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Dipyrromethene Scandium Complexes: Synthesis, Structure, and Catalytic Performance for 1,5-Hexadiene Polymerization

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Abstract

A series of dipyrromethene (DPM)-ligated scandium (Sc) complexes (1-3) have been prepared and characterized in moderate yields via the acid-base reaction between dipyrromethene (DPM) ligand and rare earth metal tri(trimethylsilylmethyl) complexes. They have been applied to the cyclopolymerization of 1, 5-hexadiene, and high trans cycloolefin polymers have been obtained. The effects of different alkylated aluminum on the microstructure and molecular weight of the polymer, and the effects of different complex structures on the polymer were studied.

Keywords

Scandium (Sc) complex; 1, 5-hexadiene; Cycloolefin polymers.

1. INTRODUCTION

Cycloolefin polymer is a kind of polymer material with ring structure on the main chain of molecules. Because of its unique physical and chemical properties, it has been widely used in the manufacture of various electronic and optical devices. Cyclization polymerization of unconjugated diene is an effective method to synthesize cycloolefin polymers with excellent properties. [1, 2] In 1951, Butler et al. reported solution polymerization of diallyl quaternary ammonium salt with free radicals for the first time, and obtained soluble linear polymers. Thus, it was proposed that polymer monomers with two double bonds could realize the synthesis of linear polymers through alternating "intramolecular and intermolecular" chain growth. [3] Since then, the development of catalytic systems with excellent performance, the control of selectivity in the polymerization of non-conjugated diene and the acquisition of cycloolefin polymers with rich structure have been the forefront and hotspot in the field of polymerization research at home and abroad.

In 1958, Marvel et al. used Ziegler-Natta catalytic system [$TiCl_4/Al(^iBu)_3$] to achieve the cyclopolymerization of non-conjugated dienes, and obtained polyolefin containing ring structure. [4] However, the Ziegler-Natta catalytic system has a very low catalytic activity for the polymerization of unconjugated diene, the structure of the obtained polymer is unregulated, and the product contains insoluble crosslinked polymers. In 1980, Kaminsky discovered the high activity of dicylocylchloro-zirconium [Cp_2ZrCl_2] for ethylene polymerization in the presence of methyl aluminoxane [MAO], which injected vigor into the study of metallocene catalysts. [5] Waymouth et al. studied in detail the catalytic performance of the polymerization of 1, 5-hexadiene catalyzed by diphenyl-zirconium chloride. Compared with Ziegler-Natta catalytic system, the polymerization of 1, 5-hexadiene catalyzed by diphenyl-zirconium showed higher cyclization and stereoselectivity, in which the ligand structure of diphenyl-zirconium was the main factor affecting the stereoselectivity of the cyclization. [6, 7] However, the catalytic system of dizirconium is used in a narrow range, and the study of cyclopolymerization of unconjugated diene is only limited to 1, 5-hexadiene. After 2000, with the continuous development of monometallocene complexes, people found that when used in catalytic of

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conjugated dienes polymerization monometallocene titanium and zirconium [8, 9, 10]catalyst of conjugated dienes polymerization activity is greatly increased, get some contain a double bond of the structure of the polymer, provides convenient conditions for the functionalization of polyolefin materials. However, the existence of a large number of double bond structures can not avoid the formation of cross-linked polymers. Recently, researchers have developed a large number of non-metallocene catalytic systems. Among them, Li Yuesheng et al. found that the hafnium catalytic system with pyridine amino complex could catalyze not only the cyclization polymerization of 1, 5-hexadiene but also the cyclization polymerization of 1, 7-ocdiene, with the cyclization selectivity up to 97%, and the selectivity of cis-seven-member ring was 100%. [11] Osakada's research group has made a great breakthrough in the polymerization of 1, 6-heptadiene by using nitrogen ligand complexation of non-post-ocallocene transition metal complexes. The copolymer of 1, 6-heptadiene was obtained by the copolymerization of 1, 6-heptadiene with trans - pentameric ring as the main structural unit. The copolymer of 1, 6-heptadiene and ethylene was obtained by the copolymerization of cobalt catalyzed by diimine complex system, but the molecular weight of the copolymer was lower and the molecular weight distribution was wider. However, the copolymerization of 1, 6-heptadiene with ethylene and 1, 6-heptadiene is only a mixture of two homopolymerers, which is catalyzed by the iron catalytic system of diimine complex. [12, 13]

At present, rare earth organometallic olefin polymerization catalyst has developed into a new type of olefin polymerization catalyst following Ziegler-Natta catalytic system and metallocene catalyst, which has a great application prospect in olefin polymerization industry. However, the studies on the catalytic polymerization of non-conjugated diene by rare earth metals have received little attention so far. Among them, the reported catalytic systems of Sm-Yttrium catalysts for the polymerization of 1, 5-hexadiene are far less active and selective than those of Zr catalysts [14, 15]. Lv Xiaobing et al. found that the azocyclic carbine scandium alkyl complex could catalyze the copolymerization of 1, 5-hexene and 1-hexene with high efficiency, and obtained the random copolymer of two monomers [16]. On this basis, this paper continues to investigate the catalytic performance of scandium monomer cyclopolymerization of unconjugated diene, further study the polymerization conditions and unconjugated diene structure on the polymerization activity, molecular weight and microstructure of the product.

