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Living ring-opening polymerization of *ε*-caprolactone with combinations of *tert*-butyllithium and bilky aluminium phenoxides

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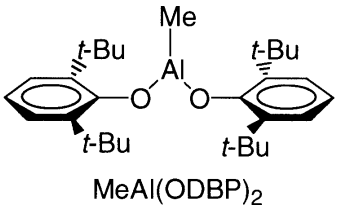
Summary

The polymerization of ε-caprolactone (ε-CL) with a combination of *tert*-butyllithium (*t*-BuLi) and bis(2,6-di-*t*-butylphenoxy)methylaluminum [$MeAl(ODBP)_2$] in toluene at 0°C proceeded in a living manner to give polymers with narrow molecular weight distributions (MWD) within a few minutes, while the polymerization with *t*-BuLi alone gave a polymer with much broader MWD. The yield of the polymer did not reach 100 % at the Al/Li ratio of 5, because the excess $MeAl(ODBP)_2$ coordinates with ε-CL to protect it from the attack by the propagating species. The polymerization with *t*-BuLi/$EtAl(ODBP)_2$ gave polymers in quantitative yields regardless of Al/Li ratio, and also narrower MWD even for higher molecular weight polymers.

Introduction

Anionic ring-opening polymerizations of ε-caprolactone (ε-CL) by alkali-metal alkyls or alkali-metal alkoxides are generally very fast, but are problematic in the control of polymer structure due to intra- and / or intermolecular transesterification reactions, that lead to the formation of macrocycles and to the broadening of molecular weight distribution (MWD). Decrease in the nucleophilicity of the initiator, through the modification of the counterion for example, has been found favorable to the propagation of linear chains compared to the macrocyclization process [1]. Thus, the living polymerizations of ε-CL have been attained by use of aluminum and zinc alkoxides such as $Al(O^{i}Pr)_3$ [2], $Zn[OAl(OR)_2]_2$ [3], $R_xAl(OR)_{3-x}$ [4,5], and (tetraphenylporphyrinato)Al(OR) [6]. The polymerizations with lanthanide compounds such as yttrium alkoxides [7, 8, 9] and $Cp^*_2SmMe(THF)$ (Cp^*_2 = pentamethylcyclopentadienyl, THF = tetrahydrofuran) [10] and with bulky titanium bis(phenolate) [11] also give polymers with narrow MWD's.

We have reported that combinations of *tert*-butyllithium (*t*-BuLi) and bulky aluminum bisphenoxides are efficient initiating systems for highly stereospecific living polymerization of methacrylates [12-21]. For example, polymerizations of primary alkyl methacrylates with *t*-BuLi/bis(2,6-di-*tert*-butylphenoxy)methylaluminum[$MeAl(ODBP)_2$] (Al/Li ≧ 2) in toluene at low temperature give highly heterotactic polymers with narrow MWD's. The existence of excess amounts of $MeAl(ODBP)_2$ over *t*-BuLi is essential for the heterotactic polymerization,



$MeAl(ODBP)_2$

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where the bulky aluminum phenoxides are expected to play roles of stabilization of the propagating species and of activation of the monomer.

In this work, we investigated the possibility of extending the capability of this initiator system to the control of the ring-opening polymerization of the cyclic ester, ε-CL, with the expectation of the stabilization of the propagating species to prevent the side reactions and the activation of the monomer through the coordination of the bulky aluminum phenoxides.

Experimental

Materials

ε-CL obtained commercially (Nacalai Tesque) was dried over calcium dihydride and fractionally distilled under reduced nitrogen pressure. Toluene was purified in the usual manner, mixed with a small amount of *n*-butyllithium, and distilled under high vacuum before use.

t-BuLi (Aldrich) in pentane was used as a heptane solution by replacing the solvent under vacuum. The concentration was determined by titration with butan-2-ol using *o*-phenanthroline as an indicator [22].

Triethylaluminum (Et_3Al), tripropylaluminum (*n*-Pr_3Al), tributylaluminum (*n*-Bu_3Al) and triisobutylaluminum (*i*-Bu_3Al) (NIPPON ALUMINUM ALKYLS) were used as toluene solutions. Trimethylaluminum (Me_3Al) in toluene was a kind gift from Tosoh Akzo.

