Synthesis of High Molecular Weight Poly(methyl methacrylate) with Extremely Low Polydispersity by the Unique Function of Organolanthanide(III) Complexes

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ABSTRACT: Polymerizations of methyl methacrylate by bis(pentamethylcyclopentadienyl)samarium hydride, $[Sm(C_5Me_5)_2H]_2$, in toluene were found to afford the polymers of $M_n > 100 \times 10^3$ with extremely low polydispersity, $M_w/M_n = 1.02$. Since the M_n increases with an increase of the conversion while M_w/M_n remains intact, the present polymerization is estimated to proceed in a living fashion. The stoichiometric reaction of $[SmH(C_5Me_5)_2]_2$ with MMA in a 1:2 ratio gives rise to the formation of an eight-membered ring intermediate, in which a Sm–enolate bond exists at the one end and at the other end a Sm---OC bond exists between the Sm and penultimate MMA unit as confirmed by X-ray work. Furthermore highly syndiotactic polymerization (95.3%) proceeded by lowering the reaction temperature to −95 °C. Methylbis(pentamethylcyclopentadienyl)lanthanide complexes such as $YbMe(C_5Me_5)_2(THF)$ and $LuMe(C_5Me_5)_2(THF)$ in addition to trimethylaluminum complexes of organolanthanide(III) like $Yb(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$, $Y(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$, and $Lu(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$ behaved in a fashion similar to that of $[SmH(C_5Me_5)_2]_2$. Organolanthanide(II) complexes such as $Yb(C_5Me_5)_2(THF)_2$, $Sm(C_5Me_5)_2(THF)_2$, and $Yb(indenyl)_2(THF)_2$ also start the living polymerizations although their initiator efficiencies are much smaller (35%) than those obtained by organolanthanide(III) complexes (>90%).

Introduction

Synthesis of high molecular weight polymers ($M_n > 100 \times 10^3$) with extremely narrow molecular weight distributions ($M_w/M_n < 1.05$) has remained unprecedented subjected in polymerizations of polar monomers. Synthesis of such compositionally pure materials must serve as benchmark for the accurate physical and chemical properties of the desired polymers. Although various living polymerization systems have been reported, no type of anionic[1] or cationic polymerization,[2] group transfer polymerization,[3] or metal carbene initiated polymerization[4] has ever achieved this end. We describe herein the first example of high molecular weight poly(methyl methacrylate) with unusually low polydispersity (molecular weight distribution), by using the unique initiating property of $(C_5Me_5)_2Ln^{III}R$ (R = H, Me) or $(C_5Me_5)_2Ln^{II}$ complexes. The utility of single component organolanthanides has already been demonstrated for polymerizations of nonpolar monomers such as ethylene and conjugated dienes.[5]

Results and Discussion

Living Polymerization of MMA with Ln(III) Complexes in Toluene. Polymerizations of methyl methacrylate (MMA) with organolanthanide(III) complexes were performed using the following complexes, as shown in Figure 1. These are bis(pentamethylcyclopentadienyl)samarium hydride, $[SmH(C_6Me_5)_2]_2$,[6] alkylmetal complexes, $LnMe(C_5Me_5)_2(THF)$ (Ln = Sm, Yb),[7] trimethylaluminum complexes with two bridging methyl groups, $Ln(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$ (Ln = Yb, Lu),[8] and a simple methylmetal complex with a rather small auxiliary ligand, $[YbMe(C_5H_5)_2]_2$.[9] The lanthanide complexes employed here were thoroughly purified by repeating the recrystallization in argon and are isolated as air and moisture sensitive single crystals. These are freely soluble in benzene and toluene. Table I summarizes the results of polymerizations using these complexes as initiator and Table II summarizes the mode of reaction using $[SmH(C_5Me_5)_2]_2$.[10] These reactions involve the following marked features. (1) The polydispersities of resulting polymers are unusually low and reach $M_w/M_n = 1.03$. (2) Polymerization proceeds very rapidly and is complete in a short period. (3) The polymerizations gave high molecular weight poly(MMA) especially when the concentration of the complex was lower than 0.2 mol %. (4) The polymerization proceeded at a wide range of reaction temperatures starting from +40 to −95 °C. (5) Highly syndiotactic polymerizations occur at lower temperatures.

These results indicate that the present polymerization proceeds in a living fashion. In fact, the M_n (number averaged molecular weight) of polymers increased linearly in proportion to the conversion irrespective of the initiator concentration, while M_w (weight averaged molecular weight)/M_n remains intact during the polymerization

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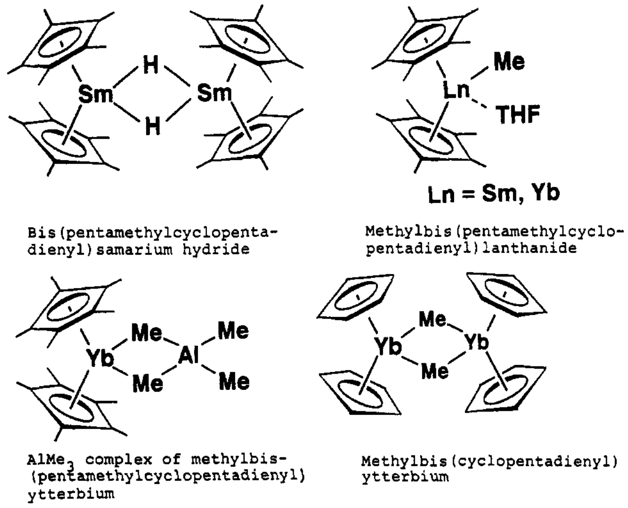


Bis(pentamethylcyclopentadienyl)samarium hydride

Methylbis(pentamethylcyclopentadienyl)lanthanide

$AlMe_3$ complex of methylbis(pentamethylcyclopentadienyl)ytterbium

Methylbis(cyclopentadienyl)ytterbium

Figure 1. Typical organolanthanide(III) initiators.

(Figure 2). Consequently, we can readily estimate that the present polymerization occurs in a living fashion. The initiator efficiency is >90% in the case of 0.2 mol % initiator concentration, while the efficiency decreases to 80% when the initiator concentration is lowered to 0.1 mol %. This is ascribable to the undesired action of a trace amount of water and oxygen contaminant in the system. In the case of $[YMe(C_5H_5)_2]_2$ with less bulky auxiliary ligands, the initiator efficiency decreased to 60%. This is presumably due to the insufficiency of the bulkiness of the ligand, and the use of the more bulky pentamethylcyclopentadienyl ligand is required to perform the living polymerization, especially at >0 °C. Although several initiator systems, i.e., bulky alkyllithium,[11] Grignard reagents such as iBuMgBr[12] and (*m*-vinylbenzyl)MgEt,[12] $Al(C_2H_5)_3{\cdot}TiCl_4$,[13] and $Al(C_2H_5)_3{\cdot}P(C_6H_5)_3$,[14] are known to produce highly syndiotactic poly(MMA) (94.3–96.6%), the molecular weights and polymer conversions are much smaller and the polydispersity is wider (1.2–1.8) than those obtained in the present work (Table III).

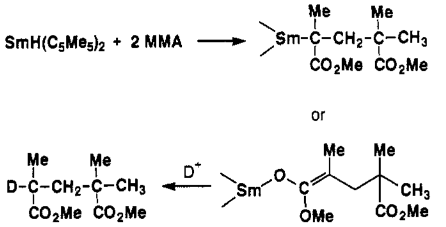
The M_n was determined conveniently by gel permeation chromatography using standard poly(MMA) whose M_w was estimated by the light-scattering method. The observed narrow M_w/M_n compares closely with the profiles of commercially available standard polystyrene ($M_n = 355 \times 10^3$, $M_w/M_n = 1.03$ and $M_n = 43.9 \times 10^3$, $M_w/M_n = 1.02$) bearing the lowest polydispersity (Figure 3).