2. PROPERTIES

2.1. Preparation and Characterization of Complexes 1, 2, 3

The ligand L_1H-L_3H of dipyrrolidene type was synthesized according to the method in literature [17]. (Figure 1)

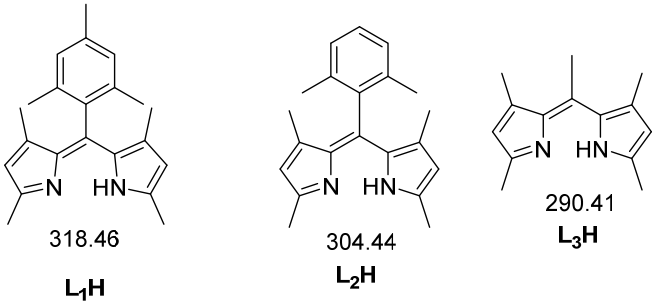

Figure 1. Dipyrrolidene type ligand

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The ^{1}H NMR spectrum of L_1H, (400 MHz, C_6D_6) δ 14.08 (s, 1H), 6.77 (s, 2H), 5.85 (s, 2H), 2.19 (s, 6H), 2.12 (s, 9H), 1.52 (s, 6H).

The ^{1}H NMR spectrum of L_2H ,(400 MHz, C_6D_6) δ 13.92 (s, 1H),7.05-7.03 (m, 1H) 6.93-6.91 (m, 2H), 5.83 (s, 2H), 2.19 (s, 6H), 2.11 (s, 6H), 1.46 (s, 6H).

The ^{1}H NMR spectrum of L_3H ,(400 MHz, $CHCl_3$) δ 12.62 (s, 1H), 6.19 (s, 2H), , 2.85 (s, 3H), 2.55 (s, 6H), 2.20 (s, 6H).

The scandium complexes(1-3) was synthesized according to the method in literature [17]. (Figure 2)

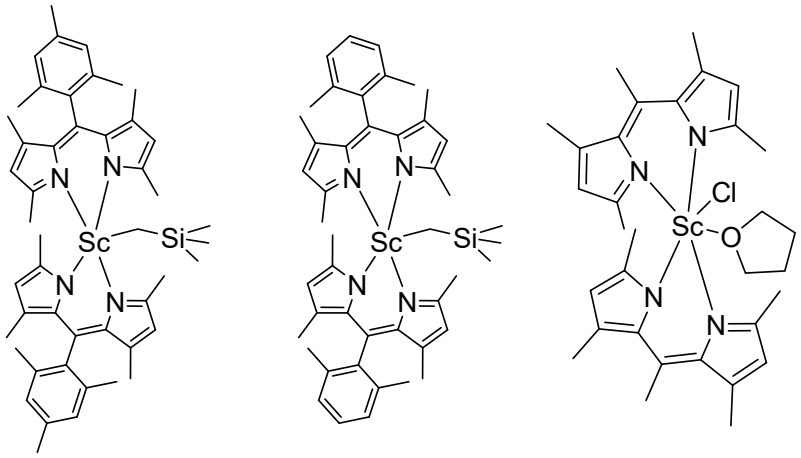

Figure 2. Dipyrromethene (DPM)-ligated scandium (Sc) complex(1-3)

The ^{1}H NMR spectrum of complex 1, (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: $C_{48}H_{61}N_4ScSi$: C, 75.16; H, 8.02; N, 7.30. Found: C, 74.79; H, 7.65; N, 6.92.

Complex 2 and 3 was synthesized by a similar method. The ^{1}H NMR spectrum of complex 2 , (C_6D_6, 400MHz, 298K) δ 7.09–7.05 (m, 2H), 6.95-6.93 (m, 4H), 5.87 (s, 4H), 2.32 (s, 24H), 1.43 (s, 12H), 0.07 (s, 9H), −0.06 (s, 2H).

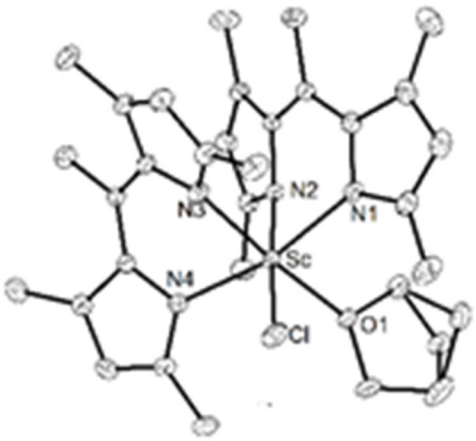

Figure 3. ORTEP drawings of the complexes 3 with thermal ellipsoids with a 30% probability. Hydrogen atoms are omitted for clarity

Partial bond lengths and bond angles of rare earth scandium metal complex 3:

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Sc1-C11 2.4386 (7), Sc1-N2 2.2412, Sc1-O1 2.2238 (17), Sc1-N3 2.211 (2), Sc1-N1 2.235 (2), Sc1-N4 2.248 (2);

