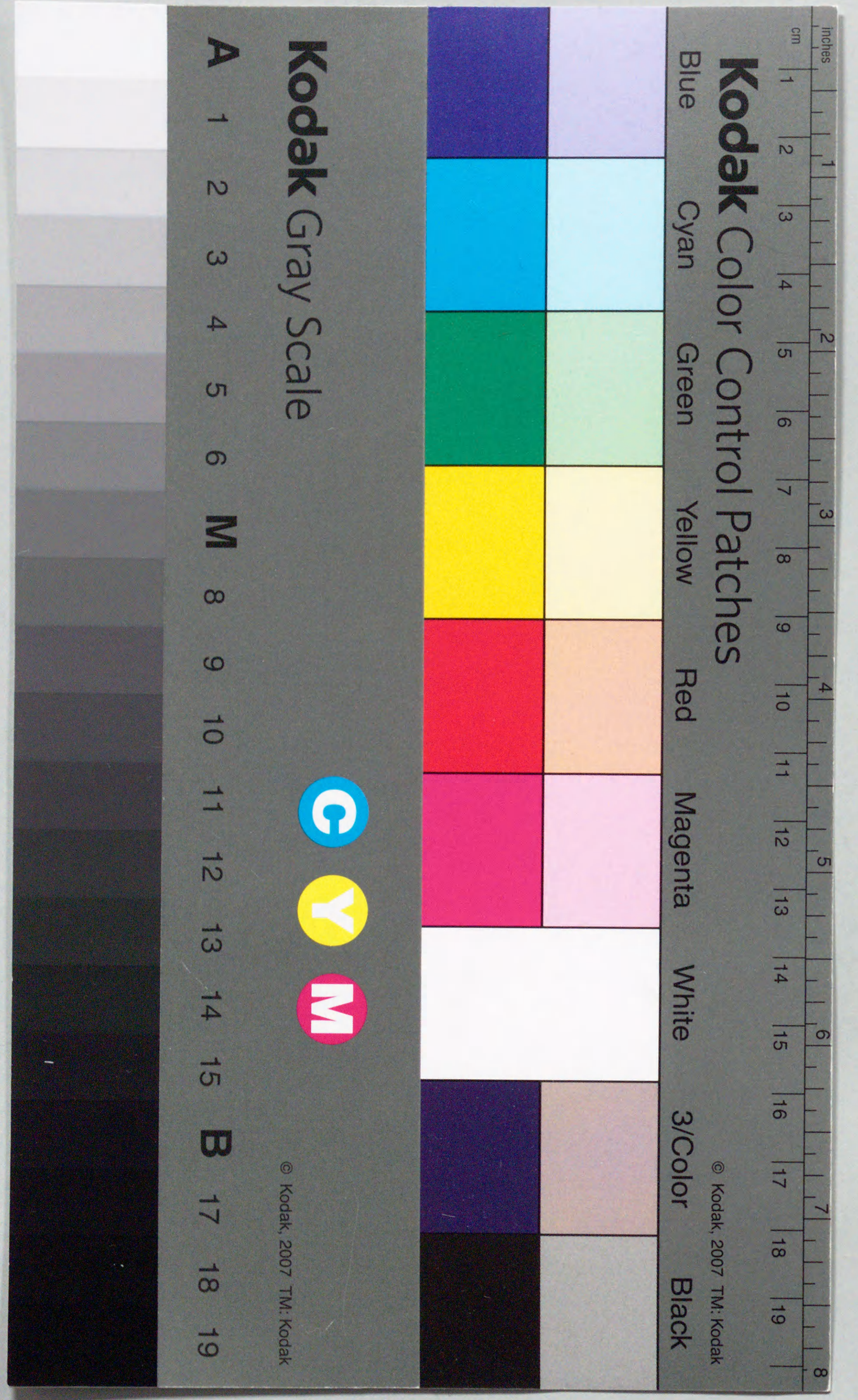

LIVING POLYMERIZATION OF POLAR MONOMERS CATALYZED BY RARE EARTH BIS(CYCLOPENTADIENYL)METAL COMPLEXES

A Doctoral Thesis
by
MASAHIRO YAMASHITA

Department of Applied Chemistry,
Faculty of Engineering, Hiroshima University

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Acknowledgement

This research has been performed under the direction of Professor Dr. Hajime Yasuda at the Department of Applied Chemistry, Faculty of Engineering, Hiroshima University.

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January, 1995

CONTENTS

Chapter 1

General Introduction

Organometallic chemistry of rare earth element had attracted little attention before 1980. In general, the isolation of rare earth metal complexes was difficult because of their strong tendency to form ate complexes owing to the high Lewis acidity and the large ionic radius of the element. Characterization of the complexes was also troublesome due to their low solubility to organic solvent. Moreover, rare earth metal complexes have been thought to exhibit only analogous reactivity to Grignard or organolithium reagents.

Use of cyclopentadienyl ligands (C_5H_5 and C_5Me_5) has changed the situation since 1980. Rare earth metal complexes with these ligands are soluble in organic solvent. A large number of rare earth metal complexes have been synthesized and their structures were characterized by X-ray analysis. In addition, the reactivities characteristic of these complexes have been revealed[1]. Various interesting reactions of the complexes with unsaturated compounds have been developed. In particular, catalytic activity for olefin polymerization has been attracted much attention since rare earth metal complexes show the activity without any cocatalyst and their activity is comparable to that of Ziegler type catalyst[2].

On the other hand, our group has developed polymerization of polar monomers by rare earth metal complexes. Living polymerization of methyl methacrylate has been achieved by the use of initiators such as $[SmH(C_5Me_5)_2]_2$ and $SmMe(C_5Me_5)_2(THF)$. High molecular weight ($M_n > 10^5$) poly(methyl methacrylate) (PMMA) with extremely narrow molecular weight distribution ($M_w/M_n < 1.05$) was obtained. Furthermore, the polymerization proceeded in a stereoselective manner giving highly syndiotactic PMMA (rr≥95%). 1:2 adduct of $SmH(C_5Me_5)_2$ and methyl methacrylate was isolated and its structure was identified by X-ray analysis and it was revealed that the polymerization proceeded through samarium enolate as an propagating species[3].

Judging from the above successful result of methyl methacrylate polymerization, further extension of this study is desirable. In this thesis, I focused on the application of the rare earth metal initiating system to lactone monomers[4]. Living polymerization of the monomers are described and the exact mechanism of the polymerization is discussed on the basis of stoichiometric reaction. In addition, I examined polymerization of protected methacrylate monomers which afforded poly(methacrylic acid) or its derivatives after deprotection. Some related investigations about

polymerization of methyl methacrylate are also described.

Outline of Each Chapter

Chapter 2 describes the living polymerization of lactones catalyzed by organo rare earth metal alkyl complexes. Polymerization of δ-valerolactone and ε-caprolactone catalyzed by $SmMe(C_5Me_5)_2(THF)$ or $[SmH(C_5Me_5)_2]_2$ gave polyesters with very narrow polydispersity ($M_w/M_n < 1.05$) and high molecular weight ($M_n > 10^5$). The fact that the number average molecular weight increases linearly in proportion to the conversion indicates that this polymerization proceeds in a living fashion. Based on the stoichiometric reactions of rare earth metal complexes with the monomers, initiation and propagation mechanisms are discussed for this system.

Chapter 3 describes the living polymerization of lactones catalyzed by organo rare earth metal alkoxide complexes, $Ln(OR)(C_5R'_5)_2$, as has been indicated as active species in chapter 2. Polymerization of δ-valerolactone and ε-caprolactone catalyzed by $YOMe(C_5R_5)_2$ (R=H,Me) gave polyesters with very narrow polydispersity and high molecular weight. The fact that the number average molecular weight increases linearly in proportion to the conversion indicates that this polymerization system belongs to the living system. Based on the stoichiometric reactions between rare earth metal alkoxide and the monomers, initiation and

propagation mechanisms are discussed.

Chapter 4 describes the polymerization of methyl methacrylate catalyzed by organo rare earth metal enolate complexes $Sm(OCR'=R''_2)(C_5R_5)_2$(R=H,Me), as has been indicated as the active species of polymerization of methacrylate in the previous work. The effect of solvent was also investigated in this part.

Chapter 5 describes the living polymerization of trimethylsilyl substituted methacrylate catalyzed by organo rare earth metal complexes. In this case, monodispersed poly(methacrylic acid) which has not been synthesized by conventional anionic polymerization was obtained upon hydrolysis. Based on the stoichiometric reactions of rare earth metal complexes with the monomers, the possibility of block copolymerization of methyl methacrylate and trimethylsilylmethacrylate was discussed.

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Chapter 2

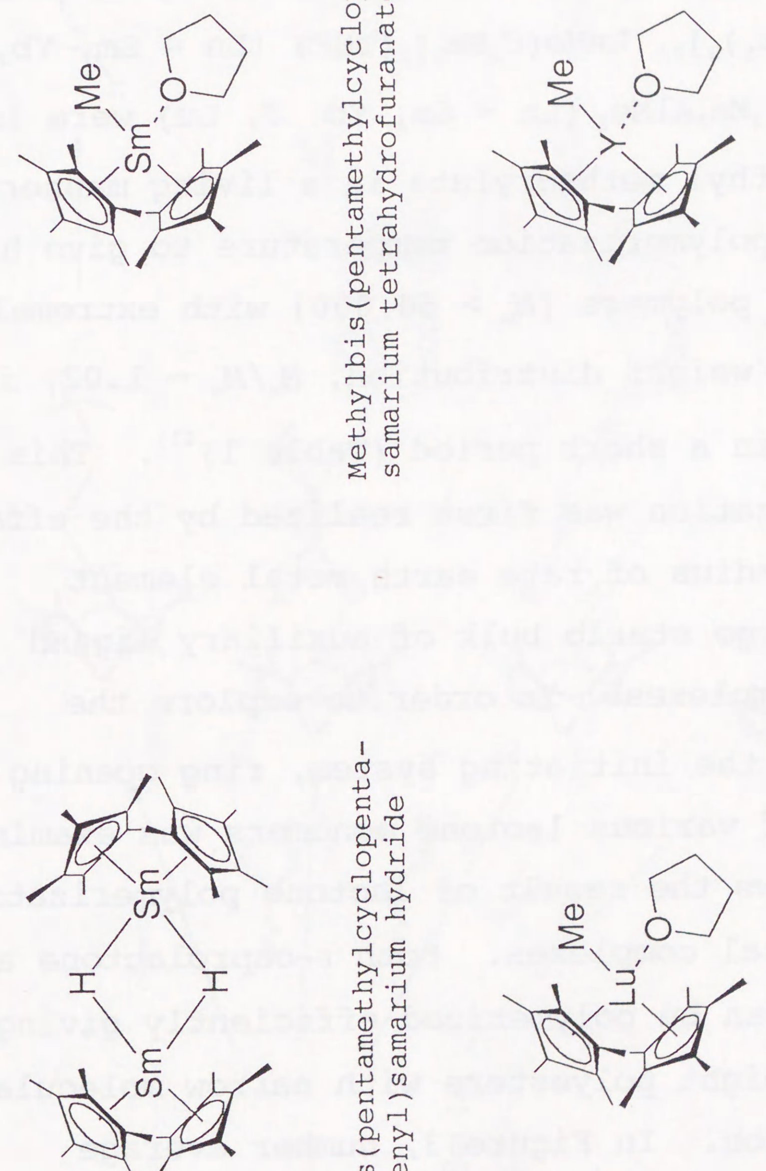
Living Polymerization of Lactones Catalyzed by Rare Earth Metal Alkyl complexes

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 by the use of initiators such as alkalimetal,5) alkaline earth metal,5) AlR_3-H_2O,6) aluminum-porphyrin,7) dialkyl-zinc-H_2O8) and CpTi(OR)$Cl_2$9) systems. Recently, it has been reported that lanthanide alkoxide(III)10) and organolanthanide(II) complexes11) can be used as extremely active catalysts for the living polymerization of these monomers.

A series of organo rare earth metal (III) complexes shows excellent catalytic activity for living polymerization of methyl methacrylate which leads to highly syndiotactic polymers with very narrow polydispersity and high molecular weight. In this study I have examined the catalytic action of organo rare earth metal complexes in polymerization of lactones, in order to realize the living polymerization and to obtain high molecular weight polymers with extremely narrow polydispersity. Stoichiometric reactions were also investigated to learn the initiation and propagation mechanism for the lanthanide assisted polymerization.

I describe herein the efficient catalytic activity of organo rare earth metal (III) complexes towards the ring opening polymerization of lactones, which provides high molecular weight polyesters with extremely narrow molecular weight distribution[12]. This chapter also deals with the initiation mechanism for polymerization of caprolactone and valerolactone by $[SmH(C_5Me_5)_2]_2$, $SmMe(C_5Me_5)_2(THF)$, $LuMe(C_5Me_5)_2(THF)$ and $YMe(C_5Me_5)_2(THF)$ (Figure 1).



Methylbis(pentamethylcyclopentadienyl) samarium tetrahydrofuranate

Methylbis(pentamethylcyclopentadienyl) yttrium tetrahydrofuranate

Bis(pentamethylcyclopentadienyl)samarium hydride

Methylbis(pentamethylcyclopentadienyl) lutetium tetrahydrofuranate

Fig. 1 Organo rare earth metal initiators

Results and Discussion

Rare Earth Metals Initiated Polymerization of Lactones. Organo rare earth metal (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 polymerize methyl methacrylate in a living manner at a wide range of polymerization temperature to give high molecular weight polymers ($M_n > 50{,}000$) with extremely narrow molecular weight distribution, $M_w/M_n = 1.02$, in high conversion in a short period (Table 1)$^{13)}$. This type of polymerization was first realized by the effect of large ionic radius of rare earth metal element together with large steric bulk of auxiliary ligand (C_5Me_5) in the complexes. In order to explore the applicability of the initiating system, ring opening polymerization of various lactone monomers was examined.

Table 2 shows the result of lactone polymerization by rare earth metal complexes. Both ε-caprolactone and δ-valerolactone can be polymerized efficiently giving high molecular weight polyesters with narrow molecular weight distribution. In Figure 3, number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers are plotted against conversion. M_n increases linearly with the conversion while M_w/M_n value remains below 1.10. These results indicate that

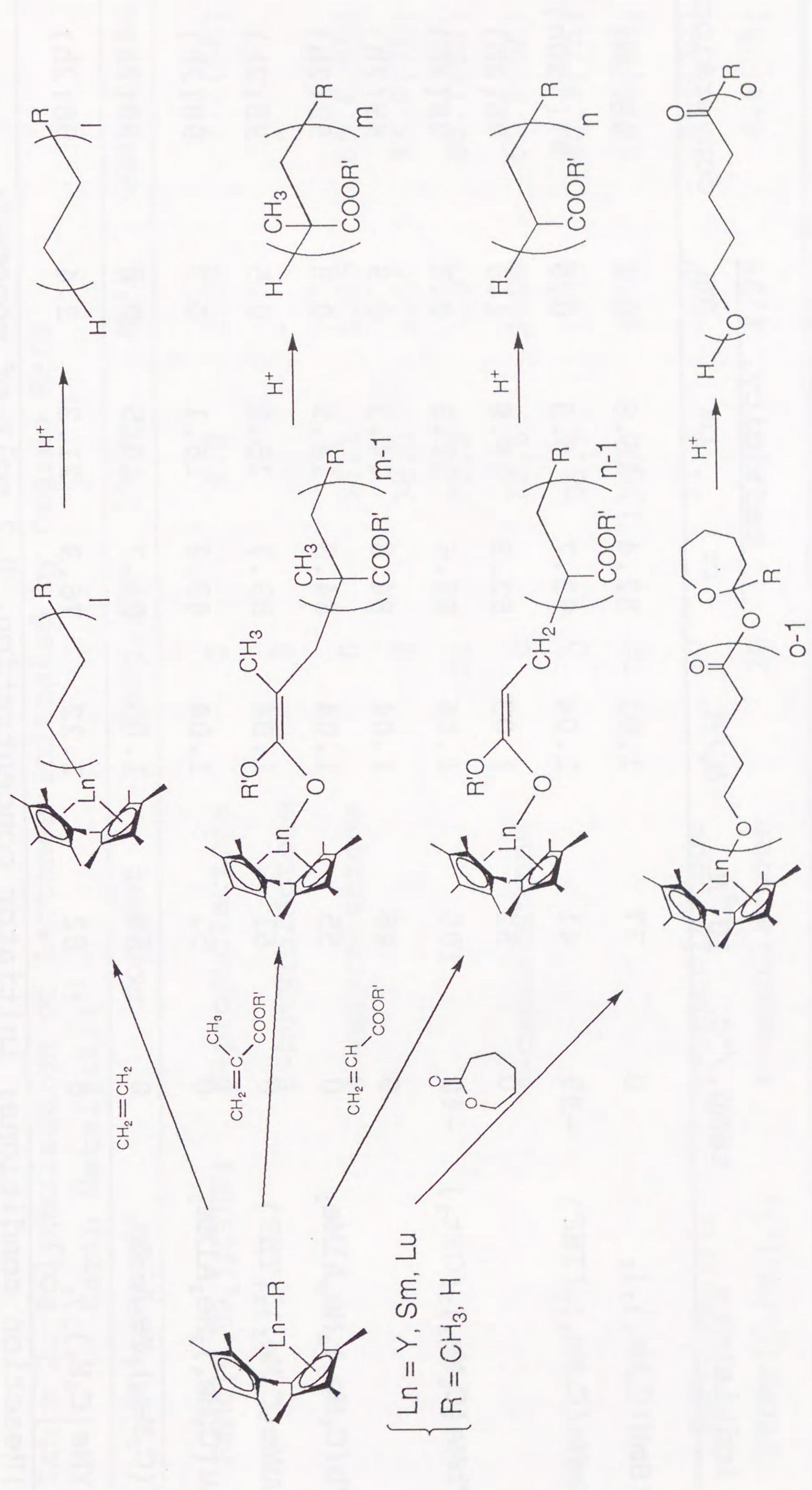


Fig. 2 Living Polymerization Catalyzed by Organolanthnide Complexes

Table 1. Characterization of Poly(methyl methacrylate) Initiated by Organo Rare Earth Metal(III)[a)]

initiators	temp./°C	$10^{-3}M_n$	M_w/M_n	tacticity, %			conversion, %
				rr	rm	mm	
$[SmH(C_5Me_5)_2]_2$	0	77	1.03	82.4	16.8	0.8	98(1h)
$SmMe(C_5Me_5)_2(THF)$	-95	41	1.04	93.7	6.3	0.0	97(150h)
	0	52	1.03	82.8	16.8	1.0	96(2h)
$YbMe(C_5Me_5)_2(OEt_2)$	-40	105	1.06	88.6	11.2	0.2	98(8h)
	0	48	1.04	84.8	14.3	0.9	99(2h)
$Yb(C_5Me_5)_2Me_2AlMe_2$	0	55	1.04	84.3	14.9	0.8	93(2h)
$LuMe(C_5Me_5)_2(THF)$	0	61	1.04	83.7	15.8	0.5	98(2h)
$Lu(C_5Me_5)_2Me_2AlMe_2$	0	51	1.04	83.2	16.1	0.7	98(2h)
$Y(C_5Me_5)_2Me_2AlMe_2$	0	53	1.03	84.7	14.5	0.8	99(2h)
$[YMe(C_5H_5)_2]_2$	0	82	1.22	76.3	21.3	2.4	98(2h)

a)Reaction conditions: initiator concentration, 0.2 mol% of monomer; solvent, toluene.

Table 2. Polymerization of Lactones Initiated by Organo Rare Earth Metal(III)[a)]

initiator	monomer	temp./°C	$10^{-3}M_n$	M_w/M_n	conversion, %
$SmMe(C_5Me_5)_2(THF)$	β-propiolactone	0	4.0	1.04	7.2(5h)
	β-butyrolactone	0	-	-	-
	δ-valerolactone	0	56.1	1.16	65.8(5h)
		0	78.0	1.15	93.0(7h)
		20	75.2	1.07	80.1(5h)
	ε-caprolactone	0	72.8	1.09	61.5(5h)
		0	86.9	1.09	80.3(7h)
		20	130.1	1.06	94.8(5h)
$[SmH(C_5Me_5)_2]_2$	ε-caprolactone	20	71.1	1.19	28.7(5h)
$[YbMe(C_5Me_5)_2]_2$	ε-caprolactone	20	18.3	1.29	4.6(5h)

a)Reaction conditions: initiator concentration, 0.2 mol% of monomer; solvent, toluene.

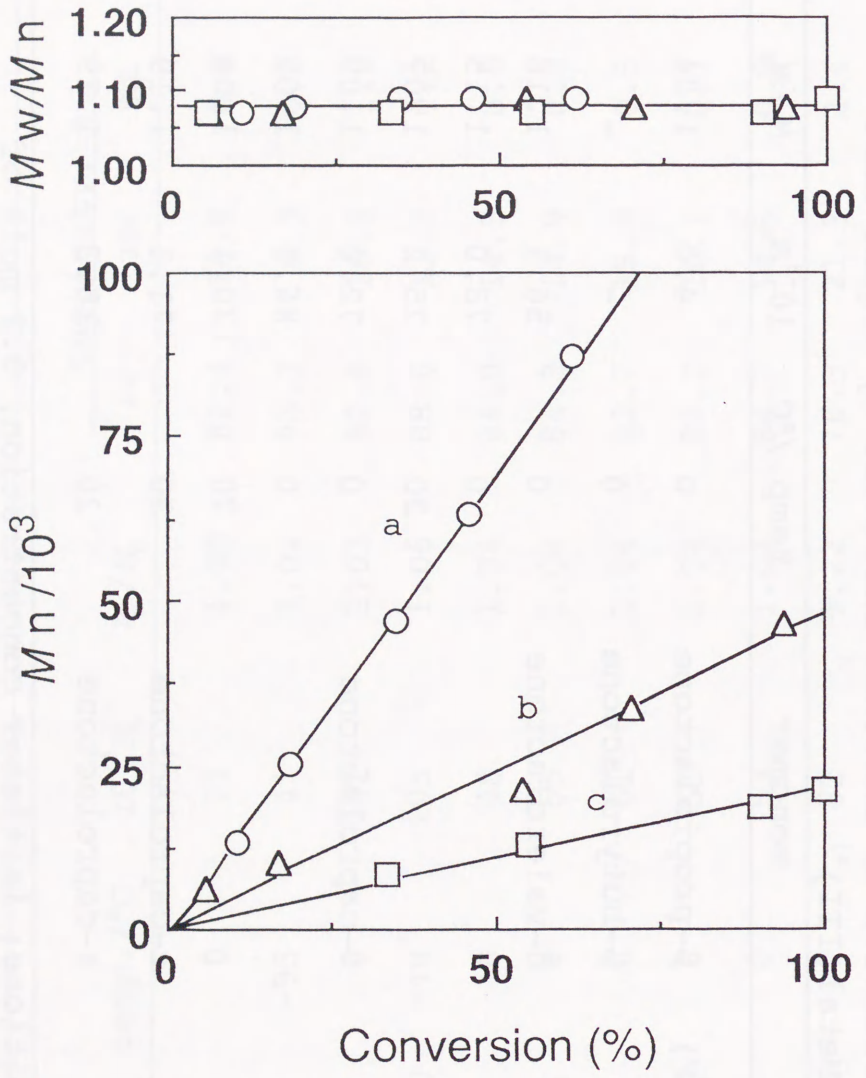


Fig. 3 Conversion vs M_n and M_w/M_n plot (a)SmMe(C_5Me_5)$_2$(THF) 0.2 mol% (b)0.5 mol% (c)1.0 mol%

the polymerization proceeded in a living manner. Figure 4 shows the relationship between M_n and catalyst concentration. It is clearly seen that M_n of the polymer can be controlled by changing the feed ratio of monomer to initiator.

The molecular weight distribution varies with the change of polymerization temperatures, i.e. the molecular weight distribution becomes wider, M_w/M_n = 1.70, when polymerization was conducted at 50 °C while it becomes narrower (M_w/M_n = 1.08) when the polymerization was carried out at 0 °C (Table 3, Figure 5).

In contrast to the above results of valerolactone and caprolactone, polymerization of β-propiolactone has failed with organo rare earth metal complexes such as SmMe(C_5Me_5)$_2$(THF) or [SmH(C_5Me_5)$_2$]$_2$. No initiation started. On the other hand, high molecular weight poly (β-propiolactone) was obtained by the use of rare earth metal alkoxide complexes such as SmOEt(C_5Me_5)$_2$(Et_2O), [YOMe(C_5H_5)$_2$]$_2$ and YOMe(C_5Me_5)$_2$(THF). Rare earth metal alkoxide initiated polymerization will be described in chapter 3.

