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# A Catalytic Approach for Cationic Living Polymerization: Sc(OTf)$_3$-Catalyzed Ring-Opening Polymerization of Lactones

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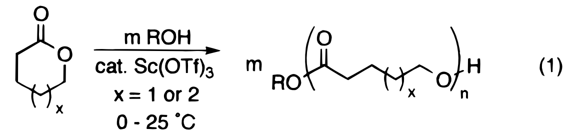
Aliphatic polyesters with a narrow molecular weight distribution (MWD) are of great interest especially for medical applications.[1] Living ring-opening polymerization of lactones[2] has been reported for that purpose mostly in an anionic or coordinated anionic fashion,[3] whereas there have been rarely found successful cationic examples in the literature.[4] Even the reported cationic living polymerization of lactones is problematic for two reasons: (i) initiators are extremely air- and moisture-sensitive; (ii) each molecule of the initiator produces, at most, only one molecule of polymer (Scheme 1a), and it is *stoichiometric* polymerization in the sense of the number of molecules. We describe herein a practical *catalytic approach* for cationic living polymerization of lactones using scandium trifluoromethanesulfonate, Sc(OTf)$_3$, as a catalyst commercially available, in which one reactive Sc(OTf)$_3$ molecule *catalytically* produces a large number of polymer molecules (Scheme 1b) and also in which contamination of protic compounds such as $H_2O$ and ROH does not suppress the catalytic activity of Sc(OTf)$_3$ for cationic polymerization (eq 1).



Rare earth metal triflates such as Sc(OTf)$_3$ have been paid more and more attention as intriguing Lewis acids in organic synthesis since Kobayashi reported that fascinating feature which is tolerance of Lewis bases.[5] We expected that these complexes could be more practical catalysts (or initiators) than those that one ever had for cationic ring-opening polymerization of lactones without strictly anhydrous conditions.[6] Polymerization of $\epsilon$-caprolactone (CL, 0.99 mmol) proceeded at 25 °C for 4 h in toluene (1 mL) in the presence of Sc(OTf)$_3$[7] (2.0 mol %) to afford poly($\epsilon$-caprolactone) (PCL) in >99% yield.[8] The number-average molecular weight ($M_n$) and the polydispersity index ($M_w/M_n$) were respectively estimated at 6900 and $1.1_3$ by SEC.[9] This polymerization appeared to have living nature by the fact that $M_n$ of polyester increased linearly as the monomer conversion increased, and $M_w/M_n$ was retained around 1.1 throughout the polymerization.[8]

We then examined the effects of the various amounts of protic benzyl alcohol (BnOH) on polymerization reactions of CL and $\delta$-valerolactone (VL)[8] (Table 1). The catalytic activity of Sc(OTf)$_3$ was not suppressed at all by the addition of BnOH, and each polymerization in the presence of various amounts of BnOH proceeded to afford PCL in a quantitative yield (entries 1−4). $M_n$ of polymer was dependent on the amount (mole percent) of BnOH. As the amount of BnOH increased, $M_n$ decreased. These results indicate that this is a *catalytic system* of cationic living polymerization in the sense of the number of molecules between polymer and reactive Sc(OTf)$_3$. The same trends were observed in polymerization of VL (entries 5−8). Higher efficiency of this *catalytic system* was proved by reactions using an excess amount of BnOH to Sc(OTf)$_3$ (Table 2). Polymerization of CL in the presence of 20 equiv of BnOH or $H_2O$ to Sc(OTf)$_3$ proceeded as expected (entries 1 and 2). The degrees of polymerization (DP's) by $^1$H NMR were respectively estimated at 50 (entry 1) and 47 (entry 2), which were consistent with the calculations based on 2 mol % of ROH (DP = 50), not on 0.10 mol % of Sc(OTf)$_3$ (DP = 1000). Polymerization in the presence of $H_2O$ afforded attractive telechelic $\alpha$-carboxylic-$\omega$-hydroxy functional PCL in a quantitative yield in a single step (entry 2).[10] Since VL is more reactive than CL (entry 3), even a lesser amount (0.05 mol %) of Sc(OTf)$_3$ was sufficient for the *catalytic approach* (entry 4). In the most successful cationic living polymerization of lactones reported before,[4] one molecule of the initiator produced, at most, one polymer molecule. On the contrary, one molecule of reactive Sc(OTf)$_3$ produced a large number of polymer molecules, up to 40 molecules (entry 4), depending on the amount of the inert ROH in this *catalytic system*.

