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ARTICLE

Controlled/Living Ring-Opening Polymerization of δ-Valerolactone Using Triflylimide as an Efficient Cationic Organocatalyst

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ABSTRACT: The polymerization of δ-valerolactone (δ-VL) using 3-phenyl-1-propanol (3-Ph-PrOH) as the initiator and trifluoromethanesulfonimide ($HNTf_2$) as the catalyst in CH_2Cl_2 at 27 °C with the $[\delta\text{-VL}]_0/[\text{3-Ph-PrOH}]_0/[HNTf_2]_0$ ratio of 100:1:0.1 proceeded homogeneously to afford a poly(δ-valerolactone) (PVL) with a narrow polydispersity index. The molecular weight determined from the ^{1}H NMR analysis, M_n = 9600 g mol^{-1}, fairly agreed with that estimated from the initial ratio of $[\delta\text{-VL}]_0/[\text{3-Ph-PrOH}]_0$, $M_{n,theo}$ = 9400 g mol^{-1}. In addition, the kinetic and chain extension experiments confirmed that the $HNTf_2$-catalyzed ROP proceeded in a living fashion. The ^{1}H NMR, SEC, and MALDI-TOF MS measurements of the obtained PVL clearly indicated the presence of the initiator residue at the chain end, showing that the $HNTf_2$-catalyzed ROP of δ-VL proceeded through a living mechanism. The $HNTf_2$-catalyzed ROP of δ-VL with functional initiators, such as 6-azido-1-hexanol, 2,3,4,5,6-pentafluorobenzyl alcohol, and *N*-(2-hydroxyethyl)maleimide, successfully afforded the corresponding end-functionalized PVL with a precise molecular control.

Introduction

An aliphatic polyester possessing biocompatible and biodegradable properties is one of the fundamental polymers for utilization in the biological and medical fields.[1−3] Thus, there are many efforts to design and synthesize advanced functional materials based on aliphatic polyesters by controlling the molecular weight, molecular weight distribution, composition, and chain end functionality.[2,4−8] Well-defined aliphatic polyesters are generally produced by the ring-opening polymerization (ROP) of cyclic esters using metallic catalysts based on Al, Zn, Ti, Sn, and Ca.[4] However, metallic residues originating from the catalysts are difficult to be removed from the obtained polyesters, which prevented the practical use of polyester-based materials for biomedical and electronic applications. Although metal-free aliphatic polyesters can be obtained using an enzymatic method, it is hard to control the precise structures of the obtained polymers.[9]

Complementing organometallic and enzymatic catalysts, the metal-free catalyst, i.e., an organocatalyst, has rapidly developed in the synthetic organic chemistry field, which has recently emerged as a suitable catalyst for the ROP of cyclic esters, to afford metal-free aliphatic polyesters.[5] For example, organocatalysts, such as *N*-heterocyclic carbene,[10−13] 4-(dimethylamino)pyridine,[14] thiourea/amine,[15,16] alcohol derivatives,[17] carboxylic acids,[18,19] guanidine,[20,21] phosphazene,[22,23] trifluoromethanesulfonic acid,[24,25] methanesulfonic acid,[25] and the $HCl\cdot Et_2O$ complex,[26−28] were found to catalyze various living ROPs of cyclic esters. However, in spite of the significant advantage of the organocatalyzed ROP from the viewpoint of material applications, the organocatalyzed ROP of cyclic esters has been insufficiently used when compared to the organometallic-catalyzed one.[4,6] Thus, it is important to evaluate the organocatalysts available for the ROP of cyclic esters in order to develop the organocatalyzed polymerization as a new polymer synthetic methodology.

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Recently, we reported that trifluoromethanesulfonimide ($HNTf_2$), a very strong Brønsted acid, could promote the group transfer polymerization (GTP) of methyl methacrylate using 1-methoxy-1-trimethylsilyloxy-2-methylpropene as the initiator to afford the highly syndiotactic poly(methyl methacrylate) without the aid of heavy metals.[29] Although $HNTf_2$ has emerged as a leading catalyst in the field of synthetic organic chemistry due to its high reactivity,[30−34] the reported employment of $HNTf_2$ is extremely limited in synthetic polymer chemistry. To the best of our knowledge, except for our $HNTf_2$-catalyzed GTP system,[29] there have been few reports dealing with $HNTf_2$ as a catalyst for polymer synthesis.[35] Thus, of great interest is the evaluation of the scope and limit of $HNTf_2$ as the organocatalyst in synthetic polymer chemistry. We now report that $HNTf_2$ is used as an organocatalyst for the ROP of δ-valerolactone (δ-VL) as the cyclic ester along with 3-phenyl-1-propanol (3-Ph-PrOH) as the initiator, as illustrated in Scheme 1. This article describes (1) the characterization and optimization of the $HNTf_2$-catalyzed ROP of δ-VL, (2) the mechanistic insight into the $HNTf_2$-catalyzed ROP of a cyclic ester using ^{1}H NMR, SEC, and MALDI-TOF MS analyses of the obtained PVL, and (3) the intrinsic advantages of the cationic ROP system using initiators that possess an inherent reactivity toward nucleophiles.

