Organolanthanide-Initiated Living Polymerizations of ϵ-Caprolactone, δ-Valerolactone, and β-Propiolactone

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ABSTRACT: Organolanthanide complexes such as $SmMe(C_5Me_5)_2(THF)$ and $[SmH(C_5Me_5)_2]_2$ initiate the living polymerizations of ϵ-caprolactone and δ-valerolactone to give high molecular weight polyesters (M_n > 70 000) with extremely narrow molecular weight distributions, M_w/M_n < 1.08, while these initiators are completely inert for the polymerization of β-propiolactone. In contrast to lanthanide alkyl complexes, lanthanide alkoxides such as $SmOEt(C_5Me_5)_2(OEt_2)$, $[YOMe(C_5H_5)_2]_2$, and $YOMe(C_5Me_5)_2(THF)$ exhibit fairly good catalytic activity for polymerizations of β-propiolactone, δ-valerolactone, and ϵ-caprolactone. The initiation mechanisms for the polymerization of lactones by $LnMe(C_5Me_5)_2(THF)$ (Ln = Sm, Yb) or $LnOR(C_5R'_5)_2$ (Ln = Sm, Y) initiators are discussed on the basis of equimolar reactions between organolanthanides and lactones.

Introduction

Ring-opening polymerization of lactones such as ϵ-caprolactone, δ-valerolactone, and β-propiolactone provides a convenient route to biodegradable polyesters, which are of great interest for a variety of practical applications.[1−4] These lactones can be polymerized with initiators containing alkali metals,[5] alkaline earth metals,[5] AlR_3-H_2O,[6] (porphinato)aluminum,[7] ZnR_2-H_2O,[8] and $CpTi(OR)Cl_2$[9] systems. Among these initiators, only the (porphinato)aluminum system provides polyesters with very narrow molecular weight distributions. More recently, lanthanide(III) alkoxides[10] and organolanthanide(II) complexes[11] have been reported to generate extremely active and living polymerization systems regarding these monomers.

We describe herein the more efficient catalytic activity of organolanthanide(III) complexes toward the ring-opening polymerization of lactones, which provides high molecular weight polyesters with extremely narrow molecular weight distributions.[12] This paper also deals with the initiation mechanism for the polymerization of ϵ-caprolactone and γ-valerolactone by $[SmH(C_5Me_5)_2]_2$, $SmMe(C_5Me_5)_2(THF)$, and $Y(OR)(C_5Me_5)_2(THF)$.

Results and Discussion

Rare Earth Metal Initiated Polymerizations of Lactones. Organolanthanide(III) complexes such as $[SmH(C_5Me_5)_2]_2$, $LnMe(C_5Me_5)_2(THF)$ (Ln = Sm, Yb, Y, Lu), and $Ln(C_5Me_5)_2Me_2AlMe_2$ (Ln = Sm, Yb, Y, Lu) were found to initiate the living polymerization of methyl methacrylate at a wide range of polymerization temperatures to give high molecular weight syndiotactic polymers (M_n > 50 000) with extremely narrow molecular weight distributions, M_w/M_n = 1.02, in high conversion over a short period.[13] This type of living polymerization was first realized by the effect of the large ionic radii (1.0−1.1 Å) of lanthanide elements together with the large steric bulk of the auxiliary ligands attached to the metal. As an extension of this study, we have explored the polymerization of other polar monomers such as lactones and alkyl acrylates[14] to find very high molecular weight polymers with very narrow molecular weight distributions. Table 1 shows the results of lactone polymerizations with some organolanthanide complexes. Both ϵ-caprolactone (CL) and δ-valerolactone (VL) gave the desired high molecular weight polymers (M_n > 75 000) with very narrow molecular weight distributions, M_w/M_n < 1.08. $SmMe(C_5Me_5)_2(THF)$ gives the highest initiator efficiency, while $[SmH(C_5Me_5)_2]_2$ and $[YbMe(C_5H_5)_2]_2$ show significantly lower efficiencies, presumably due to their high sensitivity toward monomers, i.e., lanthanide hydride is very sensitive to lactones and the reduction reaction occurs preferentially in place of polymerization.

In light of the clean and stoichiometric reactions (*vide infra*) of the initiators with 1 or 2 equiv of monomers, the observed efficiencies are rather low as shown in Table 1. This may be ascribed to the preferred reaction of water contaminated by the monomer with the organolanthanide complex. In general, thorough drying of lactones is very difficult and we employed the following method: drying over CaH_2 for more than 4 days and then drying over calcinated $CaCl_2$ for 10 days. Thus, we could attain quantitative conversion, although we still cannot neglect the some deactivations of the initiator by reaction with water. The narrowest polydispersity reported so far is M_w/M_n = 1.12 for poly(δ-valerolactone) (M_n = 12 000), obtained by tetraphenyl(porphinato)aluminum methoxide in conversions of only 85%.[7]

Thus, the $SmMe(C_5Me_5)_2(THF)$-initiated polymerization was considered to proceed in a living fashion. In fact, M_n increases linearly in proportion to the conversion, while the narrow molecular weight distribution remains constant irrespective of the catalytic concentration (Figure 1). The M_n of ϵ-caprolactone polymers increases with a decrease in the monomer to initiator ratio [initiator concentration (% monomer)] at 0 °C (Figure 2), and we can obtain poly(ϵ-caprolactone) of M_n = 260 000 with a significantly narrow molecular weight distribution by the catalytic action of $SmMe(C_5Me_5)_2(THF)$ (0.1 mol %). The molecular weight distribution varies with the change in polymerization temperature, i.e., the value becomes smallest, M_w/M_n = 1.08, when the polymerization is conducted at 0 °C, while M_w/M_n becomes larger (M_w/M_n = 1.70) when the polymerization is carried out at 50 °C. However, practically no polymerization proceeded when the polymerization temperature was lowered to −78 °C.

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Table 1. Organolanthanide-Initiated Polymerization of Lactones[a]

initiator	monomer	temp (°C)	M_n ($\times 10^{-3}$)	M_w/M_n	conversion (%)	efficiency (%)
$SmMe(C_5Me_5)_2(THF)$	valerolactone	0	78.0	1.09	93 (7 h)	59.6
	valerolactone	25	75.2	1.07	89 (5 h)	59.2
	caprolactone	0	76.9	1.08	88 (7 h)	65.2
	caprolactone	25	83.4	1.06	95 (5 h)	64.9
$[SmH(C_5Me_5)_2]_2$	caprolactone	20	142.2	1.05	65 (5 h)	26.1
$[YbMe(C_5H_5)_2]_2$	caprolactone	20	56.6	1.19	25 (5 h)	25.2

[a] Organolanthanide, 0.2 mol % of monomer, toluene solvent.

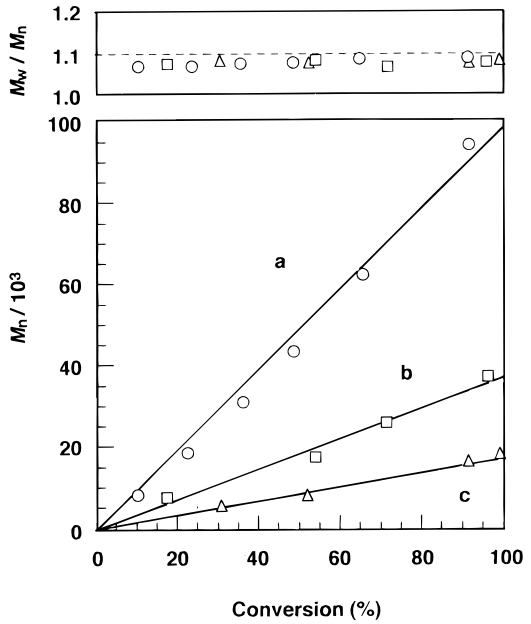

Figure 1. Conversion vs M_n and M_w/M_n plots for poly(ϵ-caprolactone): (a) 0.2, (b) 0.5, (c) 1.0 mol % $SmMe(C_5Me_5)_2$(THF). Solvent/[monomer]$_0$ = 5.0 mL/mL.

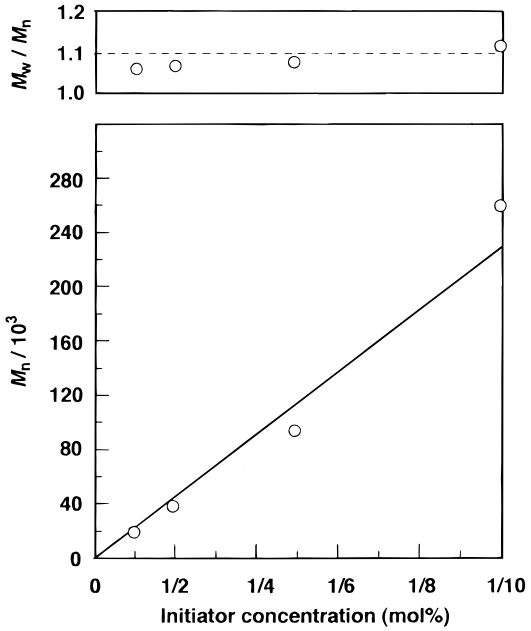

Figure 2. Initiator concentration vs M_n and M_w/M_n plots. Initiator, $SmMe(C_5Me_5)_2THF$.