Random Copolymerization of Lactones with Polar Monomers. The random copolymerization of caprolactone with valerolactone was performed with SmMe(C_5Me_5)$_2$(THF) in order to find the respective monomer

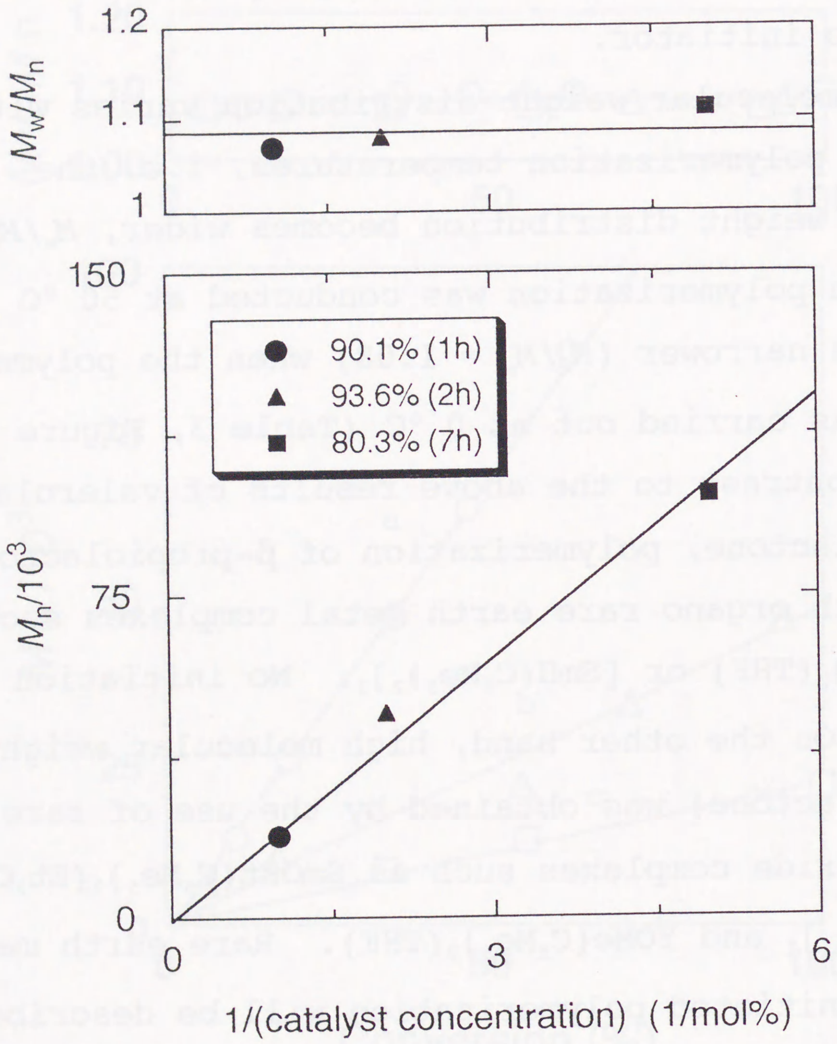


Fig. 4 Catalyst concentration vs. M_n and M_w/M_n plots.

Table 3. Effect of Polymerization Temperature[a)]

temp./°C	$10^{-3}M_n$	M_w/M_n	conversion,%
-78	-	-	trace
0	86.9	1.09	80.3
20	109.4	1.10	92.0
50	205.1	1.70	92.8

a)Reaction conditions: initiator $SmMe(C_5Me_5)_2(THF)$, initiator concentration, 0.2 mol% of monomer; solvent, toluene; polymn. time, 7h.

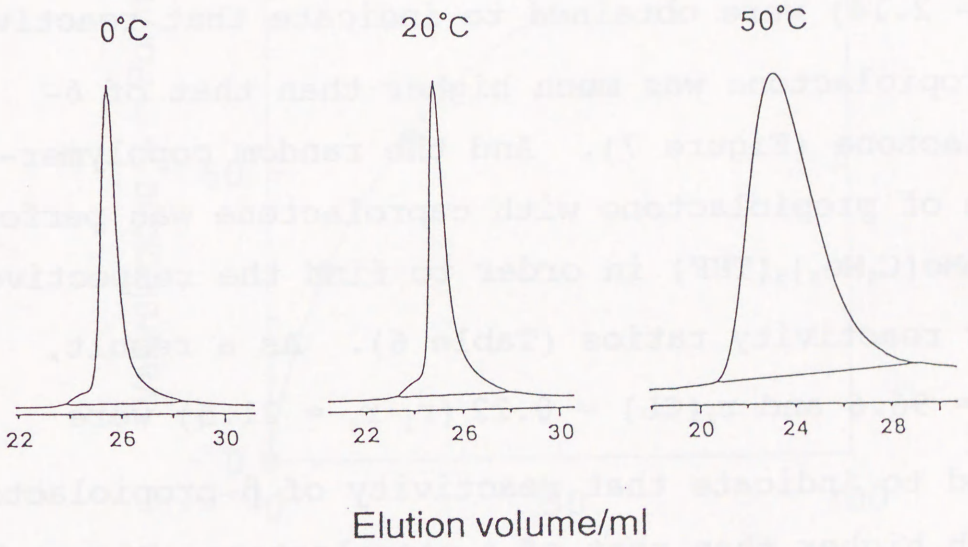


Fig. 5 GPC profile of poly(caprolactone)

reactivity ratios (Table 4). As a result, r_1(VL) = 2.82 and r_2(CL) = 0.20 ($r_1 \cdot r_2$ = 0.56) were obtained to indicate that reactivity of δ-valerolactone was much higher than that of ε-caprolactone (Figure 6).

Although homopolymerization of β-propiolactone has failed with organo rare earth metal complexes such as $SmMe(C_5Me_5)_2(THF)$ or $[SmH(C_5Me_5)_2]_2$, random copolymerization with caprolactone or valerolactone occurred easily.

The random copolymerization of propiolactone with valerolactone was performed with $SmMe(C_5Me_5)_2(THF)$ in order to find the respective monomer reactivity ratios (Table 5). As a result, r_1(PL) = 6.73 and r_2(VL) = 0.32 ($r_1 \cdot r_2$ = 2.14) were obtained to indicate that reactivity of β-propiolactone was much higher than that of δ-valerolactone (Figure 7). And the random copolymerization of propiolactone with caprolactone was performed with $SmMe(C_5Me_5)_2(THF)$ in order to find the respective monomer reactivity ratios (Table 6). As a result, r_1(PL) = 96.6 and r_2(CL) = 0.22 ($r_1 \cdot r_2$ = 21.5) were obtained to indicate that reactivity of β-propiolactone was much higher than that of ε-caprolactone (Figure 8).

These results indicate that smaller ring lactone which is highly strained readily polymerize.

Table 4. Random Copolymerization of Valerolactone (VL) with Caprolactone(CL)[a)]

VL/CL (in monomer)	VL/CL (in polymer)	$10^{-3}M_n$	M_w/M_n
10/90	33/67	27.0	1.07
25/75	56/44	44.9	1.04
50/50	83/17	59.4	1.08
75/25	87/13	34.9	1.09

a)Reaction conditions: initiator $SmMe(C_5Me_5)_2(THF)$, initiator concentration, 0.1 mol% of monomer; solvent, toluene.

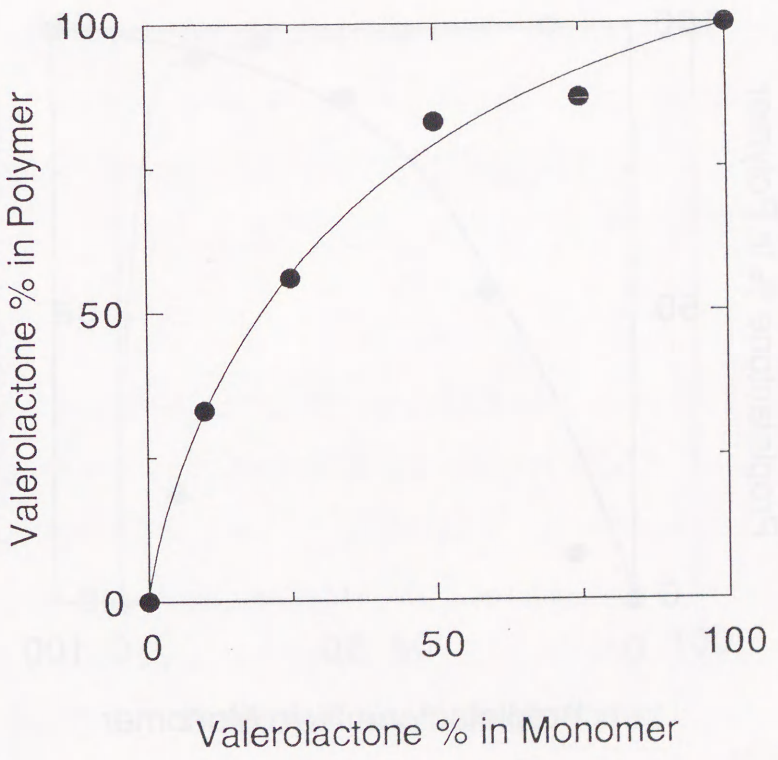


Fig. 6 Copolymer composition curve for ran-copoly(valerolactone/caprolactone)

Table 5. Random Copolymerization of Propiolactone (PL) with Valerolactone(VL)$^{a)}$

PL/VL (in monomer)	PL/VL (in polymer)	$10^{-3}M_n$	M_w/M_n
10/90	8/92	20.3	1.08
25/75	54/46	10.6	1.54
50/50	88/12	6.73	1.16
75/25	95/5	6.02	1.38

a)Reaction conditions: initiator $SmMe(C_5Me_5)_2(THF)$, initiator concentration, 0.05 mol% of monomer; solvent, toluene.

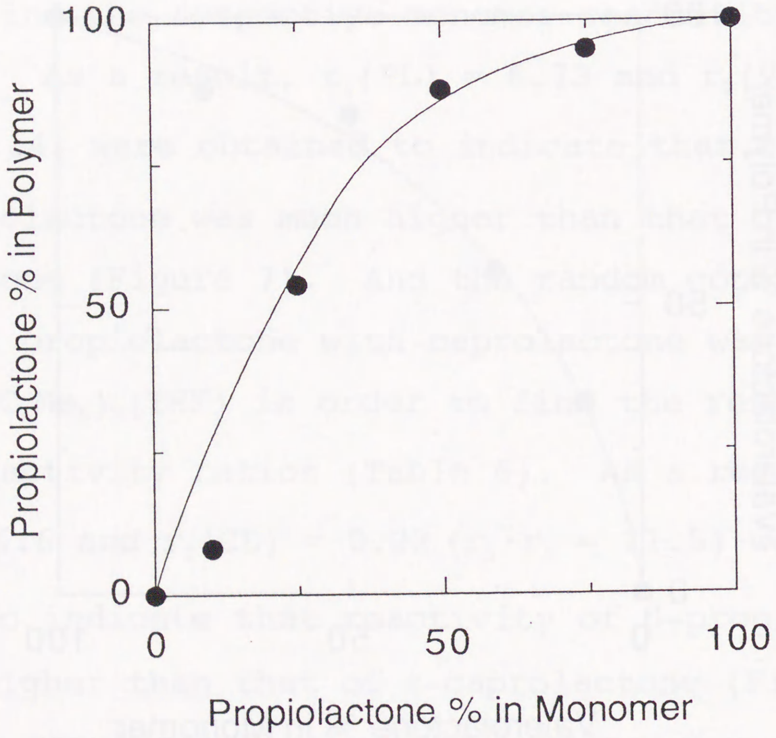


Fig. 7 Copolymer composition curve for ran-copoly(propiolactone/valerolactone)

Table 6. Random Copolymerization of Propiolactone (PL) with Caprolactone(CL)$^{a)}$

PL/CL (in monomer)	PL/CL (in polymer)	$10^{-3}M_n$	M_w/M_n
10/90	19/81	22.2	1.12
25/75	98/2	3.32	1.17
50/50	99/1	4.52	1.13
75/25	100/0	5.26	1.12

a)Reaction conditions: initiator $SmMe(C_5Me_5)_2(THF)$, initiator concentration, 0.05 mol% of monomer; solvent, toluene.

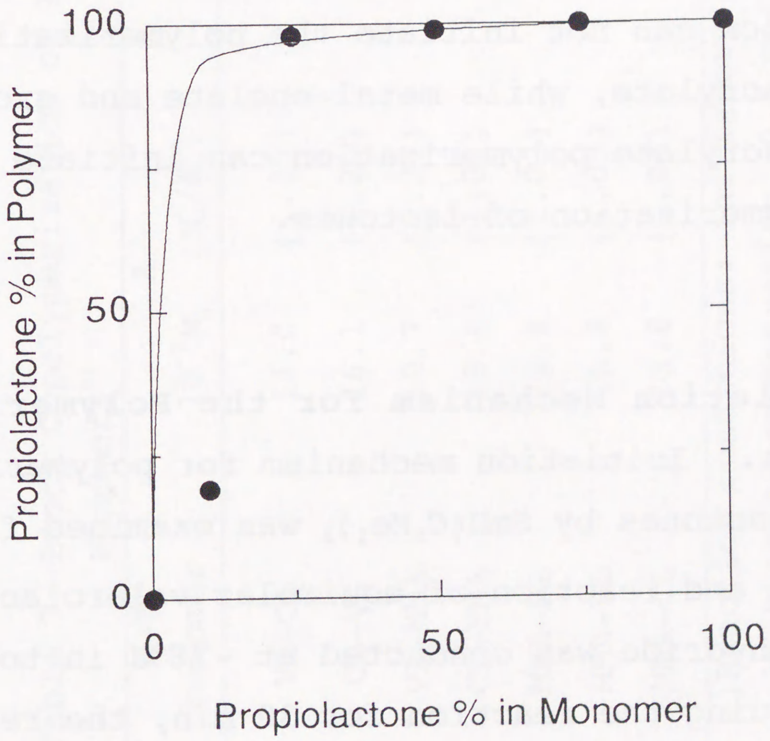


Fig. 8 Copolymer composition curve for ran-copoly(propiolactone/caprolactone)

Block Copolymerization of Lactones with Polar Monomers. Block copolymerization between caprolactone and valerolactone proceeded smoothly giving AB type block copolymers (Table 7).

Next, block copolymerization of lactones with methyl methacrylate was examined. Addition of lactone monomer after polymerization of methyl methacrylate resulted in the formation of poly(methyl methacrylate)-poly(lactone) AB type block copolymer. On the other hand, monomer addition in the reverse order afforded only poly(lactone) homopolymer. These results clearly indicate that the metal-alkoxide end group of lactone polymerization can not initiate the polymerization of methyl methacrylate, while metal-enolate end group of methyl methacrylate polymerization can initiate the ring opening polymerization of lactones.

Initiation Mechanism for the Polymerization of Lactones. Initiation mechanism for polymerization of various lactones by $SmH(C_5Me_5)_2$ was examined first. The addition and reaction of equimolar valerolactone to the samariumhydride was conducted at -78°C in toluene. After continuing the reaction for 30 min, the reaction mixture was hydrolyzed with water to give 1,5-pentanediol in ca. 50 % yield, and 1,6-hexanediol in the case of caprolactone in place of 5-hydroxyhexanol and 6-hydroxyheptanol, respectively (Figure 9). This result

Table 7. Block Copolymerization of Lactones with Other Polar Monomers[a)]

A-B	A		A-B		A/B
monomer	$10^{-3}M_n$	(M_w/M_n)	$10^{-3}M_n$	(M_w/M_n)	ratio
VL-CL	11.0	(1.39)	22.1	(1.54)	5.3:4.7
CL-VL	16.1	(1.20)	19.5	(1.28)	8.1:1.9
VL-MMA	10.7	(1.37)	10.7	(1.28)	-
CL-MMA	19.8	(1.09)	19.8	(1.07)	-
MMA-PL	14.8	(1.03)	23.1	(1.32)	5.6:4.4
MMA-VL	16.8	(1.05)	30.0	(1.11)	5.6:4.4
MMA-CL	15.8	(1.05)	36.1	(1.34)	4.7:5.3

a)Reaction conditions: initiator, $SmMe(C_5Me_5)_2(THF)$; initiator concentration, 0.5 mol% of monomer; [premonomer]/[comonomer] = 1/1, solvent, toluene.

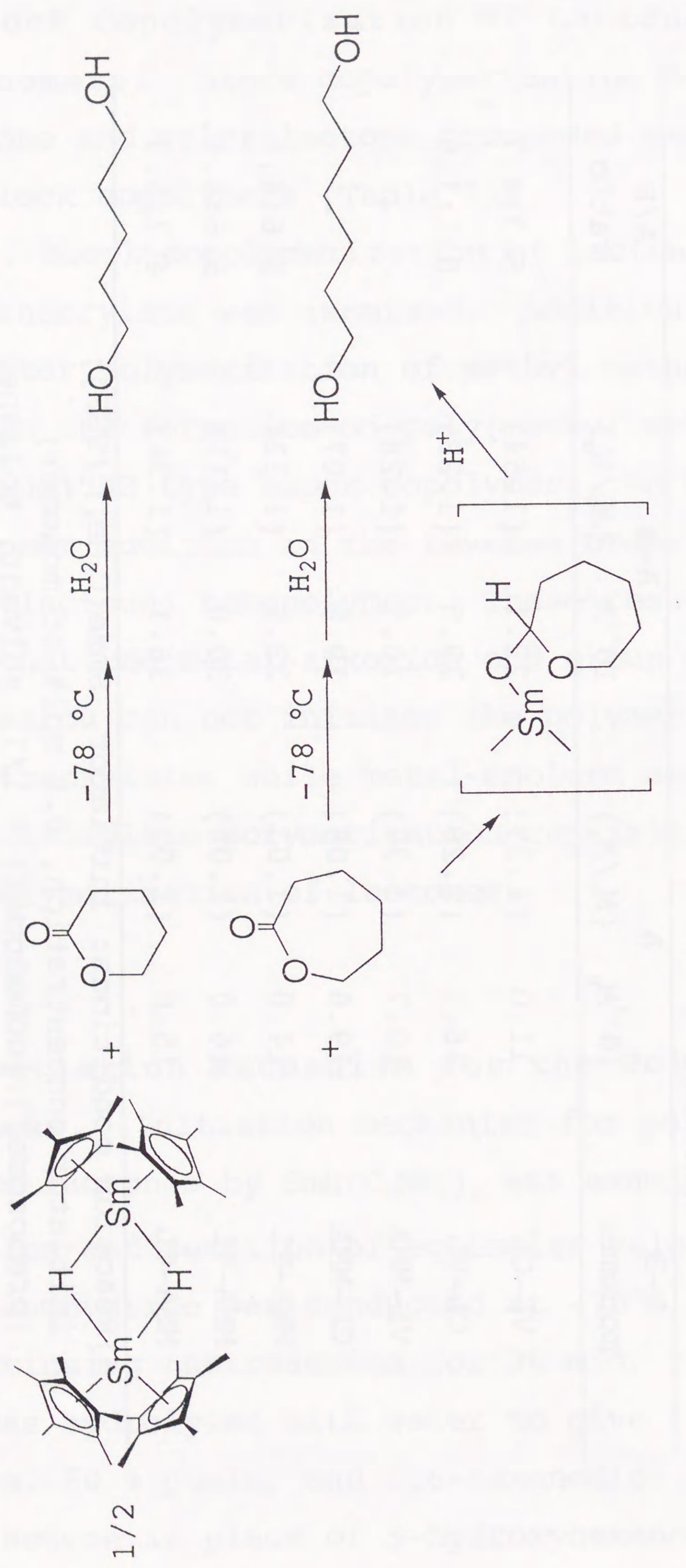


Fig. 9 Reaction of $[SmH(C_5Me_5)_2]_2$ with valerolactone

strongly indicates occurrence of reduction at the carbonyl group. By contrast to the reaction of $SmH(C_5Me_5)_2$, reaction of $SmMe(C_5Me_5)_2(THF)$ with valerolactone or caprolactone gave 5-hydroxy-2-hexanone or 7-hydroxy-2-heptanone upon hydrolysis of the product. Therefore, alkyl addition to carbonyl group occurs preferentially, in this case. (Figure 10)

To understand the mode of alkyl addition, the 1:1 reaction of valerolactone and a diamagnetic complex, $LuMe(C_5Me_5)_2(THF)$, was carried out and monitored by NMR spectroscopy (Figure 11). $SmMe(C_5Me_5)_2(THF)$ can not be used for this purpose because of the paramagnetic nature of this species. As a result, it was observed that lanthanide methyl group added to the carbonyl group of valerolactone forming an acetal linkage (ketonic carbon did not appear at around 140-149 ppm in ^{13}C NMR spectrum). In addition, the reaction of $YMe(C_5Me_5)_2(THF)$ was carried out, and gave the same result as that of $LuMe(C_5Me_5)_2(THF)$ (Figure 12).

The reaction of $LuMe(C_5Me_5)_2(THF)$ with β-propiolactone resulted in the formation of stable compound which did not react with the lactone any more. The compound was isolated and its ^1H and ^{13}C NMR spectra are shown in Figure 13, 14. A_2B_2 pattern and the chemical shifts of two methylene groups (b and c in Figure 13) clearly indicate that the structure is 1:1 adduct of