Results and Discussion

$HNTf_2$-Catalyzed ROP of δ-Valerolactone. In order to characterize $HNTf_2$ as an cationic catalyst for the living ROP of δ-valerolactone (δ-VL), we first carried out the polymerization of δ-VL using 3-phenyl-1-propanol (3-Ph-PrOH) as the initiator in CH_2Cl_2 at 27 °C with the $[\delta\text{-VL}]_0/[\text{3-Ph-PrOH}]_0/[HNTf_2]_0$ of 100:1:0.1 (Table 1, run1). The polymerization proceeded homogeneously, and the conversion of δ-VL reached 77.2% after 48 h, which was directly determined from the ^{1}H NMR spectrum of the aliquots of the polymerization mixture in $CDCl_3$. The obtained polymer was purified by quenching with immobilized base and subsequent

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Scheme 1. $HNTf_2$-Catalyzed Living Ring-Opening Polymerization of δ-Valerolactone

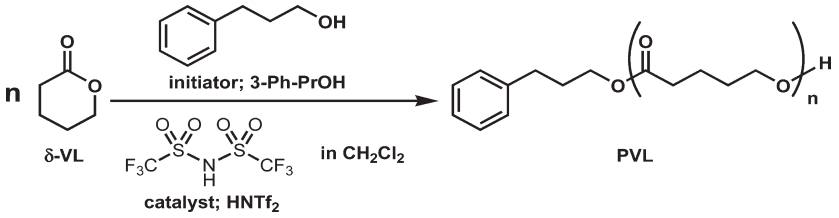


Table 1. ROP of δ-Valerolactone Using $HNTf_2$ as the Catalyst[a]

run	$[M]_0/[I]_0/[cat.]_0$	$[M]_0$ (mol L^{-1})	time (h)	conv[b] (%)	$M_{n,theo}$[c] (g mol^{-1})	$M_{n,NMR}$[d] (g mol^{-1})	M_w/M_n[d]
1	100/1/0.1	1.0	48	77.2	7900	9900	1.16
2	100/1/0.1	2.0	21	88.9	9000	9300	1.12
3	100/1/0.1	3.0	9	92.6	9400	9600	1.09
4	100/1/0.1	4.0	9	94.5	9600	10500	1.11
5	50/1/0.1	3.0	2	91.3	4700	4200	1.12
6	80/1/0.1	3.0	5	90.0	7300	7400	1.10
7	130/1/0.1	3.0	14	85.8	11300	12700	1.10

[a] Solvent, CH_2Cl_2; temperature, 27 °C. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[I]_0) \times$ conv $\times$ (MW of δ-VL) + (MW of 3-Ph-PrOH). [d] Determined by SEC in $CHCl_3$ using PSt standards.

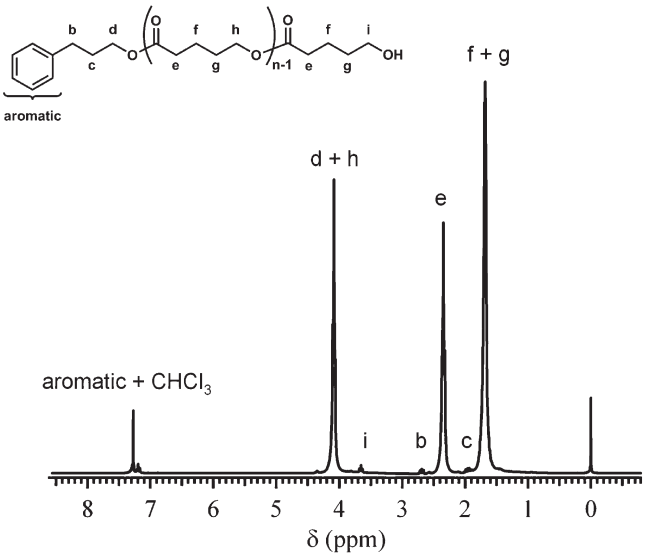


Figure 1. ^1H NMR spectrum of the obtained PVL ($[M]_0/[I]_0/[cat.]_0$ = 50/1/0.1, conversion = 91.3%, $M_{n,NMR}$ = 4200 g mol^{-1}, M_w/M_n = 1.12).