Preparation of alkylaluminum bisphenoxides [RAl(ODBP)$_2$][23 , 24]

A solution of 2,6-di-*t*-butylphenol in heptane (2 equiv.) was added slowly to a toluene solution of R_3Al (1 equiv.)[R = CH_3 , C_2H_5 , C_3H_8] at 0°C. The resulting mixture was stirred at room temperature for 24 hr. The solvent was removed under vacuum to leave a yellowish solid. The product was recrystallized three times by dissolving it in hot heptane and cooling to –30 °C. After most of the heptane was removed by a syringe and the residual heptane was evaporated under vacuum to dryness, the solid residue was dissolved in toluene and used for the polymerization reactions.

Polymerization

All the polymerizations were carried out in grass ampoules filled with dried nitrogen passed through Molecular Sieves 4A cooled at –78 °C. The polymerization was initiated by adding *t*-BuLi slowly to a toluene solution of ε-CL and RAl(ODBP)$_2$. The reaction was terminated by adding methanol containing a small amount of HCl at the polymerization temperature. The reaction mixture was poured into a large amount of hexane to precipitate the polymeric product. The precipitate was collected by filtration, washed with hexane and subsequently with water several times, and dried under vacuum at 40 °C.

Measurements

^{1}HNMR spectra of the polymers or the reaction mixtures were measured in $CDCl_3$ on a JEOL JMN-AL400 NMR spectrometer operated at 400 MHz or on a Varian Unity Inova 500 spectrometer operated at 500MHz. MWD's and number-average molecular weights ($\bar{M}$n's) of the polymers were determined by size exclusion chromatography (SEC) using a JASCO PU-980 chromatograph equipped with two Shodex SEC columns [KF-806L (8 mm i.d. X 300 mm) X 2] using THF as an eluent at 40 °C. The SEC chromatogram was calibrated against standard poly(methyl methacrylate) samples. $\bar{M}$n's of the polymers were also determined at 60 °C in toluene by using a Hitachi 117 vapor pressure osmometry (VPO).

Results and discussion

The polymerizations of ε-CL with combinations of *t*-BuLi and various aluminum compounds were carried out in toluene at 0 °C for 5 min at $[\varepsilon\text{-CL}]_0/[t\text{-BuLi}]_0 = 50$. The results are shown in **Table 1. Figure 1** shows SEC curves of the three representative polymers. The polymerization with *t*-BuLi alone gave a polymer with a broad MWD (**Figure 1a**). The polymerization with *t*-BuLi/*n*-Bu$_3$Al (1/3) (**Figure 1b**) or *t*-BuLi/*i*-Bu$_3$Al(1/3), which is an effective initiator for syndiotactic living polymerization of methacrylates [25, 26], gave polymers with broad MWD's. The polymerization with a combination of *t*-BuLi and Al(O^{i}Pr)$_3$, the latter of which has been known as an effective initiator for living polymerization of ε-CL [2], gave a polymer with broad MWD's. The polymer showed ^{1}H NMR signals due to *t*-butyl groups at 1.05 and 1.13 ppm as well as those due to isopropyl methyl protons at 1.23 ppm. The relative intensity was $(CH_3)_3C/(CH_3)_2CH = 2.12$, which means that both *t*-BuLi and Al(O^{i}Pr)$_3$ initiate the polymerization in 3/2 ratio. On the other hand, the polymerization of ε-CL with *t*-BuLi/MeAl(ODBP)$_2$(1/5) gave a polymer with narrow MWD (**Figure 1c**). The results suggest that among the aluminum compounds examined the bulky aluminum phenoxide effectively stabilizes the propagating species through coordination and the bulkiness is sufficient enough to prevent the propagating species from the possible side reactions such as intra- and intermolecular transesterifications.

Table 1 Polymerization of ε-CL with *t*-BuLi in the presence or absence of several aluminum compounds in toluene at 0℃ for 5 min [a]

Aluminum compound	Al / Li mol / mol	Yield %	$\bar{M}_n$ NMR	$\bar{M}_n$ SEC	$\bar{M}_w/\bar{M}_n$ [b]
None	0	92.1	9,000	11,300	2.41
n-Bu$_3$Al	3	100	17,200	25,300	1.97
i-Bu$_3$Al	3	99.2	11,600	20,100	2.23
Al(O^{i}Pr)$_3$	5	100	7,900	14,700	1.45
MeAl(ODBP)$_2$	5	94.2	6,100	15,500	1.15
MeAl(ODBP)$_2$ [c]	–	58.4	–	4,200	1.39

a ε-CL 5mmol, *t*-BuLi 0.1mmol, toluene 5ml.
b Determined by SEC based on the calibration with PMMA samples.
c Polymerization with MeAl(ODBP)$_2$ alone at 20℃.