In general the syndiotacticity is known to vary greatly depending upon the polymerization temperature. Therefore the temperature dependence of the tacticity as well as M_w/M_n is examined here using $[SmH(C_5Me_5)_2]_2$ as the initiator. The syndiotacticity increased to 95.3% from 75% by changing the reaction temperature from +25 to −95 °C in line with the general trend observed in polymerizations of MMA, while the polydispersity showed no change during these reactions. Syndiotacticity of the poly(MMA) was easily determined with reference to the reported triad[15] and pentad assignments.[16] Signals of ^{13}C NMR at δ 177.9, 177.6, and 176.9 are assigned to mrrr, rrrr, and rmrr, respectively (Figure 4). The ratio of these signals, 3:94:2 and 7:88:5, corresponds to 96% and 92% syndiotacticity by triad assignment.

Since the present polymerization proceeds in a living fashion, we have examined the dependence of the initiator concentration on the molecular weight of polymers together with M_w/M_n. As shown in Figure 5, the molecular weight M_n increases with a decrease of initiator concentration and reaches $M_n = 530 \times 10^3$ with $M_w/M_n = 1.04$ when the polymerization is conducted at 0 °C (initiator efficiency, 82%), while the polydispersity broadens at −78 °C to give $M_n = 420 \times 10^3$ with $M_w/M_n = 1.12$ (initiator efficiency, 48%). Such a high molecular weight polymer with narrow molecular weight distribution has never been attempted for polar monomers. Figure 6 shows the M_n vs M_w/M_n plots for all the living polymers reported in the literature since 1986,[17–52] from which we became familiar with gel permeation chromatographic analysis. Most polymers fall in a region of $M_w/M_n > 1.05$ and $M_n < 100 \times 10^3$, while the polymers obtained by $[SmH(C_5Me_5)_2]_2$ occupy a unique position.

In order to estimate the lifetime of the present growing end, 160 equiv of monomer was first polymerized (reaction is complete within 40 min at 0 °C), and after completion of the initial polymerization, 160 equiv of monomer was added again to induce the polymerization (Figure 7). At a 1-h interval, repolymerization starts and M_n increases to twice that of the prepolymer after 40 min, as expected. At a 10-h interval, 78% (area ratio) of the prepolymer survives and gives rise to the formation of living polymers ($M_w/M_n = 1.03$), while 22% of the prepolymer is decreased. This value indicates that ca. 60% of the macroanions of growing poly(MMA) survives while 18% of the macroanions is dormant. Such a long life has not been observed for any type of living polymerizations of polar monomers. The present polymerization was inert to styrene in the presence of MMA. Only homopolymerization of MMA occurred in high yields when the mixture of MMA and styrene was allowed to polymerize in ratios of 1:0.5, 1:1, and 1:10.

To get further insight into the initiation mechanism, we have demonstrated the stoichiometric reaction at 0 °C between $SmH(C_5Me_5)_2$ and MMA. Both 1:1 and 1:2 reactions gave the MMA dimer complex preferentially, $Sm(MMA)_2H$, which decomposed upon deuterolysis to afford $DCMe(CO_2Me)CH_2C(Me)_2CO_2Me$ quantitatively.



(1)

The reaction of $SmD(C_5Me_5)_2$ with MMA followed by hydrolysis gave $HCMe(CO_2Me)CH_2C(Me)(CH_2D)CO_2Me$ in a high yield. These results are indicative of the formation of a 1:2 adduct with either a Sm–enolate or Sm–α–carbon bond. In order to obtain the information on the stereoregurarity, the reaction of $YbMe(C_5Me_5)_2(THF)$ with MMA was also examined here. As a result of hydrolysis of the product, only $HCMe(CO_2Me)CH_2CMe(Et)CO_2Me$ was obtained as a racemic and meso mixture in an 87:23 molar ratio. The racemic meso ratio was determined with reference to the literature.[53] Since the $YbMe(C_5Me_5)_2$ initiated polymerization of MMA at 0 °C gave the syndiotacticity (rr) in 84% selectivity, the racemic formation in the stoichiometric reaction is in good agreement with the mode of polymerization. However, the extent of the racemization is lower than we expected (>98%). This conflict may arise from stereoirregularity occurring during the hydrolysis. In fact, hydrolysis of the tBuMgBr initiated syndiotactic oligomerizations of MMA resulted in stereoirregular cleavage in the growing end while treatment with the PhOH derivative gives a much improved stereoregularity.[54]

After expending many efforts, we succeeded in isolating $(C_5Me_5)_2Sm(MMA)_2H$ (132 °C) as crystals. To verify the

Table I. Characterization of Poly(MMA) Initiated by Organolanthanide(III) at 0 °C[a]

initiators	$10^{-3}M_n$	M_w/M_n	tacticity, % rr	rm	mm	conversion, %	initiator efficiency, %
$[SmH(C_5Me_5)_2]_2$	58	1.02	82.4	16.8	0.8	99	86
$SmMe(C_5Me_5)_2(THF)_2$	52	1.03	82.8	16.8	1.0	99	96
$YbMe(C_5Me_5)_2(THF)_2$	48	1.04	84.8	14.3	0.9	99	99
$Yb(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$	55	1.04	84.3	14.9	0.8	93	90
$LuMe(C_5Me_5)_2(THF)_2$	61	1.04	83.7	15.8	0.5	98	82
$Lu(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$	51	1.04	83.2	16.1	0.7	98	95
$Y(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$	53	1.03	84.7	14.5	0.8	99	94
$[YMe(C_5H_5)_2]_2$	82	1.22	76.3	21.3	2.4	98	60

[a] Reaction conditions: initiator concentration, 0.2 mol % of monomer; solvent, toluene, toluene/$[M_0]$ = 10 vol/vol; reaction time, 2 h.

Table II. Characterization of Monodisperse Poly(MMA) Synthesized by $[SmH(C_5Me_5)_2]_2$[a]

polymerization temp, °C	MMA/initiator charged, mol/mol	$10^{-3}M_n$	M_w/M_n	tacticity, % rr	rm	mm	conversion, % (reacn period, h)
40	500	55	1.03	77.3	21.2	1.5	99(1)
25	500	57	1.02	79.9	18.9	1.2	99(1)
0	500	58	1.02	82.4	16.8	0.8	99(1)
0	1500	215	1.03	82.6	16.9	0.5	93(2)
0	3000	563	1.04	82.3	16.9	0.8	98(3)
−78	500	82	1.04	93.1	6.4	0.5	97(17)
−95	1000	187	1.05	95.3	4.4	0.3	82(60)

[a] Reaction conditions: solvent, toluene; solvent/$[M_0]$ = 10 vol/vol. M_n and M_w/M_n were obtained by GPC after calibrating with standard polystyrene whose exact M_w was determined by light-scattering methods.

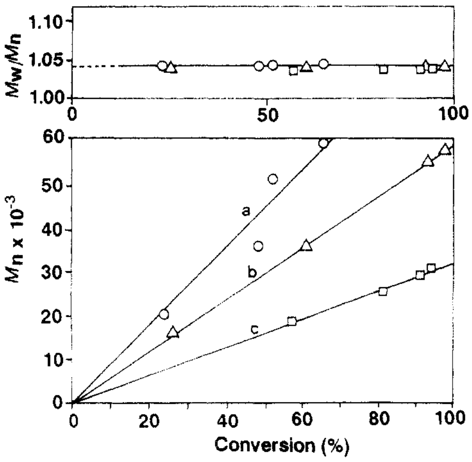


Figure 2. Conversion vs M_n and M_w/M_n plots; (a) $SmH(C_5Me_5)_2$ 0.1 mol %; (b) 0.2 mol %; (c) 0.3 mol %.

exact structure of the $SmH(C_6Me_5)_2$ adduct of 2 equiv of MMA, single crystal X-ray analysis was performed (Figure 8). Crystal data and parameters for the data collections and refinements are given in Table IV. A listing of relevant bond distances and angles is given in Tables V and VI. The adduct is tetracoordinated and bears an enolate bond at the one end, and the penultimate MMA is coordinated to the Sm atom at its CO group. Thus, the adduct has an eight-membered ring structure. The enolate group bears a *cis* configuration and binds with another MMA molecule. The O(2)—Sm bond distance is 2.186 Å, while the Sm—O(1) bond distance is elongated to 2.39 Å. This value is shorter than the Sm—O bond (2.55 Å) in $Sm(C_5Me_5)_2Cl(THF)$.[55] The O(1)—Sm—O(2) angle (94.0°) is rather wide as compared with those of $Sm(C_5Me_5)_2Me(THF)$ (89.6°),[7] $Sm(C_5Me_5)_2Cl(THF)$ (90.4°),[55] $Sm(C_5Me_5)_2I(THF)$ (88.8°),[56] and $(C_5Me_5)_2Sm[\mu\text{-}\eta^4\text{-}(C_5H_4N)CH{=}C(O)C(O){=}CH(C_5H_4N)]Sm(C_5Me_5)_2$ (76.5°)[57] as a consequence of the eight-membered ring conformation. The C(7) carbon (growing end) locates to avoid the steric congestion with the C(9) atom and the syndiotactic sequence may arise from this type of location.

