

Cis-1,4-Polymerization of Myrcene by Dipyrromethene (DPM)-ligated Scandium Monoalkyl Complex

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Abstract

Organometallics complexes are the core of coordination polymerization. A series of scandium metal monoalkyl complexes bearing dipyrromethene (DPM) ligand have been prepared in moderate yields via the acid-base reaction between the DPM ligand and scandium metal tri(trimethylsilylmethyl) complexes. In the presence of a cocatalyst such as borate and AlR_3 , these complexes 1 and 2 exhibit high activities of up to $1.8\text{--}8.3 \times 10^3$ (g of polymer)/(molLn h) and high cis-1,4 selectivities of up to 97% in the polymerization of myrcene in toluene, yielding the cis-1,4-poly myrcene with heavy molecular weights (M_n of up to 3.6×10^5 g/mol) and molecular weight distributions ($M_w/M_n = 2.0\text{--}18.6$). In addition, these complexes 1 and 2 can also promote the copolymerization of isoprene and myrcene, and obtain random copolymers with the insertion rate of isoprene varying in the range of 20 -- 76%.

Keywords

Organometallic catalysts; Myrcene; Isoprene; Coordination polymerization.

1. INTRODUCTION

Dipyrromethene ligand (DPM) is a structure consisting of two pyrrole rings connected to a methene bridge with the characteristics of planar and conjugate systems(see Figure 1), As a result, the electrically neutral chelating complex formed with various ions has good photoelectric properties, and the chelating complex formed has a very strong molar absorption coefficient in the visible light region which are very important ligands in the field of organic chemistry .[1] Since the first report of dipyrrolidene-type ligands by Hans Fischer in 1930 ,[2] dipyrrolidene-type ligands have been widely studied and applied in various fields such as organic solar cells, [3] protein and DNA markers, [4, 5]fluorescent switches, [6-8] sensors ,[7] laser dyes,[9] dye-sensitized solar cells (DSSC), [10] and luminescent materials for light-emitting devices [11] after decades of development.

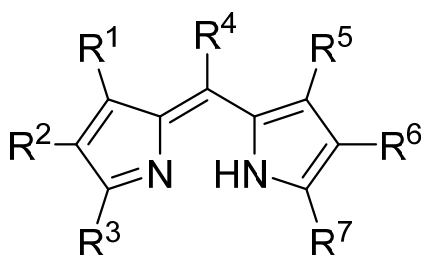


Figure 1. Dipyrrolidene (DPM) ligand

In fact, the dipyrromethene ligands (DPM) are not only rigid but also flexible, and the steric hindrance and electronic effect around the metal center can be changed by modification of the

ligand structure, and then the catalytic activity and stereoselectivity of the reaction can be regulated. And then, it has better metal coordination. [3] However, there are few rare earth metal catalysts for this ligand, especially its application in olefin coordination polymerization is still rare. So far, there is only one example of dipyrrolidene (DPM) ligated scandium metal monoalkyl complex. [12] In this paper, dipyrrolidene (DPM) ligated scandium metal monoalkyl complex have been synthesized, and catalyzed the polymerization of myrcene.

2. PROPERTIES

2.1. Materials and Method

All catalysts and the polymerization procedure were carried out in a nitrogen-filled MBraun glovebox. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$, and $\text{B}(\text{C}_6\text{F}_5)_3$ were purchased from J&K Chemical (Beijing, China). $\text{LiCH}_2\text{SiMe}_3$ (1.0 M solution in pentane) and LnCl_3 were purchased from Aldrich (St. Louis, MO, USA). $\text{Al}(\text{iBu})_3$ (1.1 M solution in hexane), AlMe_3 (1.0 M solution in Toluene), AlEt_3 (0.6 M solution in heptane), Na_2SO_4 , CaH_2 , dichloromethane, petroleum ether, and methanol were obtained from Energy Chemistry (Shanghai, China). DPM ligand [3] and $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ [13] were prepared according to the literature. Myrcene, isoprene was purchased from J&K Chemical (Beijing, China), and dried through CaH_2 . Toluene, THF, and hexane were purified by a solvent purification system (SPS-800, Mbraun, Shanghai, China) and dried over Na in the glovebox. The deuterated solvents C_6D_6 (99.6 atom% D) and CDCl_3 (99.8 atom% D) were purchased from Cambridge Isotope.