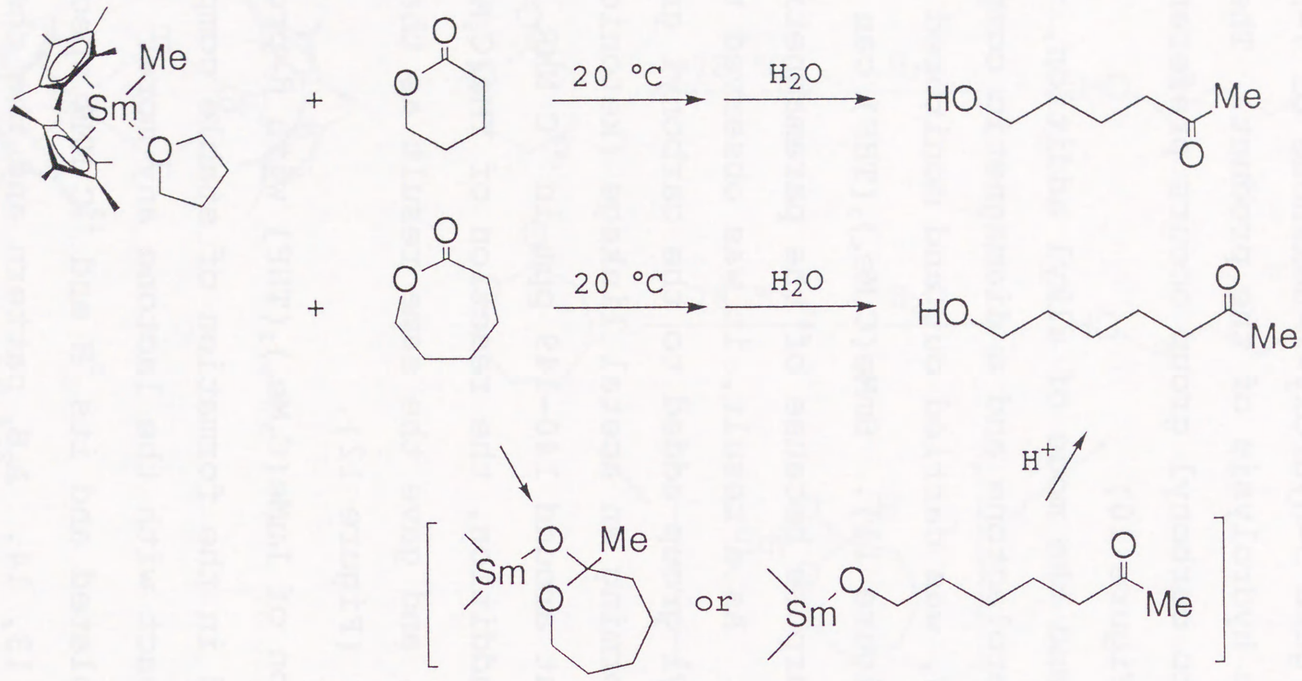


Fig. 10 Reaction of $SmMe(C_5Me_5)_2(THF)$ with valerolactone and caprolactone

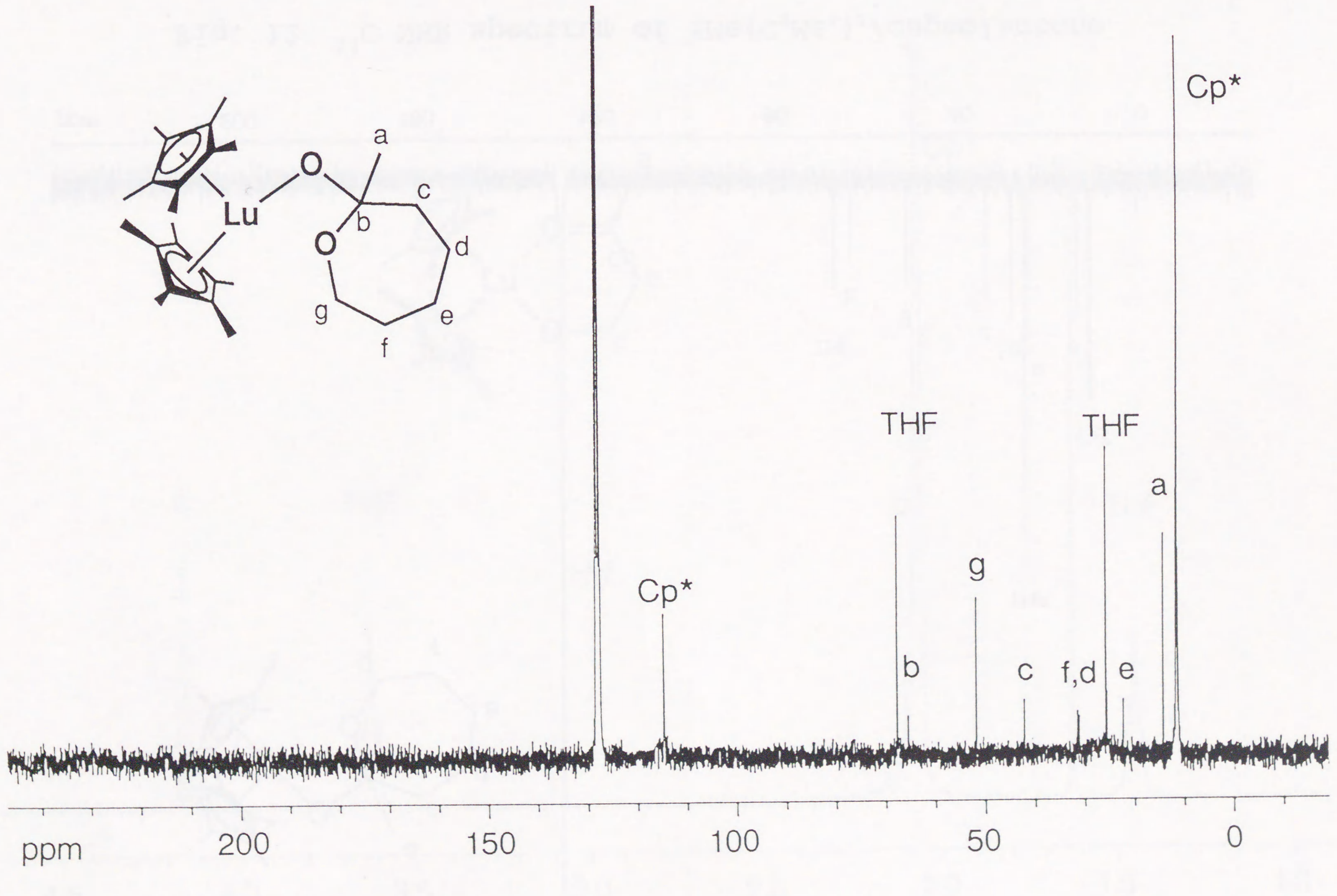


Fig. 11 ^{13}C NMR spectrum of $LuMe(C_5Me_5)_2$/capeolactone

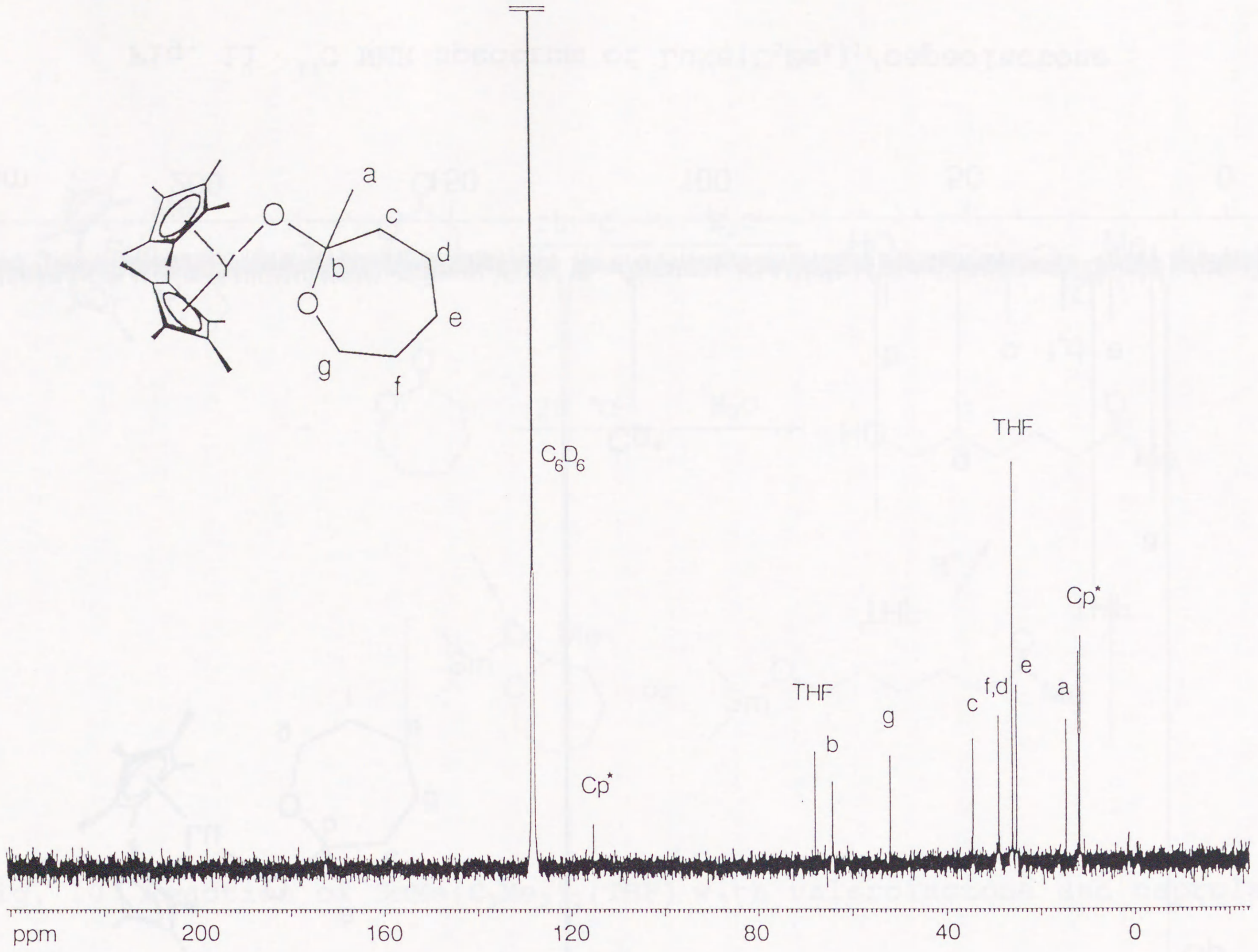


Fig. 12 ^{13}C NMR spectrum of $YMe(C_5Me_5)_2$/capeolactone

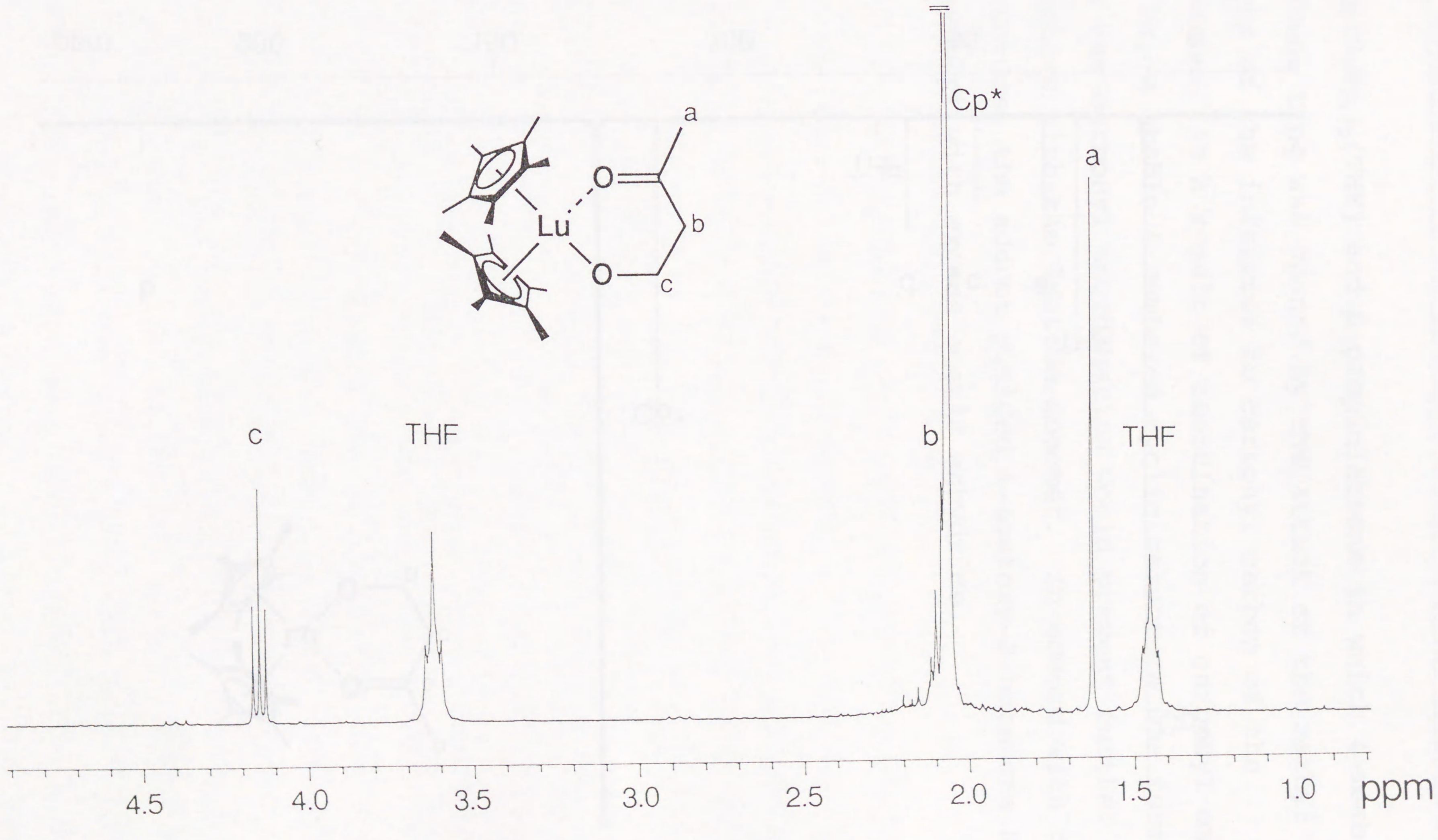


Fig. 13 ^{1}H NMR spectrum of $LuMe(C_5Me_5)_2$/propiolactone

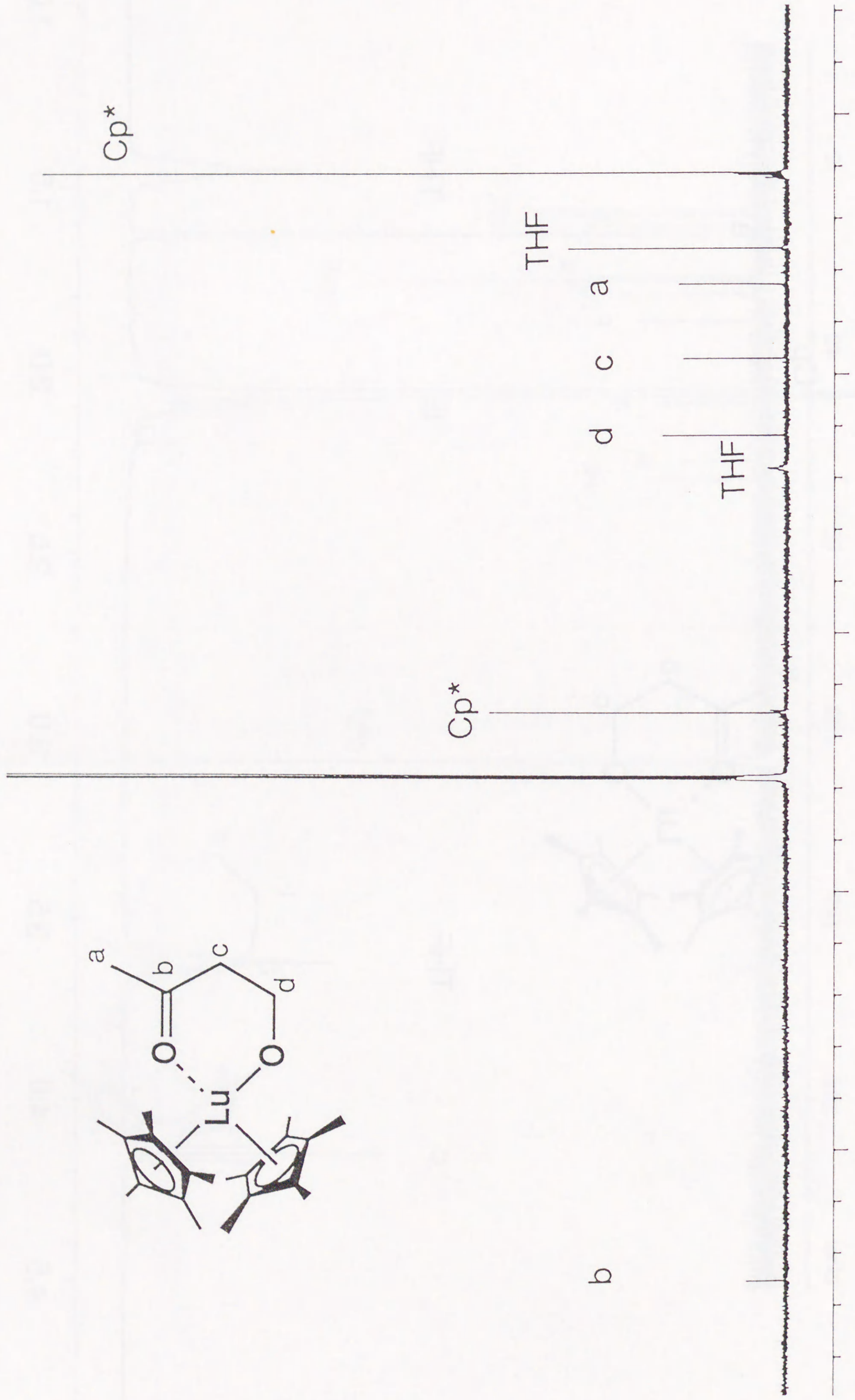


Fig. 14 ^{13}C NMR spectrum of LuMe(C$_5$Me$_5$)$_2$/propiolactone

LuMe(C$_5$Me$_5$)$_2$(THF) and β-propiolactone in which 4-membered lactone ring was opened by the attack of the methyl group of the initiator to carbonyl carbon of the lactone. As a result of coordination of carbonyl oxygen to Lu, a stable 6 membered cyclic structure was formed and the carbonyl coordination would prevent further reaction with the lactone monomer. In accord with the structure, the adduct yielded 4-acetoxy-2-butanone by treatment with excess acetic anhydride.

Experimental Section

General. All operations were conducted with standard Schlenk techniques under an argon atmosphere. NMR spectra were recorded on a JEOL EX-270 (270.0 MHz for ^{1}H and 67.5 MHz for ^{13}C nuclei), and a Brucker AMX400wb (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C nuclei). Chemical shifts of ^{1}H are calibrated using benzene (δ 7.20 ppm) in benzene-d_6 or chloroform (δ 7.26 ppm) in chloroform-d_1. Chemical shift of ^{13}C resonances are determined with reference to the carbon resonances of deuteration solvent (benzene-d_6, δ 128.0; chloroform-d_1, δ 77.0 ppm). Gas chromatographic analysis and separation of the reaction products were made with a Yanaco gas chromatograph G3810 using a column packed with Silicone DC-550 or a Yanaco gas chromatograph G3800 using a column packed with DEGS. Number averaged molecular weight and molecular weight distribution of polymers were determined by gel permeation chromatography (GPC) on a Tosoh SC-8010 high-speed liquid chromatograph equipped with a differential refractometer detector, using chloroform as a eluent at 40.0 °C. The column consisted of four columns: TSKgel G2000Hxl, TSKgel G3000Hxl, TSKgel G4000Hxl and TSKgel G5000Hxl (Tosoh Manufacturing Co., Ltd.) was used. The flow rate was 1.0 ml min^{-1}. The molecular weight

calibration curve was obtained by using standard polystyrenes : 8.70 x 10^2 (M_w/M_n = 1.10), 2.63 x 10^3 (M_w/M_n = 1.05), 5.97 x 10^3 (M_w/M_n = 1.02), 9.10 x 10^3 (M_w/M_n = 1.02), 3.79 x 10^4 (M_w/M_n = 1.01), 4.36 x 10^4 (M_w/M_n = 1.01), 9.64 x 10^4 (M_w/M_n = 1.01), 1.90 x 10^5 (M_w/M_n = 1.04), 3.55 x 10^5 (M_w/M_n = 1.02), 7.06 x 10^5 (M_w/M_n = 1.05), 1.09 x 10^6 (M_w/M_n = 1.08) and 2.89 x 10^6 (M_w/M_n = 1.09) (Tosoh Manufacturing Co., Ltd.).

Material. Tetrahydrofuran, hexane and toluene were dried over Na/K alloy and distilled just before use. In the case of the solvent used in polymerization, they were thoroughly degassed by trap-to-trap distillation just before use. Commercially purchased lactones, β-propiolactone, δ-valerolactone and ε-caprolactone were purified by the following procedure. These monomers were dried over CaH_2 for 24 hours and distilled twice under argon. Since the obtained monomers still contain ca. 30 ppm of water, they were dried over activated molecular sieves 3A under an atmosphere, and finally degassed and purified by trap-to-trap distillation just before use. Pure $Sm(C_5Me_5)_2(THF)_2$[14)], $SmMe(C_5Me_5)_2(THF)$[15)], $[SmH(C_5Me_5)_2]_2$[16)], $Sm(OEt)(C_5Me_5)_2(OEt_2)$ and $LuMe(C_5Me_5)_2(THF)$[18)] were obtained according to the known method.

Preparation of Sm(C$_5$Me$_5$)$_2$(THF)$_2$[14]. Slight excess of pentamethylcyclopentadiene (18 ml, 115 mmol) was added to a stirred dispersion of KH (4.2 g, 104.5 mmol) in 250 ml of THF, and the mixture was refluxed for 4 hours to give a dispersion of (C$_5$Me$_5$)K. A solution of C$_2$H$_4$I$_2$ (13.4 g, 47.5 mmol) in 40 ml of THF was added at once to a stirred dispersion of 1.1 equiv of Sm metal powder (40 mesh, 7.86 g, 52.3 mmol) in 1000 ml of THF. A magnetic stirring was continued for 3 hours at 20-30 °C. The color of the solution gradually changed to blue-green, as SmI$_2$(THF)$_2$ was formed. Then the (C$_5$Me$_5$)K dispersion was added to the stirred solution of SmI$_2$(THF)$_2$. The color of the solution turned purple immediately after the addition of (C$_5$Me$_5$)K and precipitation of KI occurred. After stirring the mixture for 12 hours at ambient temperature, the THF was removed by evaporation and 500 ml of toluene was added to the residue. The resulting solution of Sm(C$_5$Me$_5$)$_2$(THF)$_2$ containing (C$_5$Me$_5$)$_2$SmIK(THF)$_x$ was stirred for 12 hours and then centrifuged to remove the salt. The solvent was evaporated to dryness and the resulting Sm(C$_5$Me$_5$)$_2$ (THF)$_2$ was recrystallized from THF/hexane at -20°C to give purple crystals. Yield : 31% in one crop.

Preparation of SmMe(C$_5$Me$_5$)$_2$(THF)[15]. To a stirred solution of Sm(C$_5$Me$_5$)$_2$(THF)$_2$ (4.50 g, 8.0 mmol) in 100 ml of toluene was slowly added 5 equiv AlMe$_3$ (4.0 ml, 41 mmol). During stirring the mixture for 24 hours blue-black precipitates was generated in a red solution. Then the mixture was extracted with 500 ml of toluene to separate the resulting SmMe(C$_5$Me$_5$)$_2$(THF) from AlMe$_3$(THF) and excess AlMe$_3$. Slight concentration of the toluene solution into ca. 400 ml followed by cooling to -20 °C resulted in the formation of red crystals of (C$_5$Me$_5$)$_2$-SmMe$_2$AlMe$_2$. Recrystallization of the separated micro-crystalline substances from THF/hexane afforded SmMe(C$_5$Me$_5$)$_2$(THF) as yellow-orange crystals. Yield : 40.0%. EIMS : m/z (species, relative intensity) 424 ([^{154}Sm(C$_5$Me$_5$)$_2$]+, 80) 422 ([^{152}Sm(C$_5$Me$_5$)$_2$]+,100).

Preparation of [SmH(C$_5$Me$_5$)$_2$]$_2$[16]. Crystalline Sm(C$_5$Me$_5$)$_2$(THF)$_2$ (4.73 g, 8.4 mmol) was mixed with diphenylacetylene (1.49 g, 8.4 mmol) in the solid state and 100 ml of hexane was added. Immediately after mixing the solution turned black. Removal of the solvent after stirring overnight yielded a black material. The material was extracted with 100 ml degassed hexane. Then the resulted black hexane solution was allowed to react with H$_2$ at ambient temperature and at atmospheric pressure. The solution turned orange and orange precipitate was formed by holding it for 4 hours. The resulting solid of $[SmH(C_5Me_5)_2]_2$ was separated by centrifugation. Yield : 21.2%. EIMS : m/z (species, relative intensity) 426 ($[^{154}SmH(C_5Me_5)_2]$++1, 21) 425 ($[^{154}SmH(C_5Me_5)_2]$+,88), 424 ($[^{152}SmH(C_5Me_5)_2]$++1,24), 423 ($[^{152}SmH(C_5Me_5)_2]$+, 100).

Preparation of $(C_5Me_5)Na$. In a 300 ml round-bottom flask equipped with a condenser NaH (about. 60%, in oil, 3.0 g, 75 mmol) and 120 ml of THF were placed. Then C_5Me_5H (6.5 ml, 41.5 mmol) was added at once and the mixture was refluxed for 24 hours. Resulting pale-brown solution was centrifuged to separate excess NaH, and evaporated to dryness. The residue was washed with 40 ml of hexane and C_5Me_5Na was obtained as pale-brown powder. Yield : 91%.

Preparation of $LuCl_3$. To a mixture of Lu_2O_3 (99.9%, 10.1 g, 25.3 mmol) and NH_4Cl (6.8 g, 127 mmol) in 500 ml round-bottom flask was added ca. 300 ml of conc. HCl with stirring. The mixture was heated on a water bath until the solution becomes clear. Then the excess HCl was removed using aspirator and white solids

of mixture of hydrated $LuCl_3$ and excess NH_4Cl were obtained. In order to remove excess NH_4Cl and hydrated water, the white solids were placed in a sublimation tube and heated at 350-400 °C under reduced pressure, until sublimation of NH_4Cl is unobserved. Residual gray solids is used as anhydrous $LuCl_3$. Yield : 80%.

Preparation of $LuCl(C_5Me_5)_2(THF)$[17]**.** A solution of C_5Me_5Na (3.8 g, 24.0 mmol) in 62 ml of THF was added to a stirred suspension of anhydrous $LuCl_3$ (3.38 g, 12.0 mmol) in 100 ml of THF at room temperature and the solution was refluxed for 24 hours. Resulting brown solution was centrifuged in order to separate NaCl and THF was removed by evaporation. Toluene (150 ml) was added to the residue and the mixture was stirred for 24 hours at 25°C. After separating the salt by centrifugation, the solvent was evaporated and the crude $LuCl(C_5Me_5)_2(THF)$ was recrystallized from THF/hexane to give pale brown prisms. Yield : 25%. ^1H NMR (C_6D_6) δ 1.25 (THF,4H), 2.07 (s,30H), 3.54 (THF,4H). ^{13}C NMR (C_6D_6) δ 11.8 (C_5Me_5), 25.5 (THF), 72.3 (THF), 117.4 (C_5Me_5). EIMS : m/z (species, relative intensity) 479 ($[^{175}Lu^{35}Cl(C_5Me_5)_2$]+1, 94) 480 ($[^{175}Lu^{35}Cl(C_5Me_5)_2]$, 100) 481 ($[^{175}Lu^{37}Cl(C_5Me_5)_2]$+1, 47) 482 ($[^{175}Lu^{37}Cl(C_5Me_5)_2]$, 33).

Preparation of LuMe(C_5Me_5)$_2$(THF)[18]. To a stirred solution of LuCl(C_5Me_5)$_2$(THF) (1.57 g, 2.84 mmol) in 40 ml of THF was slowly added 2 equiv MeLi (5.7 mmol) in 7.4 ml hexane at 0 °C and then the mixture was allowed to warm to room temperature. After stirring for 6 hours the THF was evaporated to dryness and kept at 75 °C in vacuo for 12 hours in order to remove coordinated THF. Toluene (45 ml) was added to the pale yellow residue and 2 equiv of $AlMe_3$ (0.52 ml, 5.7 mmol) was added to the stirred suspension at room temperature. After the stirring was continued for 4 hours the suspension was heated at 60 °C for 1 hour to complete the reaction and then a small amount of precipitate was removed by centrifugation. Concentration of the solution followed by cooling to -20 °C resulted in the formation a pale yellow prisms of (C_5Me_5)$_2$LuMe$_2$AlMe$_2$. The crystals were separated from the solution and dissolved in a small amount of THF in order to react the coordinated $AlMe_3$ with THF. After the addition of 3-5 fold hexane, the solution was concentrated and cooled to -20 °C to result in the formation of a pale yellow prisms of LuMe(C_5Me_5)$_2$(THF). Yield : 35%. ^{1}H NMR (C_6D_6) δ -0.6 (s,3H), 1.16 (THF,4H), 2.04 (s,30H), 3.29 (THF,4H). ^{13}C NMR (C_6D_6) δ 11.7 (C_5Me_5), 24.6 (THF), 25.0 (Me), 70.5 (THF), 115.3 (C_5Me_5).

Preparation of YCl_3. To a mixture of Y_2O_3 (8.0 g, 35.4 mmol) and NH_4Cl (12 g, 224 mmol) in 500 ml round-bottom flask was added ca. 300 ml of conc. HCl with stirring. The mixture was heated on a water bath until the solution became clear. Then the excess HCl was removed by using aspirator and white solids of mixture of hydrated YCl_3 and excess NH_4Cl were obtained. In order to remove excess NH_4Cl and hydrated water, the white solids were placed in a sublimation tube and heated at 360 °C under reduced pressure, until sublimation of NH_4Cl was unobserved. Residual gray solids is used as anhydrous YCl_3. Yield : 4.77g, 34.4%.