In sharp contrast to the high reactivity of CL and VL, the polymerization of β-propiolactone has failed with alkyllanthanide or hydridolanthanide initiators such as $SmMe(C_5Me_5)_2$(THF) or $[SmH(C_5Me_5)_2]_2$. No polymerization started in this case, while the formation of a stable 1:1 adduct of $SmMe(C_5Me_5)_2$(THF) with β-propiolactone was observed (*vide infra*) as revealed by NMR. By contrast, the use of lanthanide alkoxides such as $SmOEt(C_5Me_5)_2(Et_2O)$, $[YOMe(C_5H_5)_2]_2$,[15] and $YOMe(C_5Me_5)_2$(THF) is effective to obtain high molecular weight poly(β-propiolactone), since the 1:1 adduct is destabilized in this case by the effect of the lower electron-donating property of the OR group (Table 2). In the case of the reaction of $(C_5H_4R)TiCl_2(OMe)$ with β-methylpropiolactone, a stable 1:1 addition compound was also formed after ring opening of β-methylpropiolactone, while no polymerization proceeded with this adduct.[9]

Lanthanide alkoxide initiators are also effective for the polymerization of CL and VL. This reaction again proceeds in a living fashion. In fact, M_n of poly(CL) increases linearly in proportion to the conversion, while M_w/M_n values remain intact irrespective of the conversion (Figure 3). Lanthanide alkoxides exhibit nearly the same initiator efficiency as that of lanthanide methyl complexes, and chain transfer is effectively suppressed as revealed by small values of M_w/M_n.

Random Copolymerization of Lactones. The random copolymerization of CL with VL was performed with $SmMe(C_5Me_5)_2$(THF) to understand the respective monomer reactivity ratios. As a result, r_1(VL) = 2.82 and r_2(CL) = 0.20 ($r_1 \times r_2 = 0.56$) were obtained to indicate that the reactivity of δ-valerolactone is much higher than that of ϵ-caprolactone. Although β-propiolactone was not polymerized by $SmMe(C_5Me_5)_2$(THF), random copolymerizations of β-propiolactone with ϵ-caprolactone or δ-valerolactone proceeded successfully. As a result, r_1(PL) = 16.6, r_2(CL) = 0.22, and r_1(PL) = 6.73, r_2(VL) = 0.32 were obtained with the Fineman−Ross equation by using the copolymer composition curve. Thus, largely strained β-propiolactone exhibits higher reactivity, as expected, than the ϵ-caprolactone and δ-valerolactone.

Block Copolymerization of Lactones with Polar Monomers. The block copolymerization of various polar monomers with lactones gives the fundamental aspect of the resulting polymer growing ends. For example, the polymerization of methyl methacrylate (MMA) for 30 min followed by the addition of various lactones such as β-propiolactone, δ-valerolactone, and ϵ-caprolactone in toluene (charged ratio, 1:1) gave block copolymers in 6.1:3.9 to 4.7:5.3 ratios in high conversions (60−70%) after the addition of lactones over 5 h (Table 3). In this case, a 0.7 mol % concentration of the initiator was used because the initiator efficiency is very high (>85%) for the polymerization of MMA. In fact, we could not observe the formation of the homopolymer of a lactone, i.e., lactone monomer remains in the system without polymerization. In contrast to this, the copolymer of MMA with lactone was obtained in a ca. 1:1 ratio when a 2.0 mol % catalyst concentration was used for the block copolymerizations (conversion, 89%). However, reversed addition of monomers, i.e., the polymerization of lactones followed by the addition of MMA, did not form any kind of block copolymer even when a high concentration (2−3 mol %) of the initiator was used. Only the lactone homopolymers were formed in this

Table 2. Polymerizations of Lactones by Lanthanide Alkoxides[a]

initiator	monomer	M_n ($\times 10^3$)	M_w/M_n	conversion (%)	efficiency (%)
$SmOEt(C_5Me_5)_2(Et_2O)$	PL	62	1.12	88	51.1
$[YOMe(C_5H_5)_2]_2$	PL	60	1.09	91	54.6
$YOMe(C_5Me_5)_2(THF)$	PL	63	1.10	86	49.2
$SmOEt(C_5Me_5)_2(Et_2O)$	VL	87	1.07	93	53.5
$[YOMe(C_5H_5)_2]_2$	VL	75	1.07	95	63.3
$YOMe(C_5Me_5)_2(THF)$	VL	75	1.06	92	61.3
$SmOEt(C_5Me_5)_2(Et_2O)$	CL	108	1.09	92	53.5
$[YOMe(C_5H_5)_2]_2$	CL	92	1.10	95	58.9
$YOMe(C_5Me_5)_2(THF)$	CL	89	1.12	90	57.6

[a] Initiator concentration, 0.2 mol % of monomer. Solvent, toluene. Solvent/monomer = 3.0 mL/mL. Polymerization temperature, 0 °C for 10 h.

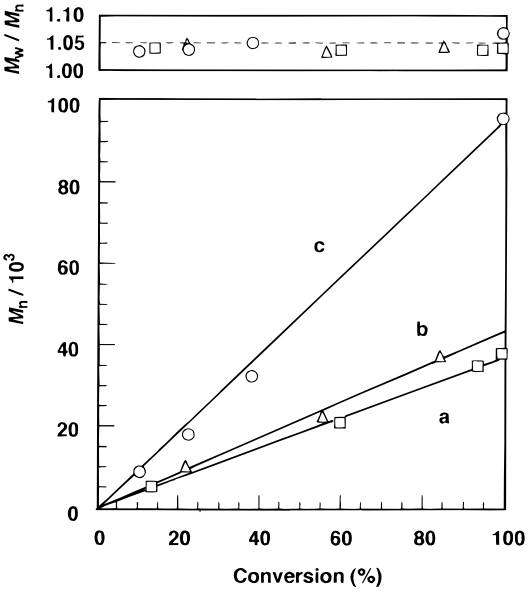

Figure 3. Conversion vs M_n and M_w/M_n of poly(ϵ-caprolactone) by lanthanide alkoxides: (a) $[YOMe(C_5H_5)_2]_2$, 0.5 mol %, (b) $YOMe(C_5Me_5)_2(THF)$, 0.5 mol %, and (c) $YOMe(C_5Me_5)_2(THF)$, 0.2 mol % of monomer.

Table 3. Block Copolymerizations of Lactones with Other Polar Monomers[a]

A, B monomers	poly(A)		poly(A-*block*-B)		A:B ratio
	M_n ($\times 10^3$)	M_w/M_n	M_n ($\times 10^3$)	M_w/M_n	
VL, CL	12.8	1.12	22.1	1.21	6.1:3.9
CL, VL	13.1	1.11	19.5	1.20	6.4:3.6
MMA, PL[b]	15.8	1.03	23.1	1.12	6.1:3.9
MMA, VL[b]	16.3	1.04	30.0	1.11	5.4:4.6
MMA, CL[b]	15.8	1.04	36.1	1.14	4.7:5.3

[a] Reaction conditions: initiator $SmMe(C_5Me_5)_2(THF)$ (1.0 mol % of lactone, 0.7 mol % of MMA); charged ratio of A and B, 1:1 mol:mol; solvent, toluene; polymerization temperature, 25 °C. [b] Polymerization time: 3 h.

case. Thus, the block copolymerization of MMA with lactones gave unimodal polymers with very narrow molecular weight distributions. Block copolymerizations of ϵ-caprolactone with δ-valerolactone and of valerolactone with ϵ-caprolactone also proceeded successfully to give the monodisperse copolymers in 80−90% yield in 6.1:3.9−6.4:3.9 ratios.

Initiation Mechanism for the Polymerization of Lactones. Stoichiometric reactions of various lactones with $[SmH(C_5Me_5)_2]_2$ were examined to understand the initiation mechanism. The 1:1 reaction of δ-valerolactone with samarium hydride was conducted at 0 °C in toluene for 1 h, and then the reaction products were hydrolyzed with water. As a result, 1,5-pentanediol was obtained in ca. 42% isolated yield on the basis of δ-valerolactone (84% yield on the basis of the Sm

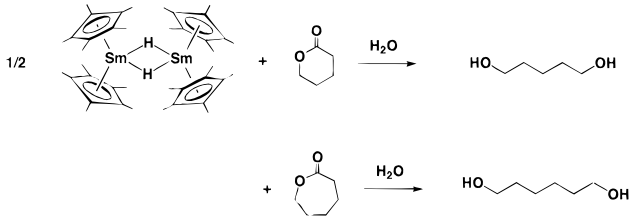

Figure 4. Reduction of lactones by $[SmH(C_5Me_5)_2]_2$.

