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RARE EARTH METAL-INITIATED POLYMERIZATIONS OF POLAR AND NONPOLAR MONOMERS

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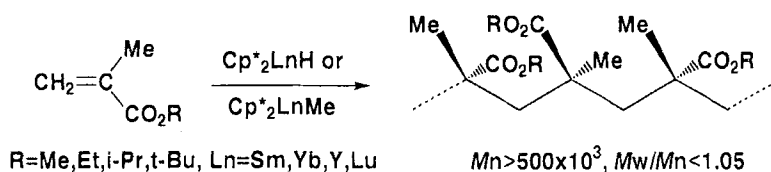
ABSTRACT

Organolanthanide(III) initiated polymerization of methyl methacrylate gave both syndiotactic and isotactic living polymers of high molecular weight. Organolanthanide(III) initiated polymerization of alkyl acrylates also gave high molecular weight poly(alkyl acrylate)s with very narrow molecular weight distribution in high yield. Molecular weights of the resulting polymers increased linearly with the conversion. Random and block copolymerizations of alkyl acrylates with methyl methacrylate were realized successfully. For the sake of development of the olefin polymerization catalyst, bulky substituents were introduced into Me_2Si bridged Cp rings and they were used as ligands for the lanthanide complexes. Tri- and divalent lanthanide complexes with such ligands showed high activity for olefin polymerization and gave high molecular weight polyolefins.

INTRODUCTION

Organolanthanide initiated living polymerization of alkyl methacrylate by the use of Cp^*SmH or Cp^*SmMe (THF) as initiator was found to give high molecular weight ($M_n > 400,000$) poly(methyl methacrylate) (Poly(MMA)) with

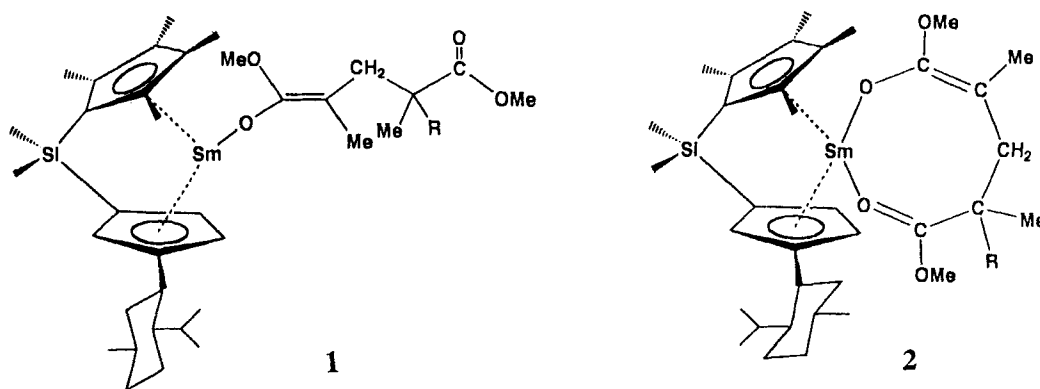
extremely narrow molecular weight distribution ($M_w/M_n < 1.05$) in high yield [1]. Furthermore, this system gave high syndiotactic poly(MMA) ($rr = 95.3\%$) when the polymerization was carried out at -95°C . We have succeeded in isolating the 1:2 adduct of Cp^*_2SmH with MMA, whose structure was determined by X-ray analysis [2]. The complex has a 8-membered cyclic structure, in which one of the terminal ends is samarium-enolate and the other end is ester group coordinated to Sm. The addition of MMA (100 equiv) to this complex resulted in the formation of poly(MMA) of $M_n = 10500$ ($M_w/M_n = 1.03$) in high yield, to indicate that the isolated complex is the real active species.



In general, living polymerizations of alkyl acrylates have been hampered due to termination reactions involving nucleophilic attack by the α -carbon. Group transfer polymerization of ethyl acrylate provided living polymers when ZnI_2 was used as a catalyst ($M_n = 3300$, $M_w/M_n = 1.03$) [3]. Aluminum/porphyrin initiator systems also give a living polymer of *t*-butyl acrylate ($M_n = 12200$, $M_w/M_n = 1.13$) [4]. More recently, organosamarium complexes, such as $(\text{C}_5\text{Me}_5)_2\text{Sm}$ and $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\eta^3\text{-CH}_2\text{CHCH-})]_2$, are reported to serve as good initiators for polymerization of methyl acrylate ($M_n = 20000$, $M_w/M_n = 1.1$) [5]. We describe herein the use of $\text{SmMe}(\text{C}_5\text{Me}_5)_2(\text{THF})$ and $\text{YMe}(\text{C}_5\text{Me}_5)_2(\text{THF})$ as efficient initiators for the living polymerization of alkyl acrylates [6].

