8014 *Macromolecules* **1996,** *29,* 8014−8016

Syndiospecific Polymerization of Methyl Methacrylate Catalyzed by Lanthanoid Thiolate Complexes Bearing a Hexamethylphosphoric Triamide Ligand

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Received March 14, 1996
Revised Manuscript Received September 10, 1996

Organolanthanoid complexes such as Cp*$_2$LnR (Cp* = η^5-C$_5$Me$_5$, R = alkyl and hydride) have attracted much interest since they are highly active catalysts for the polymerization of ethylene.[1−4] In 1992, our research group reported that Cp*$_2$LnR exhibited high activity for the polymerization of polar monomers such as methyl methacrylate (MMA) and alkyl acrylates,[5,6] as well as the ring opening polymerization of cyclic polar monomers such as ϵ-caprolactone and δ-valerolactone.[7] Our findings opened a new era in lanthanoid-complex-assisted polymerization chemistry and were followed by rapid development in this field.[8−14] Lanthanoid alkoxide complexes without cyclopentadienyl type ligands can also initiate the polymerization of polar monomers.[15−20] Okamoto and his co-workers recently reported that lanthanoid alkoxide clusters formulated empirically as [Ln(OPr^i)$_3$(LiOPr^i)$_{12}$(LiCl)$_{2-3}$] (Ln = Ce, La) were catalysts for polymerization of MMA.[21] It is uncertain that the lanthanoid metal acts as the catalyst center, since lithium alkoxides supported by lanthanoid binaphtholates were found to generate lithium enolate species[22] and lithium free lanthanoid alkoxides did not exhibit any activity for the polymerization of MMA. We expect that structurally well-defined thiolate complexes of lanthanoid elements become initiators for the polymerization of MMA on the basis of the fact that the Ln−S bond is inherently weaker than the Ln−O bond[23] and lanthanoid thiolate compounds generated *in situ* react with enones to give Michael adducts.[24] We recently prepared a series of arenethiolate complexes of lanthanoid elements by the direct reaction of metallic lanthanoid with diaryl disulfide and elucidated their structures by X-ray analysis.[25,26] Now, we have examined these lanthanoid thiolate complexes as catalyst precursors for the polymerization of polar monomers. Herein, we communicate the syndiospecific polymerization of MMA using various kinds of the lanthanoid thiolate complexes.

The polymerization of MMA proceeded in THF or toluene, and the results are summarized in Table 1.[27] Thiolate complexes of lanthanoid(III) and lanthanoid(II) such as **1a**−**c**, **2a**,**c**, **3a**,**c**, **4a**,**b** (Chart 1) were found to be initiators of the polymerization.[25,26]

Lanthanoid benzenethiolate complexes **1** and **2** that have HMPA ligands catalyzed the polymerization of MMA to give syndiotactic polymers, the tacticities (rr up to 82%) of which are comparable to those of PMMA obtained at 0 °C by Cp*$_2$LnR (Ln = Sm, Yb, Lu and Y; R = H, Me) (rr = 82−84%).[6] The 4[mm][rr]/[mr]^2 values of these syndiotactic polymers are close to 1, indicating the chain-end control mechanism.[28] Addition of strongly coordinating HMPA ligands changes the stereospecificity of **3a** in toluene from isospecific (run 7) to syndiospecific (run 9). A similar ligand effect of HMPA has been observed in the polymerization of MMA using *n*-BuMgBr in toluene/THF at −50 °C, changing syndiospecificity (rr) from 50% to 63%.[29] Thus, the coordination of HMPA ligand to lanthanide thiolate complexes improves the syndiospecificity more effectively compared with similar coordination to magnesium of Grignard reagents. Among the HMPA-free complexes, it is notable that the europium(II) complex **4b** shows a different selectivity of the polymerization that gives an isotactic PMMA (mm = 68%) in THF in good yield.[30,31] The 2[rr]/[mr] value of this polymer is 1.05, indicating the enantiomorphic site control.[28]

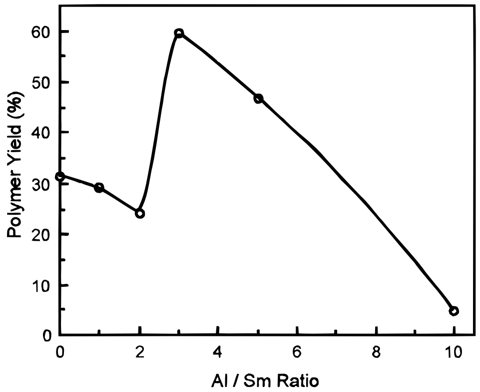


Figure 1. The yield of PMMA depending on the molar ratio of complex **3a** and cocatalyst MeAl(dbmp)$_2$. Polymerization was carried out in toluene at 0 °C for 1 h. [monomer]$_0$ = 1 M, [Sm] = 20 mM.