Preparation of YCl(C_5Me_5)$_2$(THF). A solution of C_5Me_5Na (16.3 mmol) in 19.1 ml of THF was added to a stirred suspension of anhydrous YCl_3 (1.68 g, 8.60 mmol) in 60 ml of THF at room temperature and the solution was refluxed for 4 hours. Resulting pale-brown solution was concentrated to dryness. Toluene (160 ml) was added to the residue and the mixture was stirred for overnight. After separating the salt by centrifugation, solvent was evaporated and the residue was washed by 40 ml of hexane. The crude YCl(C_5Me_5)$_2$(THF) was recrystallized from THF/hexane to give pale brown prisms. Yield : 23% in one crop. ^{1}H NMR (C_6D_6) δ 1.24 (m,4H,THF), 2.06 (s, 30H,C_5Me_5), 3.55 (m,4H,THF).

Preparation of $YMe(C_5Me_5)_2(THF)$. To a stirred solution of $YCl(C_5Me_5)_2(THF)$ (1.32 g, 2.82 mmol) in 30 ml of THF was slowly added 2 equiv MeLi (5.66 mmol) in Et_2O (7.25 ml) at 0 °C and then the mixture was allowed to warm to room temperature. After stirring for 6 hours the THF was evaporated to dryness and the mixture was kept at 75 °C in vacuo for 12 hours in order to remove coordinated THF. Toluene (30 ml) was added to the pale yellow residue and 2 equiv of $AlMe_3$ (0.55 ml, 5.66 mmol) in toluene (5.5 ml) was added to the stirred suspension at room temperature. After the stirring was continued for 4 hours the suspension was heated at 60 °C for 1 hour to complete the reaction and then a small amount of precipitate was removed by centrifugation. Concentration of the solution followed by cooling to -20 °C resulted in the formation a pale yellow prisms of $(C_5Me_5)_2YMe_2AlMe_2$. The crystals were separated from the solution and dissolved in a small amount of THF in order to react the coordinated $AlMe_3$ with THF. After the addition of 3-5 fold hexane, the solution was concentrated and cooled to -20 °C to result in the formation of a pale yellow prisms of $YMe(C_5Me_5)_2(THF)$. Yield : 25% in one crop. ^1H NMR (C_6D_6) δ -0.60 (d,3H,

Me), 1.14 (m,4H,THF), 2.05 (s,30H,C_5Me_5), 3.29 (m,4H, THF).

Polymerization of δ-Valerolactone Catalyzed by $SmMe(C_5Me_5)_2(THF)$. To a stirred solution of valerolactone (0.92 ml, 10 mmol) in 20 ml of toluene was added a toluene solution of 1/500 equivalent $SmMe(C_5Me_5)_2(THF)$ (0.010 g, 0.02 mmol) at 0 °C. After stirring for 3 hours the mixture was quenched by excess methanol.

Polymerization of ε-Caprolactone Catalyzed by $SmMe(C_5Me_5)_2(THF)$. To a stirred solution of caprolactone (1.11 ml, 10 mmol) in 40 ml of toluene was added a toluene solution of 1/500 equivalent $SmMe(C_5Me_5)_2(THF)$ (0.010 g, 0.02 mmol) at 0 °C. After stirring for 3 hours the mixture was quenched by excess methanol.

Random copolymerization of β-propiolactone with ε-caprolactone catalyzed by $SmMe(C_5Me_5)_2(THF)$. A toluene solution (1.0 ml) of $SmMe(C_5Me_5)_2(THF)$ (0.05 mmol) was added to a mixture of propiolactone and caprolactone (1:9, 25:75, 1:1, 25:75 molar ratio;

amounts of monomer: 20 mmol) dissolved in toluene (30 ml) with vigorous stirring at 0 °C. The stirring was continued for 1.5 hours, and the reaction mixture was poured into methanol. The solvent was removed by evaporation. The resulting polymer was dried under reduced pressure.

Random copolymerization of β-propiolactone with δ-valerolactone catalyzed by SmMe(C_5Me_5)$_2$-(THF). A toluene solution (1.0 ml) of SmMe(C_5Me_5)$_2$(THF) (0.05 mmol) was added to a mixture of propiolactone and valerolactone (1:9, 25:75, 1:1, 25:75 molar ratio; amounts of monomer: 20 mmol) dissolved in toluene (20 ml) with vigorous stirring at 0 °C. The stirring was continued for 1 hours, and the reaction mixture was poured into methanol. The resulting polymer was dried under reduced pressure.

Equimolar Reaction of [SmH(C_5Me_5)$_2$]$_2$ With δ-Valerolactone. Valerolactone (0.12 ml, 1.3 mmol) was added to a stirred solution of [SmH(C_5Me_5)$_2$]$_2$ (0.56 g, 0.66 mmol) in 3 ml of toluene at 0 °C and the mixture was warmed to room temperature. During stirring for 10 min the color of the solution changed from red-orange to pale yellow. After the solution was quenched by H_2O the

mixture was concentrated in vacuum. The supernatant liquid was analyzed by gas chromatograph.

Equimolar Reaction of [SmH(C_5Me_5)$_2$]$_2$ With ε-Caprolactone. Caprolactone (0.19 ml, 1.75 mmol) was added to a stirred solution of [SmH(C_5Me_5)$_2$]$_2$ (0.74 g, 0.88 mmol) in 5 ml of toluene at 0 °C and the mixture was warmed to room temperature. During stirring for 10 min the color of the solution changed from red-orange to pale yellow. After the solution was quenched by H_2O the mixture was concentrated under reduced pressure. The supernatant liquid was analyzed by gas chromatograph.

Equimolar Reaction of SmMe(C_5Me_5)$_2$(THF) with δ-Valerolactone. Valerolactone (0.043 ml, 0.46 mmol) was added to a stirred solution of SmMe(C_5Me_5)$_2$(THF) (0.23 g, 0.46 mmol) in 3 ml of toluene at 0 °C and the mixture was allowed to react at room temperature. After stirring for 10 min the color of the solution changed from yellow-orange to pale yellow. A few drops of H_2O was added to the solution (the color of the solution changed pale-yellow) and white precipitate was generated. After concentration of the supernatant liquid, the resulting product was separated by gas chromatograph.

Equimolar Reaction of $SmMe(C_5Me_5)_2(THF)$ with ε-Caprolactone. The reaction was carried out in essentially the same manner as described for the reaction of valerolactone using 0.12 g (0.23 mmol) of $SmMe(C_5Me_5)_2(THF)$ and 0.025 ml (0.23 mmol) of caprolactone.

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 0.2 ml of toluene was added 0.06 ml of valerolactone (0.65 mmol) in 0.1 ml of toluene at -78 °C. Then the mixture was allowed to warm to room temperature. The color of the solution changed from pale-yellow to pale orange. Removal of solvent by evaporation to dryness followed by extraction of the product with degassed C_6D_6 gave the sample for NMR studies. ^{13}C NMR (C_6D_6) δ 11.6 (C_5Me_5), 14.2 (a), 22.1 (e), 22.8 (d), 25.7 (THF), 51.8 (f), 65.9 (b), 70.0 (THF), 115.3 (C_5Me_5).

Equimolar Reaction of $LuMe(C_5Me_5)_2(THF)$ With ε-Caprolactone. To a NMR tube charged with 0.35 g (0.65 mmol) of $LuMe(C_5Me_5)_2(THF)$ in 0.5 ml of degassed C_6D_6, equimolar caprolactone (0.069 ml, 0.65 mmol) was added at 0 °C, and the tube was sealed. The reaction was completed in 5 min. ^{1}H NMR (C_6D_6) δ 1.2 - 1.4 (m, 6H, d, e, f), 1.46 (4H, THF), 1.64 (s, 3H, a), 2.09 (s, 30H, C_5Me_5), 2.14 (t, 2H, c), 3.62 (4H, THF), 4.44 (t, 2H, g). ^{13}C NMR (C_6D_6) δ 11.5 (C_5Me_5), 14.2 (a), 22.2 (e), 25.8 (THF), 31.2 - 31.5 (d, f), 42.2 (c), 51.8 (g), 65.5 (b), 67.8 (THF), 114.8 (C_5Me_5).

Equimolar Reaction of $YMe(C_5Me_5)_2(THF)$ With ε-Caprolactone. To a NMR tube charged with 0.026 g (0.058 mmol) of $YMe(C_5Me_5)_2(THF)$ in 0.5 ml of degassed C_6D_6, equimolar caprolactone (0.0065 ml, 0.058 mmol) was added at 0 °C, and the tube was sealed. The reaction was completed in 5 min. ^{13}C NMR (C_6D_6) δ 11.6 - 12.2 (C_5Me_5), 14.6 (a), 25.1 (e), 26.2 (THF), 29.0 - 29.5 (d, f), 34.3 (c), 52.0 (g), 64.2 (b), 67.9 (THF), 115.5 (C_5Me_5).

Equimolar Reaction of $LuMe(C_5Me_5)_2(THF)$ with β-Propiolactone. Propiolactone (0.003 ml, 0.048 mmol) in 0.1 ml of toluene was added to a stirred solution of $LuMe(C_5Me_5)_2(THF)$ (0.026 g, 0.048 mmol) in 0.2 ml of toluene at -78 °C and the mixture was allowed warm to room temperature. The color of the solution changed from pale yellow-green to pale-orange. Removal of solvent by evaporation to dryness followed by extracting with degassed C_6D_6 gave the NMR sample. A NMR tube was charged with the C_6D_6 solution and sealed. ^1H NMR (C_6D_6) δ 1.45 (4H, THF), 1.63 (s, 3H, a), 2.06 (s, 30H, C_5Me_5), 2.08 (c), 3.64 (4H, THF), 4.15 (t, 2H, d). ^{13}C NMR (C_6D_6) δ 11.6 (C_5Me_5), 26.1 (THF), 33.0 (a), 47.3 (c), 62.2 (d), 68.4 (THF), 115.8 (C_5Me_5), 225.7 (b).

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Chapter 3

Living Polymerization of Lactones Catalyzed by Rare Earth Metal Alkoxide Complexes

Introduction

In chapter 2, living polymerization of several lactone monomers was achieved by the use of organo rare earth metal initiators with metal carbon bond (e.g. $SmMe(C_5Me_5)_2(THF)$, $LuMe(C_5Me_5)_2(THF)$). High molecular weight polyesters with narrow molecular weight distribution were easily obtained by the initiating system. Stoichiometric reaction of the initiator and lactone monomer revealed that the initiation of the polymerization was nucleophilic addition of the alkyl group of the initiator to carbonyl carbon of the monomer, resulting in the formation of rare earth metal alkoxide complex after ring opening of the lactone. This result indicated that the propagating species of this polymerization had metal oxygen bond into which another lactone monomer would insert. Thus, it was suggested that rare earth metal alkoxide complexes could be used as initiators for lactone polymerization[1,2].

In this chapter, I attempted to apply rare earth metal alkoxide complexes to the initiation of lactone

polymerization. Stoichiometric reactions were also performed to understand the polymerization mechanism.

Results and Discussion

Rare Earth Metal Alkoxide Initiated Polymerization of Lactones. In the previous chapter, it has been reported that a series of organo rare earth metal complexes, $(C_5R_5)_2LnR'$ exhibits excellent catalytic activity for living polymerization of lactones. The resulting polymers have very narrow polydispersity and very high molecular weight. I proposed also the initiation and propagation mechanism for the present polymerization of lactones. Active species is metal alkoxide which is generated by addition of alkyl group of the initiator to carbonyl carbon of the monomer followed by ring opening of the lactone. As an extension of this study, I have investigated the living polymerization of lactones using pure rare earth metal alkoxide complexes as initiators.

Table 1 shows the result of lactone polymerizations with some organo rare earth metal complexes. Both ε-caprolactone (CL) and δ-valerolactone (VL) gave the desired high molecular weight polymers with very narrow molecular weight distribution. Since number average molecular weight, M_n, increases linearly in proportion to the conversion while molecular weight distribution, M_w/M_n, remains below 1.10, the present polymerization is

Table 1. Polymerization of Lactones Initiated by Organo Rare Earth Metal(III) Alkoxide[a]

initiator	monomer	Cat.%	$10^{-4}M_n$	M_w/M_n	conversion,%
$[YOMe(C_5H_5)_2]_2$	β-propiolactone	0.5	6.0	1.13	100 (18h)
	ε-caprolactone	0.2	15.8	1.04	52.0(6h)
		0.5	4.8	1.09	93.0(7h)
$YOMe(C_5Me_5)_2(THF)$	ε-caprolactone	0.2	3.3	1.03	86.6(8h)
		0.5	5.7	1.19	80.3(7h)
$SmOMe(C_5Me_5)_2(OEt_2)$	β-propiolactone	0.5	6.2	1.28	100 (18h)
	ε-caprolactone	0.2	15.8	1.28	100 (18h)

a)Reaction conditions:solvent, toluene.

considered to proceed in a living fashion (Figure 1).

As described in chapter 2, rare earth metal alkyl complexes ($SmMe(C_5Me_5)_2(THF)$, $LuMe(C_5Me_5)_2(THF)$) cannot initiate the polymerization of propiolactone. In contrast, rare earth metal alkoxide complexes efficiently polymerized the lactone affording monodisperse polymer of high molecular weight in high conversion. The mechanistic difference between the two initiating systems will be discussed below.

Initiation Mechanism for the Polymerization of Lactones Catalyzed by Rare Earth Metal Alkoxide Complexes. In order to elucidate the mechanism of the polymerization, stoichiometric reaction was carried out. The addition of equimolar caprolactone to yttrium methoxide complex followed by hydrolysis afforded only the caprolactone monomer. On the other hand, when 2 equivalent of caprolactone was used, 1:1 mixture of caprolactone and methyl 6-hydroxyhexanoate was recovered. The latter compound was formed by the addition of methoxy group to carbonyl carbon of the lactone followed by ring opening. Accordingly, when acetic anhydride was added after the 1:2 reaction, caprolactone and methyl 6-acetoxyhexanoate instead of methyl 6-hydroxyhexanoate was obtained. These results clearly indicated that ring opening of lactone molecule occurred only when additional monomers were present.

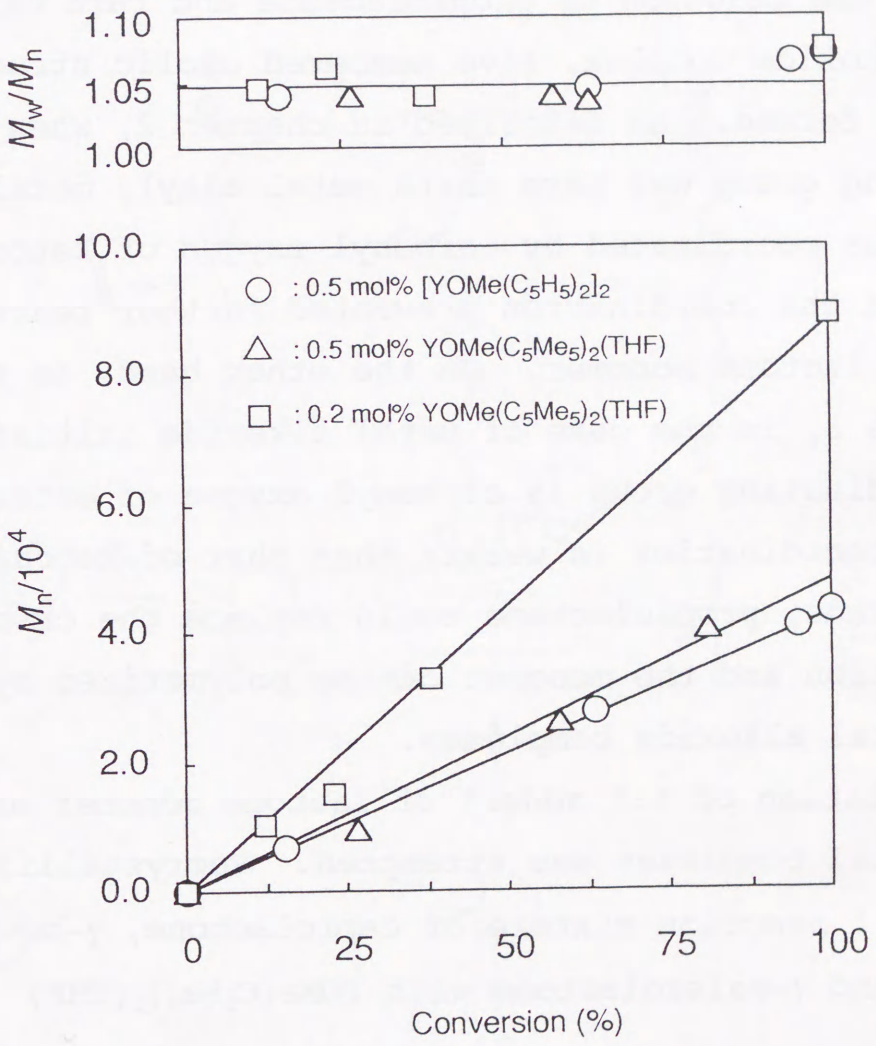

Fig. 1 Conversion vs. M_n and M_w/M_n of poly(caprolactone)

Furthermore, it was revealed that the ring opening proceeded though acyl-oxygen bond cleavage by the addition of alkoxide group to carbonyl carbon of the monomer (Figure 2).

By the reaction of propiolactone and rare earth metal alkoxide complex, five membered cyclic structure would be formed. As described in chapter 2, when the initiating group was rare earth metal alkyl, metal center was coordinated by carbonyl oxygen of ketonic group and the coordination prevented further reaction with the lactone monomer. On the other hand, as shown in Figure 3, in the case of metal alkoxide initiation, the coordinating group is carbonyl oxygen of ester group and the coordination is weaker than that of ketonic group. Thus, propiolactone could replace the carbonyl coordination and the monomer can be polymerized by rare earth metal alkoxide complexes.

Isolation of 1:1 adduct of lactone monomer and rare earth metal complexes was attempted. Recrystallization of the 1:1 reaction mixture of caprolactone, γ-butyrolactone and γ-valerolactone with $YOMe(C_5Me_5)_2(THF)$ afforded pure adduct respectively. Their ^1H NMR spectra show signals of coordinating lactone, which are significantly different from those of free lactones (Figure 4, 6 and 7). The latter two complexes were stable since the two lactone monomers could not be polymerized. On the other hand, the adduct of easily

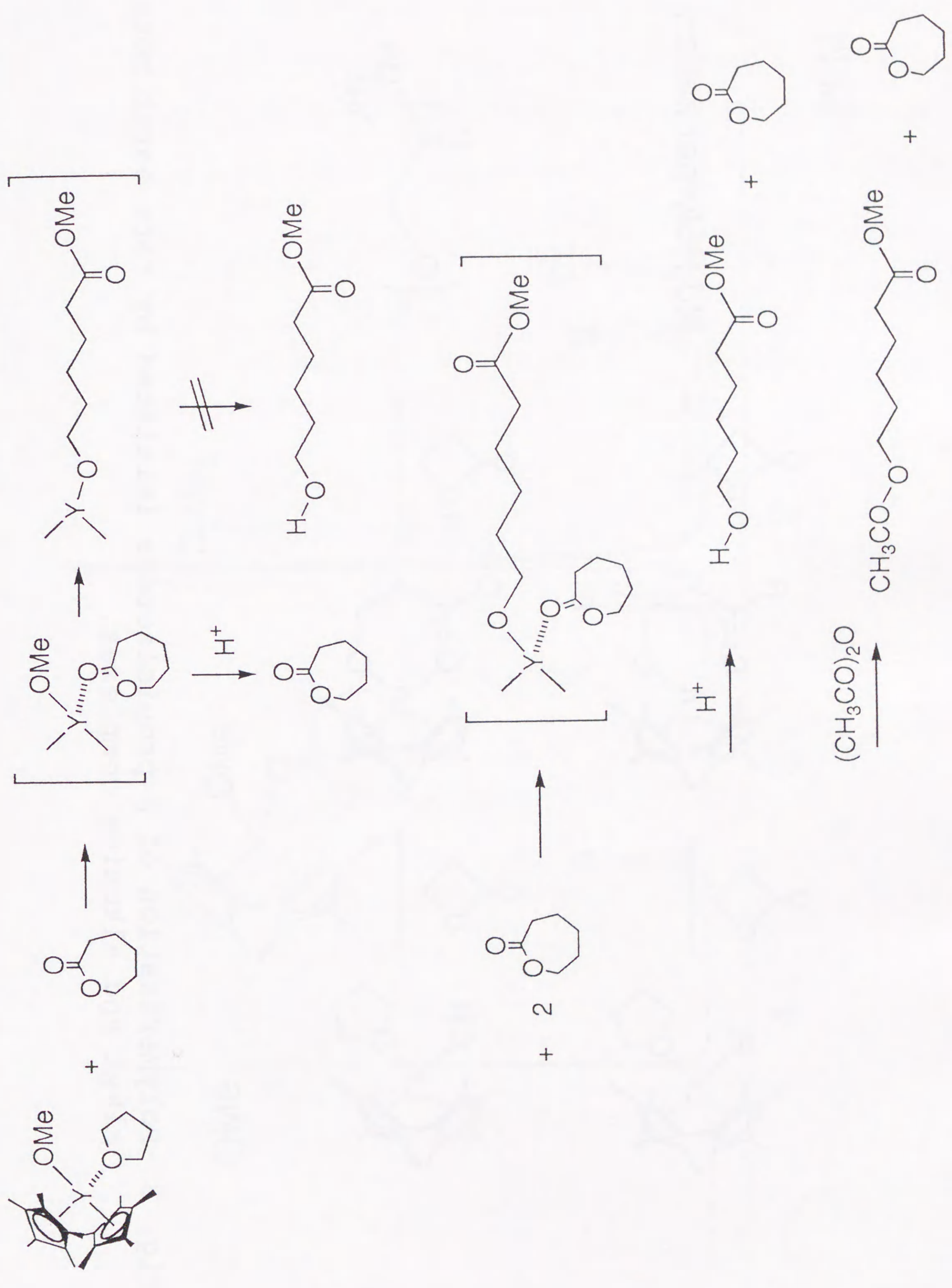

Fig. 2 Stoichiometric reaction of $YOMe(C_5Me_5)_2(THF)$ with caprolactone

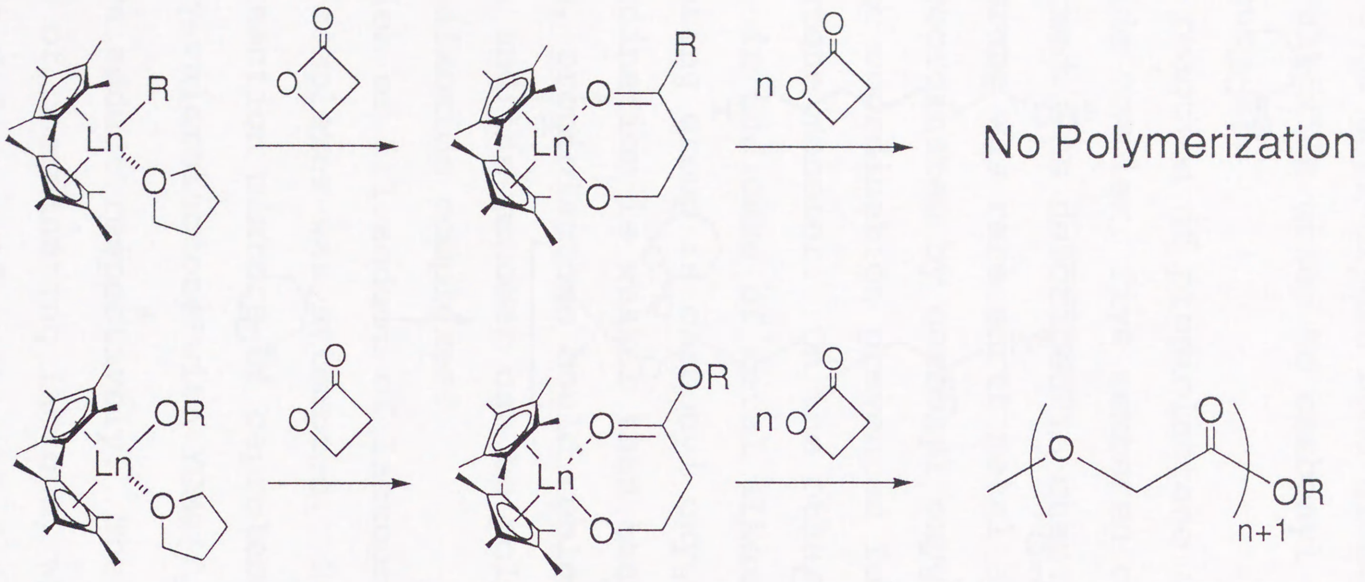

Fig. 3 Polymerization of β-propiolactone initiated by rare earth metal alkyl and alkoxide complexes.

