

DMAO-activated Rare-earth Metal Catalysts for Styrene and Its Derivative Polymerization

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Electronic Supplementary Information

Abstract The catalytic performance of rare-earth metal dialkyl complexes in combination with DMAO (dry methylaluminoxane) is explored. In the presence of 60 equivalents of DMAO, the half-sandwich complex $(C_{13}H_8CH_2Ph)Sc(CH_2SiMe_3)_2(THF)$ (**1**) is inert for styrene polymerization, but $(C_5Me_4Ph)Sc(CH_2C_6H_4NMe_2-o)_2$ (**2**) converts 18% styrene into syndiotactic polystyrene. Under the same conditions, the constrained-geometry configuration sandwich complex $(C_{13}H_8CH_2Py)Sc(CH_2SiMe_3)_2$ (**3a**) displays extremely high catalytic activity ($>6420 \text{ kg}\cdot\text{mol}_{Sc}^{-1}\cdot\text{h}^{-1}$) and perfect syndiospecific ($rrrr>99\%$) for styrene polymerization, while its lutetium (**3b**) and yttrium (**3c**) analogues are nearly inactive. Although the binary catalytic system **3a**/DMAO exhibits very low activity for 4-methoxystyrene polymerization, it is an efficient catalyst for the syndiospecific polymerization of other styrene derivatives such as 2-methoxystyrene, 4-methylthiostyrene, 4-fluorostyrene, 4-dimethylhydrosilylstyrene, alkyne-substituted styrenes and 4-methylstyrene. In addition, the binary system **3a**/DMAO can copolymerize ethylene and styrene to give alternating copolymers with a single glass transition at 80 °C and 0.4 MPa ethylene pressures. By increasing styrene feed amount from 20 mmol to 60 mmol, the styrene content slight increases from 48.2 mol% to 53.8 mol%, but the polymerization activity is obviously promoted from $240 \text{ kg}\cdot\text{mol}_{Sc}^{-1}\cdot\text{h}^{-1}$ to $532 \text{ kg}\cdot\text{mol}_{Sc}^{-1}\cdot\text{h}^{-1}$.

Keywords DMAO; Syndiotactic polystyrene; Styrene; Ethylene; Copolymerization

Citation: Zhang, Z.; Jiang, Y.; Zhang, K.; Cai, Z. Y.; Li, S. H.; Cui, D. M. DMAO-activated rare-earth metal catalysts for styrene and its derivative polymerization. *Chinese J. Polym. Sci.* 2021, 39, 1185–1190.

INTRODUCTION

Transition metal complexes play a key role in converting olefin monomers into various polymer materials.^[1–3] Thus, design and synthesis of transition metal based catalysts have attracted extensive interest from the academic and industrial fields. In contrast, cocatalysts receive much less attention although they have played a very important role in the polymerization revolution.^[4] Factually, discoveries of new and more effective cocatalysts dramatically inspire the development of polymerization technology and fundamental understanding in this field.^[5–8] For example, two-component Ziegler-Natta catalytic systems activated by alkylaluminum display very high catalytic activity for ethylene and propylene polymerization and high isotactic selectivity in the polymerization of propylene and higher α -olefin monomers. While group 4 metallocene complexes activated by alkylaluminum exhibit very low activity for ethylene polymerization,^[9] the dilemma was finally resolved by Sinn and Kaminsky *via* replacing the alkylaluminum

cocatalyst with methylaluminoxane (MAO),^[8,10] prepared by controlled hydrolysis of $AlMe_3$. Since this discovery, MAO extremely accelerates the development of homogeneous metal catalysts with high activity and has been a very important cocatalyst for group 4 metal-catalyzed olefin polymerization due to its remarkable combination of alkylating, activating and impurity scavenging properties. Despite the huge success of MAO and its derivatives MMAO, DMAO and PMAO-IP *etc.* in promoting group 4 based catalysts-mediated olefin polymerization, few rare-earth metal bis(alkyl) complexes combined with MAO or its derivatives were reported to show high activity for olefin polymerization.^[11–13]

