ORIGINAL ARTICLE

Ring-opening polymerization of ϵ -caprolactone with dilithium tetra-*tert*-butylzincate under mild conditions

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We performed ring-opening polymerization (ROP) of ϵ -caprolactone with dilithium tetra-*tert*-butylzincate (TBZL) in toluene. TBZL is a bulky zincate complex with a range of unique reactivities such as unusually low basicity and high chemoselectivity; it is a metal catalyst of low toxicity. The initiating species for ROP of ϵ -caprolactone is, however, not the *tert*-butyl anion of TBZL but the hydroxyl anion derived from a trace amount of H₂O in the system. Instead of a trace amount of H₂O in the system, a known amount of benzyl alcohol (BnOH) was added as an ROP initiator. Poly(ϵ -caprolactone) with a BnO group at the initiating chain-end was obtained, as expected. ¹H and ¹³C NMR spectra of a TBZL–BnOH mixture suggested the formation of a complex; the complex was the initiating species. The M_n increased linearly with increasing conversion. This means that the number of polymer chains is constant throughout the polymerization. The molecular weight distributions were relatively narrow, except with increased temperatures and/or prolonged polymerization times. This system does not need a high polymerization temperature or long polymerization time and uses a metal compound that has little effect on the environment. Poly(ϵ -caprolactone) with a narrow molecular weight distribution can therefore be obtained under mild conditions.

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INTRODUCTION

Aliphatic polyesters have received much attention because of their biodegradability and biocompatibility. Poly(ϵ -caprolactone) (PCL), in particular, is used industrially and medically. PCL is usually prepared by ring-opening polymerization (ROP) of ϵ -caprolactone, catalyzed by metal compounds, enzymes, organic compounds or inorganic compounds.¹ Mechanisms for ROP of ϵ -caprolactone are generally classified into four categories, depending on the catalyst: anionic, cationic, monomer-activated, or coordination–insertion ROP. Although each initiation system has advantages and disadvantages, broadening of the molecular weight distribution derived from intramolecular transesterification (back-biting), generally occurring in the later stages of anionic ROP, is especially unfavorable.

Living anionic ROP of ϵ -caprolactone with another metal catalyst, namely a combination of *tert*-butyllithium and bulky aluminum phenoxide, was reported to give polymers with narrow molecular weight distributions.² In that study, the *tert*-butyl anion initiated ROP of ϵ -caprolactone and aluminum phenoxide coordinated with the carbonyl carbon of the ϵ -caprolactone monomer. The ROP proceeded in a living manner because the bulky aluminum phenoxide stabilized the propagating species to prevent transesterification.

Here, we report the ROP of ϵ -caprolactone catalyzed by dilithium tetra-*tert*-butylzincate (TBZL), which is a metal catalyst of low toxicity. TBZL is a bulky zincate complex that has a range of unique reactivities such as unusually low basicity and high chemoselectivity.^{3–6} TBZL acts as an anionic initiator for the polymerization of

N-isopropylacrylamide in aqueous media^{3,6} or in toluene in the presence of a fluorinated alcohol or Lewis acid.⁶

On the basis of these previous reports, we considered that the ROP of ϵ -caprolactone with TBZL would also proceed by an anionic mechanism, with the *tert*-butyl anion of TBZL acting as an anionic initiator. In the present paper, the polymerization mechanism of ROP with TBZL was investigated using ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopies, size-exclusion chromatography (SEC) and matrix-assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI–TOFMS). These characterizations of the obtained PCL suggested that the initiating species for ROP of ϵ -caprolactone with TBZL is not the *tert*-butyl anion of TBZL, and unexpectedly, the ROP proceeded by a coordination–insertion mechanism.