Chart 1

Ln(SPh)$_3$(hmpa)$_3$
1
a: Ln = Sm
b: Ln = Eu
c: Ln = Yb

[{Ln(hmpa)$_3$}$_2$(μ-SPh)$_3$][SPh]
2
a: Ln = Sm
c: Ln = Yb

hmpa = hexamethylphosphoric triamide

Ln(SAr')$_3$(py)$_3$
3
a: Ln = Sm
c: Ln = Yb

[Ln(SAr')(μ-SAr')(thf)$_3$]$_2$
4
a: Ln = Sm
b: Ln = Eu

Ar' = 2,4,6-triisopropylphenyl, py = pyridine

The coordination of HMPA ligand affects also the molecular weight distribution of the polymer. Complexes **1** and **2** afforded PMMA with relatively narrow unimodal molecular weight distribution, while complexes **3** and **4** resulted in polymerization with broader or bimodal distribution. The donative coordination of HMPA ligand to the metal center of **1** and **2** weakens the Ln−S bonds[26] to accelerate the initiation step (*vide infra*), and the bulkiness of this ligand significantly retards the propagation reaction, resulting in the polymers with a relatively narrow molecular weight distribution.

Generally, the stereoregularity of polymers increases with decreasing polymerization temperature. However, these arenethiolate complexes did not polymerize MMA at −78 °C. The observed much lower activity of the thiolate complexes compared to Cp*$_2$LnR (Ln = Sm, Yb, Lu and Y; R = H, Me)[6] might be attributed to the larger bond disruption enthalpy of the Sm−S bond [*D*(Sm−SPr^n) = 73.4 kcal/mol] than that of the Sm−C bond [*D*(Sm−CH(SiMe$_3$)$_2$) = 47.0 kcal/mol].[23] The polymer-

S0024-9297(96)00387-7 CCC: $12.00

Table 1. Polymerization of MMA with Lanthanoid Thiolate Complexes[a]

					tacticity (%)				
run	catalyst	yield (%)	$\bar{M}_n/10^3$ [b]	$\bar{M}_w/\bar{M}_n$[b]	mm	mr	rr	$4[mm][rr]/[mr]^2$	$2[rr]/[mr]$
1	**1a**	24	17	1.41	1	19	80	0.89	–
2	**1a**[c]	79	28	1.77	2	21	78	1.41	–
3	**1a**[d]	<1	–	–	–	–	–	–	–
4	**1a**[e]	31	17	1.36	5	24	72	2.50	–
5	**1b**[c]	88	39	1.55	3	19	78	2.59	–
6	**1c**[c]	80	25	1.34	2	16	82	1.13	–
7	**2a**	14	16	1.34	1	19	80	0.89	–
8	**2c**	60	16	1.36	1	24	74	0.51	–
9	**3a**	44	bimodal		34	27	39	7.28	–
10	**3a**[e]	73	bimodal		56	24	20	7.78	1.67
11	**3a**/3HMPA	77	bimodal		10	11	79	26	–
12	**3a**/3HMPA[e]	96	8.3	1.70	6	20	74	4.44	–
12	**3c**	52	bimodal		21	32	47	3.86	–
13	**4a**	41	21	1.87	30	26	44	7.81	–
14	**4b**	85	29	3.58	68	21	11	6.78	1.05

[a] $[Ln] = 20$ mM, $[M]_0 = 1$ M, in THF, 0 °C, 24 h unless otherwise noted. [b] Determined by GPC analysis in THF, calibrated to a polystyrene standard. [c] $[Ln] = 20$ mM, $[M]_0 = 4$ M. [d] $[Ln] = 5$ mM, $[M]_0 = 1$ M. [e] In toluene.

Table 2. Polymerization of MMA with Lanthanoid Thiolate Complexes Assisted with $MeAl(dbmp)_2$[a]

								tacticity (%)		
run	complex	solvent	temp. (°C)	time (h)	yield (%)	$\bar{M}_n/10^3$ [b]	$\bar{M}_w/\bar{M}_n$[b]	mm	mr	rr
1	**1a**	THF	−78	24	76	27	1.74	0	13	87
2	**1a**	THF	0	24	73	25	1.44	3	27	70
3	**1c**	THF	−78	24	100	101	1.17	0	13	87
4	**1c**	THF	−78	1	22	14	1.41	12	28	60
5	**1c**	THF	0	24	75	29	1.57	2	25	73
6	**3a**	THF	−78	24	98	37	1.30	3	31	66
7	**3a**	THF	0	24	71	30	5.20	33	33	34
8	**3a**	toluene	0	24	69	12	1.44	45	32	23

[a] $[Ln] = 20$ mM, $[Al] = 60$ mM, $[M]_0 = 1$ M unless otherwise noted. dbmp = 2,6-di-*tert*-butyl-4-methyl-phenoxide. [b] Determined by GPC analysis in THF, calibrated to a polystyrene standard.

