4732 *Macromolecules* **1999,** *32,* 4732−4734

Olefin Polymerization by the (Pybox)RuX_2(ethylene)−MAO Catalyst System

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Received December 21, 1998

Introduction. Olefin polymerization by homogeneous catalysis has been one of the most attractive subjects in the field of both organometallic chemistry and catalysis. There are thus many reports concerning this topic using group 4B transition-metal complexes such as metallocene analogues,[1] hybrid "half-metallocene" analogues,[2] and others.[3] In addition, since efficient nickel-,[4] palladium-,[4] cobalt-,[5,6] and iron-based[6] catalysts have been appeared recently, the topic of late-transition-metal complexes has thus attracted particular attention. The ruthenium catalyst often exhibits both remarkable activity and selectivity in organic synthesis;[7] we are thus exploring to find an efficient olefin polymerization catalyst consisting of a ruthenium complex. In this paper, we introduce ethylene homopolymerization and ethylene/1-hexene copolymerization by ruthenium catalysis (Chart 1).[8]

Results and Discussion. The synthesis of (pybox)-$RuCl_2$(ethylene) (**1**; pybox = 2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine), which can be prepared by the treatment of $[(p\text{-cymene})RuCl_2]_2$ with pybox in CH_2Cl_2 under an ethylene atmosphere (1 atm), was according to the previous report,[9] and the iodine complex (**2**) could also be prepared in the same manner. Ethylene polymerizations by **1** or **2**−cocatalyst systems were conducted in a 100 mL stainless steel autoclave, and the results are summarized in Table 1.

It is important to note that **1** exhibits moderate catalytic activity in the presence of MAO (methylaluminoxane) solid, which was prepared from ordinary MAO (PMAO-S, Tosoh Akzo Co.) by removing toluene and $AlMe_3$ in vacuo. The use of this MAO is important in order for this catalysis to proceed at a relatively significant rate. The effect of cocatalyst is thus important for activity, and the polymerization activity in the presence of MMAO (methylisobutylaluminoxane), $AlEt_3$/$Ph_3CB(C_6F_5)_4$, or Al^iBu_3/$Ph_3CB(C_6F_5)_4$ in place of MAO solid was low. The reason for lower activity with ordinary MAO and MMAO than with the MAO solid would be due to the deactivation of the catalytically active species by $AlMe_3$ and Al^iBu_3 contained in these aluminoxanes.

These polymerization results are reproducible as depicted in Table 1 (runs 2 and 3, runs 4 and 5, runs 6 and 7, runs 10 and 11), and the solvent effect was found to be important for activity (runs 13−15). The activity was also affected by reaction temperature (runs 1−7) and Al/Ru molar ratio (runs 12 and 13). The catalytic activity decreased gradually probably due to the deactivation of catalytically active species (runs 2, 8, and 9).

Chart 1

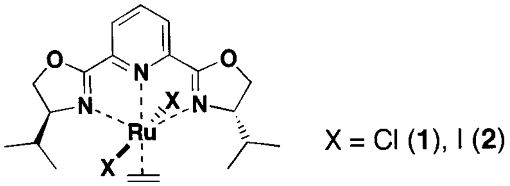

Table 1. Ethylene Polymerization by (pybox)RuX_2(ethylene)−Cocatalyst System [X = Cl (1), I (2)][a]