Elemental analyses, ^1H NMR and ^{13}C NMR, of rare-earth metal complexes were performed according to the literature. [14] Polymyrcene samples of gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) measurements were conducted according to the literature. [14]

2.2. Synthesis of Dipyrrolidene (DPM) Ligated Scandium Metal Monoalkyl Complexes

The ligand of dipyrrolidene (DPM) (L_1H - L_2H) [3] and scandium monoalkyl complex [12] were synthesized according to the method in the literature. (Figure 2)

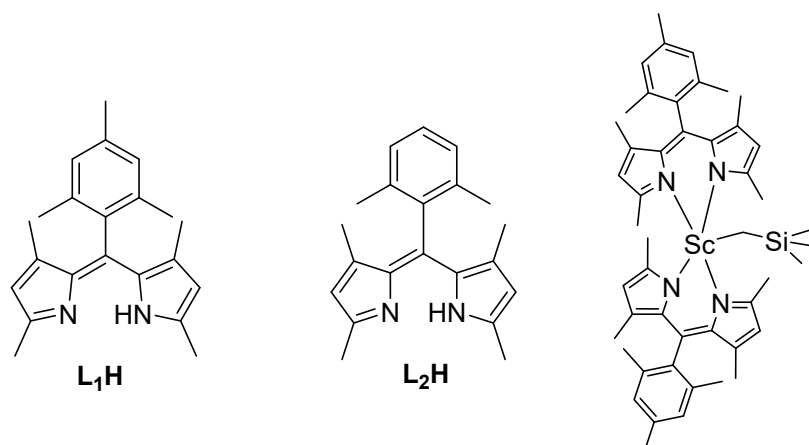


Figure 2. Dipyrrolidene(DPM) ligand and scandium monoalkyl complex

The complex showed good solubilities in THF and Tol, Insoluble in n-hexane. ^1H NMR(C_6D_6 , 400MHz, 298K) δ 6.79 (s, 4H), 5.89 (s, 4H), 2.34 (s, 18H), 2.14 (s, 12H), 1.49 (s, 12H), 0.09 (s, 9H), -0.04 (s, 2H). ^{13}C NMR(100MHz, C_6D_6) δ 145.45, 138.01, 136.52, 136.22, 129.34, 21.22, 17.52, 15.22, 14.35, 4.01, 0.03. EA: $\text{C}_{48}\text{H}_61\text{N}_4\text{ScSi}$: C, 75.16; H, 8.02; N, 7.30. Found: C, 74.79; H, 7.65; N, 6.92.

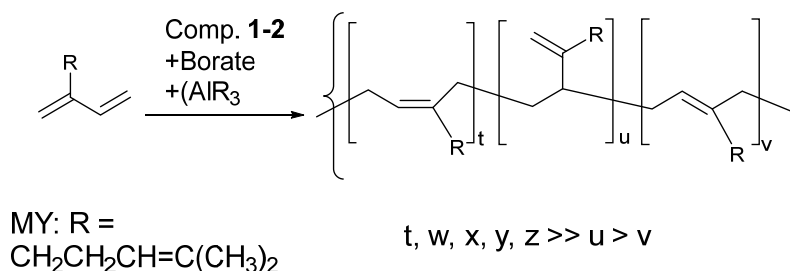
2.3. A Typical Procedure for myrcene (IP) Polymerization

A detailed polymerization procedure of myrcene is described here as a typical example. In a glovebox at 25 °C, to a toluene solution (8 mL) of $\text{Al}i\text{Bu}_3$ (181 μL , 1.1 M, 200 μmol) was added a toluene solution (8 mL) of complex 1 (0.013 g, 20 μmol), a toluene solution (2.5 mL) of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.018 g, 20 μmol), and myrcene (0.54 g, 4 mmol) in succession. In a 50 mL round bottom flask, the reaction mixture then became viscous rapidly. The flask was taken outside after 0.5 h, and then the solution was added to ethanol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent) to quench the reaction mixture. The obtained polymer was washed three times by ethanol and dried under vacuum at 40 °C to a constant weight (0.46 g, yield ca. 85%). The resulting polymer was soluble in THF and chloroform at room temperature. The isomer contents of the polymyrcene products were calculated from the ^1H and ^{13}C NMR spectra according to the literature. [15]