EXPERIMENTAL PROCEDURE

Materials

ϵ -Caprolactone (>99%) was purchased from the Tokyo Chemical Industry (Tokyo, Japan) and distilled before use. Benzyl alcohol (BnOH; >99%) was purchased from Wako Pure Chemical Industries (Osaka, Japan) and distilled before use. Toluene (super dehydrated; >99.5%), tetrahydrofuran (THF, super dehydrated; >99.5%), lithium chloride (>99%) and zinc chloride (>99.9%) were purchased from Wako Pure Chemical Industries. A THF solution of TBZL was supplied by the Tosoh Finechem (Yamaguchi, Japan). *tert*-Butyllithium (^tBuLi; 1.65 mol l^{–1} in pentane), lithium bis(trifluoromethanesulfonyl)imide (Li(SO₂CF₃)₂; 99.7%) and *n*-hexane (>95%) were purchased from the Kanto Chemical (Tokyo, Japan).

Figure 1 (a) MALDI-TOF mass spectrum of PCL prepared with TBZL. Expanded spectra at the range of 800–970 m/z (b), and of 1480–1650 m/z (c).

Measurements

The 400-MHz ^1H NMR spectra were obtained using an ECX-400 spectrometer (JEOL, Tokyo, Japan). The number-average molecular weights (M_n) and the polydispersity indexes (M_w/M_n) of the polymers were determined using SEC, calibrated against polystyrene standards. SEC was performed using an HLC 8220 chromatograph (Tosoh, Yamaguchi, Japan) equipped with TSK gel columns (SuperHM-M (6.5 mm ID $\times$ 150 mm) and SuperHM-H (6.5 mm ID $\times$ 150 mm), Tosoh). Dimethylformamide containing LiBr (10 mmol L^{-1}) was used as the eluent, at 40 $^\circ\text{C}$ and a flow rate of 0.35 mL min^{-1} . The initial polymer concentration was 1.0 mg mL^{-1} . MALDI-TOFMS was performed using an Autoflex Speed-TK spectrometer (Bruker Daltonics, Billerica, MA, USA) with dithranol and NaI as the matrix and ionizing agent, respectively. The zinc and lithium contents of the THF solution of TBZL were determined by titration.

Concentration of TBZL solution

A THF solution of TBZL (~ 0.500 ml) was added to aqueous HCl (N/2, ~ 10.00 ml) containing phenolphthalein as a pH indicator. The solution was titrated with an aqueous solution of NaOH (N/2). This procedure was repeated three times.

$$\text{TBZL (mol L}^{-1}\text{)} = \frac{(M_{\text{HCl}} \times V_{\text{HCl}} - M_{\text{NaOH}} \times V_{\text{NaOH}})}{V_{\text{TBZL}}} \times \frac{1}{4}$$

TBZL contains four *tert*-butyl anions and reacts with a fourfold molar amounts of acid. The concentration of the TBZL solution was determined using the above equation. M_{HCl} , V_{HCl} , M_{NaOH} , V_{NaOH} and V_{TBZL} are the molar concentrations of HCl, the added HCl volume, the molar concentration of NaOH, the added NaOH volume and the TBZL volume, respectively. The titration and inductively coupled plasma optical emission spectroscopy showed that the THF solution of TBZL (base: 0.626 mol L^{-1}) contained 3.6 wt% zinc and 1.4 wt% lithium.

ROP of ϵ -caprolactone with TBZL

A typical polymerization procedure was as follows. ϵ -Caprolactone (0.5 g, 4.4 mmol) was diluted with toluene to a total volume of 5 ml, and this solution

(4 ml) was transferred to a glass ampoule. The ampoule was degassed and filled with nitrogen three times. TBZL (0.11 ml, 0.626 mol L^{-1} in THF solution) was added under a nitrogen atmosphere to the ampoule, which had been placed in a constant-temperature bath. Then the mixture was stirred. After the reaction, the mixture was diluted with THF and poured into *n*-hexane (200 ml). The polymer precipitate was collected by centrifugation and dried *in vacuo*. The polymer yield was determined gravimetrically.