The isolated complex is estimated to be the real active species since the addition of 100 equiv of MMA resulted in the formation of polymer with molecular weight 11 000 and M_w/M_n = 1.03 in excellent yield. These results indicate that, in the initiation step, the hydride should attack the CH_2 group of MMA to generate a transient Sm—O—C$(OCH_3){=}C(CH_3)_2$ species, and then the incoming MMA molecule may participate in a 1,4-addition to afford the eight-membered ring intermediate (Figure 9). Then in the propagation step another MMA molcular may attack the growing end, liberating the coordinated ester group. Syndiotactic polymerization should occur by repeating these reactions, where the coordination site changes alternatively. Thus, we propose the coordination anionic mechanism for the present polymerization. In fact, $[Y(C_5Me_4SiMe_3)_2OCH{=}CH_2]_2$ shows a good activity for polymerization of MMA (M_n = 78 000 with M_w/M_n = 1.15 in the case of $[M_o]/[I_o]$ = 0.2 mol/mol) whereas $[Y(C_5Me_5)_2OMe]_2$ and $Sm(C_5Me_5)_2Cl(THF)$ are completely inert to MMA. It should be noted that such an eight-membered ring intermediate was proposed by Bawn et al.[58] and Cram, Copecky, et al.[59] for isotactic polymerizations of MMA.

Since the present polymerization takes place completely, for atactic polymerization of methyl acrylate in conjunction with syndiotactic polymerization of MMA, a 1:9 mixture of methyl acrylate and MMA was copolymerized to understand the polymerization mechanism. The syndiotacticity of the MMA unit in the random copolymer obtained at 0 °C was 82% irrespective of the insertion of methyl acrylate (12%) (polymer conversion 62%, M_w/M_n = 1.05) to indicate that stereoregularity is controlled by the initiator structure of the growing end, although chain control may assist in the syndiotactic polymerization as confirmed by the temperature dependence of syndiotacticity; i.e. the syndiotacticity increases at a lower temperature. The organolanthanides(III) are inert to vinyl-4-pyridine and vinyl-2-pyridine, which are polymerizable with typical anionic initiators, since these monomers are coordinated to the metal at their N position.

Although in Ziegler–Natta catalyst systems the molecular weight of polymers can be adjusted by the addition of hydrogen, the present system was affected little by the addition of hydrogen and homopolymerization of MMA proceeded even under a hydrogen atmosphere.

Table III. Characteristics of Conventional Initiators for Syndiotactic Poly(MMA)[a]

initiators	temp, °C	$10^{-3}M_n$	M_w/M_n	tacticity, % rr	rm	mm	conversion, %
$CH_3(CH_2)_4CPh_2Li$	−78	10	1.18	83.8	15.1	1.1	100
(piperidinyl)MgEt	−78	29	2.17	91.0	7.6	1.4	93
iBuMgBr[b]	−110	15	1.84	94.3	5.7	0.0	12
mVBzMgBr[c]	−110	14	1.19	96.6	3.1	0.3	19
$Ph_3P\cdot AlMe_3$	−93	28	1.63	94.9	4.6	0.5	70
$AlEt_3\cdot TiCl_4$	−78	109	4.58	90.3	9.0	0.7	89

[a] Reaction time, 24 h. Solvent, toluene. [b] Solvent, THF. [c] VBz = vinylbenzyl.

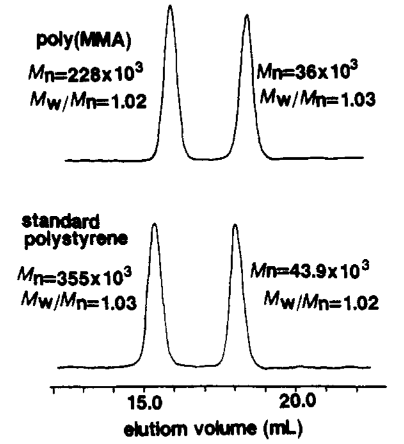


Figure 3. GPC traces of poly(MMA) and standard polystyrene.

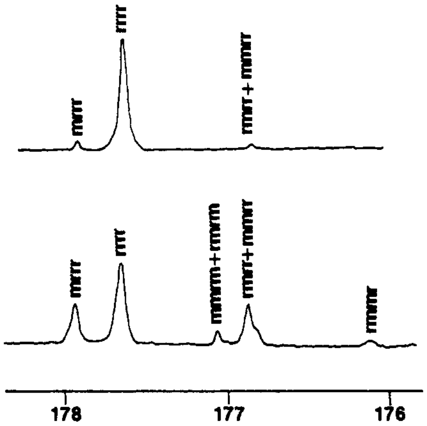


Figure 4. ^1H NMR spectra of poly(MMA) in the CO region. (a, top) $SmH(C_5Me_5)_2$ at 0 °C (syndiotacticity) 83%); (b, bottom) radical initiator (syndiotacticity 52%).

In order to establish the identity of the lanthanide metal, $LnMe(C_5Me_5)_2(THF)$ (Ln = Sm, Yb, Lu),[7,60] $Ln(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$ (Ln = Yb, Lu, Y),[8,61] and $[YMe(C_5H_5)_2]_2$[9] were examined as initiators. As a result, whole complexes used here act as living polymerization initiators, as illustrated in Figure 10. The molecular weight increased in proportion to the conversion while the M_w/M_n values were constant during the polymerization, in support of the living polymerization. The plots for polymers more than $M_n = 25 \times 10^3$ fit the calculated line well but those for polymers less than 10×10^3 deviate from the calculated line because these are soluble in a precipitating solvent, MeOH.

The syndiotacticity again increased by lowering the reaction temperature to −95 °C (Figure 11). The syndiotacticity obtained by $LnMe(C_5H_5)_2$ with a less bulky auxiliary ligand has a relatively big temperature dependence as compared with the $LnMe(C_5Me_5)_2$ or $Ln(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$ system (Ln = Sm, Y, Yb, Lu). This is ascribed to the insufficiently of the bulkiness of auxiliary ligand in controlling the stereoregularity at 0 °C, while at temperatures below −96 °C the bulkiness is sufficient to control the molecular weight distribution and stereoregularity. It should be noted that $Ln(C_5Me_5)_2(\mu\text{-}Me)_2AlMe_2$ species also conduct the living polymerization. This result suggests that the $LnMe(C_5Me_5)_2$ species produced by the attack of MMA is the real active species and the liberated $AlMe_3$ is inert for polymerization of MMA.