The well-defined homogeneous Ziegler-Natta olefin polymerization systems include, 1) highly active two component catalysts consisting of "methylalumoxane" in combination with Group 4 metallocene derivatives which may exhibit remarkable iso- or syndio-specificities in propylene polymerization with suitable modification of the cyclopentadienyl ligand, [7] and, 2) single component catalysts such as cationic group 4 metallocene alkyls, although their activities are lower than those of the methylalumoxane containing systems [8]. More recently, neutral group 3 lanthanide metallocene hydrides or metallocene alkyls have attracted much attention since these systems are active even in the absence of "methylalumoxane". For example, $[\text{rac-Me}_2\text{Si}(2\text{-SiMe}_3\text{-4-}t\text{Bu-C}_5\text{H}_2)_2\text{YH}]_2$ shows the good catalysis by itself for isospecific polymerization of propylene ($M_n = 4200$, $M_w/M_n = 2.32$) [9] and 1-olefins ($M_n > 20000$, $M_w/M_n > 1.75$). $[(\text{C}_5\text{Me}_4)\text{SiMe}_2(\eta\text{-N-}t\text{Bu})\text{Sc}(\mu\text{-H})]_2$ also catalyzes the iso-specific polymerization of 1-olefins ($M_n > 6500$, $M_w/M_n >$

1.5) [10]. However, simpler organolanthanide complexes such as $\text{LnH}(\text{C}_5\text{Me}_5)_2$ ($\text{Ln}=\text{La}, \text{Nd}$) are completely inert for polymerization of 1-olefins although these are active for polymerization of ethylene ($M_n > 590000$, $M_w/M_n < 2.03$). Among divalent organolanthanide species, only $\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{THF})$ is known to be active for polymerization of ethylene but the upper limit of the molecular weight is 24600 ($M_w/M_n = 2.28$). This paper deals with systematic studies on the catalytic action of racemo, meso and C_1 symmetric organolanthanide(II) complexes towards polymerization of ethylene and 1-olefins [11].



Isotactic Polymerizations of Methyl Methacrylate

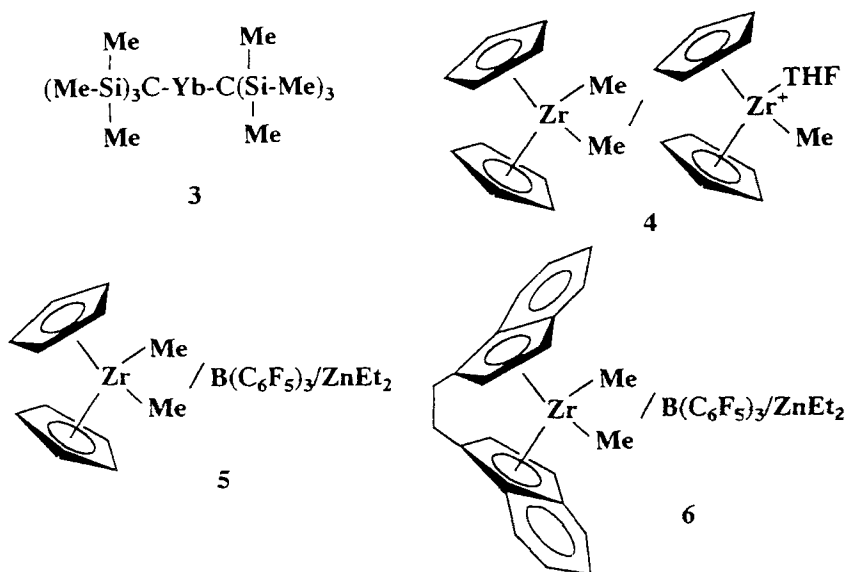
Recently, isotactic polymerization of methyl methacrylate (MMA) has been achieved ($mm = 94\%$, $M_n = 134 \times 10^3$, $M_w/M_n = 6.7$) by using $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_3\text{-}1\text{S},2\text{S},5\text{R-neomenthyl})\text{LaR}$ (**1**) [$\text{R} = \text{CH}(\text{SiMe}_3)_2$ or $\text{N}(\text{SiMe}_3)_2$], while $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_3\text{-}1\text{S},2\text{S},5\text{R-menthyl})\text{LnR}$ (**2**) [$\text{Ln} = \text{Lu}, \text{Sm}$; $\text{R} = \text{CH}(\text{SiMe}_3)_2$ or $\text{N}(\text{SiMe}_3)_2$] produce the syndiotactic poly(MMA) ($rr = 69\%$, $M_n = 177 \times 10^3$, $M_w/M_n = 15.7$) as shown in Table 1 [12]. One of the possible explanations for these reactions is that the menthyl complex produces syndiotactic polymer via a cyclic 8-membered intermediate, while neomenthyl complex produces the isotactic polymer via a noncyclic intermediate. Therefore, we can conclude that stereoregularity of polymer is determined by subtle difference of the steric bulk of complexes. In fact, isotactic polymerization of MMA ($mm = 84\%$) was realized by the use of non-metallocene system, $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{Yb}$ (**3**) [13].

In general, Ziegler-Natta catalysts such as $\text{TiCl}_4/\text{MgCl}_2/\text{AlR}_3$ and Kaminsky catalysts such as $\text{Cp}_2\text{ZrCl}_2/(\text{AlMe-O-})_n$ do not catalyze the polymerization of polar monomers such as MMA. However, a mixture of cationic species such as $\text{Cp}_2\text{ZrMe}(\text{THF})^+$ and Cp_2ZrMe_2 (**4**) have been found to catalyze the syndiotactic

TABLE 1. Living Polymerization of Methyl Methacrylate

initiator	temp. °C	$10^{-3}M_n$	obsd		tacticity		conversion, %
			M_w/M_n	rr	rm	mm	
1	-35	134	6.7	1	5	94	100
2	0	150	2.0	14	18	69	100
3	-78	15.5	1.3	7	9	84	100
4	0	90.5	1.2	1	1	98	100
5	0	482	1.38	80			64
6	0	232	1.78			80	38

polymerization of MMA (rr = 80%, $M_n = 120,000$, $M_w/M_n = 1.2-1.3$) [14]. More recently, syndio-rich polymerization of MMA was reported by using $Cp_2ZrMe_2/B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4/ZnEt_2$ (5) as catalyst and iso-rich polymerization by using $rac-Et(ind)_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$ (6) [15].