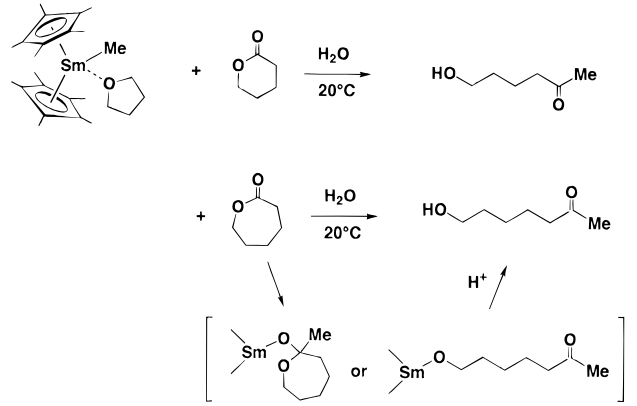

Figure 5. Stoichiometric reaction of $SmMe(C_5Me_5)_2(THF)$ with lactones.

complex, see Experimental Section) in place of the aldehyde alcohol, 4-hydroxy-1-pentanal (Figure 4). In the same manner, the 1:1 reaction of $[SmH(C_5Me_5)_2]_2$ with ϵ-caprolactone gave 1,6-hexanediol in ca. 40% yield upon hydrolysis of the product. These results strongly indicate the occurrence of reduction at the carbonyl group to produce the $(C_5Me_5)_2SmO(CH_2)_nOSm(C_5Me_5)_2$ species. In contrast to the mode of reduction by $[SmH(C_5Me_5)_2]_2$, the reaction of $SmMe(C_5Me_5)_2(THF)$ with δ-valerolactone or ϵ-caprolactone gave the keto alcohols 6-hydroxy-2-hexanone or 7-hydroxy-2-heptanone, respectively, upon hydrolysis of the products in ca. 75% isolated yield (Figure 5). Therefore, in this case, O−C(O) scission of lactones followed by alkyl addition occurred preferentially.

To understand the mode of alkyl addition directly by the ^{13}C NMR spectrum, the 1:1 reaction of ϵ-caprolactone with a diamagnetic complex, $LuMe(C_5Me_5)_2(THF)$, was examined (Figure 6). The use of $SmMe(C_5Me_5)_2$ is unsuitable for this purpose because the resulting species exhibits a paramagnetic nature. As a consequence, a lanthanide methyl group was added to the carbonyl group of δ-valerolactone, forming an acetal linkage (the ketonic carbon was not observed at around 170−220 ppm in ^{13}C NMR spectrum), which produces 6-hydroxy-2-hexanone upon acid hydrolysis. The corresponding reaction of $YMe(C_5Me_5)_2(THF)$ with ϵ-caprolactone also gave a similar compound, as revealed by the ^{13}C NMR

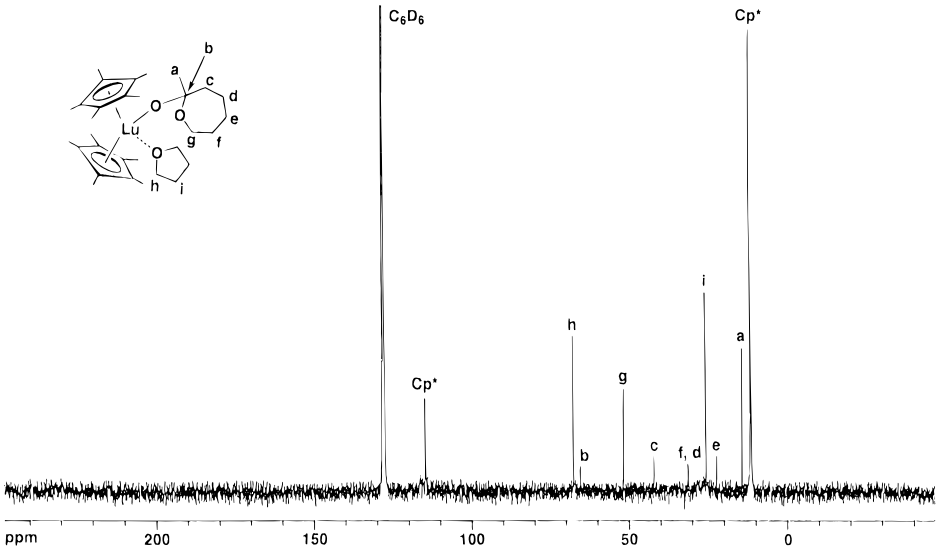

Figure 6. ^{13}C NMR spectrum of the $LuMe(C_5Me_5)_2/\epsilon$-caprolactone adduct in C_6D_6.

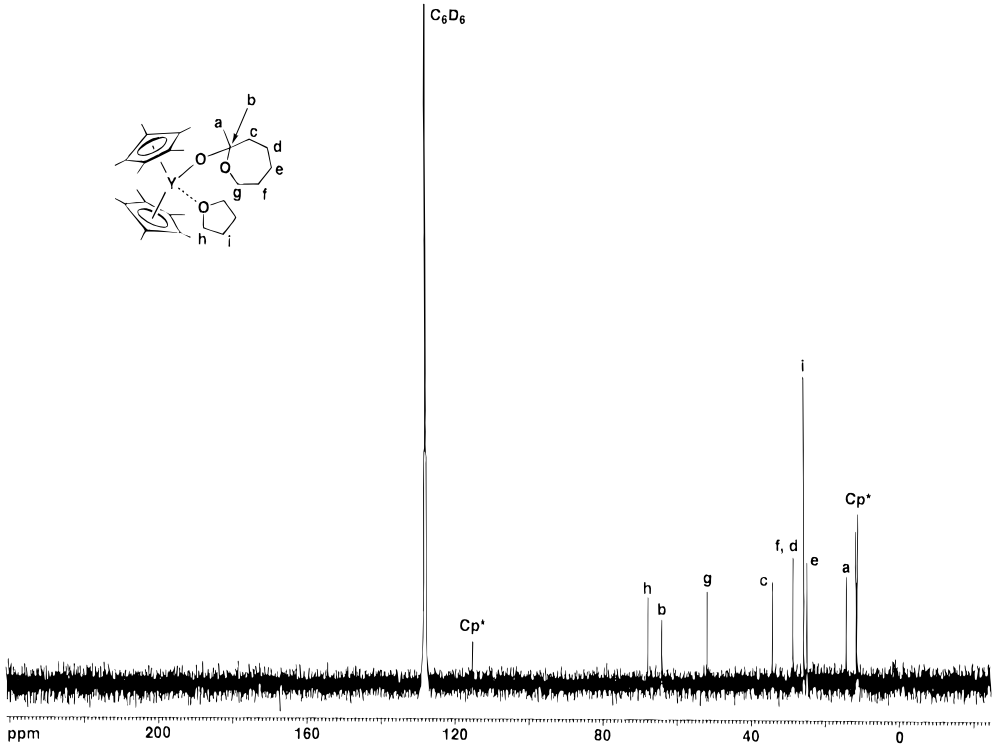

Figure 7. ^{13}C NMR spectrum of the $YMe(C_5Me_5)_2/\epsilon$-caprolactone adduct in C_6D_6.

spectrum (Figure 7). The reaction of $LuMe(C_5Me_5)_2$-(THF) with β-propiolactone gave a pure addition compound, which showed no catalytic activity for the polymerization of β-propiolactone. The isolated compound exhibits the 1:1 constitution as evidenced by ^1H NMR (Figure 8) and ^{13}C NMR spectra (Figure 9). The compound yields 1-acetoxy-3-butanone in 89% GC yield by treatment with excess acetic anhydride. This result clearly indicates the formation of 2-(acetylethoxy)-lutetium. Thus, the strained β-propiolactone molecule is stabilized by the ring opening, followed by the addition of a methyl group to C=O. Therefore, the present complex exhibits no catalytic activity for the polymerization of β-propiolactone.

However, when a lanthanide alkoxide was used as an initiator, the formation of high molecular weight polymers of β-propiolactone, δ-valerolactone, and ϵ-caprolactone was realized. The 1:1 addition reaction of these lactones to $SmOEt(OEt_2)(C_5Me_5)_2$ followed by the addition of acetic anhydride resulted in the formation of 2-(ethoxycarbonyl)ethyl acetate, 4-(ethoxycarbonyl)butyl acetate, and 5-(ethoxycarbonyl)pentyl acetate, respectively, in 70−80% yields (Figure 10). This result is consistent with the result of reaction of (porphinato)-aluminum ethoxide with ϵ-caprolactone or δ-valerolactone, which gives 4-(ethoxycarbonyl)butyl acetate or 5-(ethoxycarbonyl)pentyl acetate by the reaction of acetic anhydride.[7] However, the reaction of PL with (porphinato)aluminum largely differs from the mode of reaction with an alkoxylanthanide.[16] This reaction occurs by alkyl−acyl cleavage to give aluminum alkylcarboxylate, while in the reaction with alkoxylanthanide acyl−oxygen scission occurs preferentially to again give alkoxylanthanide.