reprecipitation using CH_2Cl_2/cold hexane as the solvent. The chemical structure of the poly(δ-valerolactone) (PVL) was confirmed by the ^1H NMR measurement (Figure 1). A more detailed discussion about the structure of the obtained PVL is described in a later section dealing with the mechanistic aspect of the $HNTf_2$-catalyzed ROP (vide infra). Importantly, the number-average molecular weight ($M_{n,NMR}$) of the obtained polymer estimated from the ^1H NMR measurement agreed fairly well with that ($M_{n,theo}$) calculated from the initial ratio of $[\delta\text{-VL}]_0/[3\text{-Ph-PrOH}]_0$. In addition, the molecular weight distribution (M_w/M_n) of 1.16, estimated from the SEC measurement, was relatively low. These results suggested that the combination of the alcohol initiator of 3-phenyl-1-propanol and $HNTf_2$ as the catalyst was suitable for the ROP of δ-VL. Thus, 0.1 mol % of $HNTf_2$ based on the initial monomer feed was found to effectively catalyze the ROP of δ-VL at ambient temperature.

The initial monomer concentration affected the control of the molecular weight and its polydispersity together with the monomer conversion for the $HNTf_2$-catalyzed ROP of δ-VL (Table 1). With the increasing monomer concentrations of

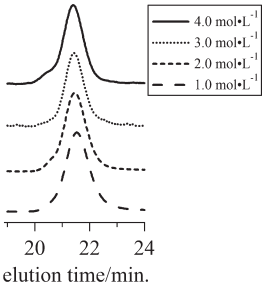


Figure 2. SEC traces of the obtained PVL with various monomer concentrations ranging from 1.0 to 4.0 mol L^{-1}.

2.0 and 3.0 mol L^{-1}, the monomer conversions were higher than that for 1.0 mol L^{-1}; 88.9% at 2.0 mol L^{-1} for 21 h and 92.6% at 3.0 mol L^{-1} for 9 h. Most importantly, for the monomer concentration of 3.0 mol L^{-1} and lower (Table 1, runs 1−3), the SEC profiles of the obtained PVLs showed unimodal and symmetric traces (Figure 2), and the polydispersity indices of the obtained PVL remained low, ranging from 1.09 to 1.16. In clear contrast, for the monomer concentration of 4.0 mol L^{-1}, the SEC profile of the obtained PVL showed a shoulder peak in the high molecular weight region (Figure 2), obviously indicating that the high monomer concentration induced the intermolecular esterification process. These results indicated that one of the suitable polymerization conditions for the $HNTf_2$-catalyzed ROP was the monomer concentration of 3.0 mol L^{-1}.

Living Nature of the $HNTf_2$-Catalyzed ROP of δ-VL. To confirm that the polymerization system proceeded through a living mechanism, we carried out the ROP of δ-VL by varying $[\delta\text{-VL}]_0/[3\text{-Ph-PrOH}]_0$ from 50 to 130 (Table 1, runs 3 and 5−7). As a direct consequence of the living nature of the $HNTf_2$-catalyzed ROP of δ-VL, the molecular weights of the resultant PVLs linearly increased with the increasing initial ratio of $[\delta\text{-VL}]_0/[3\text{-Ph-PrOH}]_0$. In addition, the obtained PVLs had molecular weights predicted from the initial ratios of $[\delta\text{-VL}]_0/[3\text{-Ph-PrOH}]_0$ and monomer conversions.

For further evidence of the living nature of the $HNTf_2$-catalyzed ROP of δ-VL, we carried out kinetic and post-polymerization experiments using $[\delta\text{-VL}]_0$ = 3.0 mol L^{-1} and $[\delta\text{-VL}]_0/[3\text{-Ph-PrOH}]_0/[HNTf_2]_0$ = 100/1/0.1. For the kinetic plots shown in Figure 3b, a distinct first-order

relationship between the reaction time and monomer conversion was observed, meaning that the monomer consumption rate was constant during the polymerization. Furthermore, the molecular weight of the obtained PVL linearly increased with the reaction time and the monomer conversion was as high as ≈95%, as shown in Figure 3a. More importantly, the number-average polymerization degrees of the obtained PVLs, which were estimated from the ^{1}H NMR analysis, were in good agreement with that calculated by the initial ratio of $[\delta\text{-VL}]_0/[\text{3-Ph-PrOH}]_0$ and the monomer conversion. In addition, the polydispersity indices of the obtained PVLs had low values ranging from 1.08 to 1.13.