Past decades have witnessed a great progress towards the design and synthesis of rare-earth metal bis(alkyl) complexes with high activity and regio- and stereo-selectivity for the olefin polymerization.^[14–21] Notably, nearly all the rare-earth metal bis(alkyl) complexes with high activity are based upon the organoborate, $PhNHMe_2B(C_6F_5)_4$, $Ph_3CB(C_6F_5)_4$ or the borane $B(C_6F_5)_3$ (Scheme 1).^[22] However, the high cost of organoborate and borane severely hinders the industrial applications of highly effective rare-earth metal catalysts. Therefore, the exploration of effective and economical cocatalysts for rare-earth metal-mediated olefin polymerization catalysts has been a challenging and meaningful task. In this contribution,

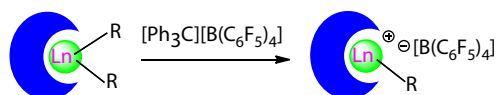
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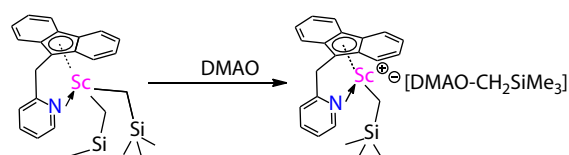
Received February 20, 2021; Accepted March 19, 2021; Published online June 2, 2021

we investigated the catalytic behaviors of rare-earth metal bis(alkyl) complexes activated by DMAO on the polymerization of styrene and its derivatives (Fig. 1). In the presence of DMAO, the constrained-geometry configuration scandium bis(alkyl) complex, **3a**, bearing a pyridyl-methylene fluorenyl ligand exhibited unprecedented high catalytic activity for styrene and its derivatives. In addition, the binary catalytic system **3a**/DMAO was also used to perform copolymerization of styrene and ethylene to give alternating ethylene-styrene copolymers.

Literature



This work



Scheme 1 Rare-earth metal cationic complexes.

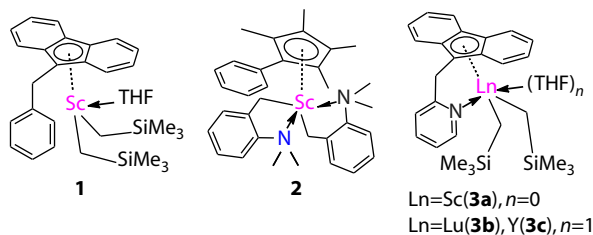


Fig. 1 Rare-earth metal bis(alkyl) complexes.

EXPERIMENTAL

General Considerations

All manipulations were performed under a dry and oxygen-free nitrogen atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified *via* a SPS system. The monomers were dried over CaH₂ under stirring for 12 h and distilled before use. Styrene, dry methylaluminoxane (DMAO) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ were purchased from Energy Chemical. Complexes **1**, **2**, **3a**, **3b**, **3c** were prepared according to the reported methods.^[23–25]

¹H- and ¹³C-NMR spectra were recorded on a Bruker AV400 (400 MHz for ¹H-NMR; 100 MHz for ¹³C-NMR) spectrometer. The molecular weight and molecular weight distribution of the polymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220 type high temperature chromatography equipped with three PL-gel 10 μm Mixed-BLS type columns at 150 °C. The glass transition temperature (*T*_g) of the polymer was measured through differential scanning calorimetry (DSC) analysis, which was carried out on a METTLER TOPEM DSC instrument under nitrogen atmosphere. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C, cooling at 10 °C/min to room temperature, and then recording the

second DSC scan from 25 °C to 300 °C at 10 °C/min.

Typical Procedure for Styrene Polymerization

In a glovebox, a toluene solution (0.8 mL) of **1a** (4.8 mg, 10 μmol) and 60 equiv. of DMAO (34.8 mg, 600 μmol) were added to a flask. Then, the mixture was stirred for 10 min. 0.52 g (5 mmol) of styrene was added to the flask. After the mixture was stirred for 5 min, the ethanol solution with BHT was injected to terminate the polymerization. The mixture was poured into a large amount of ethanol to precipitate the polymer product. The obtained white solid product was filtered and then dried under vacuum at 45 °C to a constant weight.