**Scheme 1**

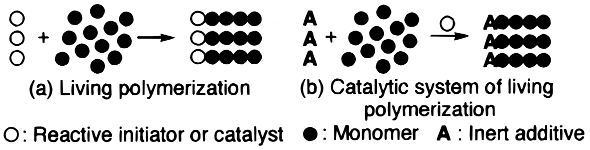


**Table 1. Polymerization of Lactones in the Presence of Various Amounts of BnOH**[a]

| entry | lactone | BnOH, mol % | time, h | yield,[b] % | $M_n$[c] × $10^{-3}$ | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|
| 1 | CL[d] | 0 | 4 | >99 | 6.9 | $1.1_3$ |
| 2 | | 2 | 2.3 | >99 | 3.5 | $1.1_3$ |
| 3 | | 5 | 2 | >99 | 2.4 | $1.1_7$ |
| 4 | | 10 | 2 | >99 | 1.6 | $1.1_8$ |
| 5 | VL[e] | 0 | 1.5 | 96 | 4.3 | $1.1_5$ |
| 6 | | 2 | 1 | 95 | 2.9 | $1.1_7$ |
| 7 | | 5 | 1 | 97 | 1.9 | $1.1_8$ |
| 8 | | 10 | 1 | 95 | 1.4 | $1.1_7$ |

[a] Sc(OTf)$_3$, 2 mol % (0.02 mmol); monomer, 1 mmol; toluene, 1 mL. [b] Isolated yield. [c] Estimated by SEC (CHCl$_3$, polystyrene standard). [d] Reaction temperature, 25 °C. [e] Reaction temperature, 0 °C.

**Table 2. Catalytic Approach for Cationic Living Polymerization**[a]

| entry | lactone | ROH (mol %) | Sc(OTf)$_3$, mol % | time, h | yield,[b] % | $M_n$[c] | $M_w$/ $M_n$[c] |
|---|---|---|---|---|---|---|---|
| 1 | CL | BnOH (2) | 0.10 | 120 | >99 | 7500 | $1.1_2$ |
| 2 | CL | $H_2O$ (2) | 0.10 | 120 | >99 | 7700 | $1.1_0$ |
| 3 | VL | BnOH (2) | 0.10 | 16 | >99 | 7500 | $1.1_5$ |
| 4 | VL | BnOH (2) | 0.05[d] | 36 | >99 | 7200 | $1.1_5$ |

[a] Sc(OTf)$_3$, 0.02 mmol; monomer, 20 mmol; toluene, 20 mL; temp, 25 °C (CL) or 0−25 °C (VL). [b] Isolated yield. [c] Estimated by SEC (CHCl$_3$, polystyrene standard). [d] Sc(OTf)$_3$, 0.01 mmol.

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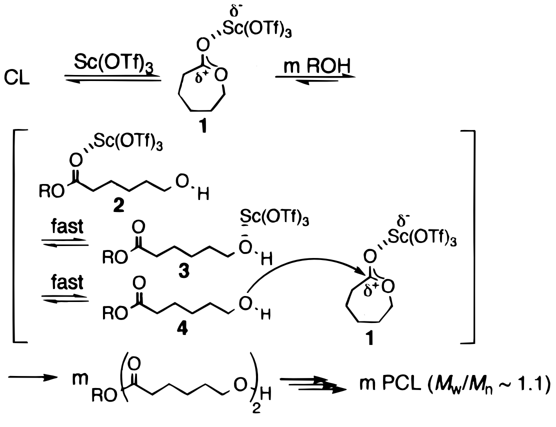
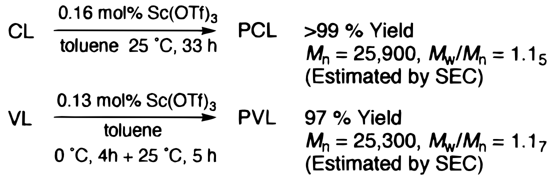
**Scheme 2. Plausible Mechanism of the Catalytic System for Cation Living Polymerization of ϵ-Caprolactone Catalyzed by $Sc(OTf)_3$**



**Scheme 3**



The plausible mechanism is shown in Scheme 2 as an activated monomer mechanism.[11−13] Coordination of CL to $Sc(OTf)_3$ affords the cationic complex **1**, followed by the electrophilic attack to ROH to produce ϵ-hydroxy ester **2**. It was supported by the fact that BnOH was consumed at the initial stage of polymerization by TLC analysis and also by formation of benzyl ester at polymer termini. The equilibria among **2**, **3**, **4**, and **1** must be rapid.[14] When $Sc(OTf)_3$ is coordinated by another CL to form **1**, the hydroxyl group of **4** (and also possibly **2**) is attacked by the electrophilic **1**. One of the characteristics of $Sc(OTf)_3$, the high number of WERC,[14] must have been essential to achieve the *catalytic approach* for cationic living polymerization. Caution should be exercised that ROH such as BnOH and $H_2O$ does not belong to the classical category of "initiators", because it is inert to CL by itself, and the reactive species here is the electrophilic complex **1**.[15] Polymerization of lactones via an activated monomer mechanism had been reported using $Et_3O^+{\cdot}PF_6^-$ or $Et_3O^+{\cdot}SbF_6^-$ in the presence of ROH,[13] where the related results were observed. Nonetheless, the concept of the *catalytic approach* for cationic living polymerization had not been realized, and those had also been limited to synthesis of relatively small molecular weight polymer ($M_n \leq 3000$) with an unsatisfactory MWD ($M_w/M_n = 1.3_1$) in CL polymerization[13] as far as we know. As shown in Scheme 3, the present system allowed one to synthesize polyesters with higher $M_n$'s with narrow MWD's in nearly quantitative yields.