The chain extension experiment also supported the living nature of the $HNTf_2$-catalyzed ROP of δ-VL. Figure 4 shows SEC traces for the chain extension experiment. A PVL with $M_{n,SEC}$ = 9200 g mol^{-1} and M_w/M_n = 1.18 was first prepared by the 93.5% conversion of 50 equiv of δ-VL using $[\text{3-Ph-PrOH}]_0/[HNTf_2]_0$ = 1/0.1. The polymerization was further carried out by the subsequent addition of 50 equiv of δ-VL to afford a PVL with $M_{n,SEC}$ = 15 400 g mol^{-1} and M_w/M_n = 1.23, indicating that the chain end group of the PVL possessed a truly living nature. Thus, the $HNTf_2$-catalyzed ROP of δ-VL was revealed to proceed through a living mechanism and produce a precisely controlled PVL at ambient temperature.

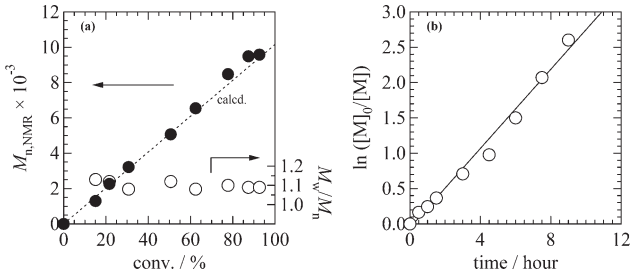


Figure 3. (a) Kinetic plots for the polymerization of δ-VL and (b) dependence of molecular weight (M_n) and polydispersity (M_w/M_n) on the monomer conversion (conv). The dashed line shows the $M_{n,theo}$ values calculated from the equation $([M]_0/[I]_0) \times \text{conv} \times (\text{MW of } \delta\text{-VL}) + (\text{MW of 3-Ph-PrOH})$.

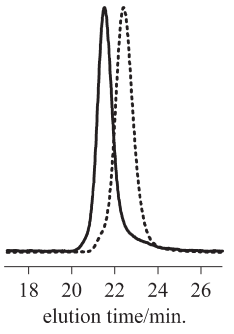


Figure 4. SEC traces of first PVL sequence (dashed line) and post-polymerization (solid line) (eluent, $CHCl_3$; flow rate, 0.8 mL min^{-1}).

We finally focused on the mechanistic aspects of the living characteristics for the $HNTf_2$-catalyzed ROP of δ-VL. We assumed a polymerization mechanism based on the analogy of the principle for the Brønsted acid-catalyzed ROP of cyclic esters, the so-called activated monomer mechanism, reported by Penczek et al., as shown in Scheme 2, because the activated monomer mechanism was estimated for a similar Brønsted acid-catalyzed ROP of cyclic esters systems.[24,26,36] First, the chain-end functionality was characterized on the basis of the ^{1}H NMR and SEC measurements (Figures 1 and 5, respectively). In the ^{1}H NMR spectrum of the obtained PVL, distinct peaks due to the initiator of 3-phenyl-1-propanol were observed. The peaks due to the phenyl protons, the benzyl protons, and the methylene protons adjacent to the ester linkage appeared in the range from 7.17 to 7.31 ppm, from 2.67 to 2.71 ppm, and from 1.94 to 2.0 ppm, respectively. In addition, the peak due to the methylene protons adjacent to the ω-chain end of the hydroxyl group was clearly observed in the range from 3.64 to 3.67 ppm. These results imply that the polymerization was initiated from 3-phenyl-1-propanol. Further evidence that 3-phenyl-1-propanol was the actual initiating agent was obtained from the SEC measurements. In Figure 5, the SEC trace of the obtained PVL monitored by an RI detector showed almost the same shape and retention time as that by the UV detector, indicating that the PVL chain possessed the 3-phenyl-1-propanol moiety at the α-chain end. These results obviously showed that 3-phenyl-1-propanol acted as the initiating agent for the ROP of δ-VL, which strongly supported the fact that the $HNTf_2$-catalyzed ROP of δ-VL proceeded through an activated monomer mechanism, as shown in Scheme 2.