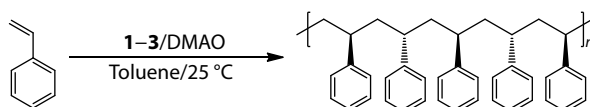
Typical Procedure for Copolymerization of Ethylene and Styrene

In a typical experiment, a 50-mL glass pressure vessel (dried in a 120 °C oven overnight prior to use) was loaded with the styrene (2.084 g, 20 mmol) and 18 mL of dry toluene inside the glovebox. A magnetic stir bar was added to the pressure vessel, and it was sealed, taken out of the glovebox, and attached to a high-pressure/high-vacuum line, then allowed to warm and equilibrate at the desired reaction temperature for 5 min using an external oil bath. The solution was saturated with 0.4 MPa of ethylene at the same time. The catalytically active species was freshly generated by mixing measured amounts of precatalyst and cocatalyst in a vial in the glovebox (in 2 mL of toluene) for 5 min. The catalyst solution was then removed from the glovebox, and quickly injected into the rapidly stirring solution, using a gastight syringe equipped with a spraying needle. After a measured time, the polymerization was quenched by addition of MeOH. All volatiles were removed from the remaining polymerization mixture, and the products were dried under high vacuum at 60 °C overnight until reaching a constant weight.

RESULTS AND DISCUSSION

Styrene Polymerization

Complexes **1–3** alone were inert for styrene polymerization and so were the binary systems **1–3**/alkylaluminum. The half-sandwich complex **1**, activated by 60 equiv. of DMAO, was first tested for styrene polymerization at 25 °C for 3 h to give a trace amount of product (Table 1, run 1). Another half-sandwich complex **2** only achieved an 18% conversion rate under the same conditions (Table 1, run 2). Surprisingly, when the constrained-geometry configuration scandium complex **3a** was used to initiate styrene polymerization, 500 equiv. of styrene were completely transformed into syndiotactic polystyrene in 5 min (Table 1, run 3). However, its lutetium and yttrium analogues **3b** and **3c** became inert again, although they can catalyze the styrene polymerization with extremely high activity in the presence of organoborate.^[23,26,27] These results indicate that increasing ancillary ligand bulk or reducing metal ionic radius facilitate to weaken the interaction strength between the anion $[\text{DMAO-CH}_2\text{SiMe}_3]^-$ and the cationic metal center, and enhance polymerization activity. The DMAO-to-complex **3a** feed ratio has a strong influence on the polymerization activity due to the “cage-like” structure of DMAO, $[-\text{Al}(\text{Me})\text{O-}]_n$.^[28] Reducing the feed amount of DMAO severely suppressed the polymerization process and broadened the molecular weight distributions due to the incomplete alkyl abstraction/activation reaction of complex **3a** (Table 1, runs

Table 1 Styrene homopolymerization using complexes **1–3a**.^a

Run	Cat.	[M]/[Ln]/[DMAO] (molar ratio)	Time (min)	Conv. (%)	Act. ^b	<i>rrrr</i> ^c (%)	<i>M_n</i> ^d (×10 ⁴)	<i>M_w</i> / <i>M_n</i> ^d	<i>T_g</i> ^e (°C)	<i>T_m</i> ^e (°C)
1	1	500/1/60	180	Trace	—	—	—	—	—	—
2	2	500/1/60	180	18	1	>99	1.37	2.31	99	272
3	3a	500/1/60	5	100	>624	>99	3.45	1.63	99	271
4	3b	500/1/60	180	Trace	—	—	—	—	—	—
5	3c	500/1/60	180	Trace	—	—	—	—	—	—
6	3a	500/1/5	120	19	5	>99	3.55	3.04	100	271
7	3a	500/1/10	120	75	19.5	>99	6.22	2.65	99	272
8	3a	500/1/20	120	100	>26	>99	5.61	1.90	98	271
9	3a	500/1/30	120	100	>26	>99	4.77	1.74	97	270
10	3a	500/1/100	5	100	>624	>99	3.09	1.70	99	271
11	3a	1000/1/60	5	100	>1248	>99	4.78	1.66	99	275
12	3a	2000/1/60	5	100	>2496	>99	10.74	1.96	101	274
13	3a	3000/1/60	5	100	>3744	>99	13.61	2.06	100	272
14	3a	5000/1/60	5	100	>6240	>99	16.34	2.17	97	273