Living Polymerization of Alkyl Acrylates

Methyl acrylate (MeA), ethyl acrylate (EtA), *n*-butyl acrylate (nBuA), and *t*-butyl acrylate (tBuA) were polymerized with $SmMe(C_5Me_5)_2$ (THF) or $YMe(C_5Me_5)_2$ (THF) in toluene at 0°C, and the results are summarized in Table 2 [6]. The initiator efficiency exceeds 65% in every case except for the tBuA system, presumably due to its increased termination reaction because of the strong electronic

TABLE 2. Polymerization of Alkyl Acrylates Catalyzed by Organolanthanide Complexes at 0°C

initiator		obsd		calcd tacticity		conversion	initiator
		$10^{-3}M_w$	M_w/M_n	$10^{-3}M_n$	(rr%)	%	efficiency,%
SmMe(C ₅ Me ₅) ₂ (THF)	MeA	48	1.04	43	33	99	89
	EtA	55	1.04	50	51(rr+rm)	94	86
	nBuA	70	1.05	64	28	99	91
	tBuA	16	1.03	13	27	99	79
YMe(C ₅ Me ₅) ₂ (THF)	MeA	50	1.07	43	33	99	86
	EtA	53	1.05	50	47(rr+rm)	96	91
	nBuA	72	1.04	64	22	98	88
	tBuA	17	1.03	13	25	99	75

effect of the bulky substituent. One can conclude that polymerizations of MeA, EtA, and nBuA proceed in a living fashion, since the M_n of poly(nBuA) initiated by SmMe(C₅Me₅)₂ (THF) increases linearly with conversion, while M_w/M_n remains constant and narrow irrespective of the initiator concentration (Figure 1). The M_n of poly(MeA) and poly(EtA) was also linearly related to conversion when the initiator concentration was fixed at 0.2 mol% (Figure 2).

The apparent rate of polymerization is very fast, and it follows the order nBuA > EtA > MeA, while the order was reversed in the case of alkyl methacrylates, MMA > EtMA > nBuA. The observed apparent rates of polymerization for MeA, EtA, and nBuA at 0°C and -78°C are listed in Table 3. In order to further define the present initiator system, the effect of catalyst concentration on the polymerization was examined. When the initiator concentration was decreased from 0.1 to 0.02 mol% , one can obtain high molecular poly(EtA) of $M_n = 500,000$ with a very narrow molecular weight distribution ($M_w/M_n = 1.06$) (Figure 3).

To penetrate the initiation mechanism, the 1:1 or 1:2 reactions of SmMe(C₅Me₅)₂ (THF) with methyl acrylate and *t*-butyl acrylate were examined. Quenching of the 1:2 reaction mixture of SmMe(C₅Me₅)₂ (THF) and methyl acrylate gives CH₃CH₂^bCH(COOMe)CH₂^eCH(COOMe)H in 65-78% yield; i.e. the CH₂(b) signal absorb at 1.57 ppm and CH₂(e) signals at 1.8 ppm as revealed by the decoupling experiment. More efficient initiation was observed in the case of 1:2 reaction of *n*-butyl acrylate with SmMe(C₅Me₅)₂ (THF), which gives, upon hydrolysis, CH₃CH₂^bCH(COObu)CH₂^eCH(COObu)H in 96% at 0°C (Figure 4). These results agree with the result of hydrolysis of the 1:2 molar reaction of [SmH(C₅Me₅)₂]₂ with MMA. Therefore, we can readily estimate that polymerization is initiated by the addition of acrylate to an enolate species (Figure 5).

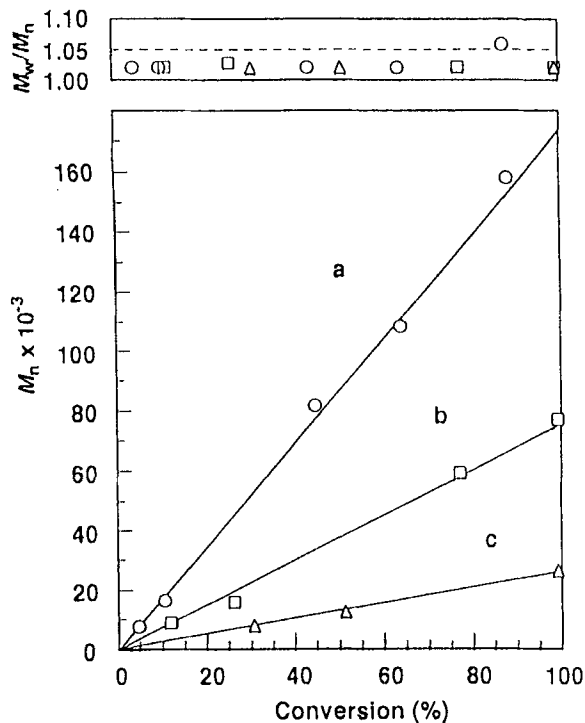


Figure 1. M_n and M_w/M_n vs. conversion plots for polymerization of nBuA. $\text{SmMe}(\text{C}_5\text{Me}_5)_2(\text{THF})$ concentration, a) 0.1, b) 0.2, c) 0.5 mol%.