3. TESTS

3.1. Homopolymerization of Myrcene by Scandium Monoalkyl Complex 1/Activator/ AlR_3 Ternary Systems

Table 1. Cis-1,4-Polymerization of myrcene by scandium monoalkyl complex 1/activator/ AlR_3 ternary systems^a



entry	Cat.	A ^b	AlR_3	[IP]/[Sc]	t (min)	T (°C)	Y (%)	A ^c	Microstructure (%) ^d			M _n ^e 10 ⁴	M _w /M _n ^e	T _g ^f (°C)
									1,2-	c-1,4-	3,4-			
1	1	A	$\text{Al}i\text{Bu}_3$	200	1440	25	100	2.3	0	97	3	36	3.75	-63
2	2	A	$\text{Al}i\text{Bu}_3$	200	1440	25	89	2.0	16	80	4	1.5	18.6	-62
3	2	2A	$\text{Al}i\text{Bu}_3$	200	1440	25	85	1.91	9	76	15	10	6.1	-62
4	1	B	$\text{Al}i\text{Bu}_3$	200	1440	25	95	2.14	0	98	2	20	2.5	-65
5	1	C	$\text{Al}i\text{Bu}_3$	200	1440	25	90	2.0	0	90	10	21	5.19	-63
6	1	A	AlMe_3	200	1440	25	80	1.8	0	91	9	1	5.4	-63
7	1	A	AlEt_3	200	1440	25	82	1.84	0	82	18	1	11.2	-62
8	1	A	$\text{Al}i\text{Bu}_3$	200	1440	0	85	0.95	0	98	2	132	2.0	-64
9	1	A	$\text{Al}i\text{Bu}_3$	200	180	50	92	8.3	0	94	6	21	4.16	-63
10	1	A	$\text{Al}i\text{Bu}_3$	200	180	70	91	8.2	0	85	15	19	3.72	-62
11	1	A	$\text{Al}i\text{Bu}_3$	200	180	100	92	8.3	0	83	17	12	2.38	-62

^a Conditions: 20 μmol of Ln complex, 20 μmol of activator, [IP]/[Ln] = 200, 5 mL of toluene unless mentioned; ^b Activator: A = $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, B = $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$, and C = $\text{B}(\text{C}_6\text{F}_5)_3$; ^c Activity: 10³ g/molLn·h; ^d c-1,4, t-1,4, 3,4: cis-1,4, trans-1,4. Determined by ^1H , ^{13}C NMR spectra; ^e Determined by GPC in THF at 40 °C against polystyrene standard; ^f Measured by DSC.

The results showed that the complexes 1-2 had no catalytic activity as initiators in the polymerization of laurene. The ternary system composed of 1/ borate/ $\text{Al}i\text{Bu}_3$ showed better catalytic activity, selectivity and higher molecular weight than the ternary system composed of 2/ Borate/ $\text{Al}i\text{Bu}_3$ and the ternary system composed of 3/ Borate/ $\text{Al}i\text{Bu}_3$ (Table 2, entries 1–3).

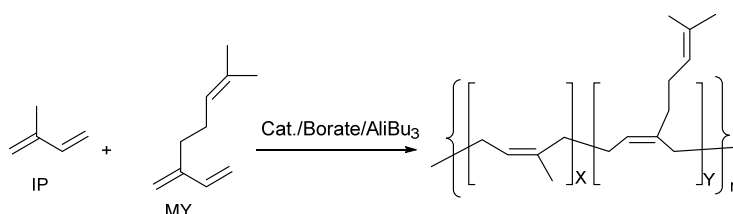
Different Borates also have great influence on the polymerization. Borate [PhMe₂NH][B(C₆F₅)₄] (B) shows lower catalytic activity and similar cis-1, 4-selectivity compared to [Ph₃C][B(C₆F₅)₄] (A), possibly due to the effect of PhNMe₂ coordination with central scandium metal. While Borate B(C₆F₅)₃ (C) showed low activity (2.0 × 10³ (g of polymer)/(molLn h)) and poor cis-1, 4-selectivity (up to 90%) (Table 2, entry 5).