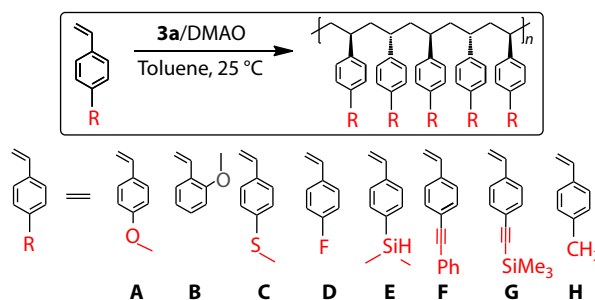
^a Conditions: complex [Ln] (10 μmol), [St]=1.0 mol/L in toluene, *T_p*=25 °C, unless otherwise noted; ^b Given in kg of polymer·mol⁻¹·h⁻¹; ^c Measured by ¹³C-NMR spectroscopy in C₆D₂Cl₂ at 100 °C; ^d Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard; ^e Determined by DSC.

6–9). Therefore, it is necessary to maintain the DMAO-to-complex **3a** feed ratio over 60:1, which is far lower than the values reported in group 4 based olefin polymerization catalysts.^[29,30] Upon increasing styrene-to-**3a** loading ratio from 500:1 to 5000:1, the polymerization activity reached 6420 kg·mol⁻¹·h⁻¹ with the monomer concentration of 1.0 mol·L⁻¹ at 25 °C (Table 1, runs 11–14). Correspondingly, the number average molecular weights of the resultant products increased from 3.45×10⁴ g·mol⁻¹ to 16.34×10⁴ g·mol⁻¹ with relatively narrow molecular weight distribution of 1.66–2.17, indicating the single-site nature of the catalytic system. All the resultant products show high melting temperatures at 270–275 °C and are insoluble in toluene, chloroform and THF,

indicating their high syndiotactic nature. The ¹³C-NMR spectrum of polystyrene produced by complex **3a** show diagnostic peaks at δ=41.3, 44.6 and 145.6 ppm, indicating the characters of perfect syndiotacticity.^[31]

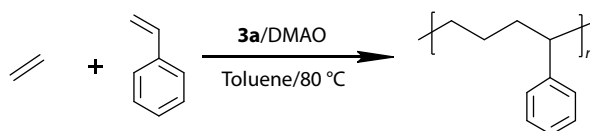
Polymerization of Styrene Derivatives

The excellent catalytic performance of the binary system **3a**/DMAO drives us to explore its catalytic behaviors for other styrene derivatives. Previously, the ternary system **3a**/ [Ph₃C][B(C₆F₅)₄]/Al*i*Bu₃ was reported to show very low catalytic activity for 4-methoxystyrene (**A**) polymerization,^[32] and, similarly, exposure of 100 equiv. of **A** to **3a**/DMAO for 15 min at 25 °C produced a trace of produce (Table 2, run 1), because the

Table 2 Homopolymerization of styrene derivatives by complex **3a**.^a

Run	Monomer	Time (min)	Yield (g)	Act. ^b	Conv. (%)	<i>rrrr</i> ^c (%)	<i>M_n</i> ^d (×10 ⁴)	<i>M_w</i> / <i>M_n</i> ^d	<i>T_g</i> ^e (°C)	<i>T_m</i> ^e (°C)
1	A	15	Trace	—	—	—	—	—	—	—
2	B	2	0.13	390	99	>99	1.40	1.03	79	243
3	C	10	0.15	90	99	>99	1.27	1.24	100	248
4	D	15	0.12	48	98	>99	2.93	1.69	107	322
5	E	15	0.16	64	99	>99	1.58	1.16	83	—
6	F	15	0.20	80	98	>99	5.71/1.98	1.11/1.18	158	—
7	G	15	0.19	76	98	>99	6.89	1.64	159	—
8	H	1	0.11	660	99	>99	4.40	1.49	110	—