Preparation of $^t\text{Bu}_4\text{ZnLi}_2$ and $^t\text{Bu}_2\text{Zn}$

$^t\text{Bu}_4\text{ZnLi}_2$ and $^t\text{Bu}_2\text{Zn}$ were prepared by the addition of 4 or 2 molar amounts, respectively, of $^t\text{BuLi}$ (1.65 mol L^{-1} in pentane) relative to ZnCl_2 in THF.^{3,4}

RESULTS AND DISCUSSION

ROP of ϵ -caprolactone with TBZL

First, we attempted the ROP of ϵ -caprolactone with TBZL in toluene at 0 $^\circ\text{C}$. The initial monomer concentration ($[M]_0$) and the $[M]_0/[TBZL]_0$ ratio were 1 mol L^{-1} and 50, respectively. The polymer was obtained at 94% yield in 10 min. M_n and M_w/M_n of the polymer were determined by SEC to be 9.0×10^3 and 2.01, respectively. The ^1H NMR spectrum indicated the formation of PCL via ROP of ϵ -caprolactone (Supplementary Figure S1). However, the resonance from the *tert*-butyl end group at 1.13 p.p.m.² was not observed in the PCL spectrum, although the *tert*-butyl anion of TBZL has been reported to initiate polymerization of *N*-isopropylacrylamide.^{3–6} The MALDI-TOF mass spectrum of the PCL showed two series of peaks, both at an interval of 114 m/z , corresponding to the repeating unit mass (Figure 1). The m/z values for the series with higher mass numbers (series A) agreed well with the monoisotopic masses of the

Scheme 1 Possible mechanism of cyclic PCL formation by ROP.

Table 1 ROP of ϵ -caprolactone with TBZL in the presence of BnOH in toluene

Run	$[M]_0$ (mol l ⁻¹)	$[M]_0/[TBZL]_0/[BnOH]_0$	Temp. (°C)	Time (h)	Yield (%)	$M_n \times 10^{-3}$		M_w/M_n^b
						Calcd	NMR ^a	
1	1.0	50/1/1	20	1	94	5.5	3.9	1.60
2	1.0	50/1/1	0	1	89	5.2	4.2	1.17
3	1.0	50/1/1	-20	1	25	1.5	1.8	1.10
4	1.0	50/1/1	-40	1	Trace	—	—	—
5	2.0	400/1/4	0	40 min	85	9.8	19.6	1.23
6 ^c	2.0	400/1/4	0	24	0	—	—	—
7 ^d	2.0	400/1/4	0	24	0	—	—	—
8 ^e	2.0	400/1/4	0	1	92	10.6	9.2	1.13
9 ^f	2.0	400/1/4	0	24	0	—	—	—
10 ^g	2.0	400/1/4	0	40 min	73	8.4	13.5	1.37

^aDetermined by ¹H NMR spectroscopy (in CDCl₃) intensity ratio.

^bDetermined by SEC in DMF, calibrated using standard PSSs.

^cLiCl was used as a catalyst instead of TBZL.

^dLiN(SO₂CF₃)₂ was used as a catalyst instead of TBZL.

^eBu₄ZnLi₂ prepared by ourselves was used as a catalyst.

^fBu₂Zn was used as a catalyst instead of TBZL.

^gBnOH was premixed with TBZL for 15 min before adding ϵ -caprolactone.

Na⁺ adducts of cyclic PCL (for example, $n = 13$, $M_{\text{theor}} = 1505.875$, $M_{\text{obs}} = 1505.890$). The m/z values for the series with lower mass numbers (series B) agreed well with the monoisotopic masses of the Na⁺ adducts of PCLs with a carboxyl group and a hydroxyl group at each chain-end (for example, $n = 13$, $M_{\text{theor}} = 1523.885$, $M_{\text{obs}} = 1523.900$).

These results suggest that the initiating species for ROP of ϵ -caprolactone is not the *tert*-butyl anion of TBZL but the hydroxyl anion derived from a trace amount of H₂O in the system. In other words, TBZL behaved not as an initiator but as a catalyst. PCL with a carboxyl group at the initiating chain-end and a hydroxyl group at the terminating chain-end was therefore considered to be produced preferentially. Furthermore, it was assumed that cyclic PCL was formed as a result of intramolecular condensation between the carboxyl and hydroxyl terminals (Scheme 1).