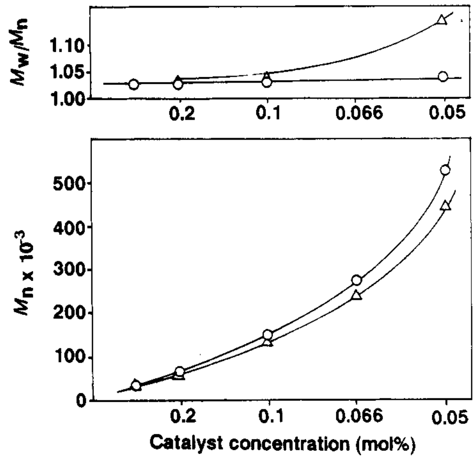


Figure 5. Dependence of M_n and M_w/M_n on the initiator concentration for the $SmH(C_5Me_5)_2$ system: (○) 0 °C; (△) −78 °C.

The rate of initial polymerization is evaluated from consumption of MMA molecules using a variety of complexes, as shown in Figure 12. The observed increasing order, Sm > Y > Yb > Lu, is in line with the order of ionic radii, Sm (1.11 Å) > Y (1.06 Å) > Yb (0.86 Å) > Lu (0.85 Å).[62] Furthermore, this order is in good agreement with the order of Cp(centroid)–Ln bond lengths, Sm (2.86–2.73 Å)[63] > Y (2.65–2.68 Å)[64] > Yb (2.31–2.35 Å)[65] > Lu (2.28–2.34 Å).[66] Thus, the activity increases with an increase of ionic radii of the elements. On the basis of this presumption, we can readily estimate that much more catalytic activity exists in La (1.22 Å) derivatives.

We can use tetrahydrofuran, diethyl ether, benzene, and even hexane instead of toluene as solvent in the case of $SmMe(C_5Me_5)_2(THF)$ and $YbMe(C_5Me_5)_2(OEt_2)$ initiators, and nearly the same results were obtained regarding the syndiotacticity, M_n, and M_w/M_n. By contrast, the tBuMgBr initiator behaves in a quite different manner; i.e. syndiotactic poly(MMA) was obtained in tetrahydrofuran[52] but isotactic poly(MMA) could be obtained in toluene.[51] Pyridine and triethylamine cannot be used as solvent because these are coordinated to the lanthanide metal and lose their activity.

Organolanthanide(III) Initiated Polymerizations of Other Methacrylates. Ethyl methacrylate (EtMA) in addition to isopropyl methacrylate (iPrMA) and *tert*-butyl methacrylate (tRuMA) can also polymerize in a living fashion with $[SmH(C_5Me_5)_2]_2$ or $LuMe(C_5Me_5)_2(THF)$ (Table VII). The observed M_w/M_n values are again sufficiently small. In these cases, the syndiotacticity decreased by reducing the bulkiness of the alkyl group in

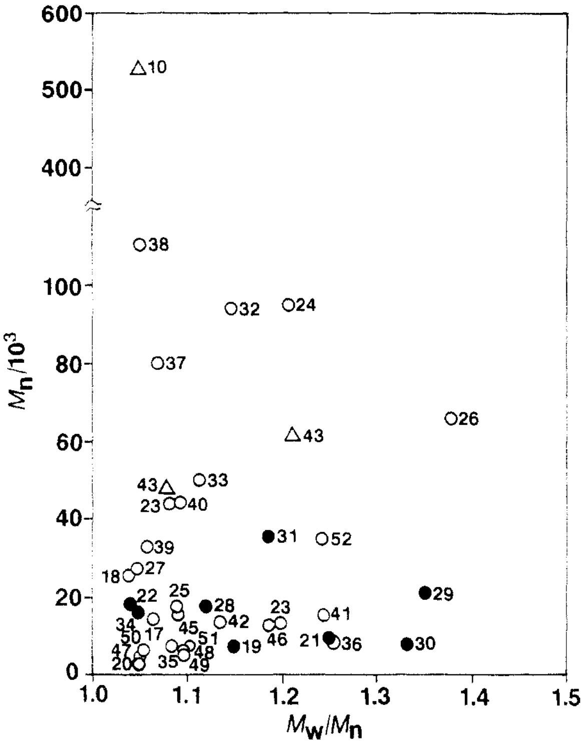


Figure 6. M_n vs M_w/M_n plots for the reported living polymers, cationic (●), anionic (○), and coordination (△) catalysts. Key: (10) MMA, $[SmH(C_5Me_5)_2]_2$; (17) α-methylstyrene, $LiC_{10}H_8$; (18) 4-(trimethylethynyl)styrene, $KC_{10}H_8$; (19) chloroethyl vinyl ether, HX/ZnX_2; (20) ε-caprolactone, EtZnOP; (21) chloroethyl vinyl ether, 1,4-bis(1-chloro-1-methylethyl)benzene/ZnI_2; (22) p-tert-butoxystyrene, HI/ZnI_2; (23) vinyl(N,N-diethylamino)dimethylsilane, BuLi; (24) 2-(3-vinylphenyl)-1,3-dioxolane, cumylpotassium; (25) 4-cyanostyrene, 1,1-bis[4′-(trimethylsilyl)phenyl]-hexyllithium; (26) acrylic esters, (5,10,15,20-tetraphenylporphinato)aluminum 1-propanethiolate; (27) propylene sulfide, (N-methyl-5,10,15,20-tetraphenylporphinato)ZnSPr; (28) isoprene, 2-chloro-2-phenylpropane/$TiCl_4$/EtOAc; (29) p-chlorostyrene, 2-chloro-2,4,4-trimethylpentane/$TiCl_4$/CH_3Cl/dimethylacetamide/2,6-di-*tert*-butylpyridine; (30) isobutylene, 1,4-bis(1-chloro-1-methylethyl)benzene/BCl_3; (31) isobutyl vinyl ether, $EtAlCl_2$; (32) MMA, (9-anthracenylmethyl)lithium; (33) 4-[N,N-bis(trimethylsilyl)amino]styrene, $LiC_{10}H_8$; (34) isobutyl vinyl ether, acetic acid/$EtAlCl_2$; (35) *tert*-butyl 4-vinylbenzoate, cumylpotassium/1,1-diphenylethylene; (36) N-phenylmaleimide, KOtBu; (37) 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline, cumylpotassium; (38) N-[(4-ethylphenyl)methylene]cyclohexamine, $KC_{10}H_1$; (39) (alkoxysilyl)styrene, $KC_{10}H_8$; (40) (4-vinylphenyl)dimethylsilane, $KC_{10}H_8$; (41) *tert*-butyl acrylate, sBuLi/LiCl; (42) δ-valerolactone, (5,10,15,20-tetraphenylporphinato)aluminum alkoxide; (43) norbornene, $Mo(CHtBu)(NAr)(OtBu)_2$; (44) norbornene, $Ta(CHtCHC_5H_8CH)(O\text{-}2,6\text{-}iPr_2C_6H_3)_2$; (45) 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline, $NaC_{10}H_8$; (46) styrene, $LiC_{10}H_8$; (47) methyl methacrylate, (α-methylstyryl)lithium; (48) methyl methacrylate, (α-methylstyryl)lithium/LiCl; (49) *tert*-butyl acrylate, methyl-α-lithioisobutylate; (50) [o-(trifluoromethyl)phenyl]acetylene, $MoCl_5$–Bu_4Sn–acetone; (51) methyl methacrylate, tBuMgBr in toluene, (52) methyl methacrylate, tBuMgBr in THF.

the methacrylates system. Random copolymerization of MMA with EtMA or iPrMA also proceeds in a living fashion. The respective monomer reactivity ratios determined from the copolymer composition curve were shown in Table VIII. MMA showed a reactivity similar to that of EtMA irrespective of the initiators, organolanthanide(III) and -(II) species, while the reactivity of MMA is larger than that of iPrMA. This trend differs greatly from the results of random copolymerization of MMA with EtMA or iPrMA by BuLi, which showed MMA(r_1):EtMA(r_2) = 1.10:0.38, MMA(r_1):iPrMA(r_2) = 2.78:0.20.[67] This conflict may arise from the longer ionic radii of the lanthanide metal. The ^1H NMR signal observed at the higher magnetic field is assigned to the poly(MMA) unit and that at the lower field to the poly(iPrMA) unit. Block copolymerization of MMA with EtMA or iPrMA also proceeds in a living fashion when the same amounts of monomer were charged succeedingly (Table IX). By taking advantage of the present block copolymerization, various types of copolymers were obtained using voluntary ratios of monomers. The M_w/M_n values are again very small. The ^1H NMR spectrum of the block copolymer derived from MMA and iPrMa is superimposable with that obtained from the respective homopolymers (Figure 13).