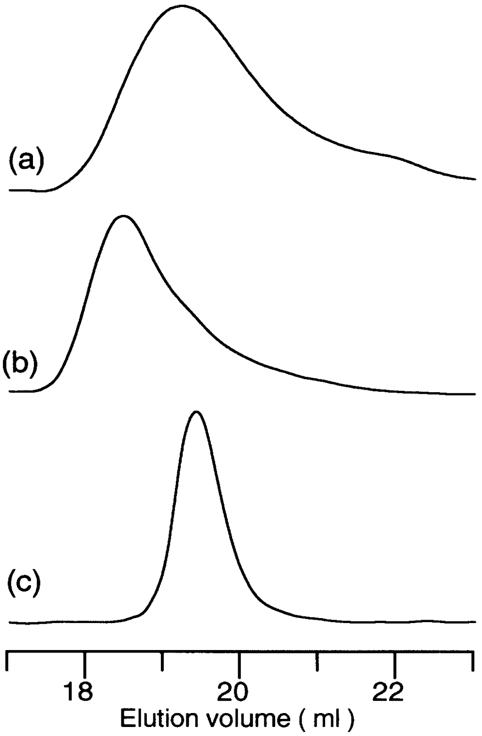


Figure 1 SEC curves of poly(ε-CL)s prepared with (a) *t*-BuLi, (b) *t*-BuLi / *n*-Bu$_3$Al (1/3 mol/mol) and (c) *t*-BuLi / MeAl(ODBP)$_2$ (1/5 mol/mol) in toluene at 0℃ for 5 min (see **Table 1**).

The $\bar{M}$n value of the poly(ε-CL) obtained with *t*-BuLi/MeAl(ODBP)$_2$ was estimated to be 6390 from the ^{1}H NMR intensity ratio of the main-chain methylene and *t*-butyl methyl protons, based on the structural information on the polymer described below. The value agrees well with that determined by VPO ($\bar{M}$n=6480) but not with that obtained by SEC ($\bar{M}$n=15520). The results mean that the SEC estimation of $\bar{M}$n of poly(ε-CL) gives the value almost twice as large as the true one. In contrast, NMR-determined $\bar{M}$n value of the poly(ε-CL) obtained with *t*-BuLi alone ($\bar{M}$n = 8950) is rather close to SEC-determined $\bar{M}$n (11320) but different from that determined by VPO (5300). The results indicate that the $\bar{M}$n determined from end - group analysis by NMR is overestimated; in other words, the polymer contains polymer molecules having no *t*-butyl end-group, which may be formed through intramolecular transesterification. On-line SEC / NMR analysis [27] of the polymer revealed that the lower molecular weight fraction contains more molecules without *t*-butyl group than the higher molecular weight one. The detail of the analysis will be reported elsewhere.