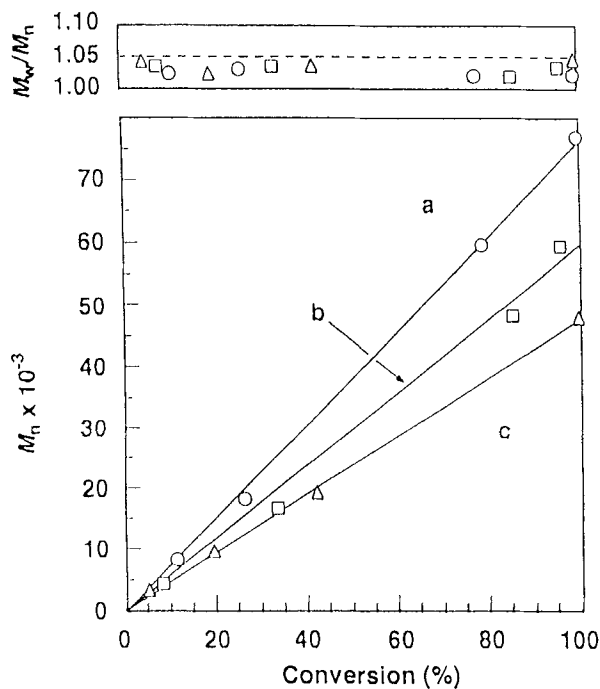


Figure 2. M_n and M_w/M_n vs. conversion plots for polymerization alkyl acrylate. Catalyst, 0.2 mol %. a) nBuA, b) EtA, c) MeA.

TABLE 3. Apparent Rate of Polymerization of Ethyl Acrylate

monomer	rate of polymerization, s-l	
	0°C	78°C
MeA	3.6	0.0001
EtA	130	0.05
nBuA	134	0.08

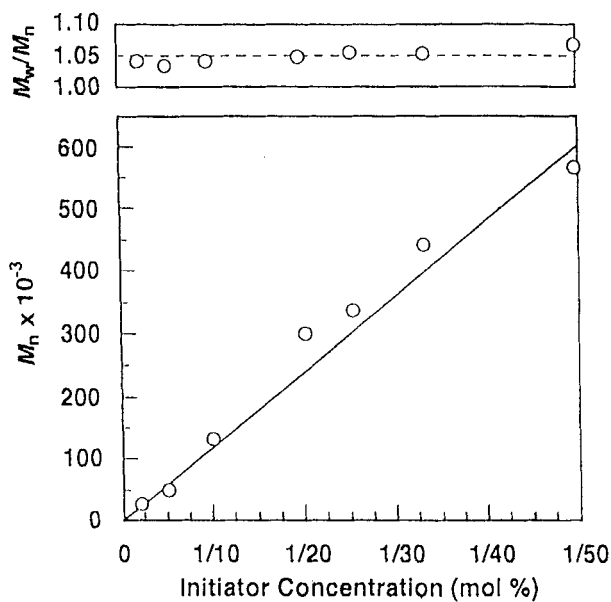


Figure 3. Effect of initiator concentration on the polymerization of ethyl acrylate.