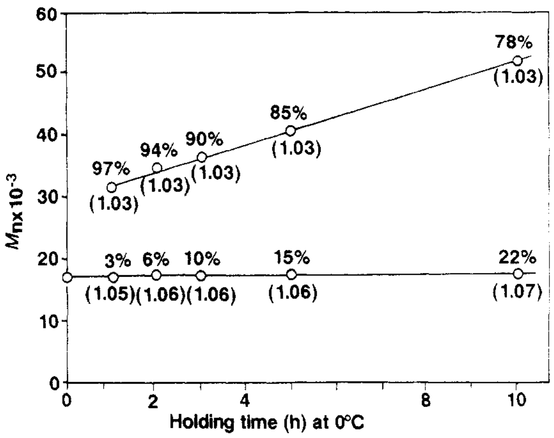


Figure 7. Lifetime of the living poly(MMA). After the addition of MMA (2.5 mmol) to $SmH(C_5Me_5)_2$ (0.015 mol) at 0 °C (polymerization completes in 40 min), the system was held for a fixed time and then 2.5 mmol of MMA was added again.

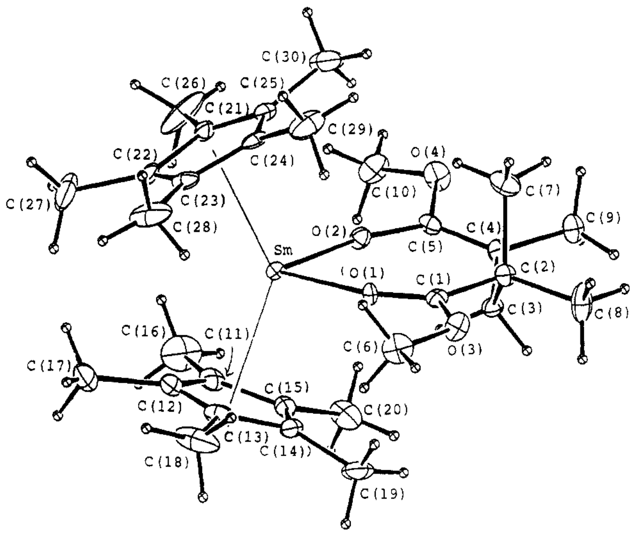


Figure 8. X-ray structure of $(C_5Me_5)_2Sm(MMA)_2H$.

Living Polymerization of MMA with Ln(II) Complexes. Organolanthanide complexes involving Yb, Sm, or Eu can exist also in oxidation state 2, Ln(II). Therefore, we have tested the polymerization using Ln(II) complexes to clarify the differences and similarities with lanthanide(III) initiators. Among the complexes tested here, $(C_5Me_5)_2Yb(THF)_2$[68] and $(C_5Me_5)_2Sm(THF)_2$[69] were found to serve as good initiators, which provide highly syndiotactic poly(MMA) with M_w/M_n = 1.09–1.11 at 0 °C. Initiation properties of $Yb(indenyl)_2(THF)$ are unique since it provides polymers with molecular weights as high as 2270 × 10^3 and a high syndiotacticity (93.8%) at −78 °C. Such a high molecular weight syndiotactic poly(MMA) has frist been prepared by using this type of lanthanide complex. The syndiotacticity again varied depending upon the polymerization temperature. In the case of $Yb(C_5Me_5)_2(THF)_2$, the syndiotacticity increases to 91.5% by

Table IV. Crystal Data and Experimental Parameters for X-ray Structure Determination of $Cp^*_2Sm(MMA)_2H$

formula	$SmO_4C_{30}H_{47}$
fw	622.1
cryst syst	monoclinic
space group	*C*2/*c*
temp, °C	25
a,[a] Å	35.808(6)
b, Å	10.503(2)
c, Å	16.620(2)
β, deg	100.64(1)
V, Å^3	6143(4)
Z	8
D_{calcd}, g cm^{-3}	1.345
F(000), e	2568
μ(Mo Kα), cm^{-1}	19.46
cryst size, mm	0.45 × 0.40 × 0.10
2θ range, deg	$6 < 2\theta < 60$
scan width, deg in 2θ	$1.52 + 0.30 \tan \theta$
scan speed, deg min^{-1}	8–16
background count, *s*	50% of peak scan
no. of reflections measd	9567
no. of reflections obsd	4040
radiation damage	no
no. of variables	316
GOF	2.22
R	0.083
R_w	0.082

[a] Least-squares refined of the θ values for 25 reflections with $2\theta > 25°$.

Table V. Selected Bond Distances (Å) in $(C_5Me_5)_2Sm(MMA)_2H$ with Estimated Standard Deviations in Parentheses

Sm–O(1)	2.39(1)	O(1)–C(1)	1.21(2)
Sm–O(2)	2.186(8)	O(2)–C(5)	1.31(1)
Sm–C(11)	2.68(1)	O(3)–C(1)	1.34(2)
Sm–C(12)	2.71(2)	O(3)–C(6)	1.41(2)
Sm–C(13)	2.73(1)	O(4)–C(5)	1.38(1)
Sm–C(14)	2.73(1)	O(4)–C(10)	1.39(2)
Sm–C(15)	2.71(1)	C(1)–C(2)	1.51(2)
Sm–C(21)	2.73(1)	C(2)–C(3)	1.58(2)
Sm–C(22)	2.78(1)	C(2)–C(7)	1.56(2)
Sm–C(23)	2.76(1)	C(2)–C(8)	1.52(2)
Sm–C(24)	2.75(1)	C(3)–C(4)	1.51(2)
Sm–C(25)	2.73(1)	C(4)–C(5)	1.35(2)
Sm–Cp(1)	2.45	C(4)–C(9)	1.45(2)
Sm–Cp(2)	2.48		

Table VI. Selected Bond Angles (deg) in $(C_5Me_5)_2Sm(MMA)_2H$ with Estimated Standard Deviations in Parentheses

O(1)–Sm–O(2)	94.0(3)	C(7)–C(2)–C(8)	108(1)
Sm–O(1)–C(1)	151(1)	C(2)–C(3)–C(4)	119(1)
Sm–O(2)–C(5)	153.3(9)	C(3)–C(4)–C(5)	116(1)
C(1)–O(3)–C(6)	118(1)	C(3)–C(4)–C(9)	118(1)
C(5)–O(4)–C(10)	118(1)	C(5)–C(4)–C(9)	125(1)
O(1)–C(1)–C(3)	122(1)	O(2)–C(5)–O(4)	117(1)
O(1)–C(1)–C(2)	125(1)	O(2)–C(5)–C(4)	129(1)
O(3)–C(1)–C(2)	113(1)	O(4)–C(5)–C(4)	114(1)
C(1)–C(2)–C(3)	109(1)	O(1)–Sm–Cp(1)	102[a]
C(1)–C(2)–C(7)	105(1)	O(1)–Sm–Cp(2)	104
C(1)–C(2)–C(8)	114(1)	O(2)–Sm–Cp(1)	106
C(3)–C(2)–C(7)	110(1)	O(2)–Sm–Cp(2)	106
C(3)–C(2)–C(8)	111(1)	Cp(1)–Sm–Cp(2)	136

[a] Cp(1) and Cp(2) are the centroids of the Cp ligands of C(11)–C(15) and C(21)–C(25), respectively.

lowering the temperature to −40 °C while lowering the polymerization temperature below −50 °C was useless because no polymerization starts at these temperatures.