More precisely, the 1:1 adducts of $YOMe(C_5Me_5)_2$-(THF) with lactones such as ϵ-caprolactone, δ-valero-

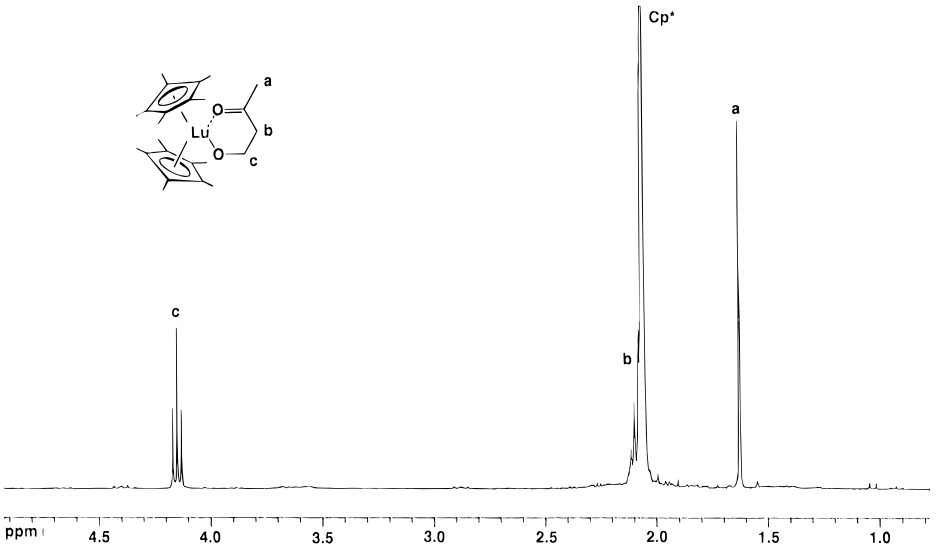

Figure 8. ^{1}H NMR spectrum of th LuMe(C_5Me_5)$_2$/β-propiolactone adduct in C_6D_6.

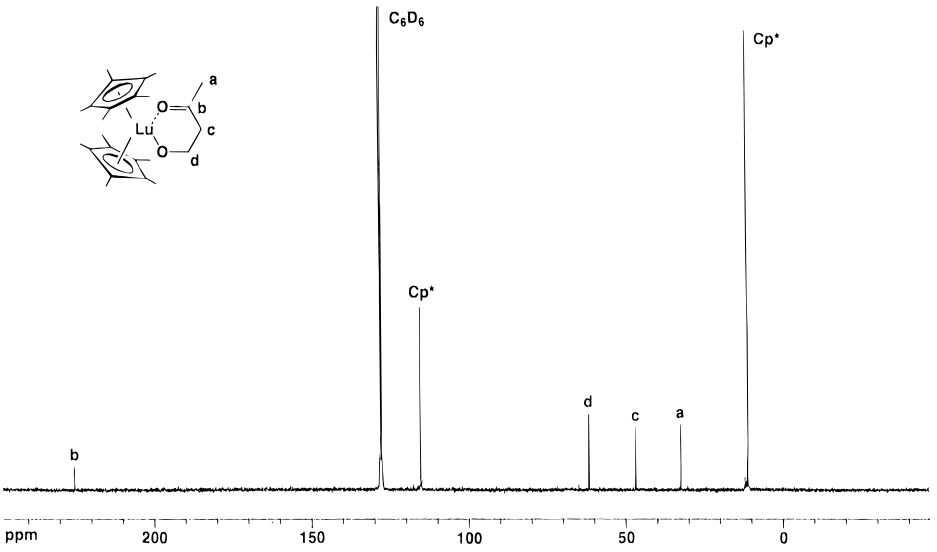

Figure 9. ^{13}C NMR spectrum of LuMe(C_5Me_5)$_2$/β-propiolactone adduct in C_6D_6.

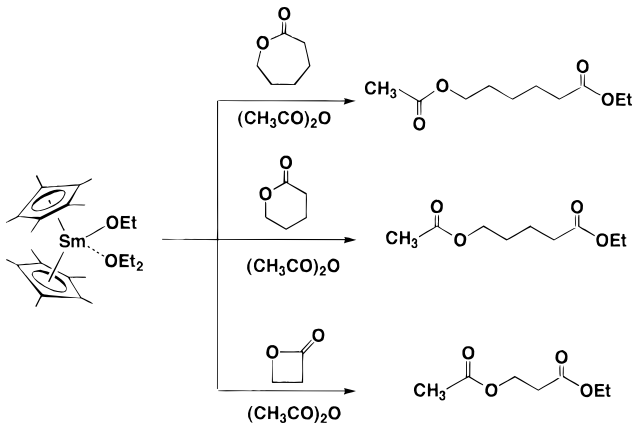

Figure 10. Reactions of lactones with SmOEt(C_5Me_5)$_2$(Et_2O).

lactone, γ-valerolactone, and γ-butyrolactone were obtained by the addition of a slight excess of lactones to the yttrium methoxide, followed by recrystallization from hexane. Figure 11 shows the isolated 1:1 ϵ-caprolactone complex of yttrium methoxide, YOMe(C_5Me_5)$_2$-(CL), which upon hydrolysis produces ϵ-caprolactone quantitatively. Chemical shift values and coupling constants for the coordinated ϵ-caprolactone molecule resemble those of metal-free ϵ-caprolactone (see Experimental Section). This adduct is stable at 0 °C for 2 h, but gradually decomposes to give the ring-opening product at room temperature. In a similar way, the 1:1 adduct of δ-valerolactone with YOMe(C_5Me_5)$_2$ is obtained in high yield, i.e., the ^{1}H NMR spectrum shows signals of OCH_3, OCH_2, $C(O)CH_2$, $CH_2(\beta)$, and $CH_2(\gamma)$ at 4.12, 3.39 (t), 2.25 (t), 0.98, and 1.143 (m) ppm, respectively. The observed spectrum resembles that of metal-free δ-valerolactone in C_6D_6, i.e., OCH_2, $C(O)CH_2$, $CH_2(\beta)$, and $CH_2(\gamma)$ signals at 3.59(t), 2.02(t), 0.93, and 1.02(m) ppm, respectively. However, we have failed in isolating the 1:1 β-propiolactone adduct of YOMe-(C_5Me_5)$_2$ because a very complex ^{1}H NMR spectrum was observed in this case, presumably due to the ring opening of β-propiolactone.

Corresponding coordination compounds, YOMe-(C_5Me_5)$_2$/γ-butyrolactone and YOMe(C_5Me_5)$_2$/γ-valerolactone, were also obtained in a similar fashion (Figures 12 and 13). These adducts again produce the γ-butyrolactone or γ-valerolactone, respectively, upon hydrolysis since these five-membered-ring monomers are completely inert toward the ring-opening polymerization. The six-coordinate *mer*-octahedral yttrium trichloride complex of ϵ-caprolactone has been isolated recently,

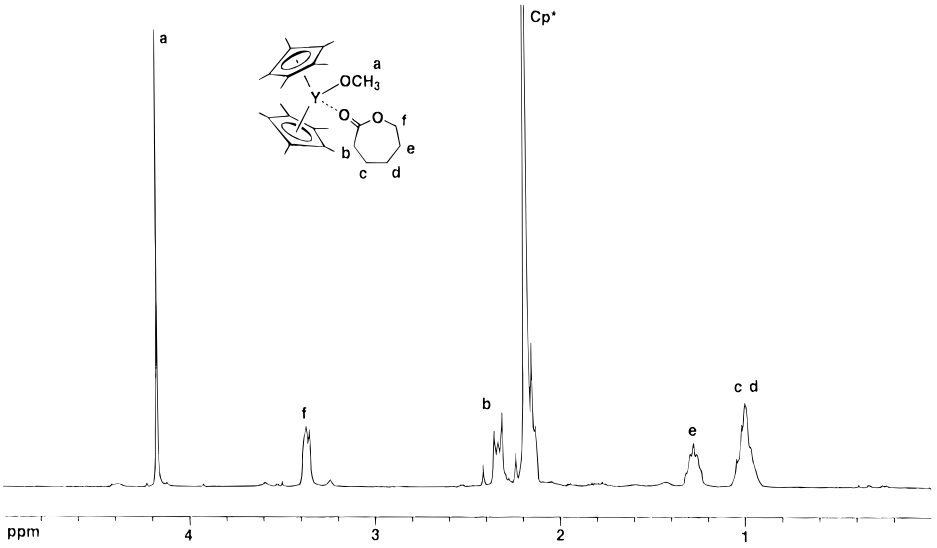

Figure 11. ^{1}H NMR spectrum of the YOMe$(C_5Me_5)_2$/ϵ-caprolactone adduct in C_6D_6.