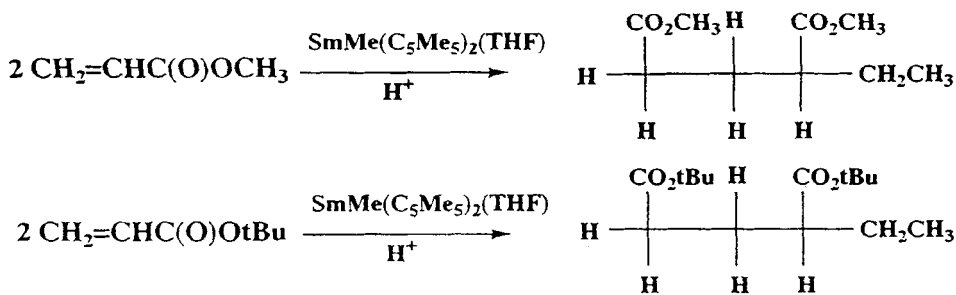


Figure 4. Hydrolysis product of the 1:2 adducts

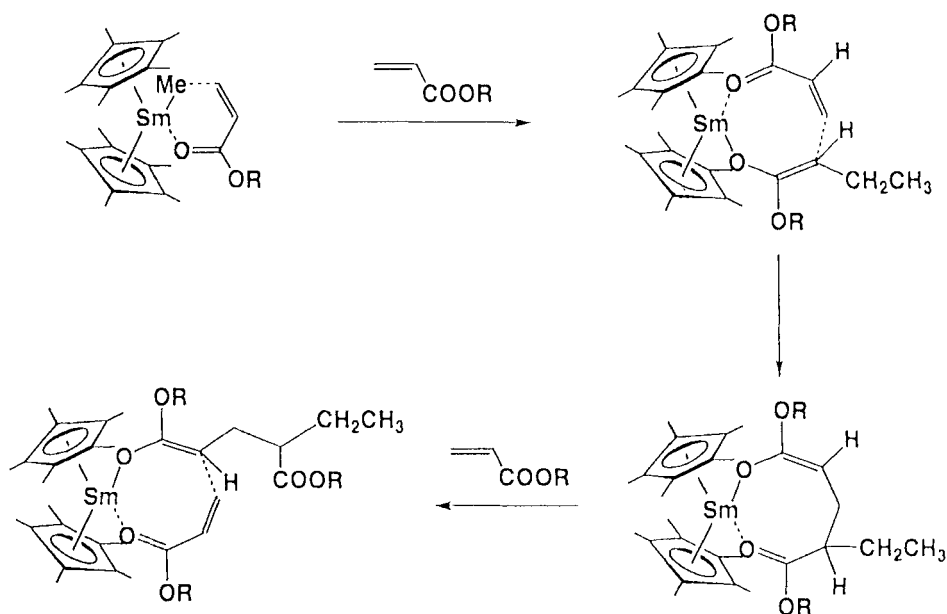


Figure 5. Proposed initiation mechanism for the polymerization of alkyl acrylate.

TABLE 4. Random Copolymerization of Alkyl Acrylate at 0°C

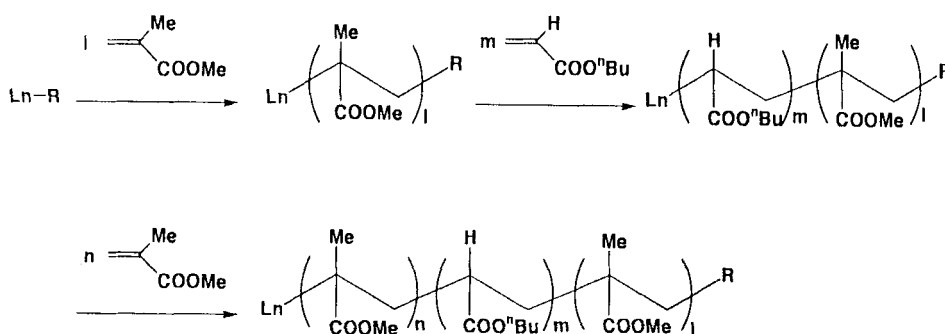
Monomers	$10^{-3}M_n$	M_w/M_n	Conversion	A/B ratio
MeA/EtA	53	1.04	99	51/49
MeA/nBuA	60	1.05	99	50/50
EtA/nBuA	65	1.05	99	50/50

The present system was found to conduct the living copolymerization of methyl acrylate with ethyl or *n*-butyl acrylate and also the copolymerization of ethyl acrylate with *n*-butyl acrylate. All systems gave high molecular weight polymers with narrow molecular weight distributions by polymerization at 0°C for 10 minutes (Table 4). The resulting copolymers are composed of equal amounts of each monomer when conversion reaches 99%. To understand the relative monomer reactivity, monomer reactivity ratios were determined using Fineman-Ross equation (Table 5). The monomer reactivity ratio of methyl acrylate is higher than that of ethyl acrylate but is nearly the same as that of *n*-butyl acrylate. In contrast to the acrylate systems, MMA exhibits much lower reactivity. Similarly, it has been

TABLE 5. Monomer Reactivity Ratio of Alkyl Acrylates

Monomers	r_1	r_2	$r_1 \times r_2$
MeA/EtA	0.959	0.597	0.573
MeA/nBuA	0.426	0.578	0.246
EtA/nBuA	0.535	0.834	0.446
MMA/MeA	0.015	19.9	0.284
MMA/EtA	0.008	15.9	0.133
MMA/nBuA	0.024	21.3	0.511

reported that methyl acrylate is much more reactive than MMA in anionic polymerization [$r_1(\text{MMA})=0.1$, $r_2(\text{MeA})=4.5$, initiator = NaNH_2], [16] while their reactivities are comparable in the radical initiating system using AIBN [$r_1(\text{MMA}) = 1.0$, $r_2(\text{MeA}) = 0.5$], [17]. Because of the different reactivities of MMA and alkyl acrylate in this initiating system, block copolymerization occurs preferentially even when a mixture of methyl methacrylate and methyl, ethyl or *n*-butyl acrylate was used.



ABA type triblock copolymers of MMA/nBuA/MMA should provide thermoplastic elastomers since MMA is a hard segment while nBuA is a soft segment, where the hard segment will act as a node and soft segments act as elastomers in the resulting network system. Thus, triblock copolymerization was conducted under the most suitable conditions; i.e. MMA was polymerized for 30 minutes, and nBuA was added at once. After completion of the polymerization of nBuA (2 minutes), MMA was again added. As a result, an ABA type triblock copolymers was formed together with AB type diblock copolymers in 1:0.2 ratio when THF was used as the polymerization solvent. Fortunately, however, we could fractionate the resulting copolymer with a mixture of CHCl_3 and hexane (1:3) as the ABA

