Polyethylene with Extremely Narrow Polydispersity obtained from the New Catalyst Systems Nb(η^5-C_5Me_5)(η^4-diene)Cl_2–MAO and Nb(η^5-C_5Me_5)(η^4-diene)$_2$–MAO

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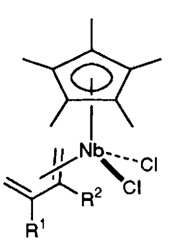
Niobium complexes Nb(η^5-C_5Me_5)(η^4-diene)Cl_2 (diene = buta-1,3-diene **1a**, isoprene **1b**, or 2,3-dimethylbuta-1,3-diene **1c**) and Nb(η^5-C_5Me_5)(η^4-2,3-dimethylbuta-1,3-diene)$_2$ **3** in the presence of a large excess of methylaluminoxane (MAO) were found to be active catalysts for the polymerization of ethylene to give polyethylene with narrow polydispersities (M_w/M_n as low as 1.05).

Polyethylene is one of the most important polymers. It has been the target of polymer chemists to synthesize virtually monodispersed polyethylene which should show superior physical properties. Recent developments in homogeneous Ziegler–Natta catalysis of cationic metallocenes of Group 4 metals and neutral Group 3 metallocenes have demonstrated control in polymerization as well as the microstructure of the polymers obtained.[1–5] Recently we found that the catalyst system of diene complexes of tantalum bearing η^5-C_5R_5 (R = H, Me) in the presence of an excess of methylaluminoxane (MAO) was active in the polymerization of ethylene.[6] This is based on the idea that M(η^5-C_5Me_5)(η^4-1,3-diene) (M = Group 5 metal) is isoelectronic with M′(η^5-C_5Me_5)$_2$ (M′ = Group 4 metal).[7] In the M(η^5-C_5H_5)Cl_2 (M = Zr and Hf)–MAO system, zirconocene is superior to hafnocene in polymerization catalysis. Thus, we continued our polymerization studies with niobium–diene complexes. In this contribution we report that niobium–diene–methylaluminoxane is an active catalyst system for the polymerization of ethylene giving high molecular mass (M_n = 2.3–4.1 × 10^4) polyethylene with the narrowest polydispersity reported to date (M_w/M_n as low as 1.05).

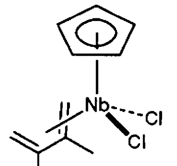
Table 1 Polymerization of ethylene catalysed by niobium-diene-MAO[a]

Run	Complex	T/°C	Activity[b] kg h^{-1} [Nb]mol^{-1}	10^{-4} M_n[c]	M_w/M_n[c]
1	**1a**	20	38.70	8.29	1.30
2	**1b**	20	19.22	3.95	1.16
3	**1c**	20	35.23	10.54	1.18
4	**1a**	0	14.50	4.95	1.07
5	**1b**	0	6.94	2.22	1.07
6	**1c**	0	21.87	8.16	1.08
7	**1a**	−20	10.65	2.36	1.05
8	**1b**	−20	1.02	0.51	1.09
9	**1c**	−20	12.71	4.10	1.05
10	**3**	20	24.65	3.07	1.18
11	**3**	0	21.95	2.82	1.13
12	**3**	−20	12.48	1.42	1.06

[a] Polymerization reactions were carried out in toluene (1.44 × 10^{-3} mol dm^{-1} [Nb]) in the presence of MAO (500 equiv.) for 1 h. [b] Polymer recovered was methanol insoluble. [c] By GPC analysis.



1a $R^1 = R^2 = H$
1b $R^1 = Me$, $R^2 = H$
1c $R^1 = R^2 = Me$



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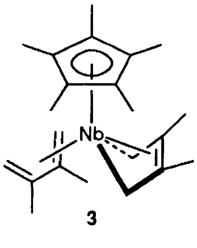

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Systems of the type Nb(η^5-C_5Me_5)(η^4-1,3-diene)Cl_2[7b] in the presence of a large excess of MAO were found to be active for the polymerization of ethylene with results shown in Table 1. The diene complexes Nb(η^5-C_5Me_5)(η^4-1,3-diene)Cl_2 were prepared by the reaction of Nb(η^5-C_5Me_5)Cl_4 with methylated allylMgCl.[7c] Treatment of Nb(η^5-C_5Me_5)Cl_4 with 2 equiv. of the 2-methylbut-2-enyl Grignard reagent in THF followed by extraction and recrystallization from hexane afforded Nb(η^5-C_5Me_5)(η^4-isoprene)Cl_2 **1b** as light green crystals in 35% yield.[7b] Similar procedures were effective for the reaction of Nb(η^5-C_5Me_5)Cl_4 with 2 equiv. of but-2-enyl and 2,3-dimethylbut-2-enyl Grignard reagents to afford similar diene complexes Nb(η^5-C_5Me_5)(η^4-buta-1,3-diene)Cl_2 **1a** (4% yield) and Nb(η^5-C_5Me_5)(η^4-2,3-dimethylbuta-1,3-diene)Cl_2 **1c** (22% yield), respectively.