Table 3. Syndiospecific Polymerization of MMA by Various Initiators

					tacticity			
initiator	solvent	temp. (°C)	$\bar{M}_n/10^3$	$\bar{M}_w/\bar{M}_n$	mm	mr	rr	ref
t-BuLi/Al(n-Bu)$_3$[a]	toluene	−78	5.51	1.17	0	8	92	38,39
(piperidinyl)$_2$Mg	toluene	−78	12[b]	–	0	7	93	40
i-BuMgBr	THF	−110	8.9	2.57	0	6	94	41
m-VBzMgCl[c]	THF	−110	9.8	1.17	0	2.4	97.6	42
$(Ph_3C)CaCl$	DME	−63	256	3.3	0	5	95	43
$[SmH(C_5Me_5)_2]_2$	toluene	−95	187	1.05	0.3	4.4	95.3	6
1c/3MeAl(dbmp)$_2$	THF	−78	101	1.17	0	13	87	this work
$TiCl_4/AlEt_3$[d]	toluene	−78	216[b]	–	0	6	94	44
$PPh_3/AlEt_3$	toluene	−78	36.8	1.44	0	9	91	45
$TASHF_2/H_2C{=}C(OMe)OTMS$[e]	THF	−90	4.55	1.11	0	19	81	46

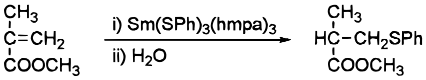
[a] Al/Li = 3. [b] $\bar{M}_v$ value. [c] *m*-Vinylbenzylmagnesium chloride. [d] Al/Ti = 5. [e] Tris(dimethylamino)sulfonium hydrogen difluoride/dimethylketene methyl trimethylsilyl acetal.

ization rate of MMA in the presence of these lanthanoid thiolate complexes could be enhanced by the use of $MeAl(dbmp)_2$ (dbmp = 2,6-di-*tert*-butyl-4-methylphenoxide)[32,33] as a cocatalyst as reported for the (TPP)-AlMe (TPP = tetraphenylporphinato) catalyst system.[34] Recently, the use of alkylaluminum aryloxides as a cocatalyst has also been reported to control the polymerization of alkyl acrylates with Grignard agents or alkyllithiums.[35−37] Thus the polymerization of MMA catalyzed by **3a** was carried out in the presence of various molar equivalents of $MeAl(dbmp)_2$, and the results are shown in Figure 1, which shows clearly that the 1:3 ratio for **3a**:$MeAl(dbmp)_2$ gave the maximum yield of the polymerization. Thus, the 1:3 ratio for catalyst:cocatalyst was used consistently for the following polymerization, and the results are summarized in Table 2. Although the catalyst systems with $MeAl(dbmp)_2$ were somewhat less stereoselective at the same temperature, the stereospecificity is similar to that observed in the corresponding Al-free systems. The polymerization of MMA at −78 °C with **1c**/3MeAl(dbmp)$_2$ (run 3) afforded PMMA with the highest syndiotacticity (rr = 87%), the highest molecular weight ($\bar{M}_n = 1.01 \times 10^5$), and the narrowest molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.17$) among the PMMAs polymerized by the lanthanoid thiolate catalyst systems.

Table 3 shows examples of catalysts for the syndiospecific polymerization of MMA. Although the reason why the initiator efficiency of **1c**/3MeAl(dbmp)$_2$ was so much decreased is not clear, this catalyst system is one of the ideal systems that afford highly stereoregular polymers with high molecular weight and narrow molecular weight distribution in good yield.

The 1:1 reaction of **1a** and MMA in THF followed by hydrolysis afforded methyl 3-(phenylthio)-2-methylpropionate (67% yield, equation 1), indicating that the polymerization was initiated by the insertion of MMA to the Ln−S bond. We assume that the 1,4-insertion generates a lanthanoid enolate species similar to the initiation reaction of the polymerization using

Cp^*_2LnR.[5,6] This type of reaction of lanthanoid thiolate compounds with α,β-unsaturated carbonyl compounds has already been reported by Fujiwara *et al.*[24] In the case of samarium(II), the reductive coupling of the monomer by divalent lanthanoids might also possibly initiate the polymerization of MMA as proposed in the systems of SmI_2[15] and Cp^*_2Sm.[11]



In conclusion, we demonstrate here that the lanthanoid thiolate complexes exhibited high catalytic activity for the polymerization of MMA. Application of these thiolate complexes as catalysts for the polymerization of polar monomers is now in progress.

Acknowledgment. The author (A.N.) thanks the Ministry of Education, Science and Culture, Japan, for financial support of this research (Specially Promoted Research No. 06101004).

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(27) The typical polymerization process is as follows: To a solution of $Yb(SPh)_3(hmpa)_3$ (44 mg, 0.04 mmol) in THF (1.19 mL) was added a 200 mM toluene solution of MeAl(dbmp)$_2$ (0.60 mL, 0.12 mmol) at −78 °C. Then MMA (0.21 mL, 0.20 g, 2 mmol) was added to the mixture at −78 °C. The reaction tube was sealed in argon and kept for 24 h at −78 °C. An excess of methanol was added to the reaction mixture. The resulting colorless polymer was collected by centrifugation and dried overnight at room temperature in vacuo. The yield was 100%.

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MA960387J