^a Conditions: complex [Sc] (10 μmol), [M]:[Sc]:[DMAO]=100:1:60; [M]=0.25 mol/L in toluene, *T_p*=25 °C, unless otherwise noted; ^b Gram polymer/(mol cationic metallocene)⁻¹·h⁻¹; ^c Measured by ¹H-NMR spectroscopy in CDCl₃ at 25 °C; ^d Determined by GPC in THF at 40 °C against a polystyrene standard; ^e Determined by DSC.

Table 3 Copolymerization of ethylene with styrene by complex **3a**.^a

Run	[St] (mmol)	Yield (g)	Act. ^b	Conv. _{St} (%)	PS cont. ^c (mol%)	M_n ^d ($\times 10^4$)	M_w/M_n ^d	T_g ^e (°C)
1	20	1.20	240	44.7	48.2	1.57	1.69	30.2
2	40	2.33	466	44.8	51.9	2.39	1.97	39.1
3	60	2.66	532	34.6	53.8	3.20	2.07	39.2

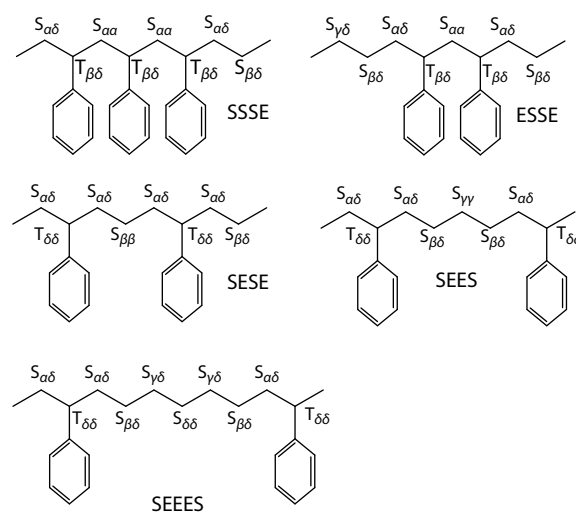
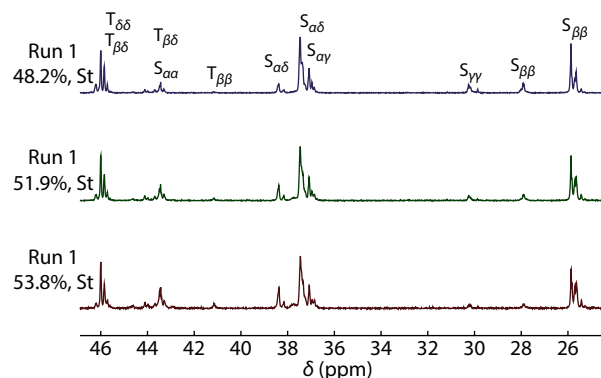
^a Conditions: complex [Sc] (10 μ mol), [Sc]:[DMAO]=1:60; toluene=20 mL, T_p =80 °C, ethylene pressure=0.4 MPa, time=30 min, unless otherwise noted; ^b Given in kg of polymer mol_{Sc}⁻¹·h⁻¹; ^c Measured by ¹H-NMR spectroscopy in CDCl₃ at 25 °C; ^d Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard; ^e Determined by DSC.

strong binding of the active metal cation Sc³⁺ with methoxy group reduces its interaction probability with vinyl group of **A**. When the methoxy group moves to the *ortho*-position of vinyl group, 2-methoxystyrene (**B**) was rapidly converted into syndiotactic product with a narrow molecular weight distribution of 1.03 (Table 2, run 2), because the *ortho*-methoxy group assisted the coordination and insertion reaction of the vinyl group.^[33] If the methoxy group was displaced by a weak base methylthio group, the catalytic activity of **3a**/DMAO was not nearly influenced and a crystalline syndiotactic poly(4-methylthiostyrene) with a melting temperature of 248 °C was produced (Table 2, run 3).^[34] Certainly, in case of styrene derivatives bearing weak polar or non-polar groups such as 4-fluorostyrene (**D**), 4-dimethylhydrosilylstyrene (**E**), alkyne-substituted styrenes (**F** and **G**) and 4-methylstyrene (**H**), **3a**/DMAO displayed high catalytic activity and perfect syndiospecificity (Table 2, runs 4–8), due to the weakest interaction of substituted groups with the active metal center.^[35–38] Even so, a bimodal poly(4-phenylethynylstyrene) was still obtained due to the side reaction of phenylethynyl group with the active metal species (Table 2, run 6).

