu, A.; Oshimura, M.; Hirabayashi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2300–2304.

(39) Oshimura, M.; Takasu, A.; Nagata, K. *Macromolecules* **2009**, *42*, 3086–3091.

(40) Kobayashi, S.; Tsuchiya, T.; Komoto, I.; Matsuo, J. *J. Organomet. Chem.* **2001**, *624*, 392–394.

(41) Hanamoto, T.; Sugimoto, T.; Jin, Y.; Inagawa, J. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1421–1426.

(42) Ishihara, K.; Kubota, M.; Yamamoto, H. *Synlett* **1996**, 265–266.

(43) Takasu, A.; Makino, T.; Yamada, S. *Macromolecules* **2010**, *43*, 144–149.

(44) Du, Y. J.; Lemstra, P. J.; Nijenhuis, A. J.; Aert, H. A. M.; Bastiaansen, C. *Macromolecules* **1995**, *28*, 2124–2132.

(45) Electron-withdrawing ligand: Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S. Z.; Hu, L.-Q.; Sung, K. S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignat'ev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasob, V. M.; Notario, R.; Maria, P.-C. J. *J. Am. Chem. Soc.* **1994**, *116*, 3047−3057.

(46) (a) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107. (b) Laidler, K. J.; King, M. C. *J. Phys. Chem.* **1983**, *87*, 2657–2664.

(47) Dubois, Ph.; Ropson, N.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1996**, *29*, 1965–1975.

(48) Stassin, F.; Jerome, R. *Chem. Commun.* **2003**, *2*, 232–233.

(49) Darensbourg, D.; Moncada, A. I.; Choi, W.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2008**, *130*, 6523–6533.

(50) Darensbourg, D. J.; Choi, W.; Richers, C. P. *Macromolecules* **2007**, *40*, 3521–3523.