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Polymerization of Styrene by Divalent Organolanthanide Catalysts under High Pressure

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Introduction

There has been intense recent interest in the use of well-defined group 4 and 3/lanthanide metal complexes as catalysts or precatalysts for the polymerization of olefins.[1] However, room-temperature polymerization of styrene catalyzed by divalent lanthanide complexes has not been developed by now.[2] In the previously reported reaction of $(C_5Me_5)_2Sm$ with styrene, a bimetallic styrene complex, $[(C_5Me_5)_2Sm]_2(\mu,\eta^2:\eta^4\text{-}CH_2CHPh)$, was formed, and no polymerization was observed in the presence of an excess amount of styrene.[3,4] Mostly, this is due to the bulky structure of styrene and the saturated coordination sphere of lanthanide complexes. Using extreme conditions in the chemical reaction systems has also attracted much intense interest now.[5,6] Here, we report the results of the polymerization of styrene by divalent samarium catalysts under high pressure, in the effort to study the effect of pressure on the coordination structure of Sm(II) complexes and the catalytic reactivity. Different from group 4 metal-based catalyst systems where a second component such as methylalumoxane (MAO) or $B(C_6F_5)_3$ has to be used to generate the catalytically active species,[1a−c,f] lanthanide complexes such as $[Cp^*Sm(OAr)Cp^*K(THF)_2]_n$ (OAr = $OC_6H_2tBu_2$-2,6-Me-4, Cp* = pentamethylcyclopentadienyl),[7] $Sm(OAr)_2(THF)_3$,[8] $(Cp^*SmOAr)_2$[7], and $Cp^*SmCp(HMPA)_2$ (Cp = cyclopentadienyl, HMPA = hexamethylphosphoric triamide) are isoelectronic to the group 4 metallocene alkyl cations and do not require a second component in polymerization.[1b,d,e] High activities in the polymerization of styrenes by these Sm(II) complexes were observed in a compressed solution.

Experimental Section

Materials. Most precatalyst compounds were synthesized according to the literature: $[Cp^*Sm(OAr)Cp^*K(THF)_2]_n$ (OAr = $OC_6H_2tBu_2$-2,6-Me-4, Cp* = pentamethylcyclopentadienyl);[7] $Sm(OAr)_2(THF)_3$;[8] $(Cp^*SmOAr)_2$.[7] Compounds $Cp^*_2Sm(THF)_2$,[9] Cp*K,[10] CpNa,[10] and KOAr[7] were also synthesized according to literature. The complex $Cp^*SmCp(HMPA)_2$ (Cp = cyclopentadienyl; HMPA = hexamethylphosphoric triamide) was synthesized by the reaction of $SmI_2(HMPA)_4$[11] with Cp*K and CpNa in two steps. To a purple THF (20 mL) solution of $SmI_2(HMPA)_4$ (1 mmol) was added Cp*K (0.174 mg, 1 mmol). After 4 h at ambient temperature, the THF solvent was removed and 20 mL of toluene was added. The resulting solution of $Cp^*SmI(HMPA)_3$ with suspended potassium salts was stirred vigorously for 1 h and then filtered, leaving a dark green filtrate solution. Then, CpNa (0.5 mL of 2 M THF solution, 1 mmol) was syringed. After 4 h, the THF solvent was removed and 20 mL of toluene was added. The suspension was stirred vigorously for 8 h and then filtered. Pump out solvent from the filtrate left dark red solid $Cp^*SmCp(HMPA)_2$ (581 mg, 82%). Diffraction quality crystals were obtained by recrystallization from the THF solution covered with hexane. And it was characterized by elemental, ^1H NMR, and X-ray analyses.[12]

Styrene was purchased from Tokyo Kassei, Co. and was dried over CaH_2 for 3 days and distilled under reduced pressure before use. Toluene was distilled from sodium/benzophenone ketyl, degassed by the freeze−thaw method (three times), and dried over fresh Na chips in a glovebox.

Polymerization Procedure. A 5-mL Teflon sample holder was transferred into a glovebox with a nitrogen atmosphere. Then, 0.1 mmol of catalyst and 3.5 mL of toluene were added, followed by 1.5 mL of styrene. The sample holder was firmly closed by a screw cap and immediately cooled to −78 °C. Pressure was applied by a direct piston-cylinder apparatus with a hydraulic press during warming to room temperature. After 2 h the pressure was released, the viscous reaction mixture transferred to a glass beaker, and MeOH (200 mL) added. The polymer was precipitated and washed with MeOH several times and dried in vacco for 2 h and at 80 °C overnight.