Ethylene (1 atm) was introduced to a solution of **1c** (2.5 mg in 4.6 ml of toluene) and MAO (500 equiv.) at 20 °C (run 3). After stirring for 1 h, the polymerization was quenched by addition of HCl-MeOH and the polyethylene (235 mg, activity = 35.23 kg h^{-1} [Nb]mol^{-1}) was recovered. Gel permeation chromatography (GPC) analysis of this sample

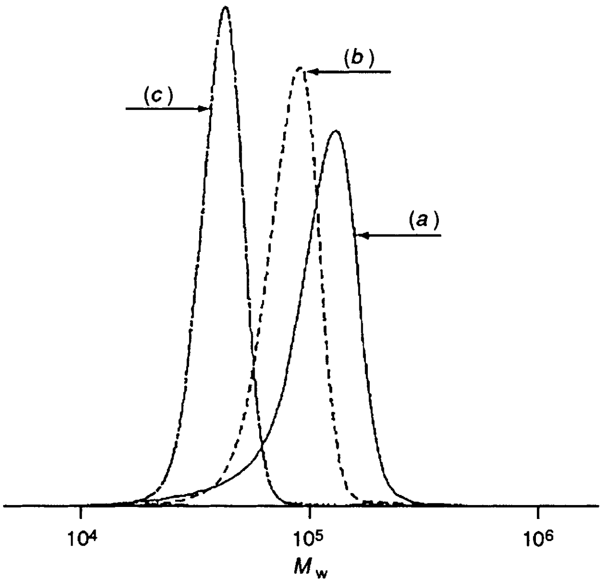

Fig. 1 GPC analyses of polyethylene obtained by the catalyst system **1c**–MAO at 20 °C (*a*) (run 3), at 0 °C (*b*) (run 6), and at −20 °C (*c*) (run 9)

showed a rather high molecular mass with a narrow molecular mass distribution ($M_n = 10.54 \times 10^4$, $M_w/M_n = 1.18$).

Methyl substitution of the coordinated diene led to a variation of the catalytic activity for the polymerization of ethylene. Complexes **1a** and **1c** have comparable catalyst activity, while complex **1b** is less active. Such a tendency has already been observed for the activity of the corresponding tantalum–diene complexes.[7] When the polymerization of ethylene was carried out in a toluene solution of **1** and MAO at lower temperatures (0 and −20 °C), very narrow polydispersities ($M_w/M_n = 1.05$–1.09) for the resulting high molecular mass polyethylene were obtained (GPC analyses for runs 3, 6 and 9 are shown in Fig. 1). We have already reported that Nb(η^5-C_5H_5)(η^4-2,3-dimethylbuta-1,3-diene)-Cl_2 **2** was an active catalyst precursor, but the resulting polyethylene had broad polydispersity.[6] This was attributed to the thermal instability of **2**. In contrast, for the more thermally stable complexes **1** narrow polydispersity of polyethylene was accomplished. The value of 1.05 for M_w/M_n (runs 7 and 9) is the narrowest polydispersity of polyethylene so far achieved.†

We also found that a bis(diene) complex of niobium, Nb(η^5-C_5Me_5)(η^4-2,3-dimethylbuta-1,3-diene)$_2$ **3**,[7b] was an active catalyst precursor for the polymerization of ethylene. The **3**–MAO system (runs 10–12) afforded polyethylene with narrow polydispersities ($M_w/M_n = 1.06$–1.18). The M_n and M_w/M_n values of polyethylene obtained indicated the catalyst efficiency, and the bis(diene) complex **3** (catalyst efficiency = 78–92%) is more catalytically active than **1c** (catalyst efficiency = 27–34%). Complex **3** has been shown to exist in two forms with the diene coordinated either *supine* or *prone* to niobium.[7b] It is anticipated that one diene moiety undergoes ligand exchange between **3** and the aluminium of MAO to generate the catalytically active species[6] and a diene aluminium species.[8]

In conclusion we have found that the niobium–diene–MAO catalytic system is more active then the tantalum–diene–MAO system and also displays the narrowest polydispersity (M_w/M_n = 1.05) to date.

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Footnote

† Narrow polydispersities for polyethylene have been reported for the following homogeneous catalysts; [LuH(η^5-C_5Me_5)$_2$]$_2$ (M_w/M_n = 1.37),[5b] [Cr(η^5-C_5Me_5)(thf)$_2$Me]$^+$ (M_w/M_n = 1.63),[9] [Co(η^5-C_5Me_5)-{P(OMe)$_3$}(CH_2CH_2Me)]$^+$ (M_w/M_n = 1.17)[10] and [RhL(Me)(OH)-(OH_2)]$^+$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) (M_w/M_n = 1.6).[11]

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