Different alkyl aluminum has an important effect on the polymerization activity and selectivity. The complexes 1/ borate/AlMe₃ and 1/ borate/AlEt₃ exhibited activities of 1.8 × 10³ (g of polymer)/(molLn h) and 1.84 × 10³ (g of polymer)/(molLn h) with cis-1, 4-selectivity of 91% and 82%, which is similar to the terpolymer system composed of complex 1/ borate/Al*i*Bu₃ (Table 2, entry 6, 7). The results indicate that the weak interaction between the complex and alkyl aluminum affects the coordination and insertion reactions of myrcene monomers. Different cocatalyst alkyl aluminium have also important effects on the polymer molecular weight. Compared with the catalytic system of complex 1/ borate/Al*i*Bu₃, the molecular weight of polymers obtained by the catalytic system of complex 1/ borate /AlMe₃ and complex 1/ borate/AlEt₃ is much lower (Table 2 entry 1, 6, 7), this may be due to the fact that AlEt₃ and AlMe₃ are more prone to chain transfer reactions.

The resulting polymyrcene exhibited good solubility in THF and CHCl₃. The ¹H and ¹³C NMR spectra in CDCl₃ indicated that the resulting polymyrcene adopted almost complete cis-1,4-microstructures. GPC data showed that the molecular weight of polymyrcene was 1.0× 10⁴–3.6× 10⁵ g/mol, lower than that of polyisoprene [12], and the molecular weight distribution was wider (PDI = 2.0–18.6), indicating that a cross-linking reaction occurred. DSC data showed that the glass transition temperature of polymyrcene was relatively high (-65~- 62°C).

3.2. Copolymerization of Myrcene and Isoprene by Scandium Monoalkyl Complex 1/Activator/AlR₃ Ternary Systems

Table 2. Copolymerization of myrcene and isoprene by scandium monoalkyl complex 1/activator/AlR₃ ternary systems^a



entry	Cat.	A	AlR ₃	[IP] (mmol)	[My] (mmol)	MY Cont	A ^b	Mnc 10 ⁴	Mw/Mn ^c	Tg ^d (°C)
1	1	A	Al <i>i</i> Bu ₃	8	0	0	81	36	3.75	-60
2	1	A	Al <i>i</i> Bu ₃	6.4	1.6	20	53	1.5	18.6	-
3	1	A	Al <i>i</i> Bu ₃	5.33	2.66	27	46	46	6.1	-62
4	1	A	Al <i>i</i> Bu ₃	4	4	51	25	25	5.6	-58
5	1	A	AlMe ₃	4	4	50.6	15	15	2.5	-
6	1	A	Al <i>i</i> Bu ₃	2.66	5.33	68	17	17	5.19	-
7	1	A	Al <i>i</i> Bu ₃	1.6	6.4	76	13	13	3.72	-57
8	1	A	Al <i>i</i> Bu ₃	0	8	100	8	8	2.38	-62

^a Conditions: 20 μmol of [Ph₃C][B(C₆F₅)₄], 200 μmol of Al*i*Bu₃, 5 mL of toluene, 25 °C; ^b Activity: 10³ g/molLn·h. ^c Determined by GPC in THF at 40 °C against polystyrene standard; ^d Measured by DSC;

In the catalytic system of 1/[Ph₃C][B(C₆F₅)₄]/ Al*i*Bu₃, with the increase of the content of laureene monomer, the content of polymyrcene in the copolymer was increased, and the

microstructure of the copolymer also changed (table 3, entries 2–7). The copolymer of myrcene and isoprene has good solubility and can dissolve in CDCl_3 and THF. DSC data showed that the glass transition temperature (T_g) of the copolymer was -62 – -58 °C, ^{13}C NMR spectra showed that the copolymer was mainly *cis*-1,4-selective.

In summary, a series of scandium metal monoalkyl complexes bearing dipyrromethene (DPM) ligand have been prepared in moderate yields via the acid-base reaction between the DPM ligand and scandium metal tri(trimethylsilylmethyl) complexes. In the presence of a cocatalyst such as borate and AlR_3 , these complexes 1 and 2 exhibit high activities of up to 1.8 – 8.3×10^3 (g of polymer)/(mol_{Ln} h) and high *cis*-1,4 selectivities of up to 97% in the polymerization of myrcene in toluene, yielding the *cis*-1,4-poly myrcene with heavy molecular weights (M_n of up to 3.6×10^5 g/mol) and molecular weight distributions ($M_w/M_n = 2.0$ – 18.6). In addition, these complexes 1 and 2 can also promote the copolymerization of isoprene and myrcene, and obtain random copolymers with the insertion rate of isoprene varying in the range of 20 -- 76%.

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