By contrast, $Sm(C_5Me_5)_2(THF)_2$ and Yb(indenyl)$_2$(THF) show good initiation properties even at −78 °C. $Yb(C_5Me_5)_2(py)_2$ exhibits no initiating property. Since the polymers obtained here has sufficiently low polydispersities, living polymerization is expected also in these cases. The conversion vs M_n plots gave approximately straight lines irrespective of the initiator concentration while the values of M_w/M_n are constant independent of conversion and catalyst concentration, in support of the living polymerization (Figure 15). The initiator efficiency

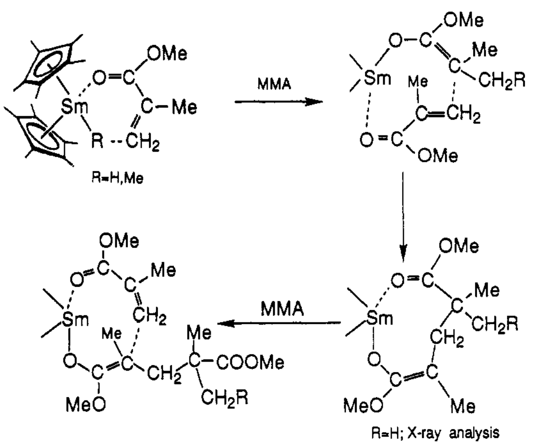


Figure 9. Proposed initiation mechanism for syndiotactic polymerization of MMA.

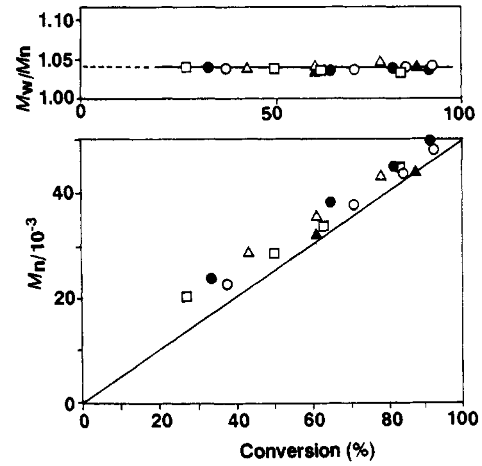


Figure 10. Conversion vs M_n and M_w/M_n for various organolanthanides(III): $Yb(C_5Me_5)_2Me_2AlMe_2$ (○); $YbMe(C_5Me_5)_2(OEt_2)$ (●); $Lu(C_5Me_5)_2Me_2AlMe_2$ (△); $LuMe(C_5Me_5)_2(OEt_2)$ (▲); $Y(C_5Me_5)_2Me_2AlMe_2$ (□).

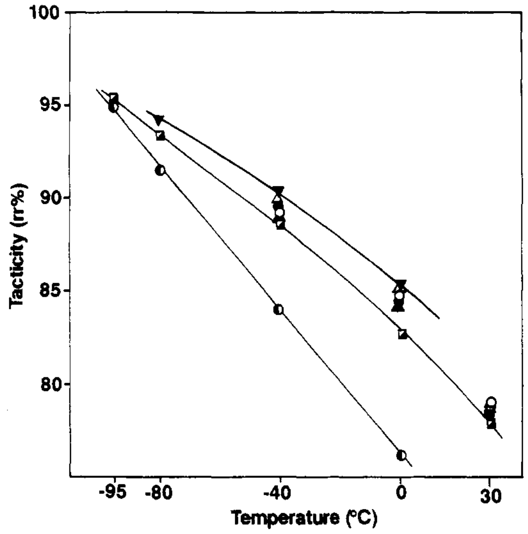


Figure 11. Dependence of syndiotacticity on the polymerization temperature; $[YbMe(C_5H_5)_2]_2$ (◐); $[SmH(C_5Me_5)_2]_2$ (◩); $Y(C_5Me_5)_2Me_2AlMe_2$ (▼); $Lu(C_5Me_5)_2Me_2AlMe_2$ (▲); $LuMe(C_5Me_5)_2(OEt_2)$ (△); $Yb(C_5Me_5)_2Me_2AlMe_2$ (●); $Yb(C_5Me_5)_2(OEt_2)$ (○).

Table VII. Living Polymerizations of Alkyl Methacrylates at 0 °C[a]

initiator	monomers	$10^{-3}M_n$	M_w/M_n	tacticity, % rr	mr	mm	conversion, %
$[SmH(C_5Me_5)_2]_2$	EtMA	72	1.03	80.9	15.5	3.6	98
	iPrMA	65	1.03	77.3	19.6	3.1	90
	tBuMA	12	1.05	78.2	18.6	3.2	25
$LuMe(C_5Me_5)_2(THF)$	EtMA	55	1.03	81.0	16.5	2.5	78
	iPrMA	54	1.04	79.8	17.2	3.0	65
	tBuMA	15	1.04	78.5	19.9	2.5	20

[a] Polymerization, 0 °C in toluene for 1 h. $[M_0]/[I_0]$ = 500 mol/mol.

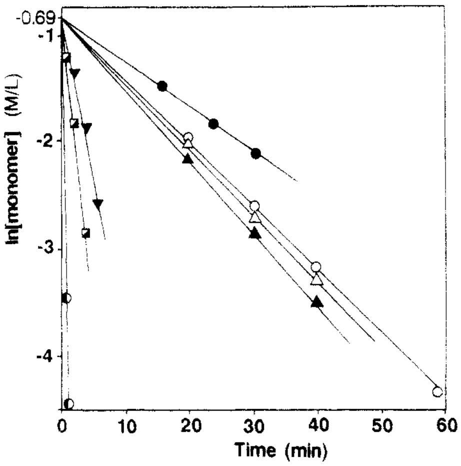


Figure 12. Apparent rates of consumption of MMA. $[M]_o$ = 0.5 mmol, $[I]_o$ = 0.01 mmol; $[YbMe(C_5H_5)_2]_2$ (◐); $[SmH(C_5Me_5)_2]_2$ (◪); $Sm(C_5Me_5)_2Me_2AlMe_2$ (■); $Y(C_5Me_5)_2Me_2AlMe_2$ (▼); $Lu(C_5Me_5)_2Me_2AlMe_2$ (▲); $LuMe(C_5Me_5)_2(OEt_2)$ (△); $Yb(C_5Me_5)_2Me_2AlMe_2$ (●); $YbMe(C_5Me_5)_2(OEt_2)$ (○).

Table VIII. Monomer Reactivity Ratio Determined with $[SmH(C_5Me_5)_2]_2$

monomer	initiators	r_1	r_2	r_1r_2
MMA/EtMA	$[SmH(C_5Me_5)_2]_2$	0.98	0.81	0.79
	$SmMe(C_5Me_5)_2(THF)$	0.99	0.83	0.82
	$Sm(C_5Me_5)_2(THF)_2$	0.99	0.82	0.81
	$Yb(C_5Me_5)_2(THF)_2$	0.95	0.78	0.74
MMA/iPrMA	$[SmH(C_5Me_5)_2]_2$	1.78	0.55	0.98
	$SmMe(C_5Me_5)_2(THF)$	1.88	0.53	1.00
	$Sm(C_5Me_5)_2(THF)_2$	1.78	0.55	0.98
	$Yb(C_5Me_5)_2(THF)_2$	1.67	0.57	0.95

Table IX. Block Copolymerization of MMA with Other Methacrylates using $[SmH(C_5Me_5)_2]_2$[a]

block copolymer	MMA unit (prepolymer) $10^{-3}M_n$	M_w/M_n	n	comonomer unit $10^{-3}M_n$	m	M_w/M_n (total)	n/m
MMA–EtMA	64	1.04	639	81	710	1.08	1/1.1
MMA–iPrMA	78	1.04	779	31	287	1.07	1/0.37
MMA–tBuMA	68	1.04	679	2	14	1.06	1/0.02

[a] To the pre-poly(MMA) was added the same amount (molar ratio) of other methacrylates, and polymerization was conducted for 30 min at 0 °C.

is 35% for 0.5 mol % concentration, but decreases to 30% and 21% for the systems of initiator concentrations of 0.2 and 0.1 mol %, respectively. This is due to the effect of contaminated H_2O and/or oxygen included in the system. Consequently, strict elimination of these impurities is essential to realize the ideal living polymerization. Conventional drying over CaH_2 is insufficient for this purpose since the monomer and solvent contain ca. 30 ppm water as revealed by Karl Fischer titration and by gas chromatography. Hence, succeeding drying over activated molecular seives 3A resulted in the upper efficiency, 38%, in the case of 0.5 mol % concentration.