run no.	complex (μmol)	cocatalyst (Al/Ru)[b]	solvent	temp (°C)	time (h)	ethylene (atm)	polymer yield (mg)	activity[c]
1	**1** (50)	MAO (500)	hexane	25	1	8	14	0.28
2	**1** (50)	MAO (500)	hexane	40	1	8	25	0.50
3	**1** (50)	MAO (500)	hexane	40	1	8	29	0.58
4	**1** (50)	MAO (500)	hexane	50	1	8	67	1.34
5	**1** (50)	MAO (500)	hexane	50	1	8	71	1.42
6	**1** (50)	MAO (500)	hexane	60	1	8	56	1.12
7	**1** (50)	MAO (500)	hexane	60	1	8	55	1.10
8	**1** (50)	MAO (500)	hexane	50	0.5	8	51	2.04
2	**1** (50)	MAO (500)	hexane	50	1	8	71	1.42
9	**1** (50)	MAO (500)	hexane	50	2	8	83	0.83
10	**1** (50)	MAO (500)	hexane	50	1	12	105	2.10
11	**1** (50)	MAO (500)	hexane	50	1	12	107	2.14
12	**1** (50)	MAO (250)	hexane	50	1	6	15	0.30
13	**1** (50)	MAO (500)	hexane	50	1	6	35	0.70
14	**1** (50)	MAO (500)	toluene	50	1	6	18	0.36
15	**1** (50)	MAO (500)	heptane	50	1	6	47	0.94
16	**2** (50)	MAO (500)	heptane	50	1	6	15	0.30
17	Ru[d](50)	MAO (500)	heptane	50	1	6	−	−
18		MAO[e]	hexane	50	1	6	−	−
19	**1** (50)	MAO[f] (500)	toluene	50	1	6	*j*	−
20	**1** (50)	$AlEt_3$/B[g] (500/3)	hexane	50	1	6	8	0.16
21	**1** (50)	Al^iBu_3/B[h] (500/3)	hexane	50	1	6	8	0.16
22	**1** (50)	MMAO[i] (500)	hexane	50	1	6	21	0.42

[a] Reaction conditions: complex 50 mmol, solvent 30 mL, 100 mL autoclave, MAO white solid (prepared by removing toluene and $AlMe_3$). [b] Molar ratio of Al/Ru. [c] Polymerization activity (kg of polymer/(mol of Ru h)). [d] $[(p\text{-cymene})RuCl_2]_2$ was used in place of **1**. [e] The reaction was attempted under the same conditions as run 13 without ruthenium complex. [f] MAO 9.5 wt % (Al) toluene solution (PMAO-S) was used in place of MAO white solid. [g] $AlEt_3$/$Ph_3CB(C_6F_5)_4$ (Ru/Al/borate = 1/500/3, molar ratio) in place of MAO was used as cocatalyst. [h] Al^iBu_3/$Ph_3CB(C_6F_5)_4$ (Ru/Al/borate = 1/500/3, molar ratio) in place of MAO was used as cocatalyst. [i] MMAO (5.8 wt % (Al) hexane solution was used in place of MAO. [j] Trace.

Table 2. Copolymerization of Ethylene with 1-Hexene by 1−MAO Catalyst[a]

run no.	1-hexene (mL)	temp (°C)	polymer yield (mg)	activity[b]	$M_w \times 10^{-4}$ [c]	M_w/M_n[c]
4		50	67	1.34	208.8	2.93
23	3	50	73	1.46		
24	3	60	86	1.72	29.4	1.89

[a] Reaction conditions: **1**, 50 mmol; hexane, 30 mL; MAO white solid, 1450 mg (Al/Ru = 500); ethylene, 8 atm; 1 h. [b] Polymerization activity (kg of polymer/(mol of Ru h)). [c] GPC data in *o*-dichlorobenzene vs polystyrene standard.

The resultant polyethylene gave high molecular weight (run 4, $M_w = 208.8 \times 10^4$), and the molecular weight distribution was relatively narrow ($M_w/M_n = 2.93$, Table 2). This result is an interesting contrast with that reported on the iron-based catalyst-containing tridentate pyridine bis-imine ligand,[6a,b] and we assume at this

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10.1021/ma981957d CCC: $18.00