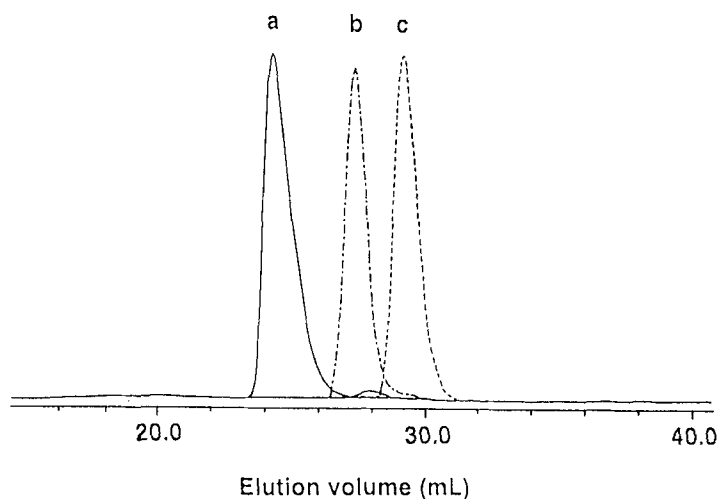


Figure 6. Gel permeation chromatograph of a) poly(MMA-*blo*-*n*BuA-*blo*-MMA) ($M_n = 144000$), b) poly(MMA-*blo*-*n*BuA) ($M_n = 36000$), and c) poly(MMA) ($M_n = 15000$).

TABLE 6. Mechanical Properties of Triblock Copolymers

Copolymer	Tensile Modulus MPa	Tensile Strength, MPa	Elongation %	Compression set at 77°C for 22 hours
poly(MMA/ <i>n</i> BuA/MMA) (20:47:33)	75	27	83	101
poly(MMA/ <i>n</i> BuA/MMA) (8:72:20)	0.8	0.7	163	58
poly(MMA/ <i>n</i> BuA/MMA) (6:92:3)	0.2	0.1	246	97
poly(MMA/EtA/EtMA) (26:48:26)	119	22	276	62

copolymer was insoluble and the AB copolymer dissolved. The resulting ABA type triblock is largely free from contamination by the AB copolymer (Figure 6). The mechanical properties of the resulting triblock copolymers were evaluated by several methods as shown in Table 6. Poly(MMA) has a large tensile modulus and large tensile strength but has very low elongation and low Izod impact strength. Furthermore, poly(MMA) does not show any decrease in compression set (typical rubber shows 20-30%). In sharp contrast to the properties of poly(MMA), the

TABLE 7. Characterization of Block Copoly(TMSMA/MMA)

feed ratio		poly(MMA)		poly(MMA/TMSMA)		yield, %
MMA	TMSMA	M_n	M_w/M_n	M_n	M_w/M_n	
50	33	5,100	1.08	10,400	1.35	99
200	132	16,600	1.04	40,500	1.36	98

TMSMA MMA		poly(TMSMA)		poly(TMSMA/MMA)		yield, %
TMSMA	MMA	M_n	M_w/M_n	M_n	M_w/M_n	
67	124 ^a	9,300	1.28	60,500	1.10	99
67	124 ^b	8,900	1.13	28,100	1.17	82

^a Reaction time, 5 minutes. ^b Reaction time, 2 minutes.

triblock copolymer (8:72:20) shows 58% compression set. In this case, the Izod impact strength is 400 J/m, while hardness was lowered to 20 JISA. The most interesting property lies in the relatively large elongation(160%). In contrast to this triblock copolymer, the triblock copolymers composed of MMA/nBuA/MMA in 6:91:3 or 25:51:24 ratios show the increased compression set of 97 or 101%, respectively, indicating that these polymers exhibit no elastic properties. Thus, a suitable ratio is required for elastic properties of these triblock copolymers. In essentially the same way, triblock copolymerization of MMA/EtA/EtMA was performed. The resulting copolymer is composed of 26:48:26 ratio and has an elongation of 276% and a compression set of 62%.

Block Copolymerization of TMSMA with MMA

As an extension of this study, we have performed the block copolymerization of trimethylsilyl methacrylate (TMSMA) with MMA. The resulting copolymer should bring about the formation of an adhesive material composed of poly(CH₂CMeCOOH/CH₂COOMe). SmH(C₅Me₅)₂ initiated polymerization of MMA followed by the addition of TMSMA or the polymerization of TMSMA followed by the addition of MMA both produced the desired polymer, which produce the adhesive polymer upon hydrolysis. Characterization of the block copoly(TMSMA/MMA) is shown in Table 7.

Single Site Polymerization of Ethylene and 1-Olefins

The racemic divalent organolanthanide complex, SiMe₂(2-SiMe₃-4-tBu-C₅H₂)₂Sm(THF)₂ (7), was prepared as purple crystals (mp 155.6°C) by the reac-