In order to provide direct evidence that the $HNTf_2$-catalyzed ROP of δ-VL was initiated by 3-phenyl-1-propanol and occurred via an activated monomer mechanism, a MALDI-TOF MS measurement was carried out, as shown in Figure 6. From the MALDI-TOF MS analysis of the obtained PVL, only one series of peaks was observed, which perfectly agreed with the molecular weight of PVL possessing the 3-phenyl-1-propanol residue and the hydroxyl chain end. This result means that the $HNTf_2$-catalyzed ROP of

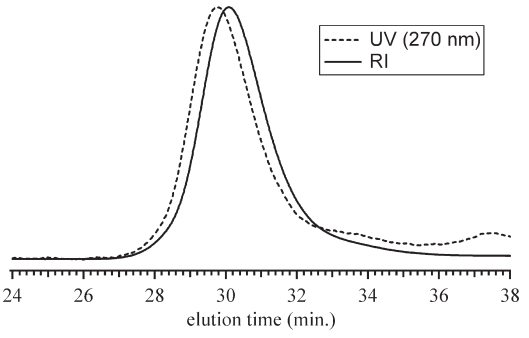
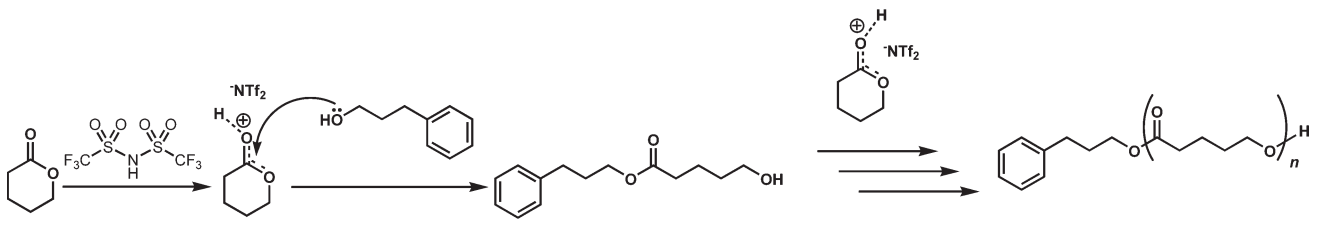


Figure 5. SEC traces of the obtained PVL ($[M]_0/[I]_0/[cat.]_0$ = 50/1/0.1, conversion = 91.3%, $M_{n,NMR}$ = 4200 g mol^{-1}, M_w/M_n = 1.12) (eluent, DMF containing 0.01 M LiCl; flow rate, 0.4 mL min^{-1}).

Scheme 2. Activated Monomer Mechanism for the $HNTf_2$-Catalyzed ROP of δ-VL



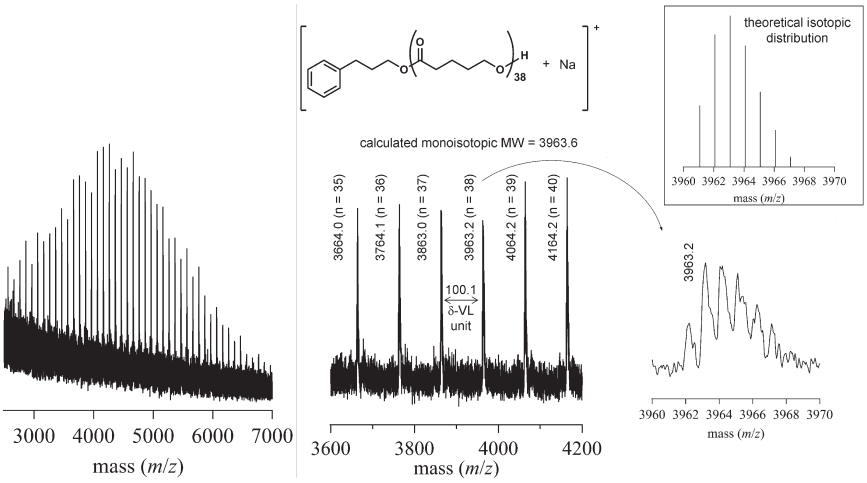


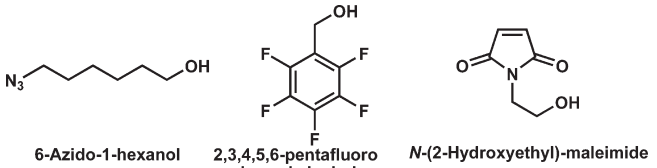
Figure 6. MALDI-TOF MS spectra in reflector mode of the obtained PVL ($[M]_0/[I]_0/[cat.]_0$ = 50/1/0.1, conversion = 91.3%, $M_{n,NMR}$ = 4200 g mol^{-1}, M_w/M_n = 1.12).