Analysis. The yield was determined by weighing, and the molecular weight and polydispersity were determined against the polystyrene standard by gel permeation chromatography (GPC) with a differential refractometer (RI) at 40 °C. The ^{13}C NMR and ^1H NMR spectra of polystyrene were recorded at 130 °C in *o*-dichlorobenzene[13] by using a JNM-EX 270 (FT, 270 MHz) spectrometer.

Results and Discussion

The reactivities of different Sm(II) complexes in the polymerization of styrene under high pressure are given in Table 1.

The bimetallic complex $[Cp^*Sm(OAr)Cp^*K(THF)_2]_n$, developed very recently in our laboratory,[7] shows reactivity in the polymerization of styrene.[14] Under high pressure (750 MPa), it gave polystyrene with a much higher molecular weight ($M_n = 23 \times 10^4$; $M_w/M_n = 2.92$) and higher conversion (78.5%) than those of the reaction under normal pressure ($M_n = 2.17 \times 10^4$; $M_w/M_n = 2.17$; conversion = 29.2%). Although this precatalyst was not soluble in toluene, the reaction system became homogeneous in several minutes when the styrene monomer was added. To check the reactivity of the possible decomposed components of this catalyst, the blank reactions of Cp*K and KOAr with styrene were also carried out and no reactivity was observed even under high pressure. Complexes $Sm(OAr)_2(THF)_3$, $(Cp^*SmOAr)_2$, and $Cp^*SmCp(HMPA)_2$ are inactive in the polymerization of styrene at ambient conditions, but they all can catalyze the polymerization of styrene under high pressure. In the compressed solution, the opportunity of the monomer molecule to coordinate to samarium ions was apparently increased, which is necessary for the initiation of the polymerization reaction. Although the dimeric complex $(Cp^*SmOAr)_2$ is unsolvated, no reaction was observed when mixed with excess styrene at 1 atm. It means that this dimeric structure is very stable. Under high pressure, due to the attack by a styrene molecule, the equilibrium between $(Cp^*SmOAr)_2$ and $Sm(Cp^*)_2$ plus $Sm(OAr)_2$ may be assumed;[8] meanwhile, the latter component $Sm(OAr)_2$ catalyzed the polymerization of styrene under this high-pressure condition while the former Cp^*_2Sm was inactive. For this reason, the polystyrene obtained in this reaction was similar

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Table 1. Reactivities of Sm(II) Complexes in the Polymerization of Styrene[a]

	0.1 MPa			750 MPa		
precatalyst[b]	10^{-4} M_n[c]	M_w/M_n[c]	conversion (%)	10^{-4} M_n[c]	M_w/M_n[c]	conversion (%)
[Cp*Sm(OAr)Cp*K(THF)$_2$]$_n$	2.17	2.17	29.2	23.00	2.92	78.5
Sm(OAr)$_2$(THF)$_3$		no reaction		2.60	1.56	100
(Cp*SmOAr)$_2$		no reaction		1.11	2.73	21
Cp*SmCp(HMPA)$_2$		no reaction		1.65	2.46	18
Cp*Sm(OAr)(HMPA)$_2$		no reaction			no reaction	
Cp$_2^*$Sm(THF)2		no reaction			no reaction	

[a] Polymerization conditions: polymerization period 2 h, styrene 1.5 mL, toluene 3.5 mL, reaction contains 5 mL, catalyst 0.1 mmol, room temperature. [b] Cp*K and KOAr were also checked in these reaction conditions; neither of them showed any reactivity in the polymerization of styrene at 0.1 or 750 MPa. [c] Determined against polystyrene standards by GPC with a differential refractometer (RI) at 40 °C.

Table 2. Pressure Dependence of Yield, M_n, M_w/M_n, Proportion of Racemic Diad, and Activity of Catalyst for the Polymerization of Styrene by Sm(OAr)$_2$(THF)$_3$[a]

pressure (MPa)	conversion (%)	10^{-4} M_n[b]	M_w/M_n[b]	acti.[c] (g/mol·h)	Pr[d]
100	9.0	0.40	1.35	600	0.52
250	64.5	2.06	1.29	4400	0.52
500	99	2.07	1.85	>7320	0.60
750	99	2.60	1.56	>7320	0.61
1000	99	1.71	1.86	>7320	0.59

[a] Reaction conditions: polymerization period 2 h, styrene 1.5 mL, toluene 3.5 mL, catalyst 0.1 mmol, room temperature. [b] Determined against polystyrene standard by GPC with a differential refractometer (RI) at 40 °C. [c] Activity of catalyst, g of polystyrene/mol of catalyst·hour. [d] Proportion of racemic diad, determined by ^{13}C NMR.