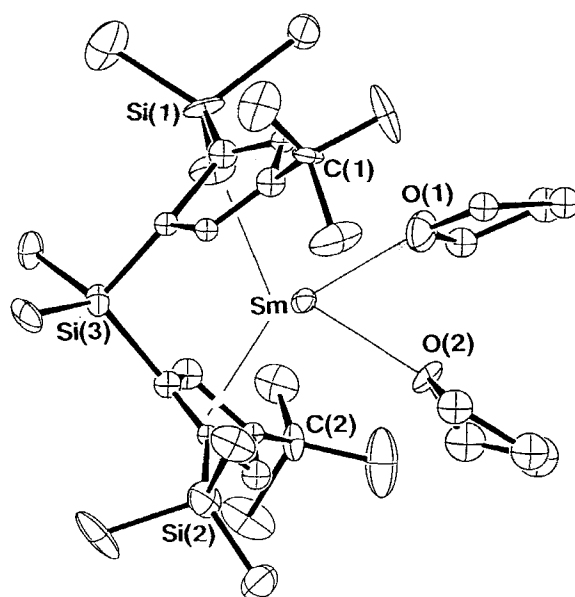


Figure 7. X-ray structure of $\text{SiMe}_2(2\text{-SiMe}_3\text{-4-tBu-C}_5\text{H}_2)_2\text{Sm}(\text{THF})_2$ (**1**).

tion of $\text{SiMe}_2(2\text{-SiMe}_3\text{-4-tBuC}_5\text{H}_2)_2\text{K}_2$ with SmI_2 in THF. Single X-ray analysis clearly reveals the racemic structure (Figure 7). The Cp'(centroid)-Sm-Cp'(centroid) bite angle is 117.08° , 18.6° smaller than that of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ containing no SiMe_2 bridge [18]. On the other hand, the meso isomer was prepared by reaction of $\text{Me}_2\text{Si}(\text{C}_5\text{H}_3\text{-tBu})_2\text{Li}_2$ with 0.5 equivalent of $\text{ClSiMe}_2\text{OSiMe}_2\text{Cl}$ followed by the reaction of the resulting product with $\text{BuLi}/^t\text{BuOK}$ to form $\text{Me}_2\text{Si}(\text{SiMe}_2\text{OSiMe}_2)(\text{C}_5\text{H}_2\text{-tBu})_2\text{K}_2$, which was then reacted with SmI_2 in THF. The molecular structure of the resulting $\text{Me}_2\text{Si}(\text{SiMe}_2\text{OSiMe}_2)(\text{C}_5\text{H}_2\text{-tBu})_2\text{Sm}(\text{THF})_2$ (**8**) (mp 168.3°C) was determined by X-ray analysis (Figure 8). The Cp'(centroid)-Sm-Cp'(centroid) bite angle is 116.9° , again ca. 19° smaller than the non-bridged complexes.

Finally, C_1 symmetric lanthanide metallocene, $\text{Me}_2\text{Si}[2,4\text{-(SiMe}_3)_2\text{C}_5\text{H}_2][3,4\text{-(SiMe}_3)_2\text{C}_5\text{H}_2]\text{Sm}(\text{THF})_2$ (**9**), was obtained as air and moisture sensitive crystals by reaction of $\text{Me}_2\text{Si}[2,4\text{-(SiMe}_3)_2\text{C}_5\text{H}_2]_2\text{K}_2$ with SmI_2 in THF. Trimethylsilyl groups substituted at the 2,4-position should migrate to the 3,4-position during the reaction. Thus, purple crystals were obtained exclusively (mp 145°C).

Ethylene polymerization was explored by using resulting three types of complexes in the absence of methyl alumoxane (Table 8). The meso isomer

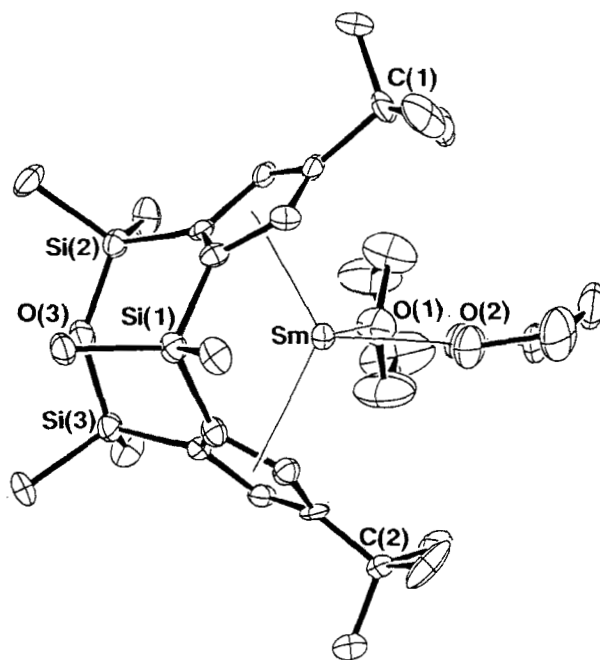


Figure 8. X-ray structure of $\text{Me}_2\text{Si}(\text{SiMe}_2\text{OSiMe}_2)(\text{C}_5\text{H}_2\text{-tBu})_2\text{Sm}(\text{THF})_2$ (**2**).