Table 2. Synthesis of End-Functionalized PVL by the $HNTf_2$-Catalyzed ROP of δ-VL Using Functional Initiators[a]

run	initiator	conv[b] (%)	$M_{n,theo}$[c] (g mol^{-1})	$M_{n,NMR}$[d] (g mol^{-1})	M_w/M_n[d]
8	6-azido-1-hexanol	92.0	4700	4700	1.12
9	2,3,4,5,6-pentafluorobenzyl alcohol	80.9	4200	5100	1.17
10	*N*-(2-hydroxyethyl)-maleimide	91.0	4700	6300	1.11

[a] [M] = 3.0 mol L^{-1}; $[M]_0/[I]_0/[cat.]_0$ = 50/1/0.1; time = 2 h; solvent, CH_2Cl_2; temperature, 27 °C. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[I]_0) \times$ conv × (MW of δ-VL) + (MW of initiators). [d] Determined by SEC in $CHCl_3$ using PSt standards.

Chart 1. Chemical Structures of the Employed Functional Initiators



δ-VL proceeded in a living manner without any side reactions, such as backbiting and transesterification reactions, thus supporting the fact that the $HNTf_2$-catalyzed ROP of δ-VL proceeded through the activated monomer mechanism,[24,26,36] in which 3-phenyl-1-propanol was obviously the initiator.

Synthesis of the End-Functionalized PVLs with Clickable Groups. To provide an intrinsic advantage of the $HNTf_2$-catalyzed ROP of δ-VL, we finally focused on the synthesis of the end-functionalized PVLs using functional initiators. We selected 6-azido-1-hexanol, 2,3,4,5,6-pentafluorobenzyl alcohol, and *N*-(2-hydroxyethyl)maleimide as the functional initiators (Chart 1) because they are well-established click-ready functional groups.[37−39] However, the 2,3,4,5,6-pentafluorobenzyl and maleimide moieties are well-known to easily react with nucleophiles, such as thiols and amines, which, in turn, directly required the polymerization system to be cationic. Furthermore, organo-azide compounds possess the potential danger of explosion when treated together with heavy metals, which is one of the advantages of utilizing the organocatalytic approach. Table 2 lists the synthetic results of the end-functionalized PVLs. All the $HNTf_2$-catalyzed ROP of δ-VL using 6-azido-1-hexanol, 2,3,4,5,6-pentafluorobenzyl alcohol, and *N*-(2-hydroxyethyl)maleimide proceeded in a well-controlled manner to afford the corresponding PVLs with predictable molecular weights and narrow polydispersity indices. The $M_{n,NMR}$ values of the obtained PVLs estimated from ^{1}H NMR measurement showed good agreement with the $M_{n,theo}$ values calculated from the $[\delta\text{-VL}]_0/[\text{functional initiator}]_0$. In addition, the introduction of these functional groups at the α-position of the obtained PVLs was confirmed by a ^{1}H NMR analysis (see Supporting Information). Thus, we first revealed that $HNTf_2$ was an efficient organocatalyst for the ROP of the lactone affording well-defined polyester-based materials.

Conclusions

The combination of alcohol derivatives as the initiators and $HNTf_2$ as the catalyst was revealed to be an efficient cationic catalyst for the ROP of δ-valerolactone, which proceeded in a living manner and produced well-controlled PVLs. The $HNTf_2$-catalyzed ROP of δ-VL was achieved using functional initiators, such as the 6-azido-1-hexanol, 2,3,4,5,6-pentafluorobenzyl alcohol, and *N*-(2-hydroxyethyl)maleimide, to afford the end-functionalized PVLs with click-ready moieties, showing a high tolerance to the functional group for the $HNTf_2$-catalyzed living ROP system. To the best of our knowledge, this is the first demonstration of the strong Brønsted acid of the $HNTf_2$-catalyzed living ROP system for cyclic esters, which leads to this new concept in synthetic polymer chemistry.

Experimental Section

Materials. Dichloromethane (>99.5%; water content <0.001%) was purchased from Kanto Chemical Co., Inc., and distilled over CaH_2 under an argon atmosphere. δ-Valerolactone (δ-VL; 99%, Kanto Chemical Co., Inc.) was distilled over CaH_2 under reduced pressure. Trifluoromethanesulfonimide ($HNTf_2$) was available from Sigma-Aldrich Chemicals Co. and used as received. 3-Phenyl-1-propanol was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI), and distilled over CaH_2 under an argon atmosphere. The weak base anion exchange resin, Amberlyst A21, was commercially available and used as received. *N*-(2-Hydroxyethyl)maleimide[40] and 6-azido-1-hexanol[41] were synthesized according to previously reported methods. 2,3,4,5,6-Pentafluorobenzyl alcohol was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI), and used as received.