ROP of ϵ -caprolactone with TBZL in the presence of BnOH

Instead of a trace amount of H₂O in the system, a known amount of BnOH was added as an ROP initiator. The results of the ROP of ϵ -caprolactone in the presence of BnOH and TBZL are summarized in Table 1. The $[M]_0$ and $[M]_0/[TBZL]_0/[BnOH]_0$ ratios were 1–2 mol l⁻¹ and 50/1/1 to 400/1/4, respectively. ROP of ϵ -caprolactone in toluene at 20 °C gave a polymer with a broad molecular weight distribution (run 1). When the polymerization temperature

Figure 2 ¹H NMR spectrum of PCL prepared with TBZL in presence of BnOH (run 5, in CDCl₃ at 25 °C).

was decreased, the polymer yields and M_w/M_n values of the polymers that were obtained (runs 2 and 3) decreased. Polymerization at -40 °C gave no polymer (run 4).

In the ¹H NMR spectrum of the polymer obtained at 0 °C, benzyl group resonances were observed at 5.12 and 7.33–7.37 p.p.m. (Figure 2). The MALDI-TOF mass spectrum of the polymer showed a set of peaks at an interval of 114 m/z (Figure 3), and the values were consistent with the monoisotopic masses of Na⁺ adducts of PCL with a BnO group at the initiating chain-end and a hydroxyl group at the terminating chain-end (series C, for example, $n = 20$, $M_{\text{theor}} = 2412.409$, $M_{\text{obs}} = 2412.549$). However, a set of peaks corresponding to the monoisotopic masses of Na⁺ adducts of PCLs with a carboxyl group and a hydroxyl group at each end (series B, for example, $n = 7$, $M_{\text{theor}} = 839.477$, $M_{\text{obs}} = 839.501$) was observed in the lower mass region. These results indicate that BnOH can initiate the ROP of ϵ -caprolactone catalyzed by TBZL, as expected. In addition, cyclic PCL was not obtained by ROP in the presence of BnOH. The mechanism of generation of cyclic PCL in the absence of BnOH is not definite at the present stage. However, these results suggested that the cyclic PCL obtained by H₂O-initiated ROP was formed by an intramolecular condensation between the carboxyl and hydroxyl terminals.

TBZL is considered to be a tetrahedral dianion-type zincate, ^tBu₄Zn²⁻Li⁺.⁵ It was assumed that Li⁺ in TBZL acted as a Lewis acid catalyst in this polymerization system. LiCl or LiN(SO₂CF₃)₂ was therefore added instead of TBZL to examine the effect of Li⁺ on ROP of ϵ -caprolactone. However, neither LiCl nor LiN(SO₂CF₃)₂ exhibited

Figure 3 (a) MALDI-TOF mass spectrum of PCL prepared with TBZL in presence of BnOH (run 5). Expanded spectra at the range of 800–970 m/z (b), and of 2390–2560 m/z (c).

any catalytic activity in the ROP of ϵ -caprolactone, even with longer polymerization times (runs 6 and 7).