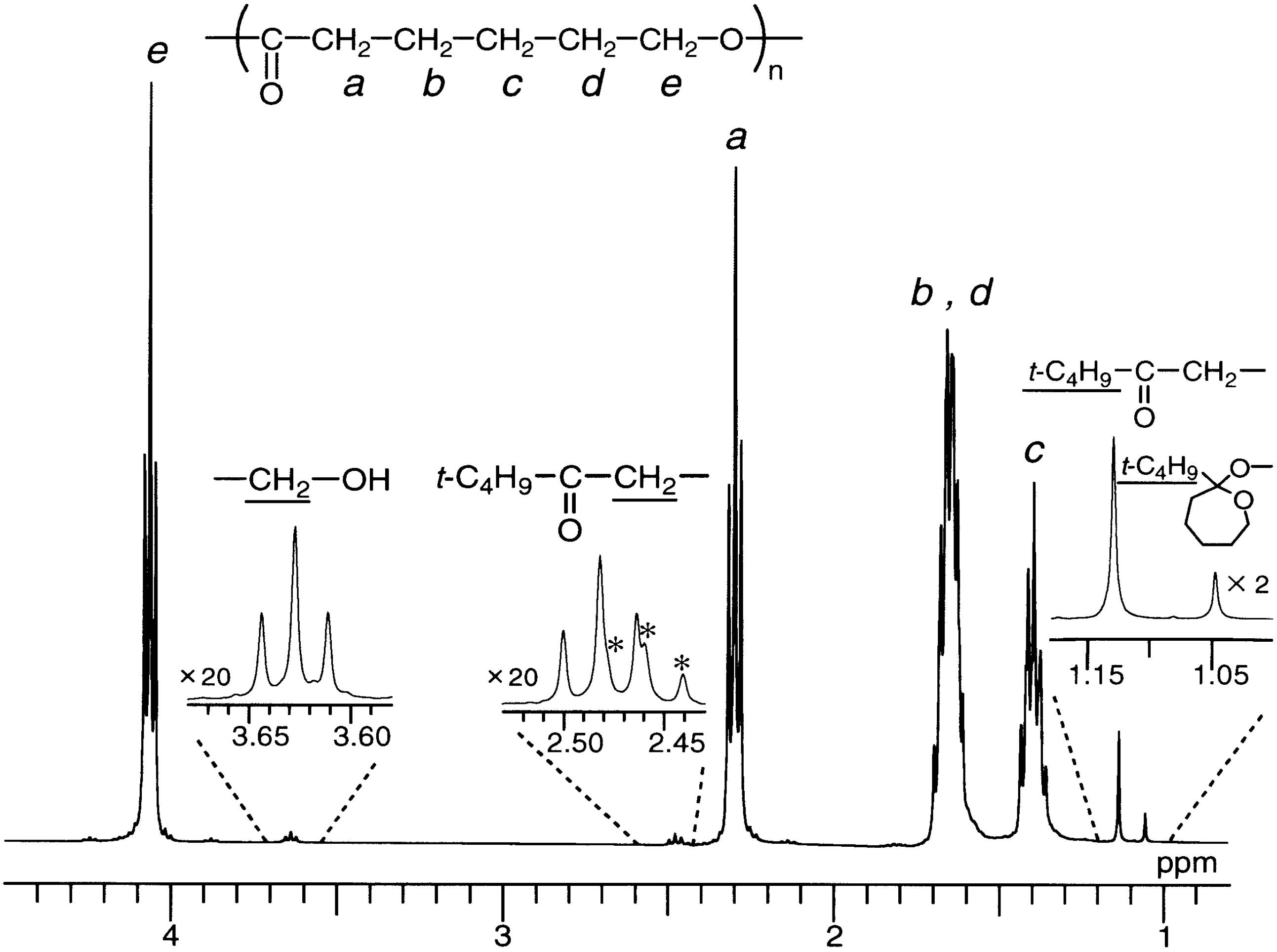


Figure 2 400MHz ^{1}H NMR spectrum of poly(ε-CL) prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1 / 5 mol / mol) in toluene at 0°C for 5 min (CDCl$_3$, 55°C).
*^{13}C satellite signal of peak *a*.

Figure 2 shows ^{1}H NMR spectrum of poly(ε-CL) prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1 / 5) in toluene at 0 °C for 5 min. The spectrum shows two singlet peaks at 1.05 ppm and 1.13 ppm ascribable to the *t*-butyl groups at the initiating chain-end but no signals due to 2,6-di-*tert*-butylphenoxy group. These results suggest that the polymerization is initiated by *t*-BuLi but not by MeAl(ODBP)$_2$. In fact, the polymerization of ε-CL with MeAl(ODBP)$_2$ in toluene at 0 °C gave no polymer for 24 hr, though the polymerization at 20 °C produced an oligomeric product in a low yield (see **Table 1**).

The spectrum also shows a triplet signal at 3.63 ppm assignable to the methylene protons adjacent to the hydroxyl group at the terminating chain-end. The result indicates that the polymerization proceeds with an alkoxide as the propagating species. In addition to the triplet signal due to the main-chain methylene protons, CH_2(***a***), adjacent to the ester carbonyl carbon, a small triplet signal is observed at 2.48 ppm, which is ascribable to methylene protons adjacent to ketonic carbonyl carbon from its chemical shift value. In the ^{13}C NMR spectrum of the poly(ε-CL), the ketonic carbonyl carbon was observed at 215.84 ppm along with a strong ester carbonyl signal at 173.98 ppm. **Figure 3** shows part of ^1H-^1H COSY spectrum of poly(ε-CL) ($\bar{M}$n = 2300) formed with *t*-BuLi/MeAl(ODBP)$_2$ (1/5) in toluene at 0 °C for 10 s. The triplet signal at 2.48 ppm shows a correlation peak with the major *t*-butyl signal at 1.13 ppm, their relative intensity being found 9 : 2 as expected. The results indicate the presence of *t*-Bu-C=O group which should form through the attack of *t*-BuLi to the carbonyl carbon of ε-CL and locate at the beginning of the chain. Thus, the major initiation process is depicted by **Scheme 1A.**