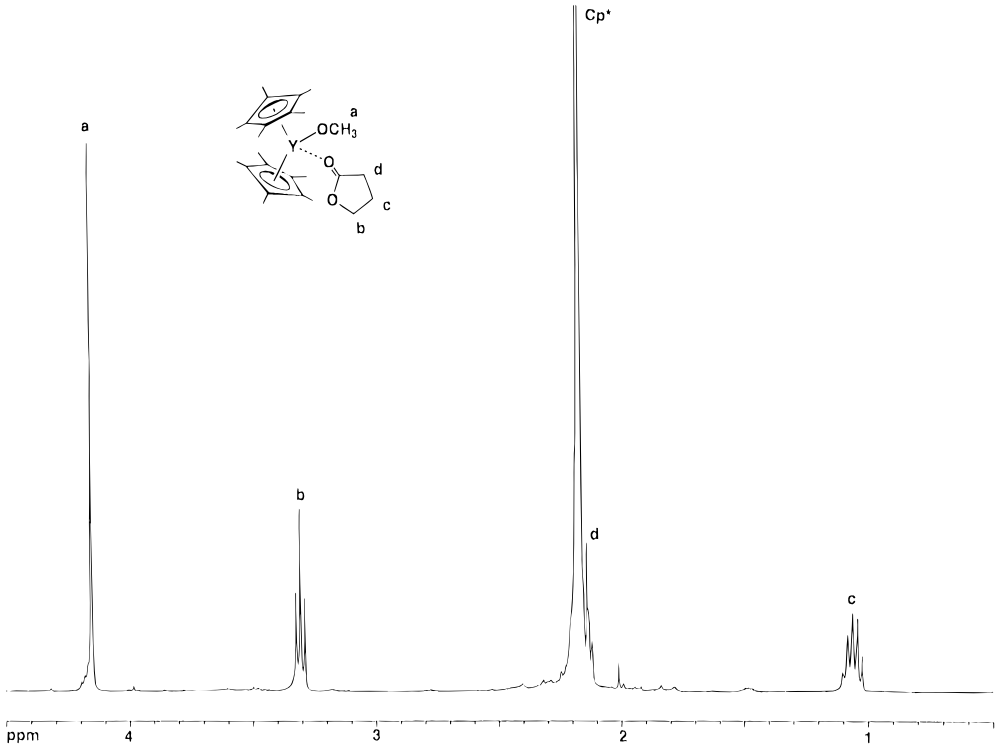

Figure 12. ^{1}H NMR spectrum of the YOMe$(C_5Me_5)_2$/γ-butyrolactone adduct in C_6D_6.

where three ϵ-caprolactone molecules coordinate as a monodentate ligand through its carbonyl oxygen.[17] Similarly, a six-coordinate *fac*-octahedral yttrium trichloride/ϵ-caprolactone complex, $YbCl_3(C_6H_{10}O_2)(THF)_2$, was also obtained.[17]

The addition of 2 equiv of ϵ-caprolactone to YOMe-$(C_5Me_5)_2$ resulted in the formation of white solid, which upon hydrolysis gave an ester alcohol together with 1 equiv of ϵ-caprolactone (Figure 14). This result indicates that ring opening occurs by the attack of the MeO group on the O−C(O) group of ϵ-caprolactone to result in the formation of the $(C_5Me_5)_2LnO(CH_2)_5C(O)OCH_3$ species. Treatment of the resultant product with acetic anhydride produces $CH_3C(O)O(CH_2)_5C(O)OCH_3$. Thus, incoming ϵ-caprolactone performed the ring-opening reaction in the presence of one equimolar amount of ϵ-caprolactone coordinated to the metal.

Experimental Section

General. All operations were conducted with Schlenk techniques under an argon atmosphere. Tetrahydrofuran, hexan, and toluene were dried over Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. Commercially purchased lactones such as β-propiolactone, δ-valerolactone, and ϵ-caprolactone were dried over CaH_2 for 4 days and then dried over calcinated $CaCl_2$ for more than 10 days. Gas chromatographic analysis and the separation of the reaction products were made with a Yanako G3810 gas chromatograph using a column packed with Silicone DC-550 or DEGS. NMR spectra were recorded on a JEOL-EX270 or a Bruker AM 400 spectrometer (400.13 MHz for ^{1}H and 100.03 MHz for ^{13}C nuclei). Chemical shifts were calibrated by using benzene (7.2 ppm) or chloroform (7.26 ppm). Number-average molecular weights and molecular weight distributions of polymers were determined by gel permeation chromatography on a Tosoh SC-8010 high-speed liquid chromatograph equipped with a differential refractometer detector, using $CHCl_3$ as eluent at 40

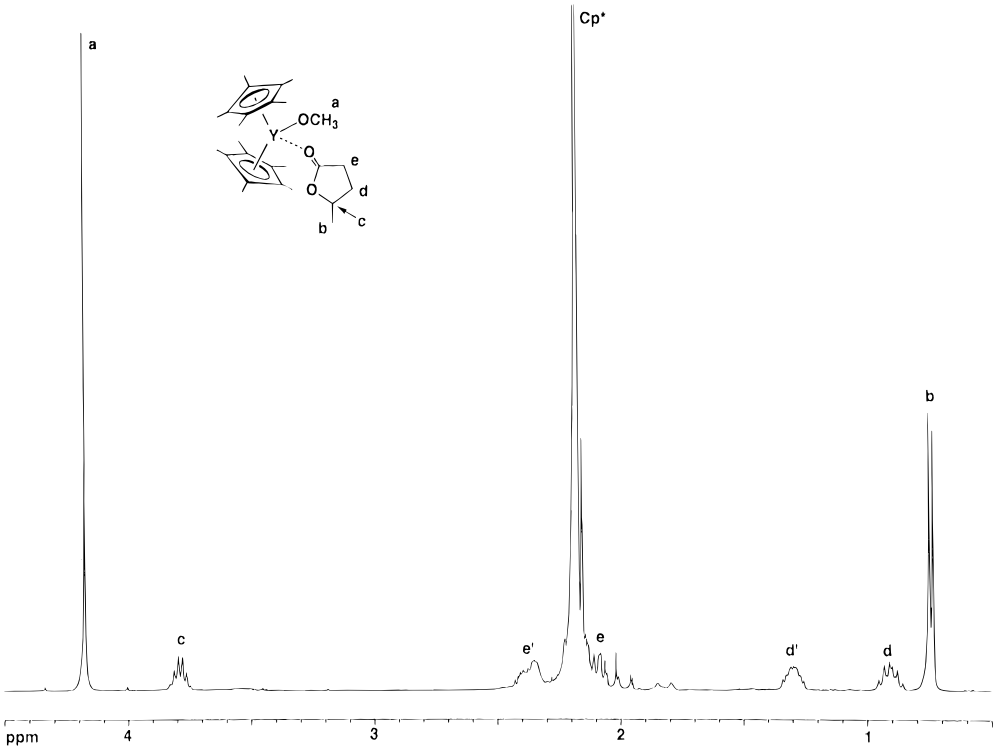

Figure 13. ^{1}H NMR spectrum of the YOMe(C_5Me_5)$_2$/γ-valerolactone adduct in C_6D_6.

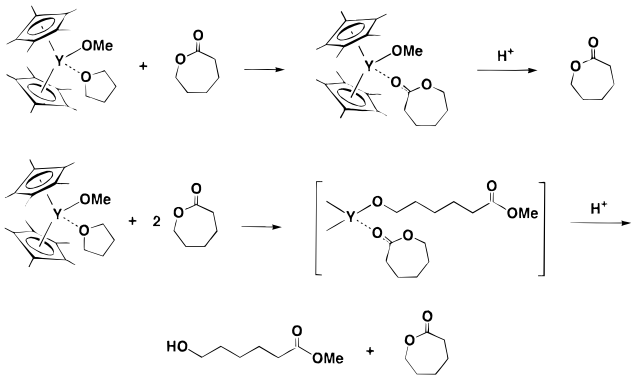

Figure 14. Stoichiometric reaction of ϵ-caprolactone with YOMe(C_5Me_5)$_2$(THF).

°C. There were four columns: TSK gel G5000Hxl, G4000Hxl, G3000Hxl, and G2000Hxl. The flow rate was 1.0 mL/min. The molecular weights and molecular weight distributions of polymers were determined by using a universal curve plotted with standard polystyrene: 8.70×10^2, $M_w/M_n = 1.10$; 3.79×10^4, $M_w/M_n = 1.01$; 7.06×10^5, $M_w/M_n = 1.05$; 2.89×10^6, $M_w/M_n = 1.06$.