Figure 4 (top) shows the time-conversion curve for polymerization with an initial monomer concentration of $[M]_0$ and $[M]_0/[TBZL]_0/[BnOH]_0$ ratios of 2 mol l^{-1} and 400/1/4, respectively (run 5). After 5 min of initiation, an aliquot was removed from the reaction mixture, using a syringe, by flushing with N_2 gas; the aliquot was mixed with $CDCl_3$ for NMR spectroscopy or with n -hexane to precipitate the polymer for SEC (sample **a**). Similar procedures were performed after 10, 15, 20, 30 and 40 min of initiation (samples **b–f**, respectively). The monomer conversion was determined from the integral intensities of the NMR signals of the $-CH_2-O-CO-$ methylene protons in the monomer and polymer. The $M_{n,NMR}$ values were estimated by chain-end analysis of the NMR signals of the benzyl protons and those of the $-CH_2-O-CO-$ methylene protons based on the assumption that polymerization was initiated by BnOH only. The time-conversion curve and $\ln([M]_0/[M])$ versus time plots suggest that there was a significant induction period, probably because of slow initiation, but the polymerization rate after the induction period was first order with respect to the monomer concentration. Similar behaviors were observed in the ROP of ϵ -caprolactone with aluminum alkoxides^{7,8} or commercial yttrium isopropoxide.⁹ The M_n increased linearly with increasing conversion. This means that the number of polymer chains is constant throughout the polymerization.

The SEC profile of sample **a** was unimodal and a narrow molecular weight distribution was observed (Figure 5, $M_w/M_n = 1.08$). As the polymerization proceeded, the shoulder in the higher molecular weight region increased, resulting in an increase in M_w/M_n . This suggests that nucleophilic attack by the hydroxyl group at the

terminating chain-end occurs preferentially at the carbonyl carbon on ϵ -caprolactone rather than at the carbonyl carbon on the polymer main chain and intermolecular esterification took place to a certain extent. Similar observations have been reported for the ROP of δ -valerolactone using trifluoromethanesulfonimide as a catalyst at high monomer concentrations.¹⁰ Although intramolecular condensation between the carboxyl and hydroxyl terminals was suppressed, intramolecular transesterification between the hydroxyl and carbonyl terminals on the polymer main chain arise slightly after monomer consumption. So, those shoulders in SEC become bigger and bigger. With lower monomer concentration ($[M]_0 = 1 \text{ mol } l^{-1}$), SEC chart of the PCL did not have definite shoulder at the latter term of the ROP.

Proposed mechanism of ϵ -caprolactone polymerization catalyzed by TBZL

The mechanism of the ROP of ϵ -caprolactone catalyzed by TBZL was investigated. 1H NMR of the supplied TBZL solution indicated that the TBZL solution included not only tBu_4ZnLi_2 but also tBu_2Zn (Figure 6a). To clarify the actual catalyst, tBu_4ZnLi_2 and tBu_2Zn were prepared separately by the addition of 4 and 2 molar amounts, respectively, of tBuLi relative to $ZnCl_2$.^{3,4} The 1H NMR spectra confirmed the successful synthesis of tBu_4ZnLi_2 and tBu_2Zn (Figures 6b and c). The ROPs of ϵ -caprolactone catalyzed by the obtained tBu_4ZnLi_2 and tBu_2Zn were performed. ϵ -Caprolactone was hardly consumed in the ROP catalyzed by tBu_2Zn , even after 24 h (run 9). In contrast, tBu_4ZnLi_2 catalyzed the ROP of ϵ -caprolactone (run 8). Furthermore, the $\ln([M]_0/[M])$ versus time plots indicated that there is an induction period in the ROP catalyzed by the tBu_4ZnLi_2 prepared by us (Figure 7). These results indicate that the ROP of

Figure 4 Plots of conversion (top) and $\ln([M]_0/[M])$ (middle) versus time, and $M_{n,NMR}$ versus conversion (bottom; dashed line indicates theoretical line), for ROP of ϵ -caprolactone with TBZL in presence of BnOH (run 5).

ϵ -caprolactone is not catalyzed by $t\text{Bu}_2\text{Zn}$ and $t\text{Bu}_4\text{ZnLi}_2$ is the actual catalyst for the ROP of ϵ -caprolactone. Molecular weights calculated by ^1H NMR spectra were nearly twice as large as the theoretical values obtained when BnOH was added four times than TBZL (runs 5 and 10). In this case, not only BnOH and TBZL, but also ϵ -caprolactone should be considered. Decrease of TBZL caused low initiation efficiency owing to the difficulty of initiation than propagation in this case.