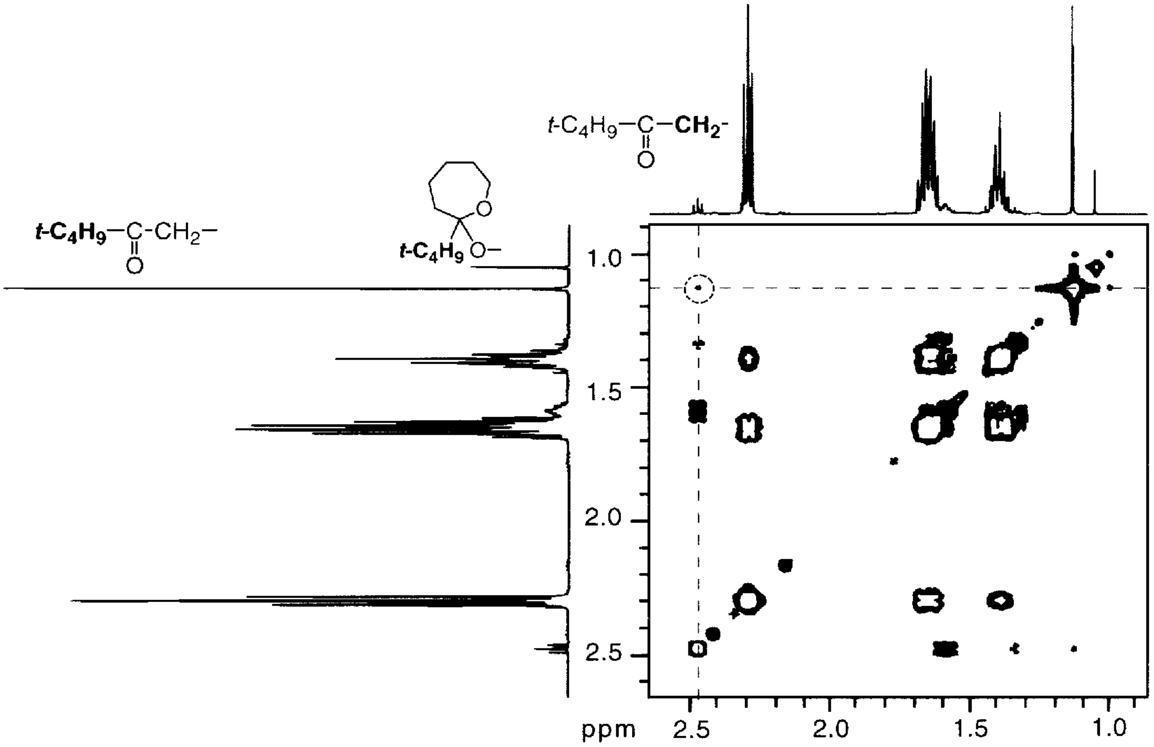
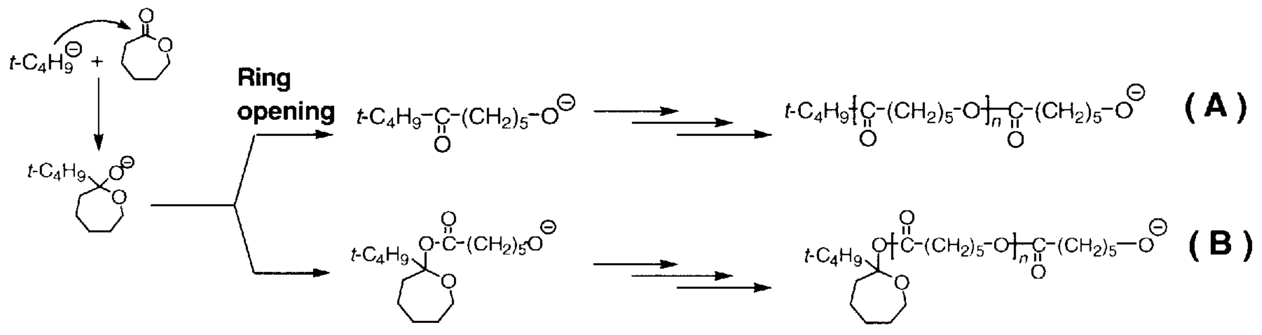


Figure 3 500 MHz H - H COSY NMR spectrum of poly(ε–CL) ($\bar{M}$n = 2300) prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1 / 5) in toluene at 0°C for 10 s (CDCl$_3$, 55°C).