Scheme 1

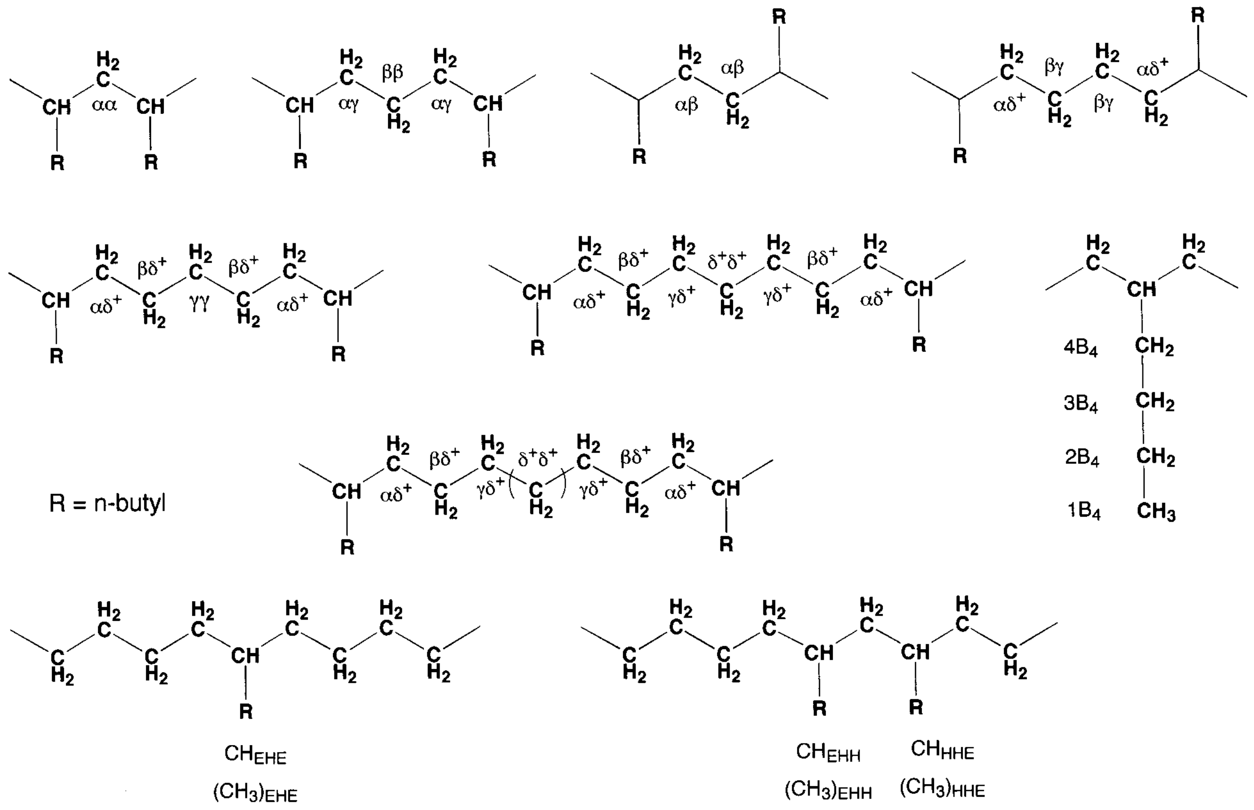

Table 3. Monomer Sequence Distribution of Ethylene/1-Hexene Copolymer Prepared by 1−MAO Catalyst[a]

run no.	[1-hexene][b] (mol %)	triad sequence distribution[b] (%)						diads			
		EEE	HEE + EEH	HEH	EHE	EHH + HHE	HHH	[EE]	[EH]	[HH]	r_Er_H[c]
24	27.16	34.16	31.46	7.22	20.30	6.78	0.08	49.89	46.64	3.47	0.32

[a] Detailed polymerization conditions, see Table 2. [b] Determined by ^{13}C NMR spectra. [c] $r_Er_H = 4[\mathrm{EE}][\mathrm{HH}]/[\mathrm{EH}]^2$.

stage that the difference of M_w value is probably due to the cocatalyst (MMAO containing $\mathrm{AlMe_3}$ and $\mathrm{Al}^i\mathrm{Bu}_3$ and MAO solid containing a trace amount of $\mathrm{AlMe_3}$) that reduces the extent of chain-transfer reaction by removing $\mathrm{AlMe_3}$ in this catalysis. Only one peak was observed in ^{1}H and ^{13}C NMR spectra of these polymers [δ 29.4 (^{13}C) and 1.45 ppm (^{1}H), respectively, in *o*-dichlorobenzene-d_4 at 130 °C), indicating that the resultant polyethylene does not have a carbon branch.

