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Rapid Report

Combination of 8-aminoquinoline nickel dichloride and Cp_2ZrCl_2 catalysts for ethylene polymerization

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Abstract: Polyethylene has been modified and synthesized *in situ* by a combination of Cp_2ZrCl_2 and 8-aminoquinoline nickel dichloride catalysts with methylaluminoxane co-catalyst. The results indicate that the crystallinity and T_m of polyethylene both decrease with increasing Ni/Zr mol ratio when the Ni catalyst is added first. Oligomers formed by 8-aminoquinoline nickel dichloride within a certain Ni/Zr mol ratio could be completely converted into polymer. Three methods used to introduce catalysts to the reaction system resulted in different products. Polyethylene with the lowest melting point, crystallinity and the highest degree of branching resulted when the Zr catalyst was added after that of the Ni compound.

Keywords: ethylene polymerization; Cp_2ZrCl_2; 8-aminoquinoline nickel dichloride; combination catalysts; *in situ* modification and polymerization

INTRODUCTION

The combination of early/late transition metal catalysts in ethylene polymerization is a research field of rising interest,[1–3] and includes those based on cationic nickel(II), palladium complexes and homogeneous zirconium,[1] SHOP-type nickel(II)-based ethylene oligomerization catalyst with heterogeneous titanium, and homogeneous zirconium or chromium based polymerization catalysts.[2,3] They provide medium- and low-density polyethylene otherwise obtained via the copolymerization of ethylene and α-olefin monomers. 8-Aminoquinoline nickel dichloride under certain conditions has a high activity (1×10^7 mol ethylene (mol Ni)$^{-1}$ h^{-1})[4]; the main product was a mixture of C_6–C_{14} olefins with some lower α-olefins. The metallocene catalyst Cp_2ZrCl_2 showed good catalytic activity for homopolymerization of ethylene and copolymerization of ethylene with α-olefin monomer.[5,6]

In this paper, we report the first results on the *in situ* modification and polymerization of ethylene with combinations of 8-aminoquinoline nickel dichloride and homogeneous Cp_2ZrCl_2 catalyst. The 8-aminoquinoline nickel dichloride produced oligomers *in situ*, while further copolymerization of the oligomers with ethylene was promoted by Cp_2ZrCl_2. Copolymerization with ethylene of the oligomers produced *in situ* formed branched polyethylene. Three combination methods were used: method (1), the nickel catalyst first oligomerized ethylene monomer to give oligomers, then the Cp_2ZrCl_2 was added, method (2), the catalysts were added simultaneously; and method (3), after Cp_2ZrCl_2 had been added the nickel catalyst was added.

EXPERIMENTAL

Materials and analytical procedures

Methylaluminoxane (MAO) in toluene (10 wt%) was from the Aybemarle Co (USA). Toluene was dried over 4 Å molecular sieves, and then refluxed with benzophenones over Na/K alloy for 24 h. 8-Aminoquinoline nickel dichloride was prepared as previously described. Cp_2ZrCl_2 was obtained from Aldrich Co (USA). Polymerization grade ethylene monomer, produced by Beijing Yanshan Petrochemical Co (China), was used without further purification.

^{13}C NMR spectra of polymers were measured on a

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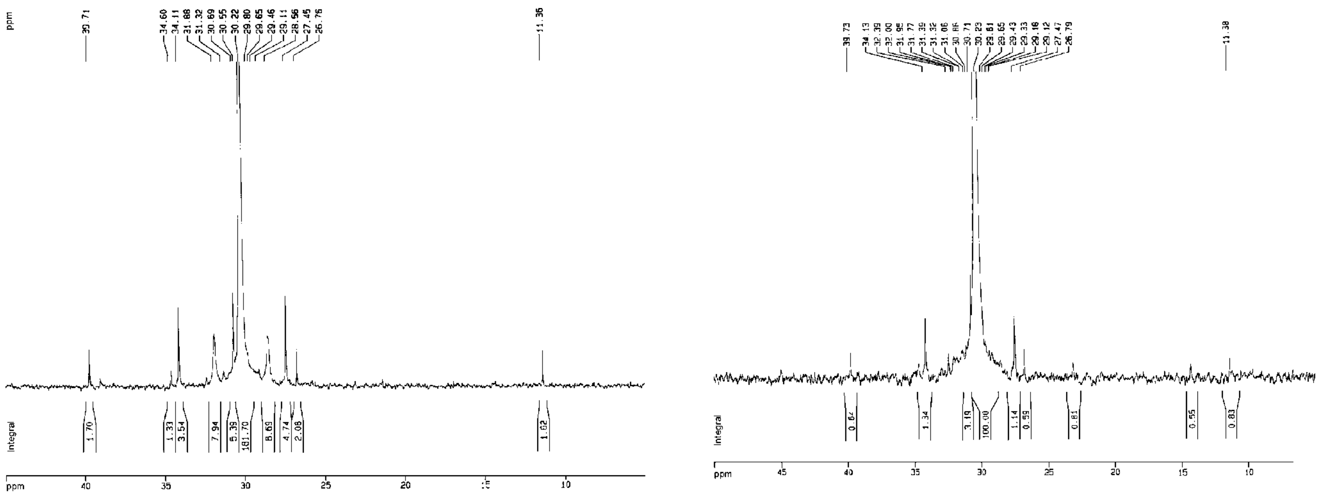

a

b

Figure 1. ^{13}C NMR results for polyethylene: (a) entry 2 in Table 1; (b) entry 3 in Table 1.