TABLE 8. Ethylene Polymerization Initiated by Organosamarium Complexes with Bridged Bis(substituted cyclopentadienyl) Ligand

initiator	polymn. time	activity	efficiency	$10^{-4}M_n$	M_w/M_n
	min	kg PE/mol h	%		
meso-tBu-Sm(II)	5	146	87	1.9	3.29
(7)	10	470	256	4.7	3.49
Cl-Sm(II)	15	15	1	100.8	1.60
(8)	30	16	2	150.5	1.80
rac-tBu-Sm(II)	1	62	2	11.6	1.43
(9)	3	139	32	35.6	1.60
non-bridge-Sm(II)	5	6	4	1.6	2.14

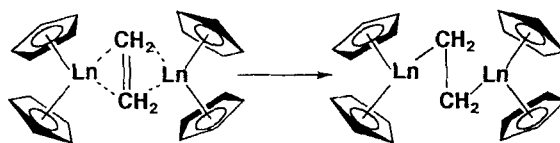
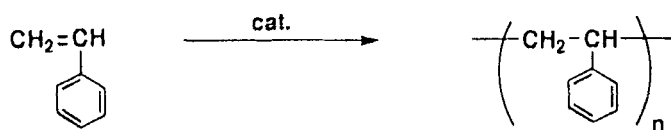


Figure 9. Initiation mechanism for polymerization of ethylene catalyzed by rare earth metal(II) complexes.

exhibits the highest initiating activity, as compared with the racemic and C_1 symmetric complexes as well as the non-bridged metallocene derivatives, (1-SiMe₃-3-tBuC₅H₄)₂Sm(THF)₂[non-bridged Sm(II)]. However, the molecular weights of polyethylene thus obtained are relatively small: <50,000, even when the initiator concentration was adjusted to be very low and reaction period was elongated to 2 hours. Thus, chain transfer occurs frequently as the catalytic efficiency exceeds 100% and polydispersities broadened to 2.5-3.5. In contrast to these complexes, the C_1 symmetric lanthanide metallocene provides the highest molecular weight of polyethylene: >1000,000, with a very narrow molecular weight distribution, despite a very low initiator efficiency of 1.0-2.0%. Thus, the initiation by C_1 symmetric lanthanide metallocene barely occurs, but once initiation started, the polymerization proceeded in a living fashion. The racemic lanthanide metallocene exhibits intermediate activity compared as compared with the meso and C_1 symmetric species, and it gives intermediate molecular weight. Since the divalent organolanthanide should initiate the polymerization by insertion of ethylene into two organolanthanides as found in the case of diphenylacetylene, azobenzene, dinitrobenzene, stilbene and butadiene, the initiation array may be given in Figure 9. Then the meso structure assumes the loosest packing while the C_1 symmetric structure assumes the tightest packing. Therefore, the meso-isomer shows the highest activity and the C_1 symmetric complex shows the lowest activity.



Styrene Polymerization

Styrene polymerization was performed by using binary initiator systems such as Nd(acac)₃-AlR₃ or Nd(P₅₀₇)₃-AlR₃ [P₅₀₇ = iC₈H₁₇P(O)OH(O-iC₈H₁₇)] and syndio[^]rich polystyrene was obtained in the ratio of Al/Nd = 10-12 [19]. More

recently, $\text{Gd}(\text{OCOR})_3/\text{iBu}_3\text{Al}/\text{Et}_2\text{AlCl}$ catalytic system was found to initiate the copolymerization of styrene with butadiene. However, this system gives only atactic polystyrene [20]. $\text{Sm}(\text{O-iPr})_3/\text{AlR}_3$ or $\text{Sm}(\text{O-iPr})_3/\text{AlR}_2\text{Cl}$ ($\text{Sm}/\text{Al} = 1-15$) catalytic system also conduct the polymerization of styrene to give a high molecular weight polymers ($M_n = 300,000$) with low polydispersity but the resulting polymer is atactic [13]. The cationic polymerization of styrene by $\text{Ln}(\text{CH}_3\text{CN})_9(\text{AlCl}_4)_3$ (CH_3CN) was also examined [21]. The activity increases in the order La (conversion 73%) $> \text{Tb} = \text{Ho} > \text{Pr} = \text{Gd} > \text{Nd} > \text{Sm} = \text{Yb} > \text{Eu}$ (conversion 54%). The M_n decreased by raising the polymerization temperature from 0°C (20×10^3) to 60° (13×10^3). More recently, single component initiator $[(\text{tBuCp})_2\text{LnCH}_3]_2$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$) was found to initiate the polymerization of styrene at relatively high temperature, 70°C , i.e. conversion is 96% for $[(\text{tBuCp})_2\text{NdCH}_3]_2$ and the resulting M_n is 3.3×10^4 [22]. However, stereoregularity is very poor. The activity varies greatly depending upon lanthanide element and the catalytic activity increases in the order $\text{Nd} > \text{Pr} > \text{Gd} \gg \text{Sm} = \text{Y}$ (the Sm and Y complexes shows almost no activity). Therefore, radical initiation mechanism is conceivable for this reaction. Styrene polymerization was also performed successfully by single component initiator, $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sm}(\text{THF})_2$, $[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{Sm}$, and $\text{La}(\text{C}_5\text{Me}_5)[\text{CH}(\text{SiMe}_3)_2]_2$ (THF) at 50°C in toluene without the addition of any cocatalyst (M_n $1.5-1.8 \times 10^4$, M_w/M_n $1.5-1.8$) [13]. However, only atactic polymers were obtained in these cases. Thus, synthesis of syndiotactic polystyrene was not realized by rare earth metal complexes, by sharp contrast to the formation of highly syndiotactic polystyrene catalyzed by $(\text{C}_5\text{Me}_5)\text{TiCl}_3/(\text{AlMe-O})_n$ (syndiotacticity $> 95\%$) [22].

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