Copolymerization of Ethylene and Styrene

Inspired by the above-mentioned results, **3a**/DMAO was utilized to initiate the copolymerization of styrene and ethylene. Delightfully, the binary system **3a**/DMAO indeed displayed high catalytic activity (240 kg mol_{Sc}⁻¹·h⁻¹) in the copolymerization of ethylene and styrene at 0.4 MPa ethylene pressure and 80 °C. With the styrene feed increasing from 20 mmol to 60 mmol, the catalytic activity dramatically increased from 240 kg·mol_{Sc}⁻¹·h⁻¹ to 532 kg·mol_{Sc}⁻¹·h⁻¹. The trend is consistent with that by using fluorenyl *N*-heterocyclic carbene scandium bis(alkyl)s.^[39–41] Notably, enlarging the styrene-to-**3a** feed ratio at a constant ethylene pressure only resulted in a slight increment of styrene incorporation in copolymer from 48.2 mol% to 53.8 mol%, and their DSC curves only show a single T_g (30.2–39.2 °C) without the melting peaks of polyethylene or syndiotactic polystyrene segments (Figs. S30–S32 in the electronic supplementary information, ESI). The ¹³C-NMR spectra of the resultant copolymers reveal that the overall pattern of signals keeps constant and is close to that observed in alternating ethylene-styrene copolymers (Figs. 2 and 3).^[42,43]

The resonance peak at δ 41.0 ppm assigned to the triad sequence SSS is very weak even in the high styrene content,^[44] indicating that **3a** prefers to initiate the alternating copolymerization of styrene with ethylene rather than their homo-

**Fig. 2** Possible monomer sequences in ethylene/styrene copolymers.**Fig. 3** Aliphatic region of ¹³C-NMR spectra recorded for ethylene/styrene copolymers from Table 3 (100 MHz, CDCl₃, 25 °C).

polymerization. This result is in sharp contrast to the multi-block ethylene-styrene copolymers formed by the half-sandwich scandium catalysts.^[31]

CONCLUSIONS

In summary, we have demonstrated that the syndiospecific polymerization of styrene and its derivatives could be realized by a binary catalytic system consisting of constrained-geometry

configuration scandium catalyst **3a** and DMAO. The high catalytic activity is mainly attributed to the presence of a pyridyl side arm in the fluorenyl ring, which reduces the openness around the active metal center and enhances the gap between the active cationic metal center and the anion $[\text{DMAO-CH}_2\text{SiMe}_3]^-$. Furthermore, the absence of AlMe_3 make DMAO a superior alkylating agent and then the stabilized cation-like complex is generated by the reaction of **3a** with a small amount of DMAO. In addition, the binary system **3a**/DMAO also displays high activity and perfect syndiospecificity for the polymerization of polar and non-polar styrene derivatives. Although complex **3a** shows high catalytic activity for the homopolymerization of ethylene and styrene, the copolymerization of ethylene and styrene catalyzed by complex **3a**/DMAO produced only alternating ethylene-styrene copolymers despite of the different ethylene/styrene feed ratios. This attributes to the constrained-geometry configuration around the active metal center, which impedes the consecutive insertion of bulky styrene and enhances the tendency of alternating enchainment of styrene and ethylene. This study sheds new light on how to design high active rare-earth metal olefin polymerization catalysts combined with DMAO.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2583-2>.

ACKNOWLEDGMENTS

This work was partially financially supported by the National Natural Science Foundation of China (Nos. 51773193 and 52073275).

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