Bruker MSL-300 (Switzerland), in 1,2-dichlorobenzene-d_4 at 135 °C and are shown in Fig 1. The branching was determined according to the method of Alexson *et al.*[5] GPC was performed on a Waters Alliance (USA), GPCV2000 instrument with trichlorobenzene as solvent. DSC traces were obtained on Perkin-Elmer (UK), series 7 thermal analysis system at a heating rate of $10\,°C\,min^{-1}$ under N_2 and the data reported are from the second scanning run. The melting heat of polyethylene samples obtained from DSC data was used to calculate polyethylene crystallinity according to the equation

$$\alpha_c(\%) = \Delta H_f/\Delta H_{f\alpha} \times 100$$

in which ΔH_r is the hypothetical heat of fusion of a perfect crystalline material and the published ΔH_{ra} value is $269.9\,J\,g^{-1}$.[6]

Polymerization of ethylene

Ethylene polymerizations were carried out in a 200 ml Schlenk-type glass reactor equipped with a magnetic stirrer. After evacuating air and moisture from the reactor for about 30 min, the first catalyst and MAO were weighed into the reactor sequentially under a nitrogen atmosphere. Polymerization started when 50 ml toluene as solvent was introduced and nitrogen in the reactor was twice replaced by ethylene monomer. The polymerization was carried out for a certain time and the second catalyst and MAO were added. When the reaction finished, acidic ethanol solution was quickly injected in order to terminate the polymerization while the reactor was brought to 0 °C. Part of the solution was sent for GC–MS analysis. The precipitated polymer was collected and washed several times with ethanol and then dried under vacuum at 50 °C for 24 h. A 5890 series II gas chromatograph and a 5971 series mass selective detector (GC-MS) were used to determine the oligomers in the final products by back calculation from the observed amount of oligomers remaining in the reaction solution.

RESULTS AND DISCUSSION

Effect of Ni/Zr mol ratio on ethylene polymerization

In method (1), ethylene was first oligomerized by 8-aminoquinoline nickel dichloride with MAO as the cocatalyst, and Cp_2ZrCl_2 was then added to copolymerize ethylene and oligomers with MAO as co-catalyst. Entries 1–6 in Table 1, showing the DSC results indicate that with increasing Ni/Zr mol ratio, the degree of branching increased, and that the melting point and the crystallinity of polyethylene decreased. In addition, the polydispersity of polymers were all broader than that of polyethylene obtained with pure Cp_2ZrCl_2 catalyst (entry 6). When the Ni/Zr mol ratio was less than five, there were no oligomers observed in the final product, meaning that all oligomers produced were turned into copolymer. At a ratio of more than five times the amount of nickel complex to zirconocene, the oligomers increased with increasing the Ni/Zr ratio, and the reactivity of Zr catalyst decreased from 12.46×10^6 to 3.42×10^6 (g PE) (mol Zr)$^{-1}$ h^{-1}. There was no 'comonomer effect', in which the activity of Cp_2ZrCl_2 catalyst had previously been observed to increase with increasing the proportion of α-olefin monomer in the copolymerization of α-olefin with ethylene.[7] This would indicate that here there was competition for ethylene monomer between the Zr and Ni catalysts. The more Ni catalyst, the more oligomers were produced, due to the [Ni—C] centre being of greater reactivity than [Zr—C]; thus more branched polyethylene was obtained (Table 1). Hence the melting and crystallinity of polyethylene decreased with increasing Ni/Zr mol ratio. Table 2 shows that there were great differences in oligomer