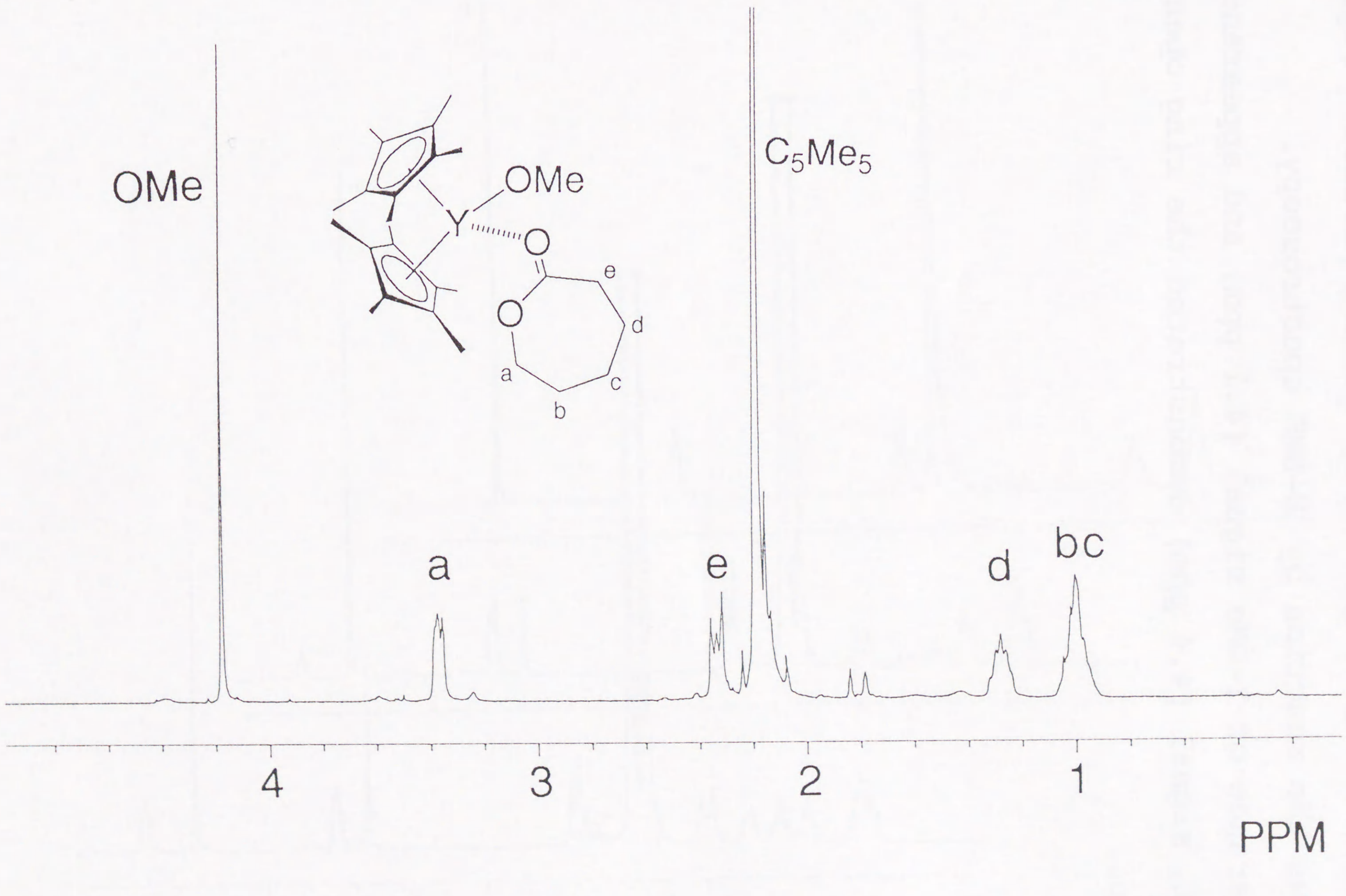

Fig. 4 ^{1}H NMR spectrum of $YOMe(C_5Me_5)_2$(caprolactone) polymerizable caprolactone reacted gradually by standing for several hours to give ring opening product. Figure 5 follows the reaction by ^{1}H-NMR spectroscopy. Disappearance of Y-OMe signal (4.1 ppm) and appearance of Y-OCH$_2$ signal (4.4 ppm) demonstrated the ring opening reaction.

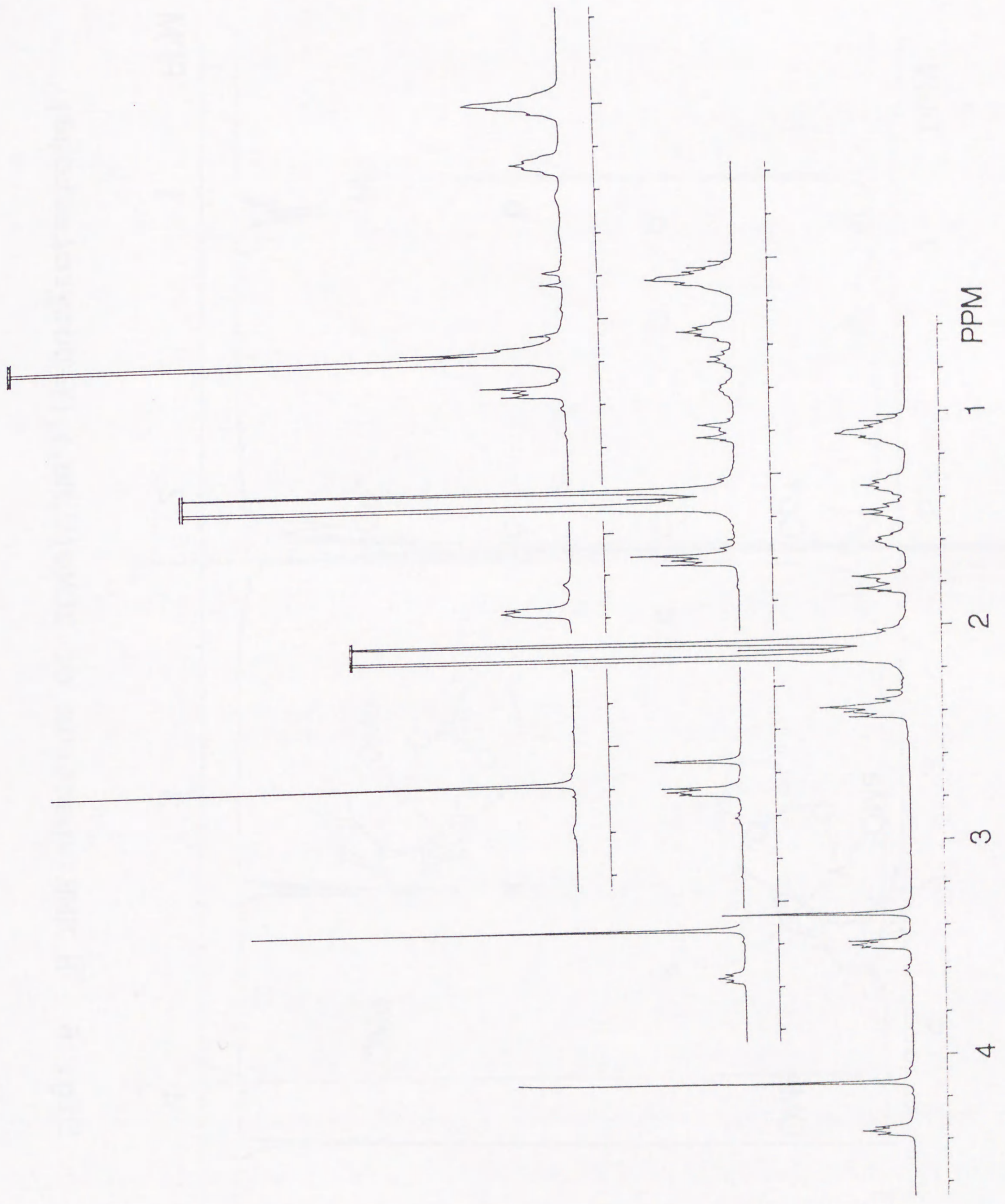

Fig. 5 Transformation of YOMe(C$_5$Me$_5$)$_2$(caprolactone)

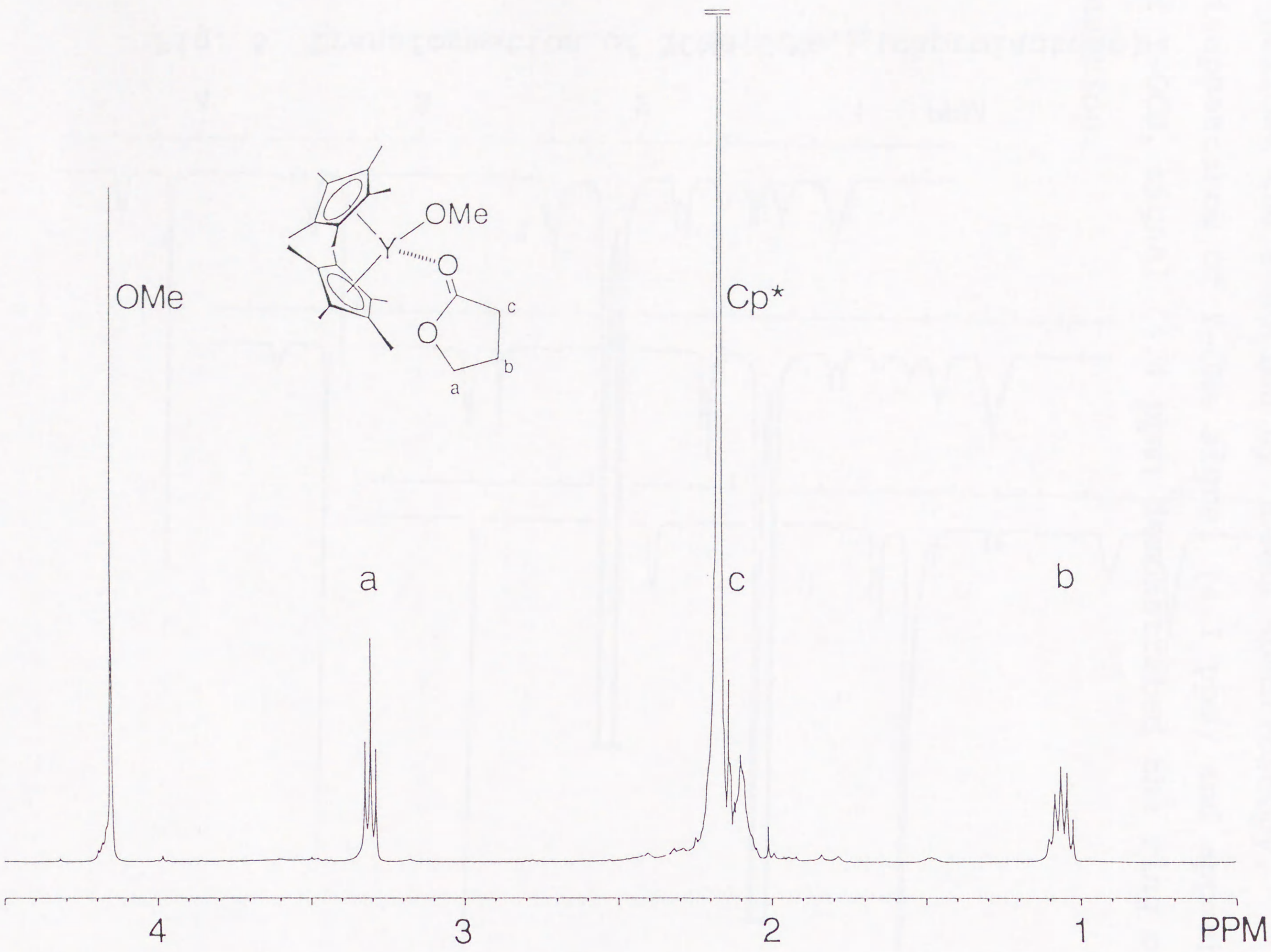

Fig. 6 ^{1}H NMR spectrum of YOMe(C_5Me_5)$_2$(γ-butyrolactone)

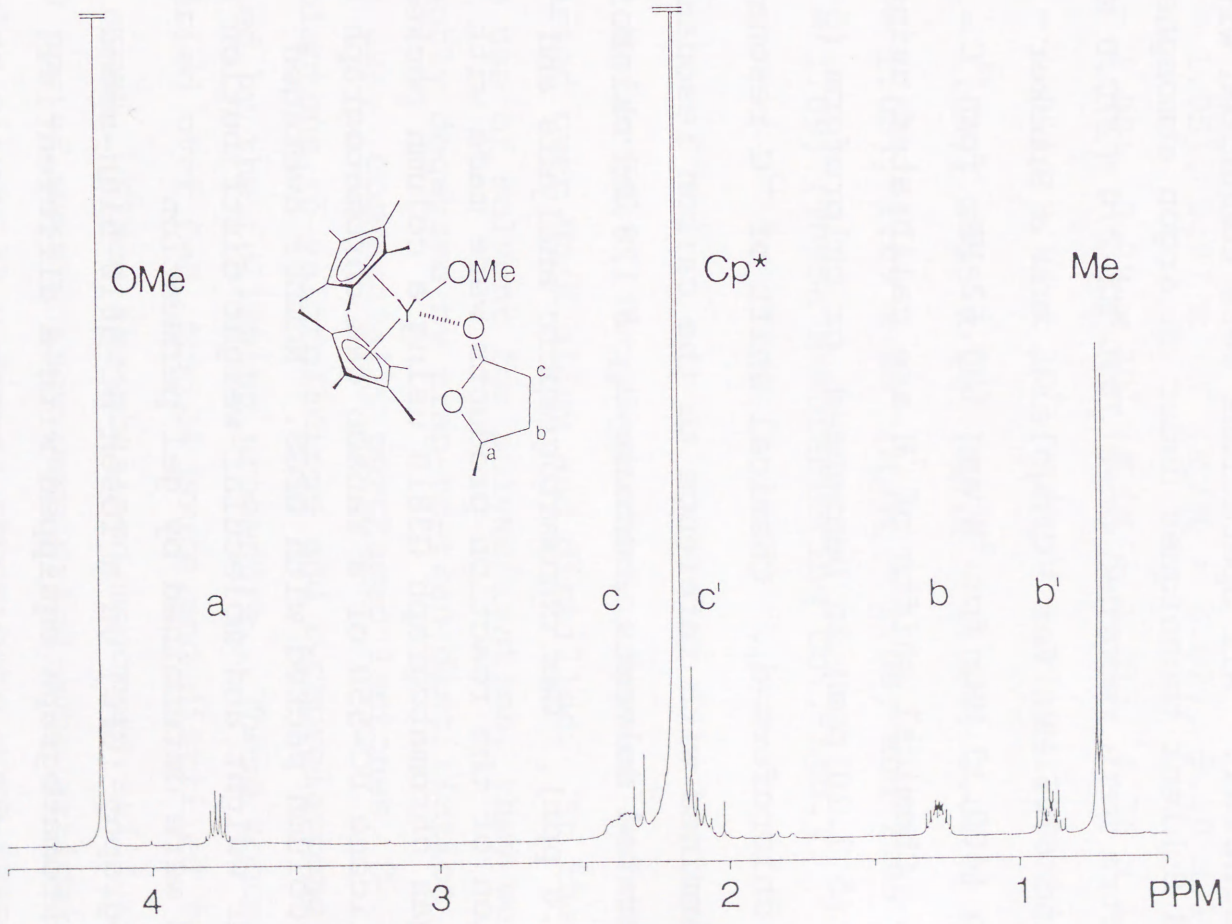

Fig. 7 ^{1}H NMR spectrum of YOMe(C_5Me_5)$_2$(γ-valerolactone)

Experimental Section

General. All operations were conducted with standard Schlenk techniques under an argon atmosphere. NMR spectra were recorded on a JEOL EX-270 (270.0 MHz for ^{1}H and 67.5 MHz for ^{13}C nuclei), and a Brucker AMX400wb (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C nuclei). Chemical shifts of ^{1}H are calibrated using benzene (δ 7.20 ppm) in benzene-d_6 or chloroform (δ 7.26 ppm) in chloroform-d_1. Chemical shift of ^{13}C resonances are determined with reference to the carbon resonances of deuterated solvents (benzene-d_6, δ 128.0; chloroform-d_1, δ 77.0 ppm). Gas chromatographic analysis and separation of the reaction products were made with a Yanaco gas chromatograph G3810 using a column packed with Silicone DC-550 or a Yanaco gas chromatograph G3800 using a column packed with DEGS. Number averaged molecular weight and molecular weight distribution of polymers were determined by gel permeation chromatography (GPC) on a Tosoh SC-8010 high-speed liquid chromatograph equipped with a differential refractometer detector, using $CHCl_3$ as a eluent at 40.0 °C. The column consisted of four columns: TSKgel G2000Hxl, TSKgel G3000Hxl, TSKgel G4000Hxl and TSKgel G5000Hxl (Tosoh Manufacturing Co., Ltd.) was used. The

flow rate was 1.0 ml min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes : 8.70 x 10^2 (M_w/M_n = 1.10), 2.63 x 10^3 (M_w/M_n = 1.05), 5.97 x 10^3 (M_w/M_n = 1.02), 9.10 x 10^3 (M_w/M_n = 1.02), 3.79 x 10^4 (M_w/M_n = 1.01), 4.36 x 10^4 (M_w/M_n = 1.01), 9.64 x 10^4 (M_w/M_n = 1.01), 1.90 x 10^5 (M_w/M_n = 1.04), 3.55 x 10^5 (M_w/M_n = 1.02), 7.06 x 10^5 (M_w/M_n = 1.05), 1.09 x 10^6 (M_w/M_n = 1.08) and 2.89 x 10^6 (M_w/M_n = 1.09) (Tosoh Manufacturing Co., Ltd.).

Material. Tetrahydrofuran, hexane and toluene were dried over Na/K alloy and distilled. In the case of the use of solvent for polymerization, they were thoroughly degassed by trap-to-trap distillation just before use. Commercially purchased lactones, β-propiolactone, δ-valerolactone and ε-caprolactone were purified by the following procedure. These monomers were dried over CaH_2 for 24 hours and distilled twice under argon. Since the obtained monomers still contain ca. 30 ppm of water, they were dried over activated molecular sieves 3A under an atmosphere more than 4 days, and was finally degassed and purified by trap-to-trap distillation just before use. Pure $Sm(C_5Me_5)_2(THF)_2$, $[SmH(C_5Me_5)_2]_2$, $SmMe(C_5Me_5)_2(THF)$, $SmOEt(C_5Me_5)_2(OEt_2)$,

$[YOMe(C_5H_5)_2]_2$, and $YOMe(C_5Me_5)_2(THF)$ were obtained according to the known method.

Preparation of $Sm(C_5Me_5)_2(THF)_2$. The complex, $Sm(C_5Me_5)_2(THF)_2$ was prepared in the same procedure described in chapter 2.

Preparation of $SmMe(C_5Me_5)_2(THF)$. The complex, $SmMe(C_5Me_5)_2(THF)$ was prepared in the same procedure described in chapter 2.

Preparation of $SmOEt(C_5Me_5)_2(Et_2O)$4). An orange powder of $[SmH(C_5Me_5)_2]_2$ (0.71 g, 0.84 mmol) was dissolved in 20 ml of diethyl ether. Immediately after mixing the color of the solution changed from yellow-orange to bright yellow. After the mixture was held at 20 °C for 30 min, volatiles were evaporated by flash distillation to result in the formation of yellow powder. The powder was extracted with 20 ml of hexane and then the hexane solution was concentrated and cooled to -20 °C to give yellow crystals of $Sm(OEt)(C_5Me_5)_2(OEt_2)$. Yield : 42% (0.30 g).

Preparation of $YCl(C_5H_5)_2(THF)$. A solution of $(C_5H_5)Na$ (15.5 mmol) in 8.6 ml of THF was added to a stirred suspension of anhydrous YCl_3 (1.51 g, 7.73 mmol) in 40 ml of THF at room temperature and the solution was refluxed for 24 hr. Resulting brown solution was centrifuged in order to separate NaCl and THF was removed by evaporation. Toluene (80 ml) was added to the residue and the mixture was stirred for 24 hr at room temperature. After separation of the salt by centrifugation, solvent was evaporated and the crude $YCl(C_5H_5)_2(THF)$ was recrystallized from THF/hexane to give pale brown prisms. Yield : 59.5 %.

Preparation of $[YOMe(C_5H_5)_2]_2$. Crystalline $YCl(C_5H_5)_2(THF)$ (0.68 g, 2.10 mmol) was mixed with NaOMe (0.13 g, 2.4 mmol) in the solid state. Then 30 ml of THF was added with vigorous magnetic stirring. After stirring for 36 hr the THF suspension was evaporated to dryness and the solid was extracted with toluene to yield white powder of $[YOMe(C_5H_5)_2]_2$. Yield : 9.0 %. EIMS : m/z (species, relative intensity) 219 ($[(C_5H_5)_2{}^{89}Y]^+$, 18.8), 435 ($[(C_5H_5)_2{}^{89}Y(OMe)_2{}^{89}Y(C_5H_5)]^+$, 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).

Preparation of $YCl(C_5Me_5)_2(THF)$. A solution of $(C_5Me_5)Na$ (32.0 mmol) in 49.5 ml of THF was added to a stirred suspension of anhydrous YCl_3 (3.29 g, 16.8 mmol) in 80 ml of THF at room temperature and the solution was refluxed for 3-4 hours. Resulting brown solution was centrifuged in order to separate NaCl and THF was removed by evaporation. Toluene (150 ml) was added to the residue and the mixture was stirred for 24 hr at room temperature. After separation of the salt by centrifugation, solvent was evaporated and the crude $YCl(C_5Me_5)_2(THF)$ was recrystallized from THF/hexane to give pale brown prisms. Yield : 63.5 %. ^1H NMR (C_6D_6) δ 1.19 (THF,4H), 2.06 (s,30H), 3.53 (THF,4H). ^{13}C NMR (C_6D_6) δ 11.7 (C_5Me_5), 25.3 (THF), 72.2 (THF), 118.0 (C_5Me_5).

Preparation of $YOMe(C_5Me_5)_2(THF)$. Crystalline $YCl(C_5Me_5)_2(THF)$ (1.01 g, 2.16 mmol) was mixed with NaOMe (0.12 g, 2.2 mmol) in the solid state. Then THF (40 ml) was added and the mixture was stirred. After stirring for overnight the mixture was evaporated to dryness and the resulting solid was extracted twice with toluene to yield white powder. Recrystallization from THF/hexane gave pale yellow-green prisms of YOMe $(C_5Me_5)_2(THF)$. Yield : 60.9%.

Polymerization of ε-Caprolactone catalyzed by $[YOMe(C_5H_5)_2]_2$. A solution of $[YOMe(C_5H_5)_2]_2$ (0.025 g, 0.05 mmol) in 0.2 ml of toluene was added to a toluene solution of 1000 or 400 equivalent (500 and 200 equivalent as a monomeric $YOMe(C_5H_5)_2$) caprolactone (5.54 ml, 50 mmol and 2.22 ml, 20 mmol) at 0 °C. After stirring fixed time (0.5, 1, 3, 6, and 18 hours) the solution was quenched with excess methanol.

Polymerization of ε-Caprolactone catalyzed by $YOMe(C_5Me_5)_2(THF)$. A solution of $YOMe(C_5Me_5)_2(THF)$ (0.023 g, 0.05 mmol) in 0.2 ml of toluene was added to a toluene solution of 500 or 200 equivalent caprolactone (5.54 ml, 50 mmol and 2.22 ml, 20 mmol) at 0 °C. After stirring fixed time (1, 2, 5, 12, and 18 hours) the solution was quenched with excess methanol.

Equimolar Reaction of $SmOEt(C_5Me_5)_2(OEt_2)$ with δ-Valerolactone. Valerolactone (0.0074 ml, 0.08 mmol) was added to a stirred solution of $Sm(OEt)(C_5Me_5)_2$ (OEt_2) (0.043 g, 0.08 mmol) in 3 ml of toluene at 0 °C and the mixture was allowed to warm to room temperature. During the mixture was stirred for 10 min stirring the color of the solution changed from yellow to pale-yellow. Then the solution was quenched by acetic anhydride and concentrated. The supernatant liquid was analyzed by gas chromatograph.

Equimolar Reaction of SmOEt$(C_5Me_5)_2(OEt_2)$ with ε-Caprolactone. The reaction was carried out in essentially the same manner as described for the reaction of valerolactone using 0.092 g (0.17 mmol) of Sm(OEt)$(C_5Me_5)_2(OEt_2)$ and 0.019 ml (0.17 mmol) of caprolactone.

Equimolar Reaction of SmOEt$(C_5Me_5)_2(OEt_2)$ with β-Propiolactone. Propiolactone (0.13 ml, 2.13 mmol) was added to a stirred solution of Sm(OEt)$(C_5Me_5)_2(OEt_2)$ (1.15 g, 2.13 mmol) in 5 ml of toluene at 0 °C and the mixture was allowed to warm to room temperature. During the mixture was stirred for 5 min the color of the solution changed from yellow to pale-yellow. Then the solution was quenched by a few drops of H_2O. The supernatant liquid was analyzed by gas chromatograph.

Equimolar Reaction of YOMe$(C_5Me_5)_2$(THF) with ε-Caprolactone (I). Caprolactone (0.035 ml, 0.31 mmol) was added to a stirred solution of YOMe$(C_5Me_5)_2$

(THF) (0.15 g, 0.31 mmol) in 5 ml of toluene at -78 °C and the mixture was allowed to react at room temperature. After stirring for 10 min the solution was quenched with acetic anhydride (0.03 ml, 0.31 mmol) and neutralized by aqueous $NaHCO_3$. During these process, white precipitate was emerged. After concentration of the supernatant liquid, the resulting product was separated by gas chromatograph and TLC.