Instruments. The ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-A400II instruments. The polymerization was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, O_2 < 1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. The size exclusion chromatography (SEC) in $CHCl_3$ was performed at 40 °C (0.8 mL min^{-1}) using a Jasco GPC-900 system equipped with a set of two Shodex K-805 L columns (linear, 8 mm × 300 mm). The SEC in DMF containing lithium chloride (0.01 mol L^{-1}) was performed at 40 °C using a Jasco high-performance liquid chromatography (HPLC) system (PU-980 Intelligent HPLC pump, CO-965 column oven, RI-930 Intelligent RI detector, and Shodex DEGAS KT-16) equipped with a Shodex Asahipak GF-310 HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 5 μm; exclusion limit, 4×10^4) and a Shodex Asahipak GF-7 M HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 9 μm; exclusion limit, 4×10^7) at the flow rate of 0.4 mL min^{-1}. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the obtained polymers was performed using an Applied Biosystems Voyager-DE STR-H equipped with a 337 nm nitrogen laser (3 ns pulse width). A total of 512 shots were accumulated for the spectra at a 25 kV acceleration voltage in the reflector mode and calibrated using insulin (TAKARA BIO, Inc.) as the internal standard. Samples for the MALDI-TOF MS were prepared by mixing the polymer (5.0 mg mL^{-1}, 10 μL), a matrix (dithranol, 25 mg mL^{-1}, 10 μL), and a cationization agent (sodium trifluoroacetate, 3.0 mg mL^{-1}, 10 μL) in THF.

Polymerization of δ-Valerolactone. A typical procedure for the polymerization is as follows: δ-VL (0.6 g, 6.0 mmol) was added to a solution of 3-phenyl-1-propanol (8.2 mg, 60 μmol) in CH_2Cl_2 in a glovebox. The CH_2Cl_2 stock solution of $HNTf_2$ (1.7 mg, 6.0 μmol) was then added to the solution to initiate the polymerization at 27 °C under an argon atmosphere. The polymerization was quenched after 9 h by the addition of Amberlyst A21. Before the Amberlyst A21 addition, we obtained a portion of the polymerization mixtures for determining the monomer conversion. The monomer conversion was directly determined from the ^{1}H NMR measurements of the polymerization mixtures after the addition of a small amount of triethylamine. The polymer was isolated by reprecipitation from CH_2Cl_2 in cold hexane. Yield: 72.0%. SEC (RI): $M_{n,SEC}$ = 18 800 g mol^{-1}, M_w/M_n = 1.09. ^{1}H NMR ($CDCl_3$) ppm: 7.17−7.31 (m, 5H, aromatic), 4.58 (bs, 1H, OH), 4.08 (t, 193H, CH_2O polymer backbone, Ph−$CH_2CH_2CH_2O$ initiator), 3.65 (t, 2H, CH_2OH), 2.69 (t, 2H, Ph−CH_2CH_2 initiator), 2.34 (m, 191H, C(=O)CH_2 polymer backbone), 1.96 (m, 2H, Ph−$CH_2CH_2CH_2O$ initiator), 1.69 (m, 382H, CH_2CH_2 polymer backbone).