Scheme 1

The minor *t*-butyl signal at 1.05 ppm does not show correlation peak with the -COCH$_2$- signal. A possible structure is shown in **Scheme 1B**, where the alkoxide formed by the attack of *t*-BuLi adds ε-CL before it undergoes ring opening. ^{13}C NMR spectrum shows a small signal at 79.64 ppm ascribable to ketalic carbon attaching two oxygen atoms corresponding to the chain-end structure depicted in **Scheme 1B**. Further investigation on the structure of the minor initiating end-group is now in progress. NMR-determined $\bar{M}n$ values in Tables are based on the assumption of the end-group structures describes above.

Table 2 Polymerization of ε-CL with *t*-BuLi / MeAl(ODBP)$_2$ with various Al / Li ratios in toluene at 0℃ for 5 min [a]

Al / Li	Yield[b]	$\bar{M}n$		$\bar{M}w$ / $\bar{M}n$ [c]
mol / mol	%	NMR	SEC	
0	92.1	9,000	11,300	2.41
1	100	6,300	16,200	1.19
2	98.9	6,400	16,200	1.19
3	96.3	6,700	16,300	1.19
5	94.2	6,400	15,500	1.15
10	89.7	5,700	14,700	1.15

a ε-CL 5mmol, *t*-BuLi 0.1mmol, toluene 5ml.
b Determined by ^{1}H NMR analysis of the reaction mixture.
c Determined by SEC based on the calibration with PMMA samples.

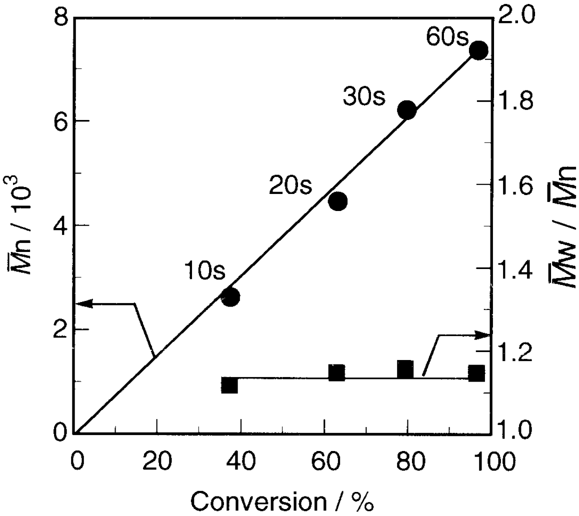


Figure 4 Relationships of $\bar{M}n$ and $\bar{M}w$ / $\bar{M}n$ with conversion in the polymerization of ε-CL with *t*-BuLi / MeAl(ODBP)$_2$ (1 / 5 mol / mol) at [ε-CL]$_0$ / [*t*-BuLi]$_0$ in toluene at 0°C.

As shown in **Figure 4**, the $\bar{M}n$'s of poly(ε-CL)s formed with *t*-BuLi/MeAl(ODBP)$_2$ (1/5) at 0 °C increased linearly with conversion while their MWD's were kept narrow. The results indicate the livingness of this polymerization. The conversion of this polymerization became close to 100% for 1 min, but did not reach 100% even when the polymerization time was extended to 1 hr.

Table 2 shows the effects of the ratio of MeAl(ODBP)$_2$ to *t*-BuLi in the polymerization at 0 °C for 5 min. The yield of the polymer reached 100% at the Al/Li = 1, but decreased with increasing Al/Li ratio. The results suggest that the excess MeAl(ODBP)$_2$ coordinates with ε-CL to prevent it from the attack of the propagating anions, probably due to the steric hindrance around the carbonyl group of the coordinated monomer. This is contrasting to the case of the polymerization of methacrylates with *t*-BuLi/MeAl(ODBP)$_2$, where MeAl(ODBP)$_2$ coordinates with the carbonyl group of the monomer so that ß-CH$_2$ group becomes more electrophilic to be attacked by the propagating anions [12-15]. In other words, the main role of the bulky aluminum phenoxide in the polymerization of ε-CL is the stabilization of the propagating species to prevent transesterifications.