Equimolar Reaction of YOMe$(C_5Me_5)_2$(THF) with δ-Valerolactone (I). The reaction was carried out in essentially the same manner as described for the reaction of caprolactone using 0.21 g (0.45 mmol) of YOMe$(C_5Me_5)_2$(THF) and 0.042 ml (0.45 mmol) of valerolactone.

Equimolar Reaction of YOMe$(C_5Me_5)_2$(THF) with ε-Caprolactone (II). Caprolactone (0.085 ml, 0.77 mmol) was added to a stirred solution of YOMe$(C_5Me_5)_2$ (THF) (0.36 g, 0.77 mmol) in 5 ml of toluene at -78 °C and the mixture was allowed to react at room temperature. After stirring for 10 min, the solution was quenched with $PhCH_2Br$ (0.18 ml, 1.54 mmol) and neutralized by aqueous $NaHCO_3$. During these process, white precipitate was emerged. After concentration of the supernatant liquid, resulting product was separated by gas chromatograph and TLC.

Equimolar Reaction of YOMe(C_5Me_5)$_2$(THF) with ε-Caprolactone (II). The reaction was carried out in essentially the same manner as described for the reaction of caprolactone using 0.59 g (1.28 mmol) of (C_5Me_5)$_2$Y(OMe)(THF) and 0.42 ml (0.45 mmol) of valerolactone.

Equimolar Reaction of YOMe(C_5Me_5)$_2$(THF) with ε-Caprolactone (III). Caprolactone (0.094 ml, 0.85 mmol) was added to a stirred solution of YOMe(C_5Me_5)$_2$ (THF) (0.39 g, 0.85 mmol) in 5 ml of toluene at -78 °C. White precipitate was formed and was washed by a small amount of hexane. Recrystallization from toluene gave white crystalline solids of YOMe(C_5Me_5)$_2$(caprolactone).

Equimolar Reaction of YOMe(C_5Me_5)$_2$(THF) with γ-Valerolactone. The reaction was carried out in essentially the same manner as described for the reaction of caprolactone using 0.027 g (0.057 mmol) of YOMe(C_5Me_5)$_2$(THF) and 0.054 ml (0.057 mmol) of γ-valerolactone.

Equimolar Reaction of YOMe(C_5Me_5)$_2$(THF) with γ-Butyrolactone. The reaction was carried out in essentially the same manner as described for the reaction of caprolactone using 0.72 g (1.56 mmol) of YOMe(C_5Me_5)$_2$(THF) and 0.13 ml (1.69 mmol) of γ-butyrolactone.

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Chapter 4

Polymerization of Methyl Methacrylate Catalyzed by Organo Rare Earth Metal Enolate Complexes

Introduction

It has been reported that organo rare earth metal (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) conduct the living polymerization of methyl methacrylate at wide range of polymerization temperature to give high molecular weight polymers ($M_n > 50,000$) with extremely narrow molecular weight distribution, $M_w/M_n = 1.02$, in high conversion in a short period.

1:2 adduct of $SmH(C_5Me_5)_2$ and methyl methacrylate was isolated and its structure was revealed by X-ray analysis. In the complex, methyl methacrylate dimer bonded to Sm in an enolate form at one end and in a carbonyl coordination in another end forming 8 membered cyclic structure (Figure 1)[1,2]. When additional monomer was added to the 1:2 adduct, living polymerization restarted efficiently. Therefore such a cyclic structure with metal enolate bond was regarded as a real propagation species.

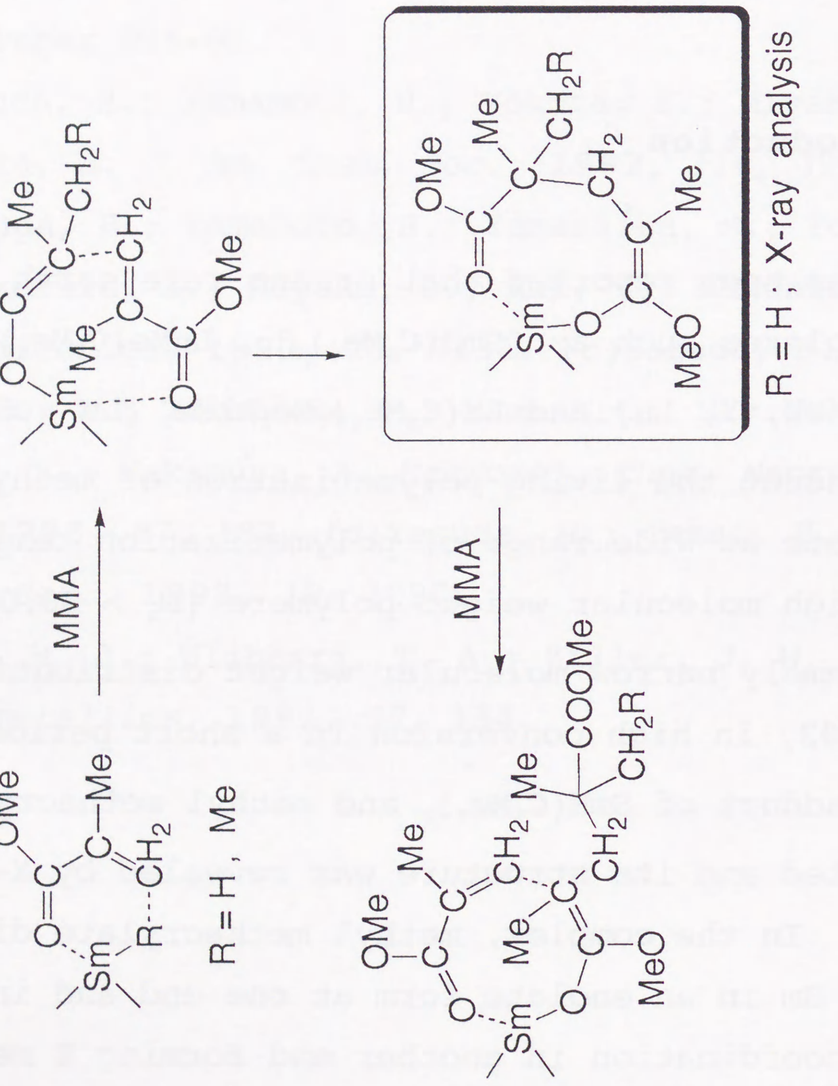

Fig. 1 Polymerization mechanism of methyl methacrylate initiated by organosamarium(III) complex[1]

The above result indicated that rare earth metal complexes with enolate structure could polymerize methyl methacrylate in a living manner. In this chapter, I prepared rare earth metal enolate complexes and examined their initiating ability for methyl methacrylate polymerization.

The effect of solvent on tacticity of poly(methyl methacrylate) was also investigated in this part.

This chapter also deals with the synthesis of complexes which have the structure of σ_s-symmetry and C_1-symmetry and the polymerization of methyl methacrylate catalyzed by these complexes to consider the possibility of regulating the tacticity of poly(methyl methacrylate) by modification of the steric environment around metal center.

Results and Discussion

Polymerization of Methyl Methacrylate Catalyzed by Organo Rare Earth Metal Enolate Complexes. Following the procedure reported by Evans et al.[3)], rare earth metal enolate complexes with C_5Me_5, $Y(OCH_2{=}CH_2)(C_5Me_5)_2(THF)$ (<u>1</u>) and $C_5H_4(TMS)$ $[Y(OCH_2{=}CH_2)\text{-}\{C_5H_4(TMS)\}_2]_2$ (<u>2</u>) were prepared. ^1H NMR spectra of these complexes are shown in Figure 2, 3. The enolate structure of these complexes was confirmed by the appearance of the characteristic signals of $OCH{=}CH_2$ group (<u>1</u> 3.93, 4.02 and 6.29 ppm, <u>2</u> 4.07, 4.28 and 6.29 ppm).

These complexes showed a good activity for polymerization of methyl methacrylate giving high molecular weight poly(methyl methacrylate) in excellent yield (Table 1). This result is in accord with the fact that the X-ray structure of the 1:2 adduct of $SmH(C_5Me_5)_2$ and methyl methacrylate was samarium enolate form.

Influence of Solvent on Tacticity of Poly(methyl methacrylate) Catalyzed by $SmMe(C_5Me_5)_2$ (THF). The effect of solvent on the tacticity of poly(methyl methacrylate) was investigated. Hatada et al. demonstrated the effect of solvent on the tacticity

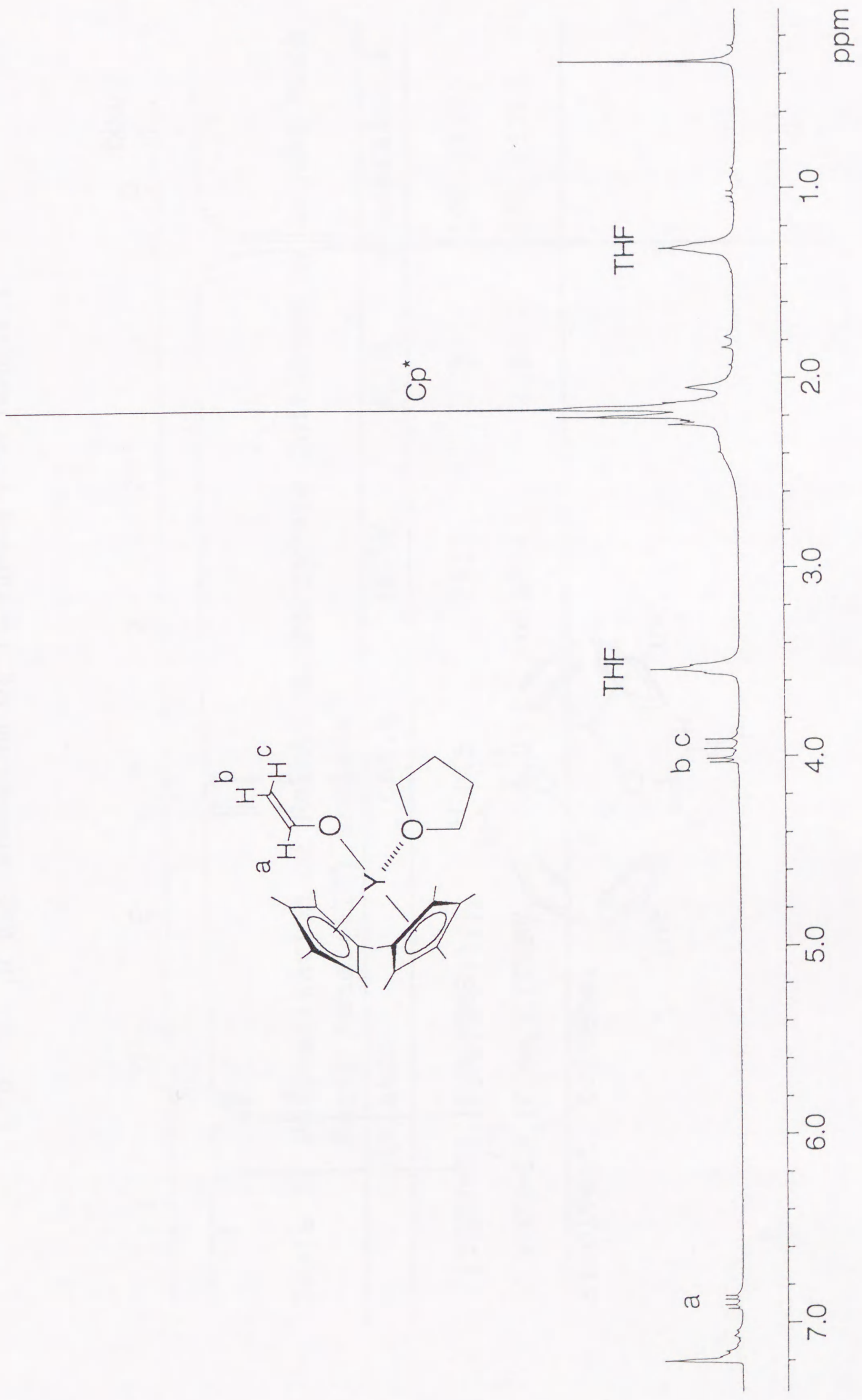

Fig. 2 ^1H NMR spectrum of $YOCH{=}CH_2(C_5Me_5)_2(THF)$

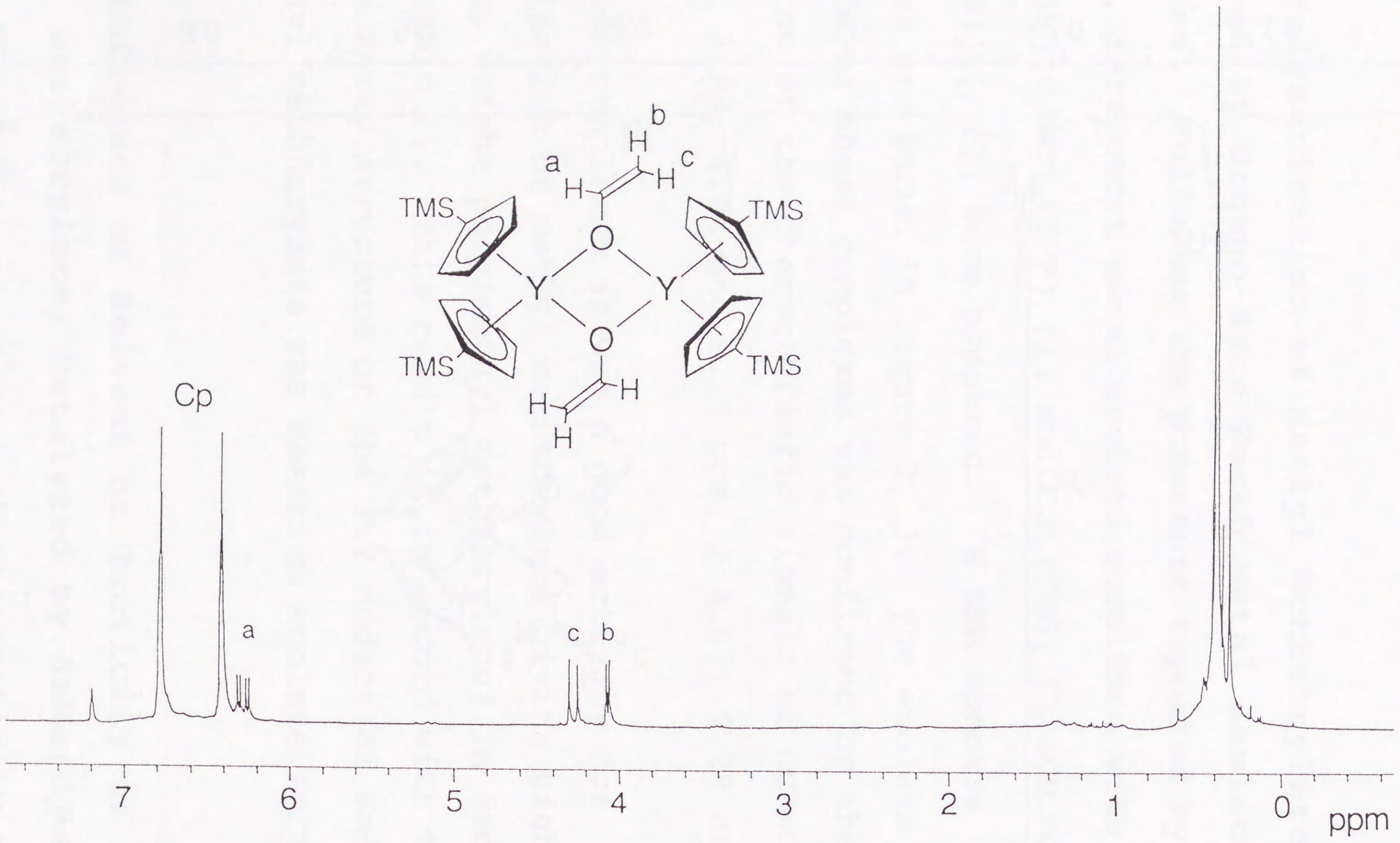

Fig. 3 ^{1}H NMR spectrum of [YOCH=CH$_2${C$_5$H$_4$(TMS)}$_2$]$_2$

Table 1. Polymerization of Methyl Methacrylate Initiated by Organo Rare Earth Metal(III) enolate[a)]

initiator	Cat.%	$10^{-3}M_n$	M_w/M_n	conversion,%
[YOCH=CH$_2${C$_5$H$_4$(TMS)}$_2$]$_2$	0.5	24.7	1.53	100 (12h)
YOCH=CH$_2$(C$_5$Me$_5$)$_2$(THF)	0.2	50.4	1.98	100 (12h)

a)solvent, toluene.

of poly(methyl methacrylate) catalyzed by Grignard reagents. The syndiotactic polymers were obtained in toluene, while isotactic polymers were obtained when tetrahydrofuran was used as solvent[4]. Table 2 shows the results of polymerization of methyl methacrylate in various solvents. All polymerizations afforded syndiotactic polymers (rr ≈ 80%), even when toluene and tetrahydrofuran was used as solvent. However, when triethylamine were used as solvent, polymers were obtained in a bimodal fashion. In this case, white precipitate was generated after stirring the mixture for 1 minute. This precipitate should be $Sm[O\text{-}C(OMe)=CH\text{-}(CH_3)](NEt_3)(C_5Me_5)_2$ or $Sm(MMA)_2Me(NEt_3)(C_5Me_5)_2$. The use of ethyl acetate resulted in the formation of no polymers, presumably due to the side reaction which inactivated the active species. Thus, the mode of the reaction differs greatly from that of Grignard reagent.

Polymerization of Methyl Methacrylate Catalyzed by σ_s- and C_1-Symmetric Rare Earth Metal Complexes. In contrast to the polymerization by Grignard reagent, change of the solvent did not influence the tacticity of resulting poly(methyl methacrylate). Next, I attempted to regulate the tacticity by modification of sterical environment around metal center. For the purpose, two types of new ligand

Table 2. Solvent Influence on Tacticity of Poly(methyl methacrylate) Initiated by $SmMe(C_5Me_5)_2(THF)$[a)]

solvent	temp./°C	time(h)	$10^{-3}M_n$	M_w/M_n	tacticity, %			conversion,%
					rr	rm	mm	
toluene	0	3	10.4	1.05	82.0	17.0	1.0	100
	-78	20	9.5	1.03	92.8	6.5	0.7	100
tetrahydrofuran	0	6	9.0	1.01	75.8	16.9	7.3	100
	-78	20	7.0	1.02	86.0	9.7	4.3	100
triethylamine	0	6	245 4.3	2.61 1.12	73.4	20.8	5.8	83.6
	-78	20	51.9 2.0	1.55 1.10	79.6	14.2	6.2	32.6
ethylacetate	0	3	-	-	-	-	-	trace
	-78	20	-	-	-	-	-	trace

a)Reaction conditions: initiator concentration, 1.0 mol% of monomer.

were prepared.

Three substituents were introduced into Me_2Si-bridged cyclopentadienyl rings. Since one of the substituent (tert-butyldimethylsilyl) was larger than the others, the ligand afforded highly unsymmetrical (C_1 symmetry) complex after complexation. σ_s-symmetric complex was obtained by using a ligand with Me_2C-bridged fluorenyl and cyclopentadienyl rings. Steric effect of these modified ligands would be expected to result in the stereoregulation of poly(methyl methacrylate).

As shown in Figure 4 and 5, bistrimethylsilylmethyl and hydride complexes with these ligands were synthesized. Table 3 and 4 show the result of methyl methacrylate polymerization by these complexes. All of them exhibited high activity for the polymerization to give poly(methyl methacrylate) efficiently. However, syndiotactic polymers (rr ≈ 80%) were obtained in all cases, indicating that such ligand modifications were not effective for the stereoregulation.

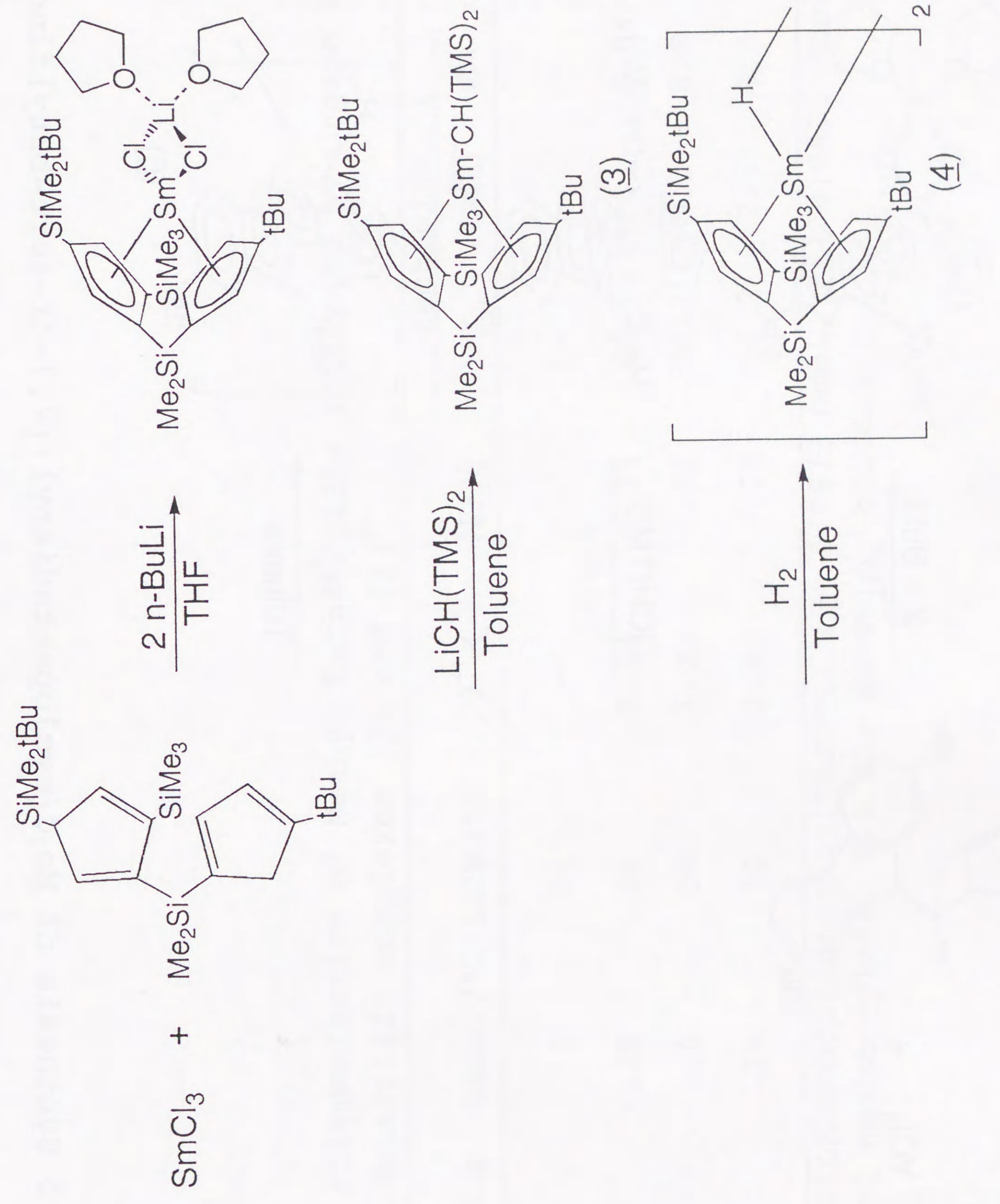

Fig. 4 Synthesis of Me_2Si(2-trimethylsilyl-4-tert-butyldimethylsilyl-cyclopentadienyl)(3-tert-butylcyclopentadienyl)SmR

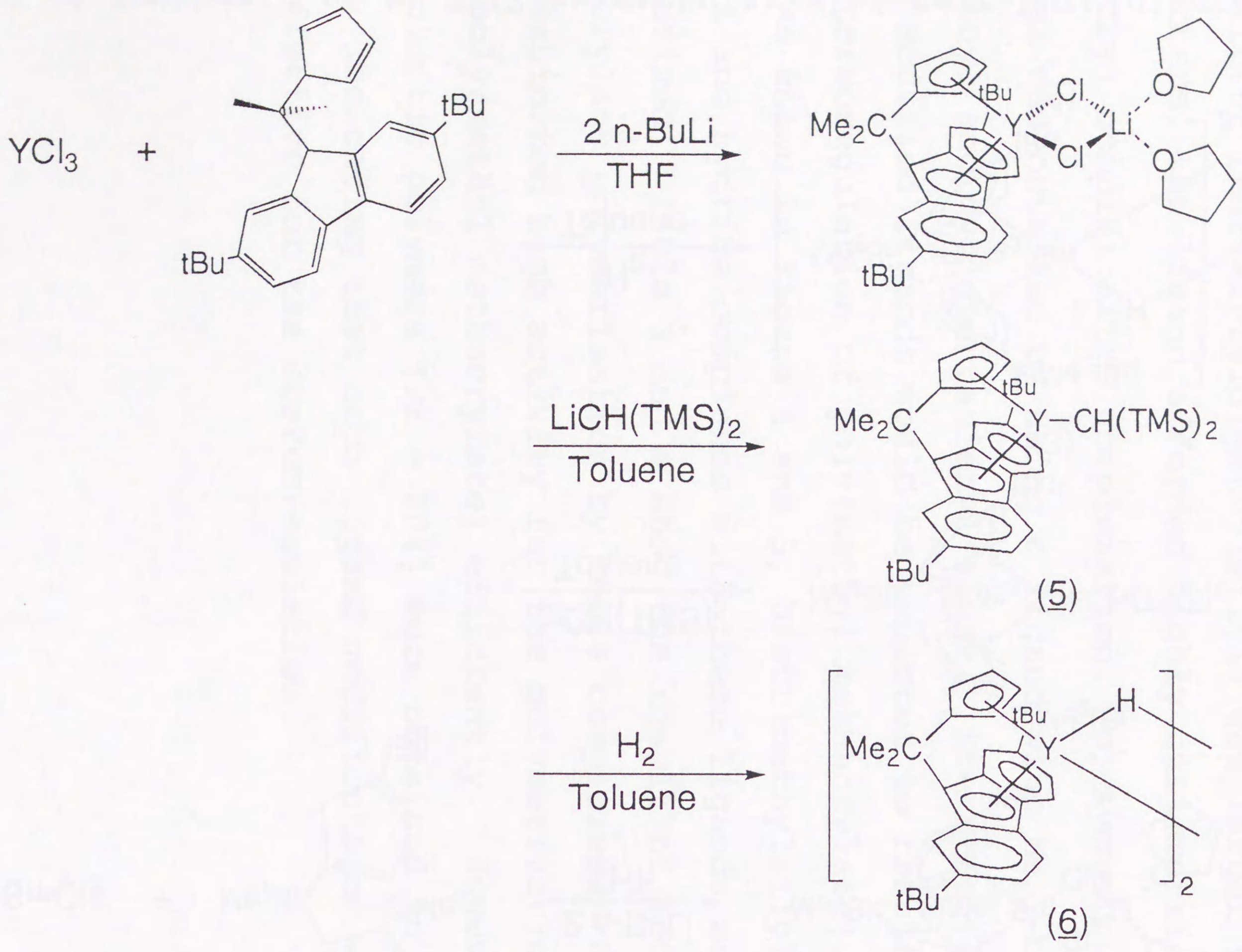

Fig. 5 Synthesis of Me_2C(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)YR

Table 3. Polymerization of Methyl Methacrylate Initiated by Organo Rare Earth Metal(III) Complexes (3) and (4)$^{a)}$

initiator	temp./°C	time(h)	$10^{-4}M_n$	M_w/M_n	tacticity, % rr	 rm	 mm	conversion,%
(3)	0	24	-	-	-	-	-	trace
	-78	24	9.93	6.74	80.2	11.3	8.5	100
(4)	0	36	1.02	1.03	86.1	5.1	8.8	38.8
	-78	12	2.80	9.75	84.2	7.9	8.0	100

a)Reaction conditions: initiator, (3) 0.0672 mmol, (4) 0.0406 mmol; methyl methacrylate, 8.0 ml; solvent, toluene.