Table 3. Pressure Dependence of Yield, M_n, M_w/M_n, and Activity of Catalyst for the Polymerization of Styrene by [Cp*Sm(OAr)Cp*K(THF)$_2$]$_n$[a]

solvent	pressure (MPa)	conversion (%)	10^{-4} M_n[b]	M_w/M_n[b]	acti.[c] g/mol·h
tol.	0.1	29.2	2.17	2.17	2000
tol.	250	99	20.97	2.84	>6849
tol.	500	52.0	12.91	2.94	3561
tol.	750	78.5	23.0	2.92	5386
THF	100	17.0	3.81	3.40	1150
THF	250	99	18.87	3.01	>6849
THF	500	99	18.79	3.14	>6849
THF	750	99	16.70	3.47	>6849
THF	1000	99	20.06	3.56	>6849

[a] Reaction conditions: polymerization period 2 h, styrene 1.5 mL, toluene 3.5 mL, catalyst 0.1 mmol, room temperature. [b] Determined against polystyrene standard by GPC with a differential refractometer (RI) at 40 °C. [c] Activity of catalyst, g of polystyrene/mol of catalyst·hour.

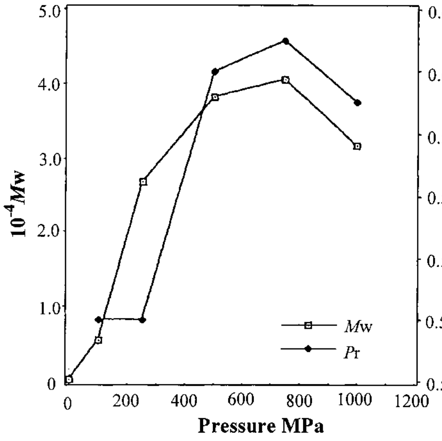

Figure 1. Pressure dependence of the proportion of racemic diad and molecular weight for the polymerization of styrene by Sm(OAr)$_2$(THF)$_3$.

to that in the Sm(OAr)$_2$(THF)$_3$ catalyst system but the conversion was much lower under the same reaction conditions. Different from this dimeric complex, a similar heteroleptic complex bearing both Cp* and OAr and stabilized by two HMPA molecules was inactive in the reaction with styrene even under high pressure probably due to the strong coordination power and steric bulk of the neutral ligand HMPA.[11] The complex Cp$_2^*$Sm(THF)$_2$ was also inactive in the polymerization of styrene under high pressure because of the bulky and rigid pentamethylcyclopentadienyl ligands which hindered the reaction. Interestingly, when one of the two pentamethylcyclopentadienyl ligands was replaced by a small cyclopentadienyl group (Cp*SmCp(HMPA)$_2$), the polymerization of styrene took place under high pressure, although the Sm atom was coordinated by two HMPA ligands.

Pressure dependence of the monomer conversion, molecular weight, molecular weight distribution, activity of catalyst, and the racemic diad proportion of polystyrene backbones for the polymerization of styrene by Sm(OAr)$_2$(THF)$_3$ and [Cp*Sm(OAr)Cp*K(THF)$_2$]$_n$ are shown in Tables 2 and 3. At 250 MPa the polymerization of styrene by Sm(OAr)$_2$(THF)$_3$ was carried out for 2 h, which gave atactic polystyrene ($P_r = 0.52$) with the molecular weight $M_n = 20\,600$. The molecular weight distribution was narrow ($M_w/M_n = 1.29$). Further experiments with pressures between 0.1 MPa and 1 GPa revealed that the rate was considerably enhanced as the pressure was increased and that the molecular weight was apparently enhanced between 0.1 and 250 MPa but was almost not changed as the pressure increased from 500 MPa to 1 GPa. It was very interesting to note that the proportions of racemic diad in the polystyrenes produced under pressures larger than 500 MPa (Pr = 0.59−0.61) were considerably larger than those synthesized under lower pressures ($P_r = 0.52$); see Figure 1. This suggested that the steric effect for forming syndio-rich atactic polystyrene was enhanced under high pressure. The molecular weight of polystyrene was slightly dropped to 17 100 at a higher reaction pressure of 1.0 GPa. It can be assumed that high viscosity[15] retards the diffusion of the monomer to the active center and decreases the rate of chain propagation while chain termination via β-H transfer to the metal should be independent of the monomer concentration. There are two ways in which the pressure can affect the polymerization rate: the pressure increases the initiation rate of this reaction and decreases the rate of chain propagation under very high pressure. This was similar to the polymerization of hex-1-ene by zirconocene catalysts.[6]

It was also valuable to note that the Sm/K bimetallic catalyst [Cp*Sm(OAr)Cp*K(THF)$_2$]$_n$ can polymerize styrene under high pressure even in THF. It was clear that the complex [Cp*Sm(OAr)Cp*K(THF)$_2$]$_n$ had an equilibrium to KOAr and Cp*$_2$Sm(THF)$_2$ in THF[7] and it was inactive in the polymerization of styrene at 1 atm. Also, the decomposed components KOAr and Cp$_2^*$Sm(THF)$_2$ were inactive in the polymerization of styrene even under high pressure. It is assumed that the high pressure forced the equilibrium back to the catalyst side and initiated the polymerization reaction. The molecular weight of the polystyrene obtained by [Cp*Sm(OAr)Cp*K(THF)$_2$]$_n$ in THF showed a similar pressure dependence as that in toluene; see Table 3.