When EtAl(ODBP)$_2$ was used in place of MeAl(ODBP)$_2$, the polymerization proceeded quantitatively regardless of the Al/Li ratio (**Table 3**), and the polymer with narrowest MWD was obtained at Al/Li = 2. To compare the coordination ability of MeAl(ODBP)$_2$ and EtAl(ODBP)$_2$, ^{1}HNMR spectroscopic coordination experiment was carried out for an equimolar ternary mixture of ε-CL : MeAl(ODBP)$_2$: EtAl(ODBP)$_2$ in toluene at 0°C (**Figure 5**). Both of MeAl(ODBP)$_2$ and EtAl(ODBP)$_2$ show a pair of signals due to coordinated and free species. The relative intensity indicates that 70% of ε-CL coordinate with $MeAl(ODBP)_2$ and 30% with $EtAl(ODBP)_2$. The results suggest that the coordination of $EtAl(ODBP)_2$ to ε-CL is weaker than that of $MeAl(ODBP)_2$, and imply that the coordination of $EtAl(ODBP)_2$ to the propagating anions is also weaker so that the reactivity of the propagating anion is higher.

Table 3 Polymerization of ε-CL with *t*-BuLi / $EtAl(ODBP)_2$ with various Al / Li ratios in toluene at 0℃ for 5 min[a]

Al / Li	Yield[b]	$\bar{M}n$		$\bar{M}w$ / $\bar{M}n$ [c]
mol / mol	%	NMR	SEC	
0	92.1	9,000	11,300	2.41
1	100	6,800	9,100	1.53
2	100	6,600	14,700	1.11
3	99.7	6,600	15,300	1.13
5	99.4	6,300	14,500	1.14
10	100	6,000	13,300	1.15

a ε-CL 5mmol, *t*-BuLi 0.1mmol, toluene 5ml.
b Determined by ^1H NMR analysis of the reaction mixture.
c Determined by SEC based on the calibration with PMMA samples.

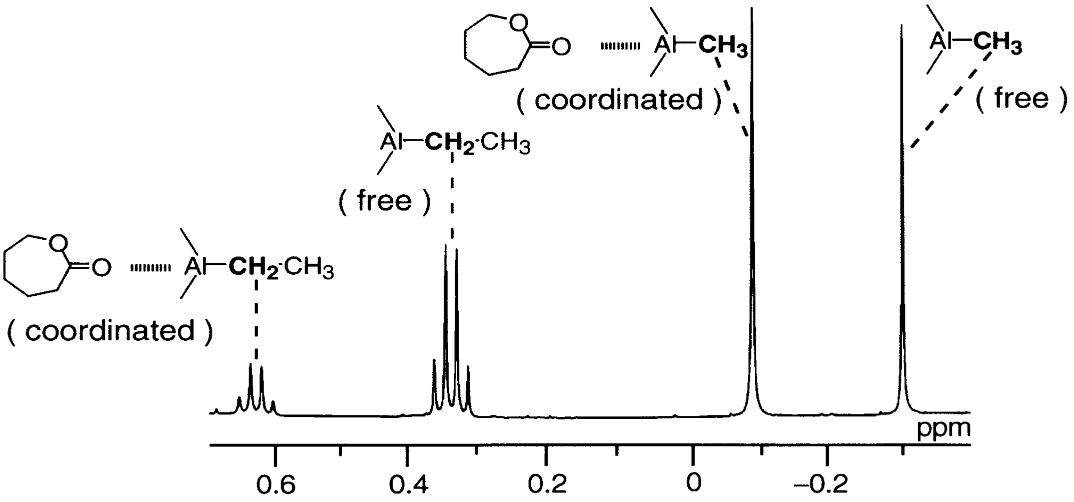


Figure 5 500MHz ^1H NMR spectrum of an equimolar mixture of ε-caprolactone, $MeAl(ODBP)_2$ and $EAl(ODBP)_2$ measured in toluene-d_8 at 0℃.

Table 4 summarizes the results of the polymerization with *t*-$BuLi/RAl(ODBP)_2$ (1/2) (R = Me, Et or Pr) at $[ε\text{-CL}]_0/[t\text{-BuLi}]_0$ ratios of 100 and 200. Polymers were obtained within 5 min in high yields at any conditions. The polymers obtained at the $[ε\text{-CL}]_0/[t\text{-BuLi}]_0$ = 100 with $MeAl(ODBP)_2$ showed broader MWD than those obtained with $EtAl(ODBP)_2$ and with $PrAl(ODBP)_2$.