Table 1. Polymerization of ethylene with Cp_2ZrCl_2 and nickel catalysts

Entry no	Ni (μmol)	Zr (μmol)	Oligomer (g)	PE (g)	Activity[a]	T(°C)	α(%)[b]	M_w/M_n	$M_n \times 10^5$	$CH_3/1000CH_2$
1	24	2	1.04	3.42	3.42	115.8	35.6	4.13	0.14	–[d]
2	20	2	0.94	3.47	3.47	117.2	41.6	3.89	0.39	29.3
3	16.5	3.3	0	7.45	4.52	122.6	43.5	4.61	0.27	8.9
4	4	2	0	8.37	8.37	124.1	44.1	7.94	0.46	6.0
5	2	2	0	9.82	9.82	128.1	45.4	4.98	0.26	–
6	0	2	0	12.46	12.46	133.8	54.2	2.33	2.65	–
7	2	0	1.22	0						
8	4	2	0	8.23	8.23	128.2	60.6	2.52	0.43	–
9	4	2	0.02	3.48	3.48	115.7	31.8	3.93	1.14	–
10	4	2	0.07	4.18	4.18	122.8	47.3	4.38	0.88	–
11	4	2	0	1.24	1.24	128.6	55.2	2.62	0.42	–
12	4	2	0.03	1.12	1.12	131.2	32.5	5.00	1.18	–

[a] Reaction conditions: $T = 25$ °C; for entries 8 to 10 the reaction temperature is 50 °C, 0 °C and −20 °C respectively; 50 ml toulene as solvent: Al/(Ni + Zr) = 1000, $t = 30$ min.

[b] Crystallinity: $X_e = \Delta H/\Delta H_{n1} \times 100\%$, $\Delta H_{n2} = 269.9\,J\,g^{-1}$.

[c] Entries 1–5 and 8–10, method (1); entry 11, method (2); entry 12, method (3).

[d] —, Not determined.

distribution depending on whether a combination of Ni/Zr catalysts or pure Ni catalyst was used. No C_4 and C_6 oligomers were observed for pure 8-aminoquinoline nickel dichloride, but when Cp_2ZrCl_2 was added (Ni/Zr > 5), the α-olefin disappeared, but some olefins still remained (entry 2). Upon increasing the percentage of Ni catalyst, the chain of oligomers became shorter (C_4 and C_6; entry 1), implying that the Zr catalyst affected the reactivity of Ni catalyst.

Effect of polymerization temperature

In entries 8, 4, 9 and 10 in Table 1, the reaction temperatures were 50, 25, 0 and −20 °C, respectively, and method (1) was used. At low reaction temperatures (0, −20 °C), there was still a small amount of oligomers in entries 9 and 10, but only C_4 exists in the final products. From the activity and crystallinity of polymers in Table 1, the Ni catalyst gave the best catalytic capability in competition with Cp_2ZrCl_2 catalyst at 0 °C, and the polyethylene had the lowest melting point and crystallinity. At higher temperatures (25, 50 °C), the polyethylene produced had a relatively higher melting point and crystallinity because the 8-aminoquinoline nickel complex had a low reactivity, and no activity at all above 50 °C. These results indicate that the branching of final products depended greatly on the reactivity of 8-aminoquinoline nickel dichloride in this reaction system.

Effect of order of catalyst addition

When the mol ratio of Ni/Zr was fixed the order of addition of the two catalysts significantly affected the property of polymers produced see entries 4 (method 1), 11 (method 2) and 12 (method 3). In Table 1, compared with that produced using pure Cp_2ZrCl_2, the polyethylene produced by three different combined catalysts had lower crystallinity, melting point and reactivity of polymerization. In method (1), the branching mostly depended on the percentage of oligomers produced in advance. In method (2), by adding the two catalysts at the same time (entry 1, Table 1), all the oligomers produced by the Ni catalyst took part in copolymerization. No oligomers were detected in the final toluene solution. In method (3), polyethylene had no branching as determined by ^{13}C NMR (entry 12, Table 1). There are two possible reasons for the process. One is that the polyethylene chains produced by Zr catalyst prevented contact between Ni active centres and ethylene; the other is that the activity of Ni catalyst decreased due to the exothermicity of the ethylene polymerization catalysed by Cp_2ZrCl_2.

Table 2. Proportions[a] of oligomers

Entry in Table1	Proportion (%)									
	C_4	α-C_4	C_6	α-C_0	C_1	α-C_1	C_{10}	α-C_{10}	C_{12}	α-C_{12}
1	20.3	12.3	78.7	0		0	0	0	0	0
2	58.3	47.6	41.7	0	0	0	0	0	0	0
7	0	0	0	0	72.7	15.0	27.1	7.6	0.2	0
9	100	66.7	0	0	0	0	0	0	0	0
10	100	66.7	0	0	0	0	0	0	0	0
12	100	100	0	0	0	0	0	0	0	0

[a] C_n proportions include α-C_n.

CONCLUSIONS

Polyethylene has been modified *in situ* by using a Cp_2ZrCl_2 and 8-aminoquinoline nickel dichloride combination catalytic system. Oligomers produced by 8-aminoquinoline nickel dichloride with a certain Ni/Zr mol ratio could be completely converted to polymer. The crystallinity and T_m of polyethylene both decrease when the mol ratio of Ni/Zr increases. Polyethylene had the lowest melting point, crystallinity and more branches if the Ni catalyst was added before the Zr catalyst.

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