Table 4. Polymerization of Methyl Methacrylate Initiated by Organo Rare Earth Metal(III) Complexes (5) and (6)$^{a)}$

initiator	temp./°C	time(h)	$10^{-5}M_n$	M_w/M_n	tacticity, % rr	rm	mm	conversion, %
(5)	0	3	5.12	1.66	78	19	3	99.7
	-20	3	10.5	1.54	79	18	3	99.8
	-78	44	13.0	1.67	77	20	3	84.0
(6)	0	1	7.6	1.66	79	18	3	42.8
	-78	13	5.2	1.70	78	18	4	11.5

a)Reaction conditions: initiator concentration, 0.3 mol% of monomer; solvent, toluene.

Experimental Section

Preparation of $[YCl\{C_5H_4(TMS)\}_2]_2$. A solution of $C_5H_4(TMS)Na$ (28.8 mmol) in 23.6 ml of THF was added to a stirred suspension of anhydrous YCl_3 (3.13 g, 16.0 mmol) in 130 ml of THF at room temperature and the solution was refluxed for 20 hours. Resulting pale-brown solution was centrifuged in order to separate NaCl and THF was removed to dryness by evaporation and kept at 75 °C in vacuo for 12 hours in order to remove coordinated THF. Toluene (150 ml) was added to the residue and the mixture was stirred for 24 hr at room temperature. After separation of the salt by centrifugation, recrystallization from toluene gave pale brown crystalline powder of $[YCl\{C_5H_4(TMS)\}_2]_2$. Yield : 60.5 %.

Preparation of $YCl(C_5Me_5)_2(THF)$. The complex, $YCl(C_5Me_5)_2(THF)$ was prepared in the same procedure described in chapter 3. Yield 29%.

Preparation of $[Y(OCH{=}CH_2)\{C_5H_4(TMS)\}_2]_2$. $Li(OCH{=}CH_2)$ (3.5 mol) in 7.0 ml of THF was added to the solution of $[YCl\{C_5H_4(TMS)\}_2]_2$ (1.36 g, 1.71 mmol) at room temperature. Immediately after the addition white precipitate generated. After stirring for 12 hours at room temperature the THF was evaporated to dryness by keeping at 75 °C in vacuo for 12 hours in order to remove coordinated THF. The white residue was extracted 4 - 5 times with 40 ml of toluene, and then a small amount of precipitate was removed by centrifugation. Evaporation of the solution to dryness resulted straw-colored solids of $[Y(OCH{=}CH_2)\{C_5H_4(TMS)\}_2]_2$. ^1H NMR (C_6D_6, ppm) δ 0.25 (s, TMS, 18H), 4.07 (d, $OCH{=}CH\underline{H}$, 1H), 4.28 (d, $OCH{=}C\underline{H}H$, 1H), 6.29 (dd, $OC\underline{H}{=}CH_2$, 1H), 6.39 and 6.78 (s, C_5H_4, 8H).

Preparation of $Y(OCH{=}CH_2)(C_5Me_5)_2(THF)$. Li-$(OCH{=}CH_2)$ (3.6 mol) in 7.2 ml of THF was added to the solution of $YCl(C_5Me_5)_2(THF)$ (0.91 g, 1.95 mmol) at room temperature. Immediately after the addition white precipitate generated. After stirring for 12 hours at room temperature the THF was evaporated to dryness. The white residue was extracted 4 - 5 times with 40 ml of toluene, and then a small amount of precipitate was removed by centrifugation. Evaporation of the solution to dryness resulted straw-colored solids of $Y(OCH{=}CH_2)(C_5Me_5)_2(THF)$. ^1H NMR (C_6D_6, ppm) δ 0.34 (s, TMS, 18H), 1.31 (m, THF), 2.16 and 2.20 (C_5Me_5), 3.53 (m, THF), 3.93

(d, $OCH{=}CH\underline{H}$, 1H), 4.02 (d, $OCH{=}C\underline{H}H$, 1H), 6.29 (dd, $OC\underline{H}{=}CH_2$, 1H).

Preparation of $Lu(OCH{=}CH_2)(C_5Me_5)_2(THF)_n$. The reaction was carried out in essentially the same manner as described above using 0.64 g (1.15 mmol) of $(C_5Me_5)_2$-LuCl(THF) and 1.15 mmol of $Li(OCH{=}CH_2)$.

Preparation of $Y(OC^tBu{=}CH_2)(C_5Me_5)_2(THF)$. The mixture of $YCl(C_5Me_5)_2(THF)$ (0.91 g, 1.95 mmol) and Li-$(OC^tBu{=}CH_2)$ (0.64 g, 6.05 mol) was dissolved in 40 ml of tetrahydrofuran at room temperature and then white precipitate generated. After stirring for 6 hours at room temperature the tetrahydrofuran was evaporated to dryness. The white residue was extracted with 80 ml of toluene, and then a small amount of precipitate was removed by centrifugation. Solid mass obtained by evaporation of the solution were further extracted with 80 ml of hexane. Evaporation of the solution to dryness resulted in the formation of straw-colored solids of $Y(OC^tBu{=}CH_2)(C_5Me_5)_2$ (THF).

Preparation of Me_3Si\{4-(tert-butyl-dimethylsilyl)-2-(trimethylsilyl)cyclopentadiene\}(3-tert-butylcyclopentadiene). To a stirring solution of 1-(tert-butyldimethylsilyl)-3-(trimethylsilyl)cyclopentadiene (7.06 g, 0.028 mol) in hexane (40 ml) was added hexane solution of 1.64 M n-butyllithium (19.0 ml, 0.0312 mol) at 0 °C, and stirred for 20 hours at room temperature. To a resulted solution tetrahydrofuran (40 ml) was added, and then dimethylsilyldichloride (3.80 ml, 0.0313 mol) in tetrahydrofuran (10 ml) was added with stirring at 0 °C and kept the mixture under same condition for 1 hour and at room temperature for 24 hours. After removal of solvent tetrahydrofuran (60 ml) was added to the residue.

Next, to a stirring solution of tert-butylcyclopentadiene (7.06 g, 0.028 mol) in tetrahydrofuran (40 ml) was added hexane solution of 1.64 M n-butyllithium (17.5 ml, 0.0287 mol) at 0 °C, and stirred the mixture for 4 hours at room temperature. Then to the previous tetrahydro-furan solution was added this solution at 0 °C and stirred for 14 hours. The mixture was poured into a large amount of water (500 ml). The solution was extracted with hexane (150 ml, twice) and organic layer was dried over Na_2SO_4. Evaporation of the product gave pale yellow liquid of Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadiene\}(tert-butylcyclopentadiene) (8.46 g, 0.0196 mol). Yield : 70.3 %.

Preparation of Me_3Si\{4-(tert-butyl-dimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl\}(3-tert-butylcyclopentadienyl)$SmCl_2Li(THF)_2$. A hexane solution of 1.64 M n-butyllithium (11.0 ml, 18.0 mmol) was added to a solution of Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadiene\}(3-tert-butylcyclopentadiene) (3.17 g, 7.36 mmol) in tetrahydrofuran (100 ml) at 0 °C, and the mixture was stirred at room temperature for 3 hours. Then the solution was dropwise added to $SmCl_3$ (2.25 g, 8.76 mmol) in tetrahydrofuran (80 ml), and the mixture was stirred for 12 hours. After the solvent was removed in vacuo, the residue was extracted with hexane (120 ml). Centrifugation of the solution followed by recrystallization from hexane gave a yellow crystals of Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl\}(3-trimethylsilylcyclopentadienyl)$SmCl_2Li(THF)_2$. Yield : 2.78 g (3.47 mmol) in one crop, 47.1 %.

Preparation of Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl\}(3-tert-butylcyclopentadienyl)$SmCH(TMS)_2$. A ether solution of 0.67 M $LiCH(trimethylsilyl)_2$ (7.0 ml, 4.69 mmol) was added to a solution Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl\}(3-trimethylsilylcyclopentadienyl)$SmCl_2Li(THF)_2$ (2.78 g, 3.47 mol) in toluene (100 ml) at 0 °C and the mixture was stirred for 24 hours at room temperature. After the removal of toluene, the residue was extracted with hexane (100 ml). Centrifugation followed by recrystallizion from hexane gave orange crystals of Me_3Si{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl}(3-trimethylsilylcyclopentadienyl)$SmCH(TMS)_2$. Yield : 1.41 g (1.91 mmol) in one crop, 55.0 %.

Preparation of 2,7-di-tert-butylfluorene. To a solution of fluorene (34 g, 0.20 mol) and 2,6-di-tert-butyl-p-cresol (44 g, 0.30 mol) in nitromethane (300 ml) was added a solution of aluminium chloride (40 g, 0.30 mol) in nitromethane (60 ml) over a period of 30 minutes at room temperature. The reaction mixture was stirred for 15 minutes and poured into a large amount of ice water (500 ml). The solution was extracted with ether (150 ml, twice) and washed with 10% NaOH aqueous solution (100 ml, twice). Then organic layer was dried over Na_2SO_4, and evaporated in vacuo. The residue was recrystallized from ethanol to give green powder of 2,7-di-tert-butylfluorene (24.0 g, 0.089 mol). Yield : 43 %.

Preparation of Me_2C(cyclopentadiene)(2,7-di-tert-butylfluorene). A hexane solution of 1.61 M n-butyllithium (46 ml, 0.075 mol) was added to a solution 2,7-di-tert-butylfluorene (18.9 g, 0.068 mol) in tetrahydrofuran (150 ml) at 0 °C. The reaction mixture was stirred at room temperature for 8 hours, and then after cooling to -78 °C 6,6-dimethylfuluvene (9.0 ml, 0.075 mol) was dropwise added taking over 20 minutes. The mixture was allowed to warm to room temperature with stirring. The solvent was removed in vacuo, and water (500 ml) was added to the residue. After extracting with ether (200 ml, twice), the ether layer was washed with water (200 ml, twice) and dried over Na_2SO_4. After the removal of solvent in vacuo, the residue was recrystallized from chloroform/methanol to give pink powder of Me_2C(cyclopentadiene)(2,7-di-tert-butylfluorene) (8.19 g, 0.021 mol). Yield : 31.4 %.

Preparation of Me_2C(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)$YCl_2Li(THF)_2$. A hexane solution of 1.61 M n-butyllithium (17.5 ml, 0.028 mol) was added to a solution Me_2C(cyclopentadiene)(2,7-di-tert-butylfluorene) (5.07 g, 0.013 mol) in tetrahydrofuran (100 ml) at 0 °C, and the mixture was stirred at room temperature for 8 hours. Then the solution was dropwise added to YCl_3 (2.83 g, 0.015 mol) in tetrahydrofuran (100 ml), and the mixture was refluxed for 12 hours. After the solvent was removed in vacuo, the brown residue was extracted with hexane. Recrystallization from hexane gave a yellow powder of Me_2C(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)$YCl_2Li(THF)_2$. Yield : 31.2 %.

Preparation of Me_2C(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)$YCH(TMS)_2$. A ether solution of 0.75 M $LiCH(TMS)_2$ (6.6 ml, 4.94 mmol) was added to a solution Me_2C(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)$YCl_2Li(THF)_2$ (2.85 g, 4.12 mol) in toluene (150 ml) at 0 °C and stirred for 12 hours under the same conditions. After the removal of toluene, the red residue was extracted with hexane. Recrystallization from hexane gave red powder of Me_2C(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)$YCH(TMS)_2$. Yield : 19.2 %.

Polymerization of methyl methacrylate catalyzed by Me_2C(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)$YCH(TMS)_2$. A catalyst Me_2C(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)$YCH(TMS)_2$ (23.3 mg, 0.0365 mmol) was dissolved in 19 ml of toluene. To the solution was added 1.0 ml of methyl methacrylate at 0 °C

with vigorous magnetic stirring. The stirring was continued for 3 hours at 0 °C. The reaction mixture was quenched with 200 ml of methanol, to give white powder of poly(methyl methacrylate).

Polymerization of methyl methacrylate catalyzed by Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl\}(3-tert-butylcyclopentadienyl)$SmCH(TMS)_2$. A catalyst Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl\}(3-tert-butylcyclopentadienyl)$SmCH(TMS)_2$ (49.7 mg, 0.67 mmol) was dissolved in 10 ml of toluene. To the solution was added 0.85 ml of methyl methacrylate at 0 °C with vigorous magnetic stirring. The stirring was continued for 12 hours at 0 °C. The reaction mixture was quenched with excess of methanol/hexane, and white powder of poly(methyl methacrylate) was obtained.

Polymerization of methyl methacrylate catalyzed by Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl\}(3-tert-butylcyclopentadienyl)SmH. A catalyst Me_3Si\{4-(tert-butyldimethylsilyl)-2-(trimethylsilyl)cyclopentadienyl\}(3-tert-butylcyclopentadienyl)$SmCH(TMS)_2$ (30.0 mg, 0.41 mmol) was dissolved in 10 ml of toluene. The solution was degassed and charged with H_2, and stirred there for 1 hour. The color of the solution changed from orange to yellow. The solution was added to 0.85 ml of methyl methacrylate at 0 °C with vigorous magnetic stirring. The stirring was continued for 12 hours at 0 °C. Finally, the reaction mixture was quenched with excess of methanol/hexane to provide white powder of poly(methyl methacrylate).

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Chapter 5

Living Polymerization of Trimethylsilyl Substituted Methacrylate Catalyzed by Organo Rare Earth Metal Complexes

Introduction

In 1982, Nakahama et al. found the anionic living polymerization of tert-butyldimethylsilyl substituted 4-vinylphenol. In this case, monodispersed poly(4-vinylphenol) ($M_w/M_n < 1.1$) was obtained quantitatively upon hydrolysis of silyl group. This is the first example of anionic living polymerization of the functional monomer, which is generally very difficult by conventional method[1].

In a similar manner, poly(methacrylic acid) and poly(hydroxyethyl methacrylate) have been prepared by the polymerization of their protected monomer ($CH_2=CMeCOOSiMe_3$ and $CH_2=CMeCOOCH_2CH_2OSiMe_3$) followed by hydrolysis (deprotection). However, stereoselective polymerization of these monomers has not been achieved so far. Judging from the result of methyl methacrylate polymerization by rare earth metal complexes[2], the initiating system would be expected to polymerize the

protected methacrylate monomers stereoselectively. Physical properties of stereoregulated water soluble polymers thus obtained may be interesting from an industrial point of view.

In this chapter, rare earth metal complexes were applied to the polymerization of various protected methacrylate monomers.

Results and Discussion

Rare Earth Metal Initiated Polymerization of Trimethylsilyl Methacrylate. Polymerization of trimethylsilyl methacrylate (TMSMA) was examined first. Table 1 shows the result of the polymerization catalyzed by $SmMe(C_5Me_5)_2(THF)$ and $[SmH(C_5Me_5)_2]_2$. The product was obtained as a water soluble poly(methacrylic acid) by the treatment with methanol. Both the initiators afforded poly(methacrylic acid) with narrow molecular weight distribution in good yield. Figure 2 shows the relationship between M_n and M_w/M_n against conversion. M_n increases linearly with the conversion retaining M_w/M_n value below 1.10. These results indicated that the polymerization of TMSMA by rare earth metal initiators proceeded in a living manner. Furthermore, TMSMA was polymerized stereoselectively affording highly syndiotactic poly(methacrylic acid) (rr ≥ 90%). The stereoselectivity was calculated from the peak intensity ratio in carbonyl region of ^{13}C-NMR spectrum (Figure 3).

From the above results, it is obvious that the mechanism of polymerization here is quite similar to that of methyl methacrylate polymerization. As shown in Figure 1, the reaction is estimated to proceed through an 8 membered cyclic intermediate, which is the origin of the high stereoselectivity.

Table 1. Polymerization of Trimethylsilyl Methacrylate Initiated by Organosamarium(III) Complexes[a)]

initiator	time(h)	$10^{-4}M_n$	M_w/M_n	conversion,%
$[SmH(C_5Me_5)_2]_2$	1	1.33	1.05	27.6
	6	4.67	1.11	96.5
$SmMe(C_5Me_5)_2(THF)$	0.5	2.45	1.03	10.3
	1	1.33	1.05	27.6
	2	4.55	1.06	42.9

a)Reaction conditions: initiator concentration, 1.0 mol% of monomer; solvent, toluene.

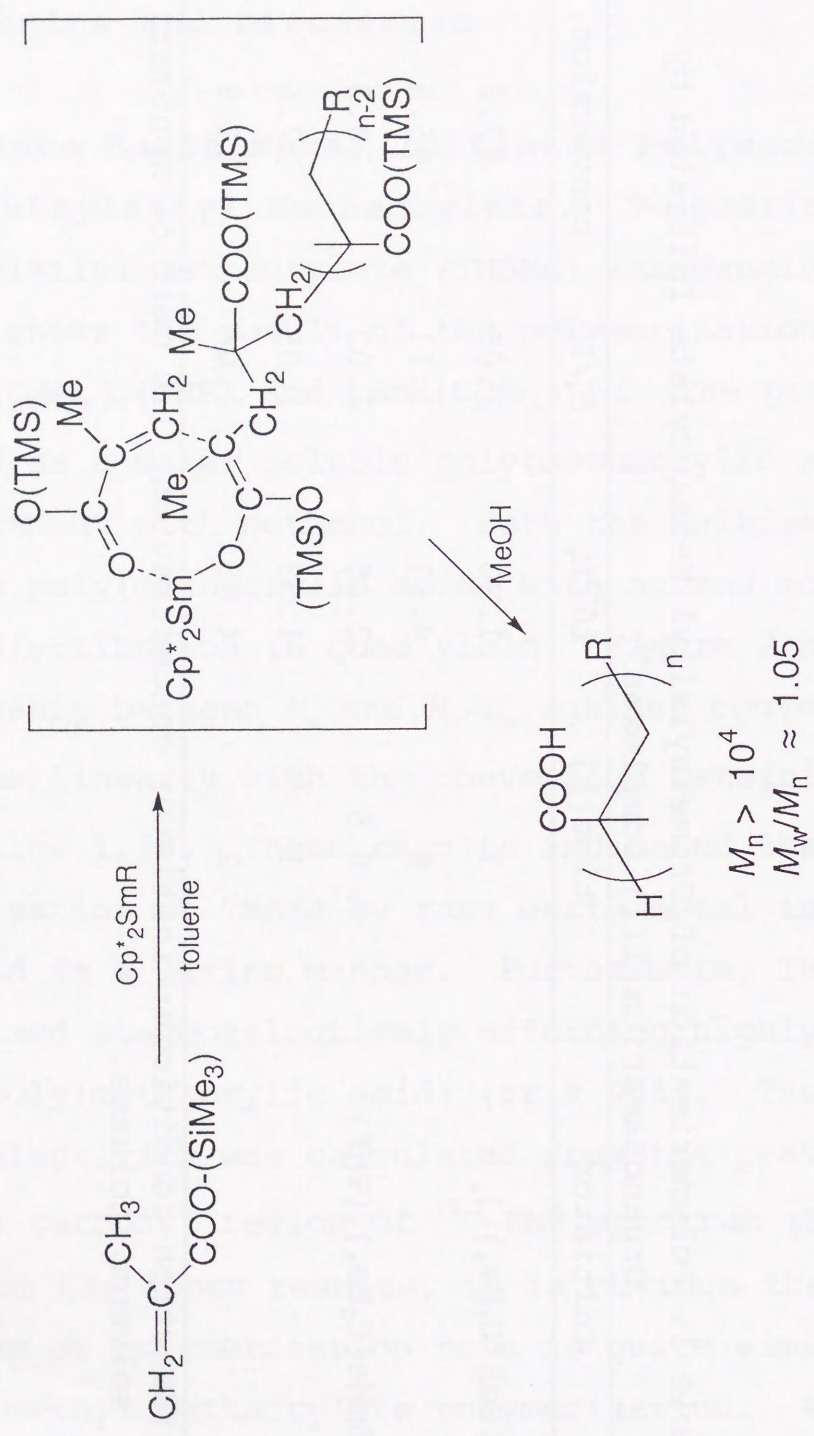

Fig. 1 Polymerization of trimethylsilyl methacrylate.

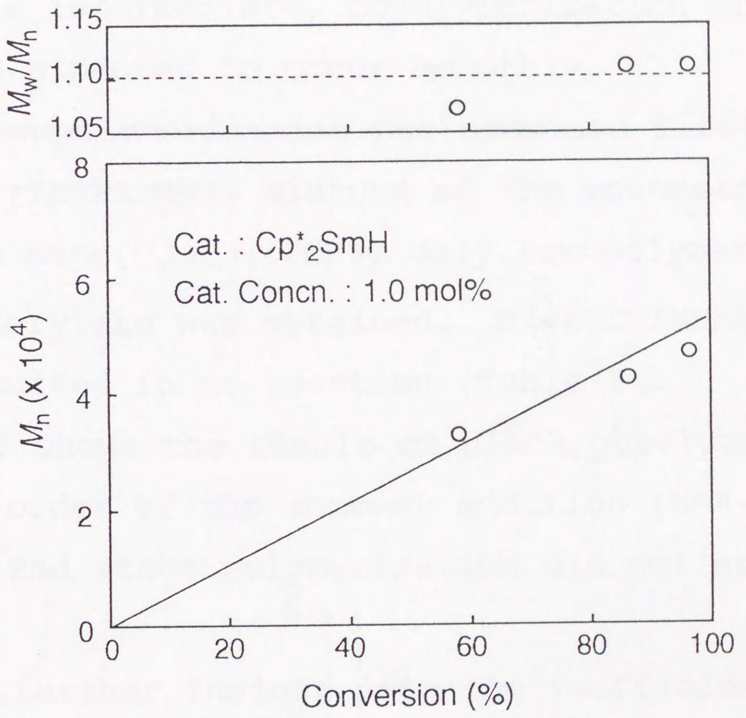

Fig. 2 Conversion vs. M_n and M_w/M_n of poly(methacrylic acid) generated by polymerization of trimethylsilyl methacrylate.