Preparation of Organolanthanide Complexes. Preparations of SmMe(C_5Me_5)$_2$(THF) and [SmH(C_5Me_5)$_2$]$_2$ were carried out with reference to the literature.[18,19] LuMe(C_5Me_5)$_2$-(THF) was synthesized according to the procedure reported by Evans.[20]

Preparation of Lanthanide Alkoxides. SmOEt(C_5Me_5)$_2$(OEt_2) was synthesized by reaction of [SmH(C_5Me_5)$_2$]$_2$ with diethyl ether with reference to the literature.[21] [YOMe-(C_5H_5)$_2$]$_2$ was synthesized by reaction of YCl(C_5H_5)$_2$(THF)[22] with NaOMe. The starting compound, crystalline YCl(C_5H_5)$_2$-(THF), was synthesized by the addition of a THF solution (8.6 mL) of C_5H_5Na (15.5 mmol) to the stirred suspension of anhydrous YCl_3 (1.51 g, 7.73 mmol) in THF (40 mL) at room temperatur. The mixture was refluxed for 24 h. The resulting brown solution was centrifuged to separate the resulting NaCl, and the THF solution was evaporated to dryness. Toluene (80 mL) was added to the residue and centrifugation was carried out again to remove the salt. Recrystallization from THF/hexane solution gave YCl(C_5H_5)$_2$(THF) as pale brown prisms (yield, 35%). The resulting YCl(C_5H_5)$_2$(THF) (0.68 g, 2.10 mmol) was mixed with NaOMe (0.13 g, 2.4 mmol) in the solid state. Then THF (30 mL) was added with vigorous magnetic stirring, which was continued for 24 h. After evaporation of the solution to dryness, the solid was extracted with toluene to give a white powder of [YOMe(C_5H_5)$_2$]$_2$: isolated yield, 25% on the basis of NaOMe; dimer structure was estimated from the mass spectrum; EI mass (relative intensity) m/z 219 ([(C_5H_5)$_2$Y]+, 18.8), 438 ([(C_5H_5)$_2$^{89}Y(OMe)$_2$^{89}Y(C_5H_5)]$^+$, 100.0), 469 ([(C_5H_5)$_2$^{89}Y(OMe)^{89}Y(C_5H_5)$_2$]$^+$, 7.0), 500 ([(C_5H_5)$_2$^{89}Y-(OMe)$_2$^{89}Y(C_5H_5)$_2$]$^+$, 64.6); ^{1}H NMR (benzene-d_6) δ 6.19 (C_5H_5, 10H), 2.88 (MeO, 3H); ^{13}C NMR (benzene-d_6) δ 51.8 (MeO), 11.7 (C_5H_5). Anal. Calcd: C, 52.82; H, 5.20; O, 6.40; Y, 35.58. Found: C, 52.78; H, 5.24; O, 6.56; Y, 35.42 (metal oxide method).

Synthesis of YOMe(C_5Me_5)$_2$(THF) was carried out by the addition of NaOMe (0.12 g, 2.2 mmol) to YCl(C_5Me_5)$_2$(THF) (1.01 g, 2.16 mmol)[23] in the solid state, followed by the addition of THF (40 mL) with stirring. After the mixture was stirred overnight, the solution was evaporated to dryness and the resulting solid was extracted twice with toluene to yield a white powder. Recrystallization from THF/hexane gave yellow-green prisms of YOMe(C_5Me_5)$_2$(THF): isolated yield, 61%; ^{1}H NMR (benzene-d_6) δ 1.28 (m, 4H, THF), 2.09 (s, 30H, C_5Me_5), 3.49 (m, 4H, THF), 4.18 (s, 3H, OMe); ^{13}C NMR (benzene-d_6) δ 11.26 (CH_3), 25.2 (THF), 54.58 (THF), 54.65 (OMe), 115.3 (C). Anal. Calcd for $C_{25}H_{41}O_2Y$: C, 64.95; H, 8.88; O, 6.94; Y, 19.23. Found: C, 64.91; H, 9.01, O, 6.98; Y, 19.1 (metal oxide method).

Living Polymerization of Lactones by SmMe(C_5Me_5)$_2$-(THF) and [SmH(C_5Me_5)$_2$]$_2$. An initiator, SmMe(C_5Me_5)$_2$-(THF) (10 mg, 0.02 mmol), was dissolved in 10 mL of dried toluene. To the toluene solution was added 1.1 mL of ϵ-caprolactone (10 mmol) using a syringe at 0 °C with vigorous magnetic stirring. The stirring was continued for 10 h at 0 or 25 °C. Then the mixture was poured into excess MeOH to induce the precipitation of the polymer. The resultant polymer was dried *in vacuo*. In the same manner, δ-valerolactone (1.0 mL, 10 mmol) or β-propiolactone (0.62 mL, 10 mmol) was added and the mixture was stirred for 10 h at 25 °C. Then the resultant mixture was poured into excess MeOH to induce the precipitation of the polymer.

To the solution of ϵ-caprolactone or δ-valerolactone (10 mmol) in toluene (10 mL) was added a toluene solution (1 mL)

of purple single-crystalline $[SmH(C_5Me_5)_2]_2$ (8 mg, 0.02 mmol). Then the solution was stirred for 10 h at 20 °C to conduct the polymerization. The polymerization of lactones with $YbMe(C_5Me_5)_2(THF)$ was carried out in the same manner as described for $SmMe(C_5Me_5)_2(THF)$-initiated polymerization.

Living Polymerization of Lactones by $YOMe(C_5Me_5)_2(THF)$ and $[YOMe(C_5Me_5)_2]_2$. To a toluene solution (4−5 mL) of ϵ-caprolactone (10 mmol), δ-valerolactone (10 mmol), or β-propiolactone (10 mmol) was added a toluene solution (1 mL) of colorless crystalline $YOMe(C_5Me_5)_2(THF)$ (10 mg, 0.02 mmol) or $[YOMe(C_5Me_5)_2]_2$ (4.9 mg, 0.02 mmol) with vigorous stirring at 0 °C. The stirring was continued for 10 h at 25 °C, and the reaction mixture was poured into excess MeOH (100 mL) to induce the precipitation of the polymers in 88−95% conversion.

Living Polymerization of Lactones by $SmOEt(C_5Me_5)_2(OEt_2)$. The crystalline $SmOEt(C_5Me_5)_2(Et_2O)$ (10 mg, 0.02 mmol) was dissolved in 1 mL of toluene. To the toluene solution was added 0.93 mL of δ-valerolactone (10 mmol) using a syringe at 0 °C with vigorous magnetic stirring. The stirring was continued for 10 h at 0 °C. Then the mixture was poured into excess MeOH to induce the precipitation of the polymer. The resultant polymer was dried *in vacuo*. In the same manner, ϵ-caprolactone (1.1 mL, 10 mmol) was added to a toluene solution of $SmOEt(C_5Me_5)_2(Et_2O)$ (10 mg, 0.02 mmol), and stirring was continued for 10 h at 0 °C to conduct the polymerization.

Block Copolymerization of Lactones with Polar Monomers. To the toluene solution (20 mL) of methyl methacrylate (10 mmol, 1.07 mL) was added a toluene solution (1 mL) of $SmMe(C_5Me_5)_2(THF)$ (0.7 mol % of methyl methacrylate). The mixture was stirred for 1 h and then lactones (10 mmol) were added to this solution. After the mixture was stirred for 5 h at 25 °C, the resultant polymer solution was poured into excess methanol to precipitate the polymer. The block copolymer of δ-valerolactone with ϵ-caprolactone was obtained as described in the following. To a toluene solution (10 mL) of δ-valerolactone (10 mmol, 0.93 mL) was added a toluene solution (1 mL) of $SmMe(C_5Me_5)_2(THF)$ (1.0 mol % of δ-valerolactone). The mixture was stirred for 3 h at 25 °C, and then ϵ-caprolactone (10 mmol, 1.1 mL) was added. After the mixture was stirred the mixture for 5 h at that temperature, the resultant polymer solution was poured into excess methanol and the precipitated solid was dried *in vacuo*. The composition ratio of the resulting copolymer was determined by ^1H NMR.