1 also exhibits moderate catalytic activity for copolymerization of ethylene with 1-hexene. An attempt for 1-hexene polymerization with **1**−MAO catalyst (1-hexene, 10 mL; **1**, 50 mmol; Al/Ru = 500, room temperature, 1 day) gave only a trace amount of poly(1-hexene) or oligomer. Note that incorporation of 1-hexene could be confirmed by the ^{13}C NMR spectrum of poly(ethylene-*co*-1-hexene) in *o*-dichlorobenzene-d_4 (Figure 1).[10] This is an interesting contrast with that by the iron-based catalyst system, in which incorporation of α-olefin seemed very difficult.[6c] We assume that the active species in this ruthenium catalysis is similar to that in iron-based catalysis, because these are iron(II) or ruthenium(II) complexes containing similar triimine-based ligands. The difference presented here might be thus due to the original nature of ligand or due to the nature of centered metal (iron or ruthenium). One possible explanation is that the pybox ligand would have a more open space around the active metal center than the 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine ligand,[6] which would facilitate the coordination of 1-hexene.

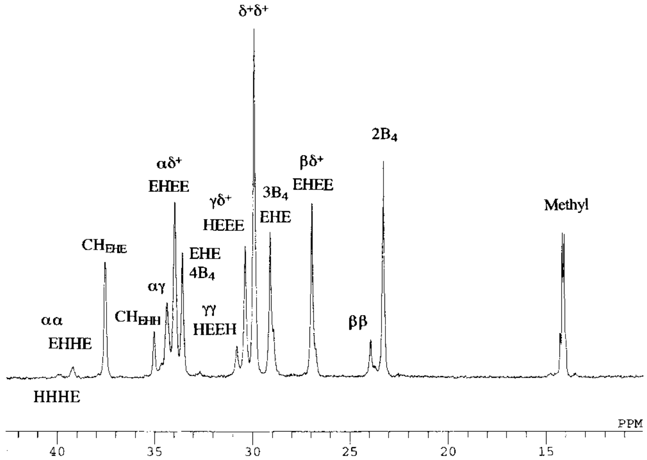

Figure 1. ^{13}C NMR spectrum of poly(ethylene-*co*-1-hexene) prepared by **1**−MAO catalyst (run 24, Tables 2 and 3, in *o*-dichlorobenzene-d_4 at 50 °C).

Further studies with various ligands and metals are now in progress.

The molecular weight distribution (M_w/M_n) of the resultant copolymer was 1.89, and the molecular weight decreased compared with that of the homopolymer (Table 2). All resonances in the ^{13}C NMR spectrum of the copolymer could be assigned (Figure 1, Scheme 1), and peaks corresponding to 2,1-insertion of 1-hexene could not be observed. In addition, resonances corresponding to HHHE (αα) and $\mathrm{CH_{HHH}}$ were negligible, and this might be due to the extremely low activity for 1-hexene polymerization under the same conditions. Triad sequence distributions of the poly(ethylene-*co*-1-hexene) are summarized in Table 3, and a small r_Er_H value (r_E and r_H are monomer reactive ratios of ethylene and 1-hexene) was obtained. This result indicates that the copolymerization does not proceed in a random manner.

We have shown that (pybox)$RuCl_2$(ethylene) catalyzes ethylene homopolymerization and ethylene/1-hexene copolymerization in the presence of cocatalyst. We believe that the information presented here is important to understand or to design better catalysts with late-transition-metal complexes for polyolefin synthesis. We are currently exploring the effect of substituents, especially in the pybox-based ligand; more detailed results will be introduced in the near future.

Acknowledgment. K.N. expresses his thanks to Prof. Masafumi Hirano (Tokyo University of A&T) for discussions. K.N. also expresses his heartfelt thanks to the Tosoh Akzo Corporation for donating MAO (PMAO-S) and MMAO (MMAO-3A) and to Tosoh Co. Ltd. for GPC analysis in *o*-dichlorobenzene.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of polyethylene (run 10) prepared by **1**−MAO catalyst and GPC data (runs 4 and 24) for the resultant polymers; experimental details for general experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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