In conclusion, we presented a novel concept of a *catalytic approach* for cationic living polymerization of lactones using $Sc(OTf)_3$. Here are characteristics of this system: (1) Commercially available $Sc(OTf)_3$ emerged as an excellent catalyst for cationic polymerization of lactones under mild conditions, and it was reactive in the presence of excess protic compounds and easy to handle under air. (2) One reactive $Sc(OTf)_3$ molecule catalytically produced a large number of polymer molecules with a narrow MWD.[16] (3) Analytically pure polyester was readily obtained in nearly quantitative yields (≥95%) from an organic layer washed with water to remove the water-soluble catalyst after the monomer was completely consumed, and no further purification was required. We believe this *catalytic approach* for cationic living polymerization could be a strong candidate to develop more powerful and practical polymerization methodologies for various monomers that are polymerized under the cationic conditions. Further work on the mechanistic details by spectroscopic methods and application to various monomers is in progress.

**Supporting Information Available:** Details of polymerization and discussion of the living nature of polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

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(3) For examples: (a) Aluminum alkoxides: Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982. Dubois, P.; Jérôme, R.; Teyssie, P. *Polym. Bull.* **1989**, *22*, 475. (b) Titanium alkoxide: Okuda, J.; Rushkin, I. L. *Macromolecules* **1993**, *26*, 5530. (c) Rare earth metal alkoxides: Shen, Y.; Shen, Z.; Zhang, Y.; Yao, K. *Macromolecules* **1996**, *29*, 8289. (d) Rare earth alkyl complexes: Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798. (e) As this paper was being prepared, Deng et al. reported ring-opening polymerization of CL by organoacid rare earth compounds such as $(CH_3CO_2)_3La$ and $(CCl_3CO_2)_3La$, where they could not control the molecular weight and the MWD, and proposed the "nonionic-coordination-insertion mechanism": Deng, X. M.; Yuan, M. L.; Xiong, C. D.; Li, X. H. *J. Appl. Polym. Sci.* **1999**, *71*, 1941.

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(5) (a) A comprehensive review: Kobayashi, S. *Synlett* **1994**, 689. See also ref 14. (b) Longbottom, D. *Synlett* **1999**, 2023.

(6) Quite recently, Sawamoto et al. reported controlled cationic polymerization of *p*-methoxystyrene in aqueous media with $Yb(OTf)_3$: Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3827.

(7) $Sc(OTf)_3$ was purchased from Strem Chemicals Inc. and was used after being freeze-dried in benzene prior to use. In our drying process, we estimated the real component of the complex as $Sc(OTf)_3{\cdot}H_2O$; see the Supporting Information. Lanthanide salts are notoriously difficult to obtain in an anhydrous state: Aspinall, H. C.; Dwyer, J. L. M.; Greeves, N.; McIver, E. G.; Woolley, J. C. *Organometallics* **1998**, *17*, 1884.

(8) See the Supporting Information for experimental details.

(9) Size exclusion chromatography ($CHCl_3$ as an eluent, polystyrene standard).

(10) A two-step procedure was recently reported: Trollsås, M.; Hedrick, J. L.; Dubois, Ph.; Jérôme, R. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1345.

(11) One of the reviewers suggested another possibility that $H^+$ from the complex, $[RO-Sc(OTf)_3]^-{\cdot}H^+$, could be the real catalyst instead of $Sc(OTf)_3$ itself. Because highly acid-sensitive silyl enol ether could exist in the mixture of $M(OTf)_3-H_2O-THF$, the mixture is believed to be almost neutral; see refs 5a and 14.

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(14) Kobayashi, S.; Nagayama, S.; Busujima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8287. WERC: water exchange rate constant (exchange rate constants for substitution of inner-sphere water ligand).

(15) In one of the leading reports of polymerization of epichlorohydrin via the activated monomer mechanism, Okamoto described ROH as the “molecular weight modifier”; see ref 12a.

(16) The “catalytic version” of living polymerization in a coordinated anionic fashion has been well-known as “immortal polymerization”, whose mechanism, reactive species, and living polymer termini are in sharp contrast with those of the present system; see ref 2b.

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