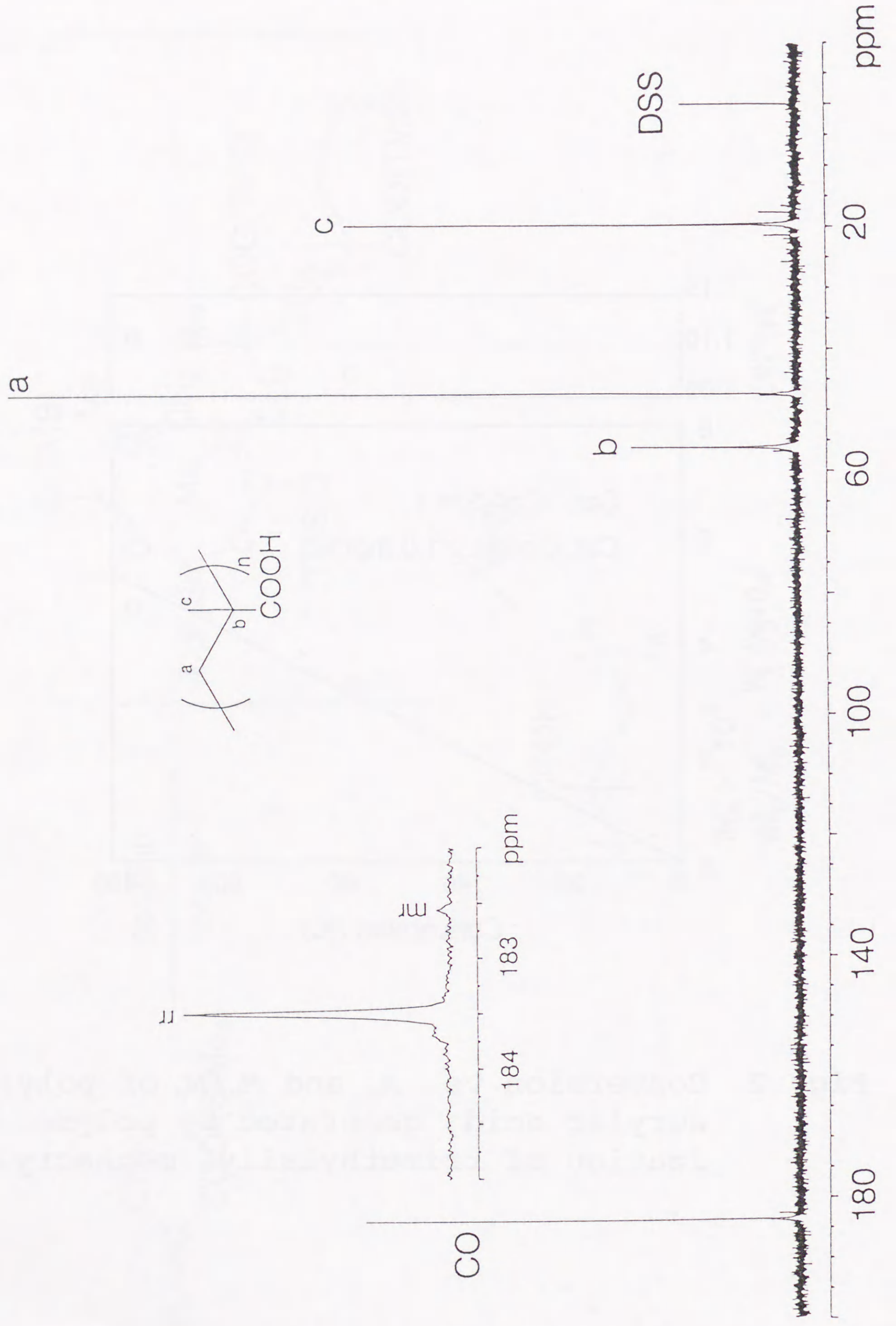

Fig. 3 ^{13}C NMR spectrum of poly(methacrylic acid) generated by polymerization of trimethysilyl methacrylate.

Block and Random Copolymerization of Trimethylsilyl Methacrylate and Methyl Methacrylate Catalyzed by SmMe(C_5Me_5)$_2$(THF). Since polymerizations of both TMSMA and methyl methacrylate by rare earth metal complexes proceeded through the similar metal enolate intermediate, copolymerization of these monomers was expected to occur smoothly.

Random copolymerization was examined first. When 1:10 to 1:3 (TMSMA:MMA) mixture of the monomers was reacted with SmMe(C_5Me_5)$_2$(THF), only homopolymer of methyl methacrylate was obtained. Higher TMSMA ratio than 1:3 resulted in no reaction (Table 2).

Table 3 shows the result of block copolymerization. In both the order of the monomer addition (MMA-TMSMA and TMSMA-MMA), 2nd stage polymerization did not start at all.

To get further insight into the inefficiency of the block copolymerization, I demonstrated the stoichiometric reaction at -78 °C between SmMe(C_5Me_5)$_2$(THF) and both methacrylates (TMSMA, MMA). Each sequential addition of the monomers in the order of TMSMA-MMA and MMA-TMSMA resulted in the formation of Sm(TMSMA)(MMA)Me and Sm(MMA)(TMSMA)Me, which decomposed upon hydrolysis to afford $CH_3CH(COOH)CH_2C(CH_3)(CH_2Me)(COOCH_3)$ and $CH_3CH(COOCH_3)CH_2C(CH_3)(CH_2Me)(COOH)$, respectively (Figure 4, 5). Thus, the addition of TMSMA to the active end of Sm-(MMA)Me and the addition of MMA to the Sm(TMSMA)Me

Table 2. Random Copolymerization of Trimethylsilyl Methacrylate and Methyl Methacrylate Initiated by $SmMe(C_5Me_5)_2(THF)$[a)]

TMSMA/MMA ratio	time(h)	$10^{-4}M_n$	M_w/M_n	conversion,%	MA content,%
1/1	15	-	-	-	-
1/2	15	-	-	-	-
1/3	5	7.73	1.17	58.3	0
1/5	5	3.31	1.11	75.2	0
1/10	5	2.12	1.21	96.2	0

a)Reaction conditions: initiator concentration, 1.0 mol% of monomer; polymn. temp., -78°C; solvent, toluene.

Table 3. Block Copolymerization of Trimethylsilyl Methacrylate (TMSMA) with Methyl Methacrylate(MMA)[a)]

A-B monomer	A $10^{-4}M_n$	A (M_w/M_n)	A-B $10^{-4}M_n$	A-B (M_w/M_n)	A/B ratio
MMA-TMSMA	1.14	(1.05)	1.14	(1.04)	-
	2.27	(1.04)	2.31	(1.03)	-
	5.69	(1.04)	5.65	(1.03)	-
TMSMA-MMA	3.72	(1.21)	3.75	(1.20)	-
	3.84	(1.18)	3.80	(1.19)	-

a)Reaction conditions: initiator, $SmMe(C_5Me_5)_2(THF)$; initiator concentration, 1.0 mol% of monomer; [premonomer]/[comonomer] = 1/1, solvent, toluene.

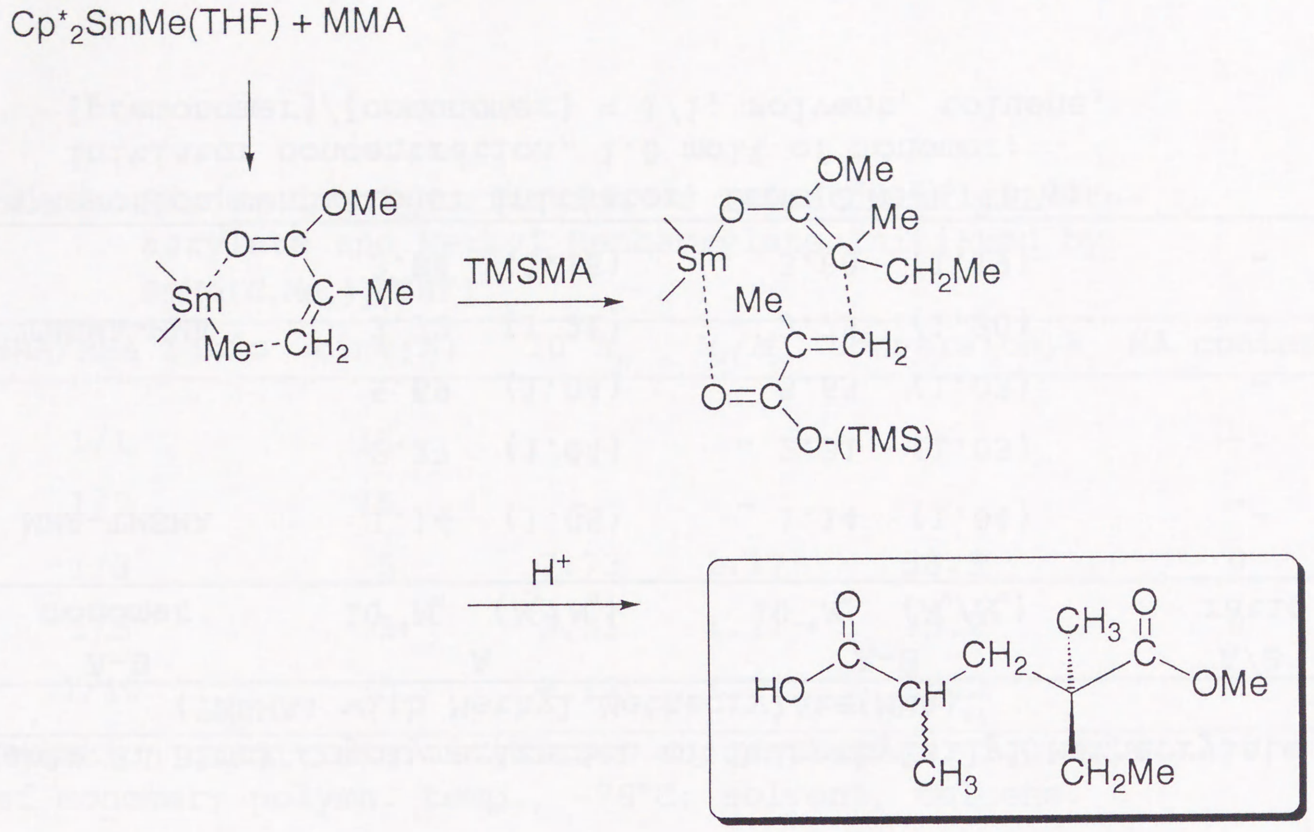

Fig. 4 Stoichiometric reaction of $SmMe(C_5Me_5)_2(THF)$ with methyl methacrylate and trimethylsilyl methacrylate.

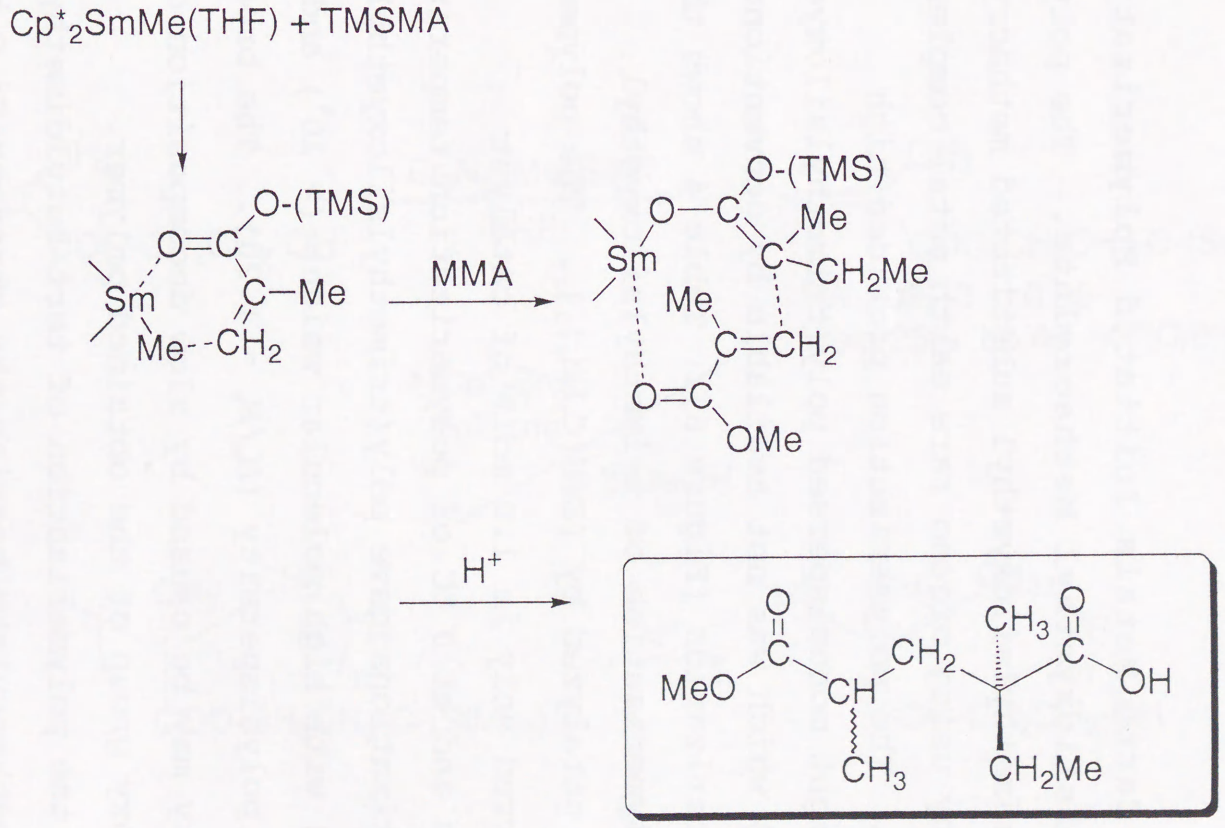

Fig. 5 Stoichiometric reaction of $SmMe(C_5Me_5)_2(THF)$ with trimethylsilyl methacrylate and methyl methacrylate.

end occurred in the stoichiometric reaction, though copolymerization between these monomers did not occur.

Rare Earth Metals Initiated Polymerization of Trimethylsiloxyethyl Methacrylate. The polymerization of trimethylsiloxyethyl substituted methacrylate could occur by using organo rare earth metal complexes as initiator. The polymerization provided high molecular weight monodispersed poly(trimethylsiloxyethyl methacrylate) which was not available by conventional anionic polymerization (Figure 6). Table 4 shows the result of polymerization of trimethylsiloxyethyl methacrylate catalyzed by $[SmH(C_5Me_5)_2]_2$. The polymerization occurred only in 1.0 mol% of catalyst concentration and at 0 °C of polymerization temperature. These polymerizations gave poly(trimethylsiloxyethyl methacrylate) with high molecular weight ($> 10^4$) and rather broad polydispersity ($M_w/M_n \approx 1.20$). The broad polydispersity may be caused by slow decomposition of trimethylsiloxy group of the obtained polymer. Accordingly, the polymerization of tert-butyldimethylsiloxyethyl methacrylate bearing the stronger Si-O bond was demonstrated. However, polymerization of this monomer was not initiated by $[SmH(C_5Me_5)_2]_2$, which might be ascribed to the steric effect of the bulky tert-butyldimethylsilyl group.

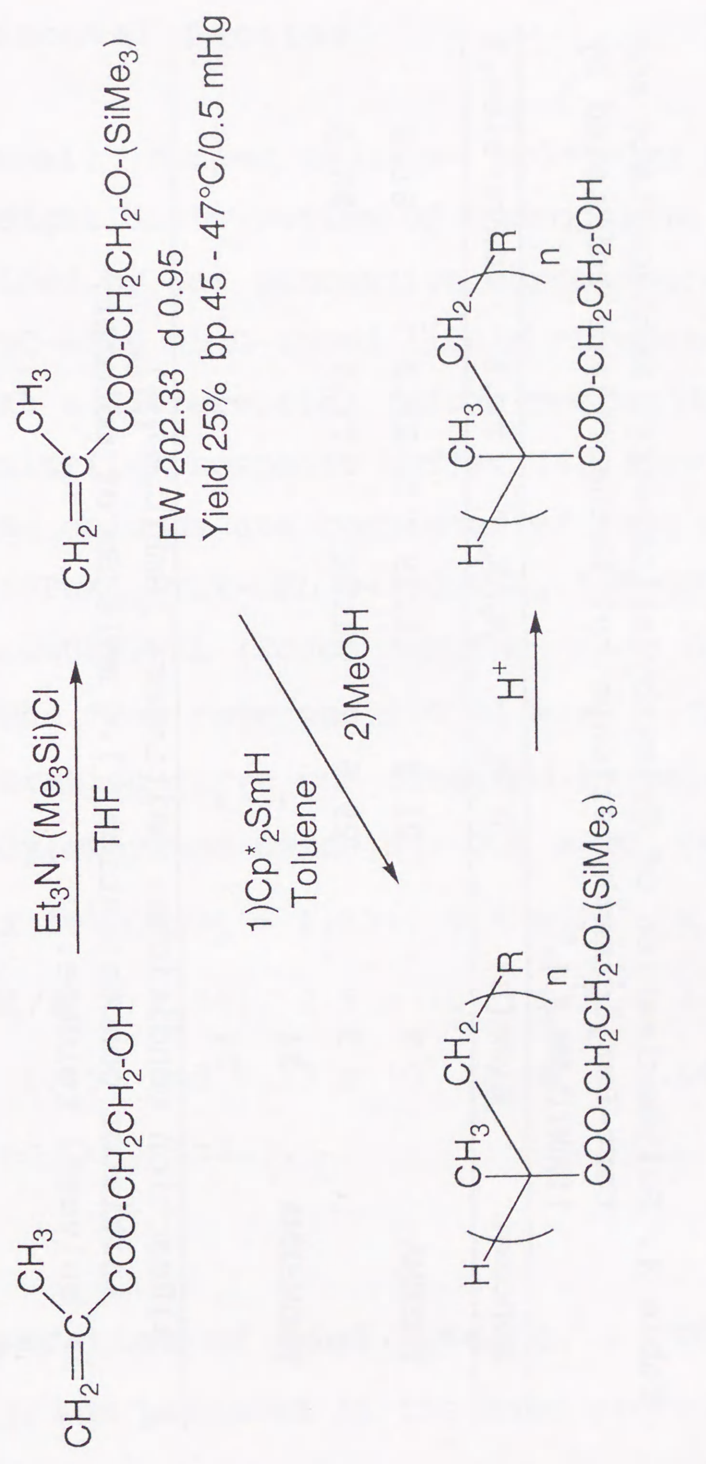

Fig. 6 Synthesis and polymerization of trimethylsiloxyethyl methacrylate.

Table 4. Polymerization of Trimethylsilyloxyethyl Methacrylate and tert-Butyldimethylsilyloxyethyl Methacrylate Initiated by $[SmH(C_5Me_5)_2]_2$ [a)]

monomer	time(h)	$10^{-4}M_n$	M_w/M_n	rr,%	conversion,%
TMSEMA	3	21.2	1.19	81.2	81.8
	3	29.5	1.24	77.3	80.3
TBDMSEMA	24	-	-	-	-
	24	-	-	-	-

a)Reaction conditions: initiator, $[SmH(C_5Me_5)_2]_2$; initiator concentration, 1.0 mol% Sm of monomer; solvent, toluene.

Experimental Section

General. Number averaged molecular weight and molecular weight distribution of hydrophilic polymers were determined by gel permeation chromatography (GPC) on a Tosoh SC-8010 high-speed liquid chromatograph equipped with a differential refractometer detector, using acetonitrile/phosphate buffer (4/1) as a eluent at 40.0 °C. The columns are consisted of four columns: TSK-GEL G3000PWXL, TSK-GEL G4000PWXL, TSK-GEL G5000PWXL and TSK-GEL G6000PWXL (Tosoh Manufacturing Co., Ltd.) was used. The flow rate was 1.0 ml min^{-1}. The molecular weight calibration curve was obtained by using TSK Standard Poly(ethylene oxide)s : 2.6×10^4 (M_w/M_n = 1.20), 4.6×10^4 (M_w/M_n = 1.10), 9.5×10^4 (M_w/M_n = 1.04), 1.7×10^5 (M_w/M_n = 1.04), 2.5×10^5 (M_w/M_n = 1.04), 5.1×10^5 (M_w/M_n = 1.05) and 9.13×10^5 (M_w/M_n = 1.08) (Tosoh Manufacturing Co., Ltd.).

Preparation of $[SmH(C_5Me_5)_2]_2$[3)]. The complex, $[SmH(C_5Me_5)_2]_2$ was prepared in the same procedure as described in chapter 2.

Preparation of $SmMe(C_5Me_5)_2(THF)$[4]. The complex, $SmMe(C_5Me_5)_2(THF)$ was prepared in the same procedure as described in chapter 2.

Preparation of trimethylsiloxyethyl methacrylate. Hydroxyethyl methacrylate (24.3 ml, 200 mmol) was added with stirring to a solution of triethyl amine (55.8 ml, 400 mmol) in THF (150 ml) at room temperature under Ar. Stirring was continued for 10 minutes under the same conditions. Trimethylsilyl chloride (38.1 ml, 300 mmol) was added with stirring at 0°C and the mixture was stirred for 24 hours at room temperature. The mixture was quenched by water and then extracted by hexane. The solution was concentrated in vacuo to produce trimethylsiloxyethyl methacrylate in 79.1 % yield [bp. 57.5 °C/1.0 mmHg].

Preparation of tert-butyldimethylsiloxyethyl methacrylate. Hydroxyethyl methacrylate (36.5 ml, 300 mmol) was added with stirring to a solution of triethyl amine (55.8 ml, 400 mmol) in THF (180 ml) at room temperature under Ar. Stirring was continued for 10 minutes under the same conditions. Tert-butyldimethylsilyl chloride (50 g, 331 mmol) was added with stirring at 0 °C and the mixture was refluxed for 7

hours and stirred at room temperature for 8 hours. The mixture was quenched by water and then extracted by hexane. The solution was concentrated in vacuo to give tert-butyldimethylsiloxyethyl methacrylate in 65.6% yield [bp. 60.7-61.7 °C/0.3 mmHg].

Polymerization of trimethylsilyl methacrylate catalyzed by $SmMe(C_5Me_5)_2(THF)$. A toluene solution of $SmMe(C_5Me_5)_2(THF)$ (0.051 g, 0.1 mmol) was added to a toluene solution of 100 equivalent trimethylsilyl methacrylate (1.79 ml, 10 mmol) at -78°C. After stirring for several hours the solution was quenched with excess methanol.

Polymerization of trimethylsiloxyethyl methacrylate catalyzed by $SmMe(C_5Me_5)_2(THF)$. A toluene solution of $[SmH(C_5Me_5)_2]_2$ (0.042 g, 0.05 mmol) was added to a toluene solution of 100 equivalent trimethylsilyl methacrylate (1.79 ml, 10 mmol) at -78°C. After stirring for several hours the solution was quenched with excess methanol.

Polymerization of tert-butyldimethylsiloxyethyl methacrylate catalyzed by $[SmH(C_5Me_5)_2]_2$. A toluene solution of $[SmH(C_5Me_5)_2]_2$ was added to a toluene solution of 200 equivalent tert-butyldimethylsiloxyethyl methacrylate at -78, 0 and 60 °C. After stirring for 3, 6, and 24 hours the solution was quenched by excess methanol.

Block copolymerization of methyl methacrylate with trimethylsilyl methacrylate catalyzed by $SmMe(C_5Me_5)_2(THF)$. Methyl methacrylate (2.14 ml, 20 mmol) was added to the toluene solution (20 ml) of $SmMe(C_5Me_5)_2(THF)$ (0.025 g, 0.05 mmol) at 0°C with vigorous magnetic stirring. The stirring was continued for 2 hours. A half of the reaction mixture was taken out and poured into methanol. The precipitated poly (Methyl methacrylate) was collected by filtration and dried in vacuum. To the rest of the mixture was added trimethylsilyl methacrylate (1.79 ml, 10 mmol) at 0°C. The stirring was continued for 4 hours, and the reaction was terminated by pouring the reaction mixture into methanol. The resulting polymer was dried under reduced pressure.

Random copolymerization of methyl methacrylate with trimethylsilyl methacrylate catalyzed by $SmMe(C_5Me_5)_2(THF)$. A toluene solution

(1.0 ml) of $SmMe(C_5Me_5)_2(THF)$ (0.051 g, 0.1 mmol) was added to a mixture of methyl methacrylate and trimethylsilyl methacrylate (1:1, 2:1, 3:1, 5:1, 10:1 molar ratio, amounts of monomer: 20 mmol) dissolved in toluene (20 ml) with vigorous stirring at -78°C. The stirring was continued for several hours (5, 6 or 15 hours), and the reaction mixture was poured into excess methanol. The resulting polymer was dried under reduced pressure.

Equimolar Reaction of $SmMe(C_5Me_5)_2(THF)$ with methyl methacrylate and trimethylsilyl methacrylate. Methyl methacrylate (0.071 ml, 0.66 mmol) was added to a stirred solution of $SmMe(C_5Me_5)_2$ (THF) (0.42 g, 0.83 mmol) in 20 ml of tetrahydrofuran at -78 °C and then trimethylsilyl methacrylate (0.148 ml, 0.83 mmol) was added and the mixture was allowed to react at room temperature. After stirring for 10 minutes the color of the solution changed from yellow-orange to pale yellow. A few drops of aqueous HCl solution was added to the solution (the color of the solution changed pale-yellow) and white precipitate was generated. After extraction with chloroform and concentration of the product, the resulting product was seperated by gas chromatograph.

Equimolar Reaction of SmMe(C_5Me_5)$_2$(THF) with trimethylsilyl methacrylate and methyl methacrylate. Trimethylsilyl methacrylate (0.11 ml, 0.61 mmol) was added to a stirred solution of SmMe(C_5Me_5)$_2$(THF) (0.390 g, 0.767 mmol) in 20 ml of tetrahydrofuran at -78 °C and then methyl methacrylate (0.082 ml, 0.76 mmol) was added and the mixture was allowed to react at room temperature. After stirring for 10 minutes the color of the solution changed from yellow-orange to pale yellow. A few drops of HCl aqueous solution was added to the solution (the color of the solution changed pale-yellow) and white precipitate was generated. After extraction with chloroform and concentration of the product, the resulting product was seperated by gas chromatograph.

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LIST OF PUBLICATIONS

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