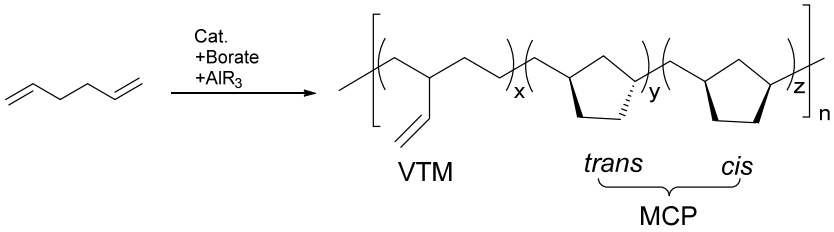
N2-Sc1-C11 176.23 (5), N2-Sc1-N4 88.53 (7), O1-Sc1-N2 85.79 (7), O1-Sc1-N1 85.72 (7), O1-Sc1-N4 102.01 (7), N3-Sc1-C11 94.90 (5), N3-Sc1-N2 88.44 (7), N3-Sc1-O1 173.93 (7), N3-Sc1-N1 91.35 (8), N3-Sc1-N4 79.70 (8), N1-Sc1-C11 98.80 (6), N1-Sc1-N2 79.34 (7), N1-Sc1-N4 165.16 (7), N4-Sc1-C11 93.78 (6).

3. TESTS

3.1. Homopolymerization of 1, 5-hexadiene catalyzed by dipyrromethene (DPM)-ligated scandium (Sc) complex(1-3)

A detailed polymerization procedure of 1,5-hexadiene is described here as a typical example: In the glove box, accurately measure 5 ml toluene solution, add 200 μmol Al^iBu_3, 20 μmol catalyst, 20 μmol co-catalyst Borate (A = $[Ph_3C][B(C_6F_5)4]$, B = $[PhNHMe_2][B(C_6F_5)_4]$, and C = $B(C_6F_5)_3$) was added to 100 mL eggplant bottles with 4 mmol 1, 5-hexadiene monomer. The reaction was carried out at room temperature. After the reaction was completed, the eggplant bottle was taken out and the reaction was terminated with 40 mL ethanol solution containing 5% polymeric inhibitor 2, 6-ditert-butyl-4-methylphenol (BHT). Then the polymer was washed out with a large amount of ethanol and dried in a vacuum oven at 40 °C to a constant weight.

Table 1 polymerization of 1, 5-hexadiene catalyzed by dipyrromethene (DPM)-ligated scandium (Sc) complex(1-3)[a]



entry	Cat.	A[b]	AlR_3	[HD]/[Sc]	t (min)	T (°C)	Y (%)	A[c]	Microstructure (%)[d] C	*trans*-	*cis*-	M_n[e] 10^4	M_w/M_n[e]
1	1	A	Al^iBu_3	200	720	25	100	2.7	100	70	30	1.9	1.42
2	1	B	Al^iBu_3	200	720	25	89	2.4	100	57	43	0.6	1.6
3	1	A	$AlMe_3$	200	720	25	85	2.3	95	51	49	0.25	1.18
4	1	A	$AlEt_3$	200	720	25	87	2.3	95	57	43	0.4	2.0
5	2	A	Al^iBu_3	200	720	25	95	2.6	100	66	34	2.8	1.25
6	3	A	Al^iBu_3	200	720	25	90	2.4	100	62	28	0.7	2.42

[a] Conditions: 20 μmol of Ln complex, 20 μmol of activator, [HD]/[Ln] = 200, 5 mL of toluene unless mentioned; [b] Activator: A = $[Ph_3C][B(C_6F_5)_4]$, B = $[PhNHMe_2][B(C_6F_5)_4]$, and **C** = $B(C_6F_5)_3$; [c] Activity: 10^3 g/mol_{Ln}·h; [d] *cis*-, *trans*-, and cyclized MCP units in the polymer. Determined by ^1H, ^{13}C NMR spectra; [e] Determined by GPC in THF at 40 °C against polystyrene standard.

1, 5-hexadiene can be catalyzed in a ternary catalytic system consisting of rare earth metal complexes 1, 2, 3/$[Ph_3C][B(C_6F_5)_4]$/ AlR_3 to obtain cyclic polymers with high molecular weight (Table 1, Entry 1-6).^{13}C NMR spectra showed that the copolymer was dominated by cis-1, 4-selective structure.^1H and ^{13}C NMR spectra showed that the highest ring formation rate of 1, 5-hexadiene was 100% and the highest cis was 70%. Alkyl aluminum has an important effect on the microstructure and molecular weight of the polymer. When Al^iBu_3 is used as the co-catalyst, the ring formation rate and cis selectivity of the polymer reach 100%, 70%, and the molecular weight of the polymer reaches 1.9 × 104 g/mol (Table 1, Entry 1, 3, 4).The structure of different

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complexes also had an effect on the polymer, among which complex 2 catalyzed the highest polymer molecule, reaching 2.8 × 104 g/mol (Table 1, Entry 1, 5, 6).

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