Equimolar Reaction of δ-Valerolactone and ϵ-Caprolactone with $[SmH(C_5Me_5)_2]_2$. To a toluene solution (5 mL) of $[SmH(C_5Me_5)_2]_2$ (0.42 g, 1.0 mmol) was added δ-valerolactone (0.1 mL, 1.0 mmol) at 0 °C. The stirring was continued for 2 h and the mixture was quenched with excess water. After concentration of the toluene-soluble part, the resulting product was separated with gas chromatography and identified as 1,5-pentanediol, as revealed by the authentic sample; isolated yield, 43%; ^1H NMR ($CDCl_3$) δ 1.43 (m, 2H), 1.58 (q, J =7.6 Hz, 4H), 2.5 (bs, OH, 2H), 3.63 (q, J = 5.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 21.90 (1C), 32.14 (2C), 62.47 (2C); mass spectrum (70 eV, relative intensity) m/z 105 (M + 1, 1.1), 102 (M − 2, 1.6), 84 (C_5H_8O, 15.4), 83 (15.2).

In the same manner, an equimolar reaction of $[SmH(C_5Me_5)_2]_2$ with ϵ-caprolactone gave 1,6-hexanediol in 42% isolated yield upon hydrolysis: ^1H NMR ($CDCl_3$) δ 1.39 (q, J = 3.5 Hz, 4H), 1.49 (bs, 2H), 1.58 (q, J = 6.5 Hz, 4H), 3.64 (q, J = 5.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 25.49 (2C), 32.62 (2C), 62.82 (2C); mass spectrum (70 eV, relative intensity) m/z 119 (M + 1, 0.2), 88 (1.7), 82 (15.8), 68 (100).

Equimolar Reaction of δ-Valerolactone or ϵ-Caprolactone with $SmMe(C_5Me_5)_2(THF)$. To a toluene solution (5 mL) of $SmMe(C_5Me_5)_2(THF)$ (0.51g, 1.0 mmol) was added δ-valerolactone (0.1 mL, 1.0 mmol) at 0 °C. The stirring was continued for 2 h and the mixture was quenched with excess water. After concentration of the toluene-soluble part, the resulting product was separated with gas chromatography and identified as 6-hydroxy-2-hexanone: GC yield, 87%; ^1H NMR ($CDCl_3$) δ 1.80 (q, J = 6.4 Hz, 2H), 1.82 (q, 2H), 2.15 (s, 3H), 2.56 (t, J = 6.9 Hz, 2H), 3.61 (t, J = 6.0 Hz, 2H), 4.80 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.01 (CH_2), 26.15 (CH_2), 29.94 (CH_3CO), 40.35 (CH_2CO), 62.05 (CH_2O), 209.63 (CO); mass spectrum (70 eV, relative intensity) m/z 117 (M + 1, 2.4), 115 (M − 1, 1.8), 98 (100), 83 (19.7).

In the same manner, an equimolar reaction of $SmMe(C_5Me_5)_2(THF)$ with ϵ-caprolactone gave 7-hydroxy-2-heptanone in 42% isolated yield: ^1H NMR ($CDCl_3$) δ 1.78 (q, J = 6.4 Hz, 2H), 1.82 (q, 2H), 1.86 (m, 2H), 2.25 (s, 3H), 2.58 (t, J = 6.9 Hz, 2H), 3.45 (t, J = 6.0 Hz, 2H), 4.75 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.88 (CH_2), 26.02 (CH_2), 26.42 (CH_2), 29.75 (CH_3CO), 40.31 (CH_2CO), 62.08 (CH_2O), 209.32 (CO); mass spectrum (70 eV, relative intensity) m/z 131 (M + 1, 1.4), 129 (M − 1, 2.5), 112 (100), 97 (17.5).

Equimolar Reaction of $LuMe(C_5Me_5)_2(THF)$ with β-Propiolactone. β-Propiolactone (0.3 mL, 4.8 mmol) dissolved in 10 mL of toluene was added to a stirred solution of $LuMe(C_5Me_5)_2(THF)$ (2.6 g, 4.8 mmol) in 10 mL of toluene at −78 °C, and the mixture was allowed to warm to room temperature. The color of the solution turns to pale yellow from yellow green. Removal of the solvent by evaporation to dryness followed by extraction with degassed C_6D_6 gave the following NMR data: ^1H NMR (C_6D_6) δ 1.63 (s, 3H, CH_3), 2.06 (s, 30H, C_5Me_5), 2.08 (t, 3H, CH_2), 4.15 (t, 2H, CH_2); ^{13}C NMR (C_6D_6) δ 11.6 (C_5Me_5), 33.0 (CH_3), 47.3 (CH_2), 62.2 (CH_2), 115.8 (C_5Me_5), 225.7 (C). Anal. Calcd for $C_{23}H_{37}O_2Lu$: C, 53.08; H, 7.12; O, 6.15; Lu, 33.65. Found: C, 53.02; H, 7.18; O, 6.22; Lu, 33.58. Treatment of the product with acetic anhydride gave 1-acetoxy-3-butanone in 88% GC yield: ^1H NMR ($CDCl_3$) δ 2.03 (t, 3H), 2.15 (t, 3H), 2.51 (t, J = 7.2 Hz, 2H), 4.05 (t, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 22.68 (CH_3), 29.92 (CH_3), 39.83 (CH_2CO), 63.54 (CH_2O), 171.04 (COO), 207.68 (CO); mass spectrum (70 eV, relative intensity) m/z 87 (M − CH_3CO, 18.8), 71 (M − CH_3CO − CH_3, 100), 55 (100).

Equimolar reaction of $LuMe(C_5Me_5)_2(THF)$ with δ-Valerolactone. To a stirred solution of $LuMe(C_5Me_5)_2(THF)$ (0.35 g, 0.65 mmol) in 5 mL of toluene was added 0.06 mL of δ-valerolactone (0.65 mmol) in 2 mL of toluene at −78 °C. Then the mixture was allowed to warm to room temperature. The color of the solution turned to pale orange from pale yellow. Evaporation of the solution to dryness followed by extraction with degassed C_6D_6 gave the following NMR data: ^{13}C NMR (C_6D_6) δ 11.6 (C_5Me_5), 14.2 (Me), 22.1 (CH_2), 22.8 (CH_2), 25.7 (THF), 51.8 (CH_2), 65.9 (CH_2), 70.0 (THF), 115.3 (C_5Me_5). Treatment of the product with acetic anhydride produced 1-acetoxy-5-hexanone in 89% GC yield: ^1H NMR ($CDCl_3$) 1.84 (q, J = 6.7 Hz, 2H), 1.88 (q, J = 6.5 Hz, 2H), 2.05 (s, 3H), 2.18 (s, 3H), 2.62 (t, J = 7.2 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.78, 20.92, 22.72, 29.95, 40.05, 63.44, 171.05, 208.1; mass spectrum (70 eV, relative intensity) m/z 115 (M − CH_3COH, 20.1), 99 (100), 83 (11.2).

Equimolar Reaction of $LuMe(C_5Me_5)_2(THF)$ with ϵ-Caprolactone. ϵ-Caprolactone (0.07 mL, 0.65 mmol) was added to a toluene solution (5 mL) of $LuMe(C_5Me_5)_2(THF)$ (0.35 g, 0.65 mmol) at 0 °C, and the mixture was allowed to warm to room temperature (25 °C). After evaporation of the mixture, the resulting white solid was extracted with hexane (20 mL) and the solution was cooled to −24 °C to induce the precipitation of $LuMe(C_5Me_5)_2(\epsilon$-caprolactone): isolated yield, 30−35%; ^1H NMR (C_6D_6) δ 1.2−1.4 (m, 6H, CH_2), 1.46 (4H, THF), 1.64 (s, 3H, CH_3), 2.09 (s, 30H, C_5Me_5), 2.14 (t, 2H, CH_2), 3.62 (4H, THF), 4.44 (t, 2H, CH_2); ^{13}C NMR (C_6D_6) δ 11.5 (C_5Me_5), 14.2 (CH_2), 22.2 (CH_2), 25.8 (THF), 31.2−31.5 (d, CH_2), 42.2 (CH_2), 51.8 (CH_2), 65.5 (CH_2), 67.8 (THF), 114.8 (C_5Me_5). Treatment of the product with acetic anhydride produces 1-acetoxy-6-heptanone in 78% yield: ^1H NMR ($CDCl_3$) δ 1.83 (q, J = 6.7 Hz, 2H), 1.85 (q, 2H), 1.88 (q, 2H), 2.05 (s, 3H), 2.17 (t, J = 7.1 Hz), 4.08 (t, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 19.99, 20.85, 20.91, 29.92, 40.05, 63.55, 171.05, 207.68; mass spectrum (70 eV, relative intensity) m/z 129 (M − CH_3COH, 16.5), 113 (100), 97 (10.0).