^1H and ^{13}C NMR spectra of ethyl acetate (as an ϵ -caprolactone model) or BnOH in the presence of an equimolar amount of the prepared TBZL were examined to clarify as to how the $t\text{Bu}_4\text{ZnLi}_2$ forms the actual active species. The ^1H - and ^{13}C -NMR spectra of ethyl acetate showed scarcely any changes, regardless of the presence of TBZL (Supplementary Figure S2). In contrast, the addition of TBZL

Figure 5 SEC chart of PCL prepared with TBZL in presence of BnOH. Polymerization time: (a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) 30 min; and (f) 40 min. Flow rate, 0.35 ml min^{-1} ; eluent, dimethylformamide/LiBr.

Figure 6 ^1H NMR spectra of (a) TBZL, (b) $t\text{Bu}_2\text{Zn}$, and (c) $t\text{Bu}_4\text{ZnLi}_2$ prepared by ourselves (in tetrahydrofuran- d_8 at 0°C).

resulted in the loss of ^1H NMR signals from the hydroxyl protons of BnOH and broadening of the resonances from the methylene protons of BnOH, with a downfield shift (Figure 8). Similarly, the ^{13}C -NMR

signals of the methylene carbons of BnOH exhibited a downfield shift. Similar observations have been reported for zinc complexes supported by maltolato ligands¹¹ and zinc complexes supported by *N,O*-ketimine ligands,¹² which are used for the ROP of cyclic esters. It is therefore assumed that ${}^t\text{Bu}_4\text{ZnLi}_2$ forms a complex with BnOH, which initiates the ROP.

The ${}^1\text{H}$ NMR spectrum of TBZL in the presence of excess BnOH (4 equiv) was recorded to confirm the hydrogen abstraction reaction of the hydroxyl group of BnOH with the *tert*-butyl group of TBZL (Figure 9). On addition of excess BnOH to the TBZL solution, the signals from the *tert*-butyl groups on TBZL disappeared. This suggests that the *tert*-butyl group reacted with the hydroxyl group on BnOH and volatilized as isobutane. A possible mechanism of the ROP of ϵ -caprolactone with TBZL in the presence of BnOH is shown in Scheme 2.

To clarify whether or not the induction period previously mentioned was caused by hydrogen abstraction and complex formation, ROP of ϵ -caprolactone was performed by adding ϵ -caprolactone after premixing TBZL and BnOH at 0 °C for 15 min. The $\ln([M]_0/[M])$

Figure 7 $\ln([M]_0/[M])$ versus time for ROP of ϵ -caprolactone with ${}^t\text{Bu}_4\text{ZnLi}_2$, prepared by ourselves, in presence of BnOH (run 8).

$[M]$) versus time plots suggest that there was a significant induction period (Supplementary Figure S3). The induction period in the ROP of ϵ -caprolactone was not caused by hydrogen abstraction and complex formation between BnOH and TBZL. MeOH was premixed with TBZL instead of BnOH and a similar ROP induction period was observed. These results suggest that the induction periods in the ROP of ϵ -caprolactone were not caused by a sterically hindered benzyloxy group generated from BnOH, but by the coordination between ϵ -caprolactone and a complex of BnOH and TBZL.

CONCLUSIONS

This system does not need a high polymerization temperature or long polymerization time and uses a metal compound that has little effect on the environment; PCL with a narrow molecular weight distribution can therefore be obtained under mild conditions. These results

Figure 9 ${}^1\text{H}$ NMR spectra of (a) TBZL and (b) excess amount of BnOH and TBZL (4/1, in tetrahydrofuran- d_8 at 0 °C).

Figure 8 ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra of (a) TBZL, (b) BnOH, and (c) equimolar mixture of BnOH and TBZL (in tetrahydrofuran- d_8 at 0 °C).

Scheme 2 Possible mechanism of ROP of ϵ -caprolactone with TBZL in presence of BnOH.

demonstrate that TBZL is an excellent candidate for catalyzing rapid ROP of ϵ -caprolactone.

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