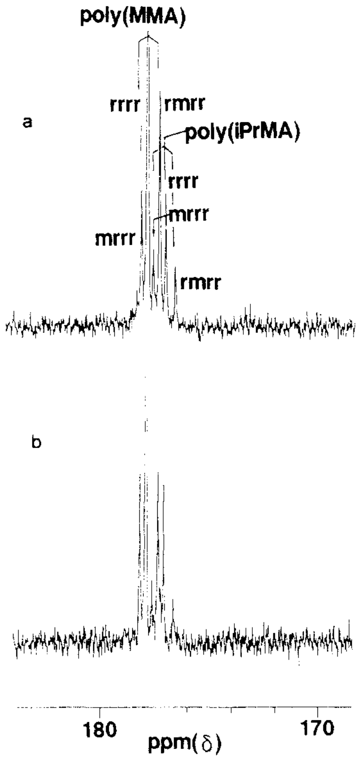


Figure 13. ^{13}C NMR spectra of a block copolymer in the CO region; (a) a mixture of poly(MMA) and poly(iPrMA) (5:1); (b) block copolymer of MMA with iPrMA (5:1).

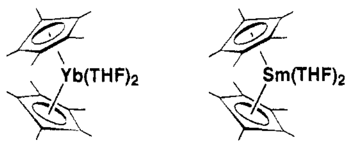


Figure 14. Typical organolanthanide(II) initiators.

Stoichiometric reactions of $Yb(C_5Me_5)_2(THF)_2$ with MMA in ratios of 1:1–1:2 however resulted in a complex mixture including $HCMe(CO_2Me)CH_2CMe_2CO_2Me$ in 35% yield. Thus, we can estimate that the real active species should be the $Yb^{III}H$ analog generated during the reaction.

T_g Measurement of Resulting Poly(MMA). A series of monodisperse poly(MMA) with variety of syndiotacticities has been obtained by using organolanthanide initiators at various temperatures. By taking advantage of the present polymers, we could measure the exact glass transition temperature (T_g) of poly(MMA). The values for 100% syndiotactic poly(MMA) have been reported to be 136–131 °C using conventional poly(MMA) with rather broad polydispersities. The glass transition points for polymers with $M_n > 30\,000$ increased with an increase of syndiotacticity and can be extrapolated to be 131 °C for 100% syndiotactic poly(MMA) (Figure 16).

Measurement of Melt Viscosity of Resulting Poly(MMA). In order to find new rheological properties of

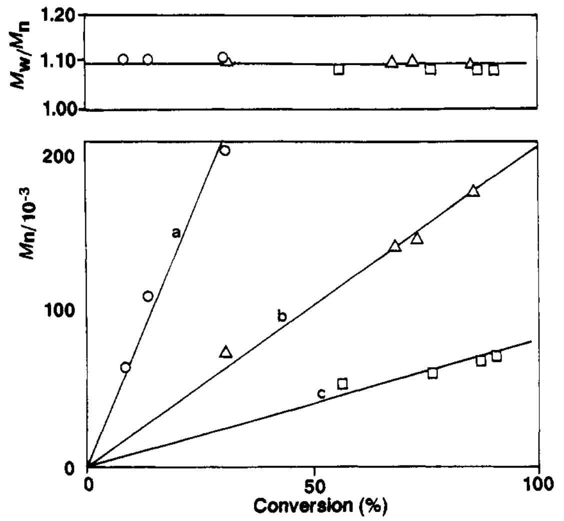


Figure 15. Conversion vs M_n and M_w/M_n plots for organolanthanide(II) systems: (a) $Yb(C_5Me_5)_2(THF)$, 0.1 mol ; (b) 0.2 mol %, (c) 0.3 mol %.

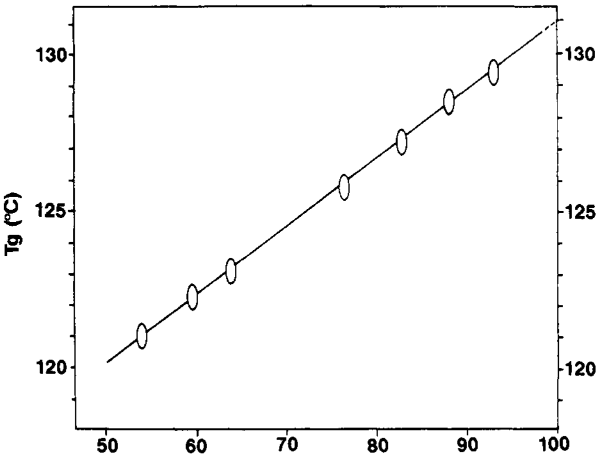


Figure 16. Dependence of T_g on the tacticity (rr %).

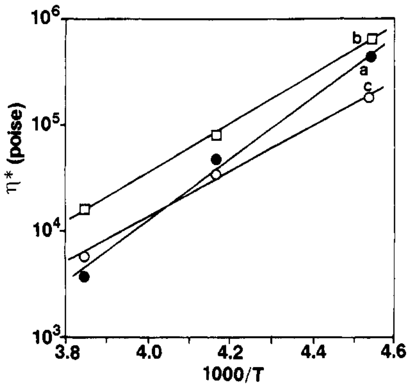


Figure 17. Temperature dependence of melt viscosity: (a) poly(MMA) prepared by $SmMe(C_5Me_5)_2(THF)$ at −90 °C (rr = 92%); (b) poly(MMA) prepared by $SmMe(C_5Me_5)_2(THF)$ at 0 °C (rr = 73%); (c) poly(MMA) prepared by radical initiator (rr = 52%).

the resulting monodisperse poly(MMA), we have measured the melt viscosity (η^*) using the polymer prepared by $SmMe(C_5Me_5)_2(THF)$ at −90 °C (a) ($M_n = 88 \times 10^{-3}$, $M_w/M_n = 1.03$, rr = 92.4%), the polymer obtained at 0 °C (b) ($M_n = 110 \times 10^{-3}$, $M_w/M_n = 1.04$, rr = 73.2), and the polymer obtained with the radical initiator (c) ($M_n = 40 \times 10^{-3}$, $M_w/M_n = 2.08$, rr = 52%). The effects of temperature on the melt viscosity are shown in Figure 17. The η^* values for polymer b are larger than that of polymer c at any temperature, and this is attributed to the difference in molecular weight. However, the behavior of polymer a differs greatly and at higher temperature η^* decreased markedly even compared with polymer c. This results from high syndiotacticity, and this property fits well for industrial high temperature molding of poly(MMA). The D-type shore hardness (5.0) and dynstat impact strength (5.0 (kg·cm)/cm^2) are nearly equal with the present samples.

Experimental Section

General Considerations. All the operations were performed under argon by using standard Schlenk techniques. Methyl methacrylate (MMA) was dried over CaH_2 for 4 days and the distillate was further dried over activated molecular sieves 3A for more than 5 days. Toluene was dried over Na/K alloy and was distilled before use. ^1H and ^{13}C NMR spectra were recorded on a JEOL GX-500 or JEOL GX-270 spectrometer. Gel permeation chromatographic analyses were run on a Tosoh Model SC-8010 using columns TSK gel G1000, G2500, G4000H, and G7000H in chloroform. The molecular weights of the polymers were determined using a calibration curve with standard poly(MMA) whose M_w was estimated from the light-scattering method.