Table 4 Polymerization of ε-CL with *t*-BuLi / $RAl(ODBP)_2$ (1 / 2 mol / mol) in toluene at 0℃ [a]

$RAl(ODBP)_2$ R =	[ε–CL] / [*t*-BuLi]	Time	Yield	$\bar{M}n$		$\bar{M}w$ / $\bar{M}n$ [b]
		min	%	NMR	SEC	
Me	100	5	96.6	14,100	29,500	1.26
Et	100	1	92.1	11,800	31,700	1.11
	100	5	99.1	12,400	25,400	1.16
	200	1	73.9	22,200	43,100	1.14
	200	2	95.2	23,800	54,600	1.16
	200	5	98.6	22,500	58,300	1.21
Pr	100	5	97.1	31,100	31,100	1.17

a ε-CL / toluene = 1 mol / L.
b Determined by SEC based on the calibration with PMMA samples.

At the [ε-CL]$_0$/[*t*-BuLi]$_0$ ratio of 200 with EtAl(ODBP)$_2$, the polymer yield reached 95% for 2 min and a polymer with narrow MWD was obtained. However, the MWD of the polymer became slightly broader at 5 min, indicating that the possible side reaction took place in the later stage of polymerization.

In conclusion, the polymerization of ε-CL with *t*-BuLi/RAl(ODBP)$_2$ at 0 °C proceeded in a living manner and gave the polymers with narrow MWD within a few minutes. This is faster polymerization than the polymerizations with aluminum and zinc alkoxides, which are known as the initiators for the living polymerization of ε-CL. This initiator system is also effective for the stereospecific living polymerization of vinyl monomers such as methacrylates and acrylates. The block copolymerization of ε-CL and these vinyl monomers are now being investigated extensively.

References

1. Sosnowski S, Slomkowski S, Penczek S and Reibel L (1983) Makromol. Chem. 184 : 2159
2. Ouhadi T, Stevens C and Teyssié Ph (1975) Makromol. Chem. Suppl. 1 : 191
3. Hamitou A, Ouhadi T, Jérome R and Teyssié Ph (1977) J. Polymer Sci., Polymer Chem. Ed. 15 : 865
4. Hofman A, Slomkowski S and Penczek S (1987) Makromol. Chem., Rapid Commun. 8 : 387
5. Dubois Ph, Jérome R and Teyssié Ph (1989) Polym. Bull. 22 : 475
6. Endo M, Aida T and Inoue S (1987) Macromolecules 20 : 2982
7. McLain SJ and Drysdale NE (1992) Polym. Prepr., Am. Chem. Sci. 33 : 174
8. Stevals WM, Ankone MJK, Dijkstra PJ and Feijen J (1996) Macromolecules 29 : 3332
9. Martin E, Dubois P and Jérome R(2000) Macromolecules 33 : 1530
10. Yamashita M, Takemoto Y, Ihara E and Yasuda H (1996) Macromolecules 29 : 1798
11. Takeuchi D, Nakamura T and Aida T (2000) Macromolecules 33 : 725
12. Kitayama T, Zhang Y, Hatada K (1994) Polym. Bull. 32 : 439
13. Kitayama T, Zhang Y and Hatada K (1994) Polym. J. 26 : 868
14. Kitayama T, Hirano T and Hatada K (1996) Polym. J. 26 : 61
15. Kitayama T, Hirano T, Y. Zhang Y and Hatada K (1996) Macromol. Symp. 107 : 297
16. Kitayama T, Hirano T and Hatada K (1996) Polym. J. 28 : 1110
17. Kitayama T, Hirano T and Hatada K (1997) Tetrahedron 53 : 15263
18. Hirano T, Kitayama T and Hatada K (1998) Polym. J. 30 : 736
19. Hirano T, Yamaguchi H, Kitayama T and Hatada K (1998) Polym. J. 30 : 767
20. Hirano T, Kitayama T, Cao J and Hatada K (2000) Macromolecules 33 : 1926
21. Hatada K and Kitayama T (2000) Polym. Int. 49 : 11
22. Watson SC and Eastham JF (1965) J. Organomet. Chem. 9 : 165
23. Maruoka K and Yamamoto H (1985) Angrew. Chem., Int. Ed. Engl. 24 : 668
24. Maruoka K, Itoh T, Sakura M, Nonoshita K and Yamamoto H (1988) J. Am. Chem. Soc. 110 : 3588
25. Kitayama T, Shinozaki T, Masuda E, Yamamoto M and Hatada K (1988) Polym. Bull. 20 : 505
26. Kitayama T, Shinozaki T, Sakamoto T, Yamamoto M and Hatada K (1989) Macromol. Chem., Supplement. 15 : 167
27. Ute K, Niimi R, Hongo S and Hatada K (1998) Polym. J. 30 : 439