When the behaviors of different catalyst systems in the polymerization of styrene under high pressure were compared, polymer conversions or reaction rates were found to vary according to the ligand environments around the samarium. Bulky and rigid ligand groups hindered the polymerization reaction even under high pressure. The reaction rates of these catalysts in the polymerization of styrene under high pressure are in this order: [Cp*Sm(OAr)Cp*K(THF)$_2$]$_n$ > Sm(OAr)$_2$(THF)$_3$ > (Cp*SmOAr)$_2$ > Cp*SmCp(HMPA)$_2$ $\gg$ Cp*Sm(OAr)(HMPA)$_2$ and Cp$_2^*$Sm(THF)$_2$ (no reaction).

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References and Notes

(1) Reviews: (a) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (b) Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, 1996. (c) Brintzinger, H.; Fisher, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (d) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Lappert, M. F., Eds.; Pergamon Press: Oxford, 1995; Vol. 4, Chapter 2. (e) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (f) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (g) Fu, P.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10747.

(2) Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ at 50 °C was recently reported to be active for polymerization of styrene: Ihara, E.; Hayakawa, T.; Saiki, A.; Yasuda, H. *Polym. Prepr. Jpn.* **1996**, *45*, 1357. Yasuda, H.; Ihara, E. *Bull Chem. Soc. Jpn.* **1997**, *70*, 1745.

(3) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219.

(4) Evans, W. J.; DeCoster, D. M.; Greaves, J. *Macromolecules* **1995**, *28*, 7929.

(5) For polymerization in solution under pressure: (a) Walling, C.; Pellon, J. *J. Am. Chem. Soc.* **1957**, *79*, 4782. (b) Symcox, R. O.; Ehrlich, P. *J. Am. Chem. Soc.* **1962**, *84*, 531. (c) Higgins, J. P.; Weale, K. E. *J. Polym. Sci., A* **1970**, *8*, 1705. (d) Yokawa, M.; Ogo, Y.; Imoto, T. *Makromol. Chem.* **1974**, *175*, 179.

(6) Fries, A.; Mise, T.; Matsumoto, A.; Ohmori, H.; Wakatsuki, Y. *Chem. Commun.* **1996**, 783.

(7) Hou, Z.; Zhang, Y.; Yoshimura, T.; Wakatsuki, Y. *Organometallics* **1997**, *16*, 2963.

(8) Hou, Z.; Fujita, A.; Yoshimura, T.; Jesorka, A.; Zhang, Y.; Yamazaki, H.; Wakatsuki, Y. *Inorg. Chem.* **1996**, *35*, 7190.

(9) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270.

(10) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271.

(11) Hou, Z.; Zhang, Y.; Wakatsuki, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 149. Hou, Z.; Wakatsuki, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1205.

(12) Results of elemental analysis for Cp*SmCp(HMPA)$_2$. Found: C, 45.41; H, 8.05; N, 11.50. Calcd. for $C_{27}H_{56}N_6O_2P_2$Sm: C, 45.73; H, 7.96; N, 11.85. ^{1}H NMR (C_6D_6, 22 °C) δ: 5.78 (s, 15H, C_5Me_5), 3.35 (br, 36H, HMPA), −2.18 (br, 5H, C_5H_5). The crystal data for Cp*SmCp(HMPA)$_2$ is as follows: $C_{27}H_{56}N_6O_2P_2$Sm, orthorhombic, $P2_12_12_1$, $a = 17.923(5)$, $b = 19.299(7)$, $c = 10.407(3)$ Å, $V = 3599(2)$ Å^3, $Z = 4$, $d = 1.309$ g cm^{-3}, $\mu = 17.552$ cm^{-1}. $R = 0.049$, $R_w = 0.057$ for 3098 unique data with $I > 3\sigma(I)$ and 343 variables.

(13) Kawamura, T.; Toshima, N. *Macromol. Rapid Commun.* **1994**, *15*, 479.

(14) Hou, Z.; Zhang, Y.; Wakatsuki, Y. Manuscript in preparation. For polymerization and copolymerization of styrene and ethylene by this type of complex, see: Hou, Z.; Tezuka, H.; Zhang, Y.; Yamazaki, H.; Wakatsuki, Y. *Macromolecules* **1998**, *31*, 8650.

(15) Je Noble, W. J.; Kelm, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 841.

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