Polymerizations of MMA Initiated by Organolanthanide(III) Complexes. A typical example is given below. To a toluene solution (20 mL) of MMA (200 mmol, 2.38 mL) was added at once the toluene solution (5 mL) of $[SmH(C_5Me_5)_2]_2$ (0.4 mmol, 165 mg) with vigorous magnetic stirring at 0 °C. After the solution was held for 40 min, the resulting polymer solution was poured into methanol (100 mL) to induce the precipitation of the polymer. The resulted polymer was permitted to stand for 5 h and was dried in vacuum.

Isolation of the 1:2 Adduct of $[SmH(C_5Me_5)_2]_2$ with MMA. To a toluene solution (50 mL) of $[SmH(C_5Me_5)_2]_2$ (2.5 mmol, 1.0 g) was added a toluene solution (5 mL) of MMA (5.0 mmol, 0.59 mL) at once at 0 °C. The orange-purple solution turns pale-orange immediately after mixing with MMA. The reaction was carried out for 10 min and after the concentration of solution to 5 mL hexane (30 mL) was added to obtain the crystals. After repeating the recrystallizations, the 1:2 adduct was obtained as orange single crystals (mp 132 °C). Deuterolysis of the product gave $DCMe(CO_2Me)CH_2CMe(CO_2Me)CH_3$. ^1H NMR (chloroform-*d*): δ (ppm) 1.12 (s, Me, 3), 1.14 (s, Me, 3), 1.18 (s, Me, 3), 2.07, 1.59 (d, CH_2, 2), 3.64, 3.65 (s, OMe, 6).

Isolation of the 1:2 Adduct of $YbMe(C_5Me_5)_2(THF)$ with MMA. A toluene solution (5 mL) of MMA (5.0 mmol, 0.59 mL) was added to a solution of $YbMe(C_5Me_5)_2(THF)$ (2.5 mmol, 1.06 g) at once at 0 °C. The reaction was carried out for 10 min. After concentration of the product to 5 mL, hexane (30 mL) was added to obtain the microcrystalline product. Hydrolysis of the product yielded $HCMe(CO_2Me)CH_2CMe(CO_2Me)C_2H_5$. ^1H NMR (chloroform-*d*): (racemic derivative) δ 0.79 (t, Me, 3), 1.12 (s, Me, 3), 1.14 (d, Me, 3), 1.38 (q, CH_2, 2), 1.42, 2.21 (dd, CH_2, 2), 3.64, 3.65 (s, OMe, 6); (meso derivative) 0.79 (t, Me, 3), 1.12 (s, Me, 3), 1.10 (d, Me, 3), 1.65 (q, CH_2, 2), 1.72, 1.98 (dd, CH_2, 2), 3.64, 3.65 (s, OMe, 6).

Preparation of $[Y(C_5Me_4SiMe_3)_2OCH{=}CH_2]_2$. The enolate was synthesized with reference to the literature.[70] $C_5H_5SiMe_3$ was lithiated with 1 equiv of BuLi in THF and was reacted with anhydrous YCl_3 (0.5 equiv) to give $(C_5H_4SiMe_3)_2YCl_2$ in 78% yield. The resulting $(C_5H_4SiMe_3)_2YCl_2$ was then reacted with $LiOCH{=}CH_2$, and the product was recrystallized in hexane. ^1H NMR (Chloroform-*d*): δ 0.25 (s, $SiMe_3$, 18), 4.07 (d, CH=CH*H*, 1), 4.28 (d, CH=C*H*H, 1), 6.29 (dd, C*H*=CH_2, 1), 6.39 and 6.78 (s, C_5H_4, 8).

Structure Determination of $Sm(C_5Me_5)_2(MMA)_2H$. A single crystal of $Sm(C_5Me_5)_2(MMA)_2H$ was inserted into a thin-walled glass capillary under argon and was mounted on a Rigaku automated four-circle diffractometer. Relevant crystal and data statistics are summarized in Table IV. Fractional atomic coordinates are given in Table X. The unit cell parameters at 20 °C were determined by a least-squares fit to 2θ values of 25 strong high-angle reflections. A sample crystal showed no significant intensity decay over the duration of a data collection. The crystal structure of the above complex was solved by the

Table X. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms in $Cp^*_2Sm(MMA)_2H$ with Estimated Standard Deviations in Parentheses[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Sm	0.10839(2)	0.23128(6)	0.10168(4)	3.20(2)
O(1)	0.1422(3)	0.043(1)	0.1529(6)	4.2(5)
O(2)	0.1430(2)	0.2648(8)	0.0083(5)	4.5(4)
O(3)	0.1691(3)	−0.1423(9)	0.1947(6)	5.9(5)
O(4)	0.1844(3)	0.338(1)	−0.0707(7)	7.0(7)
C(1)	0.1662(4)	−0.037(1)	0.1491(8)	4.1(7)
C(2)	0.1947(4)	−0.031(1)	0.0925(9)	4.6(7)
C(3)	0.1735(4)	0.013(1)	0.0048(8)	4.3(7)
C(4)	0.1887(4)	0.126(1)	−0.0355(9)	4.5(7)
C(5)	0.1710(4)	0.239(1)	−0.0296(7)	4.2(6)
C(6)	0.1444(5)	−0.156(2)	0.251(1)	7(1)
C(7)	0.2244(5)	0.071(2)	0.130(1)	7(1)
C(8)	0.2155(6)	−0.156(2)	0.087(1)	9(1)
C(9)	0.2212(5)	0.107(2)	−0.075(1)	6.2(9)
C(10)	0.1604(6)	0.441(2)	−0.093(1)	8(1)
C(11)	0.0430(4)	0.238(2)	−0.007(1)	6.0(8)
C(12)	0.0316(5)	0.212(2)	0.066(1)	8(1)
C(13)	0.0429(5)	0.094(2)	0.087(1)	6(1)
C(14)	0.0621(4)	0.041(1)	0.030(1)	4.8(8)
C(15)	0.0613(4)	0.132(2)	−0.030(1)	5.2(8)
C(16)	0.0351(7)	0.359(2)	−0.058(2)	13(2)
C(17)	0.0038(5)	0.292(3)	0.101(2)	16(2)
C(18)	0.0326(7)	0.020(3)	0.158(1)	14(2)
C(19)	0.0750(5)	−0.098(2)	0.028(1)	9(1)
C(20)	0.0759(5)	0.120(2)	−0.110(1)	9(1)
C(21)	0.1260(5)	0.473(1)	0.157(1)	4.4(8)
C(22)	0.0960(5)	0.431(2)	0.203(1)	5.9(9)
C(23)	0.1123(5)	0.334(2)	0.2562(9)	5.5(8)
C(24)	0.1498(5)	0.322(1)	0.2465(9)	4.9(7)
C(25)	0.1572(5)	0.404(1)	0.187(1)	4.8(8)
C(26)	0.1181(9)	0.577(1)	0.098(1)	14(2)
C(27)	0.0590(7)	0.500(2)	0.206(2)	15(2)
C(28)	0.0940(7)	0.268(2)	0.319(1)	13(1)
C(29)	0.1786(6)	0.237(2)	0.301(1)	11(1)
C(30)	0.1941(6)	0.431(2)	0.163(1)	10(1)

[a] Positional parameters are in fraction of cell edges, and B_{eq} is the isotropic equivalent temperature factor calculated from the corresponding anisotropic factor.

heavy-atom method and refined by full-matrix leas squares, as implemented in the TEXSAN crystallographic software package utilizing the observed reflection $[|F_o| > 3\sigma(F_o)]$. In the subsequent refinements, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the amplitudes of observed and calculated structure factors, respectively. After the anisotropic refinement of non-hydrogen atoms, all hydrogens atomes were located in the difference Fourier maps with the help of geometrical calculations and were refined isotropically.

T_g Measurement of Poly(MMA). Glass transition points of poly(MMA) with M_n = (2.5–5.0) × 10^3 obtained at various temperatures were measured with Rigaku Denki DSC 8230B and DSC 8240B.

Measurement of Melt Viscosity. Melt viscosity measurements were recorded on Rheometrics dynamic analyzer Model 700 at the frequency of 1 (rad/s) and strain = 10%.

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