Equimolar Reaction of $SmOEt(Et_2O)(C_5Me_5)_2$ with Lactones. $SmOEt(Et_2O)(C_5Me_5)_2$ (0.54 g, 1.0 mmol) was added to ϵ-caprolactone (0.11 mL, 1.0 mmol), δ-valerolactone (0.093 mL, 1.0 mmol), or β-propiolactone (0.051 mL, 1.0 mmol) dissolved in 5 mL of toluene, and stirring was continued for 2 h at room temperature. The resulting product was treated with excess acetic anhydride (2.0 mL) at room temperature,

and the products were separated by GC into 5-(ethoxycarbonyl)pentyl acetate, 4-(ethoxycarbonyl)butyl acetate, and 2-(ethoxycarbonyl)ethyl acetate, respectively, in 78, 82, and 80% GC yields. 5-(Ethoxycarbonyl)ethyl acetate: ^{1}H NMR ($CDCl_3$) δ 1.45 (q, J = 7.5 Hz, 4H), 1.49 (q, 2H), 1.59 (t, 3H), 2.16 (t, 3H), 2.51 (t, J = 7.2 Hz, 2H), 4.07 (t, J = 6.5 Hz, 2H), 4.05 (q, J = 6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.52, 19.93, 20.57, 20.88, 29.92, 39.88, 63.54, 65.03, 207.68, 208.52. 4-(Ethoxycarbonyl)-butyl acetate: ^{1}H NMR ($CDCl_3$) δ 1.43 (q, J = 7.5 Hz, 2H), 1.49 (q, 2H), 1.67 (t, 3H), 2.15 (t, 3H), 2.55 (t, J = 7.2 Hz), 4.04 (t, J = 6.5 Hz), 4.05 (q, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.88, 19.99, 20.34, 29.75, 39.80, 63.55, 65.12, 207.78, 208.56. 2-(Ethoxycarbonyl)ethyl acetate: ^{1}H NMR ($CDCl_3$) δ 1.89 (s, 3H), 2.15 (s, 3H), 2.51 (t, J = 7.2 Hz, 2H), 2.55 (q, J = 7.2 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.52, 29.92, 39.88, 63.54, 65.22, 207.68, 208.52.

Equimolar Reactions of $YOMe(C_5Me_5)_2(THF)$ with Lactones. A toluene solution (1 mL) of ϵ-caprolactone (0.11 mL, 1.0 mmol) was added to a toluene solution (5 mL) of $YOMe(C_5Me_5)_2(THF)$ (0.42 g, 0.9 mmol), and the reaction mixture was stirred for 2 h at 0 °C. After evaporation of the solution to dryness, the residue was extracted into hexane (30 mL) below 25 °C, and concentration of the product followed by cooling at −24 °C gave a colorless microcrystalline solid of the 1:1 adduct, $YOMe(C_5Me_5)_2(CL)$: isolated yield, 72%; ^{1}H NMR (C_6D_6) δ 0.98 (m, CH_2, 4H), 1.27 (q, CH_2, 2H), 2.19 (s, CH_3, 30H), 2.30 (t, CH_2, 2H), 3.38 (t, CH_2O, 2H), 4.19 (s, MeO, 3H). Hydrolysis of the 1:1 adduct with water gave 1 equiv of caprolactone in 90% yield as evidenced by GC [metal-free ϵ-caprolactone in C_6D_6 shows ^{1}H NMR signals at 1.05 (q, CH_2, 2H), 1.20 (q, CH_2, 4H), 2.18 (t, $CH_2C(O)$, 2H) and 3.55 ppm (t, CH_2O, 2H)].

In the same manner, γ-butyrolactone (0.77 mL, 1.0 mmol) and γ-valerolactone (0.94 mL, 1.0 mmol) were reacted with $YOMe(C_5Me_5)_2(THF)$ (0.42 g, 0.9 mmol) in toluene (5 mL) at 0 °C. After the mixture was stirred for 3 h, the solution was evaporated to dryness and the residue was extracted with hexane (30 mL). The resultant 1:1 adduct was obtained as a colorless microcrystalline compound by concentrating and cooling the extract to −24 °C in ca. 65−72% isolated yield: ^{1}H NMR (C_6D_6) $YOMe(C_5Me_5)_2$(γ-butyrolactone) δ 1.05 (q, CH_2, 2H), 2.12 (t, CH_2, 2H), 2.15 (s, CH_3, 30H), 3.31 (t, CH_2, 2H), 4.17 (s, MeO, 3H). Metal-free γ-butyrolactone in C_6D_6 shows ^{1}H NMR signals of the CH_2, $CH_2(CO)$, and CH_2O groups at 1.20 (m), 1.78 (m), and 3.52 ppm (m), respectively, and ^{13}C NMR signals of CH_2, $CH_2(CO)$, CH_2O, and CO at 21.78, 27.33, 67.70, and 176.67 ppm, respectively. $YOMe(C_5Me_5)_2$-(γ-valerolactone): δ 0.72 (d, CH_3, J = 6.2 Hz, 3H), 0.92, 1.30 (m, CH_2, 2H), 2.20, 2.35 (m, CH_2, 2H), 2.18 (s, CH_3, 30H), 3.79 (q, CH, 1H), 4.18 (s, MeO, 3H). Metal-free γ-valerolactone in C_6D_6 shows ^{1}H NMR signals of the CH_3, CH_2, $CH_2(CO)$, and CH groups at 0.91 (d, J = 6.2 Hz), 1.07, 1.45 (m), 1.94, 1.98 (m), and 3.94 (m), respectively, and ^{13}C NMR signals of CH_3, CH_2, $CH_2(CO)$, and CO at 20.75, 28.82, 29.36, 76.16, and 176.2 ppm, respectively.

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References and Notes

(1) Duvois, Ph.; Jacobs, C.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 2266.
(2) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419.
(3) Duda, A.; Penczek, S. *Macromolecules* **1990**, *23*, 1636.
(4) Johns, D. B.; Lenz, R. W.; Luick, A. *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science Publishers: London, 1984; Vol. 1, Chapter 7, pp 461.
(5) Nomura, R.; Ueno, A.; Endo, T. *Macromolecules* **1994**, *27*, 620. Inoue, S.; Tomoi, Y.; Tsuruta, T.; Furukawa, J. *Makromol. Chem.* **1961**, *48*, 229. Jedlinski, Z.; Kowalczuk, M.; Kurock, P. *Makromol. Chem., Macromol. Symp.* **1986**, *3*, 277.
(6) Teranishi, K.; Iida, M.; Araki, T.; Yamashita, S.; Tani, H. *Macromolecules* **1974**, *7*, 421. Teranishi, K.; Araki, T.; Tani, H. *Macromolecules* **1972**, *5*, 660.
(7) Yasuda, T.; Aida, T.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3931. Shimasaki, K.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 3076. Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982.
(8) Vergara, J.; Figini, R. V. *Makromol. Chem.* **1977**, *178*, 267.
(9) Okuda, J.; Rushkin, I. L. *Macromolecules* **1993**, *26*, 5530. Okuda, J.; Kleinhenn, T.; Konig, P.; Taden, I.; Ngo, S.; Rushkin, I. L. *Macromol. Symp.* **1995**, *95*, 195.
(10) McLain, S. J.; Drysdale, N. E. U.S. Patent 5,028,667, 1991 (assigned to E. I. du Pont de Nemours and Co.). McLain, S. J.; Ford, T. M.; Drysdale, N. E. *Am. Chem. Soc., Div. Polym. Chem.* **1992**, *33*, 463. McLain, S. J.; Drysdale, N. E. *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco, April 1992; American Chemical Society: Washington, DC, 1992; POLY-160.
(11) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330. Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 4011.
(12) For a preliminary report, see Yamashita, M.; Takemoto, Y.; Yasuda, H. Rare Earths '92, Kyoto, Japan, June 1992, Paper PIK-05.
(13) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908. Yasuda, H.; Yamamoto, H.; Yamasahita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134. Yasuda, H.; Yamamoto, H.; Takemoto, Y.; Yamashita, M.; Yokota, K.; Miyake, S.; Nakamura, A. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 187. Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097. Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3726.
(14) Ihara, E.; Morimoto, M.; Yasuda, H. *Proc. Jpn. Acad.* **1995**, *71B*, 126. Yasuda, H.; Ihara, E.; Morimoto, M.; Nodono, M.; Yoshioka, S.; Furo, M. *Macromol. Symp.* **1995**, *95*, 203. Ihara, E.; Moromoto, M.; Yasuda, H. *Macromolecules* **1995**, *28*, 7886.
(15) Evans, W. J.; Sollberger, M. S.; Shreeve, J. L.; Olofson, J. M.; Hain, J. H., Jr.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 2492.
(16) Aida, T.; Maekawa, Y.; Asano, S.; Inoue, S. *Macromolecules* **1988**, *21*, 1195. Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1983**, *16*, 1792.
(17) Evans, W. J.; Shreeve, J. L.; Doedens, R. J. *Inorg. Chem.* **1993**, *32*, 245. Evans, W. J.; Shreeve, J. L.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1995**, *34*, 576.
(18) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.
(19) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6432.
(20) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292.
(21) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.
(22) Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1985**, *85*, 672.
(23) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614.

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