Supporting Information Available: ^{1}H NMR spectra of the end-functionalized PVLs. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Barrett, D. G.; Yousaf, M. N. *Molecules* **2009**, *14*, 4022–4050.
(2) Coulembier, O.; Degée, P.; Hedrick, J. L.; Dubois, P. *Prog. Polym. Sci.* **2006**, *31*, 723–747.
(3) Ueda, H.; Tabata, Y. *Adv. Drug Delivery Rev.* **2003**, *55*, 501–518.
(4) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147–6176.
(5) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813–5840.
(6) Labet, M.; Thielemans, W. *Chem. Soc. Rev.* **2009**, *38*, 3484–3504.
(7) Kubisa, P.; Penczek, S. *Prog. Polym. Sci.* **1999**, *24*, 1409–1437.
(8) Penczek, S.; Cypryk, M.; Duda, A.; Kubisa, P.; Słomkowski, S. *Prog. Polym. Sci.* **2007**, *32*, 247–282.
(9) Kobayashi, S. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3041–3056.
(10) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, D. A.; Hagberg, E. C.; Nyce, G. W.; Waymouth, R. M.; Hedrick, J. L. *Polymer* **2006**, *47*, 4018–4025.
(11) Dove, A. P.; Li, H.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, D. A.; Waymouth, R. M.; Hedrick, J. L. *Chem. Commun.* **2006**, 2881–2883.
(12) Culkin, D. A.; Jeong, W.; Csihony, S.; Gomez, E. D.; Balsara, N. R.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2627–2630.
(13) Kamber, N. E.; Jeong, W.; Gonzalez, S.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2009**, *42*, 1634–1639.
(14) Nederberg, F.; Connor, E. F.; Möller, M.; Glauser, T.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 2712–2715.
(15) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 13798–13799.
(16) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Lundberg, P. N. P.; Dove, A. P.; Li, H.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 7863–7871.
(17) Coulembier, O.; Sanders, D. P.; Nelson, A.; Hollenbeck, A. N.; Horn, H. W.; Rice, J. E.; Fujiwara, M.; Dubois, P.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 5170–5173.
(18) Sanda, F.; Sanada, H.; Shibasaki, Y.; Endo, T. *Macromolecules* **2002**, *35*, 680–683.
(19) Casas, J.; Persson, P. V.; Iversen, T.; Córdova, A. *Adv. Synth. Catal.* **2004**, *346*, 1087–1089.
(20) Chuma, A.; Horn, H. W.; Swope, W. C.; Pratt, R. C.; Zhang, L.; Lohmeijer, B. G. G.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L.; Rice, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 6749–6754.
(21) Lohmeijer, B. G. G.; Pratt, R. C.; Leibfarth, F.; Logan, J. W.; Long, D. A.; Dove, A. P.; Nederberg, F.; Choi, J.; Wade, C.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 8574–8583.
(22) Zhang, L.; Nederberg, F.; Messman, J. M.; Pratt, R. C.; Hedrick, J. L.; Wade, C. G. *J. Am. Chem. Soc.* **2007**, *129*, 12610–12611.
(23) Zhang, L.; Nederberg, F.; Pratt, R. C.; Waymouth, R. M.; Hedrick, J. L.; Wade, C. G. *Macromolecules* **2007**, *40*, 4154–4158.
(24) Bourissou, D.; Martin-Vaca, B.; Dumitrescu, A.; Graullier, M.; Lacombe, F. *Macromolecules* **2005**, *38*, 9993–9998.
(25) Gazeau-Bureau, S.; Delcroix, D.; Martín-Vaca, B.; Bourissou, D.; Navarro, C.; Magnet, S. *Macromolecules* **2008**, *41*, 3782–3784.
(26) Shibasaki, Y.; Sanada, H.; Yokoi, M.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 4316–4320.
(27) Kim, M. S.; Seo, K. S.; Khang, G.; Lee, H. B. *Macromol. Rapid Commun.* **2005**, *26*, 643–648.
(28) Lou, X.; Detrembleur, C.; Jérôme, R. *Macromolecules* **2002**, *35*, 1190–1195.
(29) Kakuchi, R.; Chiba, K.; Fuchise, K.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 8747–8750.
(30) Cossy, J.; Lutz, F.; Alauze, V.; Meyer, C. *Synlett* **2002**, 45–48.
(31) Inanaga, K.; Takasu, K.; Ihara, M. *J. Am. Chem. Soc.* **2005**, *127*, 3668–3669.
(32) Takasu, K.; Nagao, S.; Ihara, M. *Adv. Synth. Catal.* **2006**, *348*, 2376–2380.
(33) Yamamoto, H. *Tetrahedron* **2007**, *63*, 8377–8412.
(34) Akiyama, T. *Chem. Rev.* **2007**, *107*, 5744–5758.
(35) Desmurs, J.-R.; Ghosez, L.; Martins, J.; Deforth, T.; Mignani, G. *J. Organomet. Chem.* **2002**, *646*, 171–178.
(36) Penczek, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1919–1933.
(37) Lutz, J.-F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1018–1025.
(38) Pounder, R. J.; Stanford, M. J.; Brooks, P.; Richards, S. P.; Dove, A. P. *Chem. Commun.* **2008**, 5158–5160.
(39) Becer, C. R.; Babiuch, K.; Pilz, D.; Hornig, S.; Heinze, T.; Gottschaldt, M.; Schubert, U. S. *Macromolecules* **2009**, *42*, 2387–2394.
(40) Heath, W. H.; Palmieri, F.; Adams, J. R.; Long, B. K.; Chute, J.; Holcombe, T. W.; Zieren, S.; Truitt, M. J.; White, J. L.; Willson, C. G. *Macromolecules* **2008**, *41*, 719–726.
(41) Misaka, H.; Kakuchi, R.; Zhang, C.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 5091–5096.