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Ethylene Polymerization under high pressure and temperature using Nickel-α-diimine catalyst

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Summary

The combination of 1,4–bis(2,6-diisopropylphenyl)-acenaphthenediimine-dichloro-nickel (II) (**1**) and methylaluminoxane (MAO) has been shown as being highly active in ethylene polymerization under high pressure and temperature. Herein we describe the effects of ethylene pressure and reaction temperature on polymer properties and reaction performance.

The polyethylenes synthesized with the system 1/MAO are highly branched, with 105 to 277 branches per 1000 backbone carbon atoms, depending on the reaction conditions. The branching index increases with the rise of temperature or with the decrease of ethylene pressure. These branches go from methyl to hexyl, or even farther, and present a pattern in which 1,4; 1,5 and 1,6 methyl groups appear mainly and isolated methyl groups are not present.

These branches are generated by a chain-walking system. The polyethylenes produced with these systems have a molecular weight (Mw) between 44,000 and 105,000 Daltons and polydispersions from 2,0 to 4,0, depending on reaction conditions.

The polymer molecular weight tends to decrease with the increasing temperature of polymerization.

Introduction

International competition for the development of new technologies for the production of special polyolefins has become a must. A great challenge in the petrochemical industry is the substitution of expensive polymeric materials for easily recyclable and low cost materials.

In the late 90's a new class of olefin polymerization catalysts, based on nickel or palladium and containing α-diimine ligants was discovered. The use of these catalysts was developed by Brookhart *et all* [1,2] and attracted the interest of the scientific community, since through them branched polyethylenes could be prepared without the addition of comonomer. The branches were obtained without the addition of comonomer through a mechanism called "chain walking"[1] and the products obtained were similar to low density polyethylenes (LDPE). The polymerization reactions have been well described and showed very high activities in Gibson´s activity scale [3]. This makes the majority of the research groups use very smooth reaction conditions such as room temperature and atmosphere pressure. Very few reports have described the catalytic behavior of nickel-α-diimine complex under more demanding reaction conditions.

Herein we report the influence of polymerization conditions, such as temperature and ethylene pressure in the productivity of polyethylenes and on the polyethylene properties. The temperature was between 40 and 100°C and ethylene pressure was between 30 and 60 atm.

Experimental

Materials

All operations were performed in argon atmosphere using standard Schlenk tube techniques. The catalyst precursor 1,4–bis(2,6–diisopropylphenyl)-acenaphthene-diimine-dichloronickel (II) (1) was synthesized according to methods that have been published [4] and cyclohexane was refluxed and distilled with metallic sodium. Ethylene and argon, provided by White Martins, were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (13 Å) prior to use. The cocatalyst, methylalumonoxane (MAO 5.21 wt% Al, in toluene) was purchased from Witco and used without further purification.

Instruments

Polymer molecular weight (M_w) and polydispersity (M_w /M_n) were determined by gel permeation chromatography (GPC) with a Waters 150CV equipment with three columns Styragel HT3, HT4 and HT6 (10^3, 10^4 and 10^6 Å, respectively) and a refraction index detector. A calibration curve was established using monodisperse polystyrene standards and checked with known polyethylenes. Analyses were accomplished using 2.5 mg of a sample of synthesized polyethylenes dissolved in 2.5 mL of 1,2,4-trichlorobenzene (distilled and stabilized with 0.05g/L of 2,6-di-terc-butil-4-metilfenol (BHT) at 140°C.

The polymer microstructure was qualitative and quantitatively analyzed by ^{13}C NMR. The spectra was obtained with a Varian Inova 300 spectrometer operating at 75 MHz, at 80 or 120°C, with a 71.7° flip angle, acquisition time of 1.5 s and delay of 4.0 s. Sample solutions of the polymer were prepared in *o*-dichlorobenzene and benzene-d6 (30% w/v) in a 10mm tube.

Melting temperatures were determined by means of differential scanning calorimetry (DSC 2010) with a Thermal Analyses Instrument. A 10 mg sample was heated from 40°C to 180°C at 10°C/min rate. The analyses were performed under nitrogen flux. Melting point temperatures and degree of crystallinity were determined in the second scan. The peak temperature with the highest endothermic was chosen as the melting point. Degree of crystallinity($\lambda\chi$) was calculated from the DSC traces using the enthalpies of fusion of the perfectly crystalline polyethylene (293 J/g) [5].

Polymerization

All ethylene polymerization reactions were done using a 450 mL autoclave Parr reactor with a stainless steel pipette coupled to it. Magnetic drived mechanical stirring was applied. The parameters studied in the reactions of ethylene polymerization using the catalytic system (1)/MAO were: ethylene pressure, between 30 and 60 atm and pre-heating reaction temperature, between 40 and 100°C. All reactions were carried out with a reaction time of 10 min. A typical polymerization run was performed as follows: the system was purged three times with successive vacuum cycles and refilling of argon. When the reactor was completely under argon atmosphere, it was charged with 30mL of cyclohexane and the required amount of cocatalyst solution (MAO 5.21% p/p Al). The system was pre-heated until reaching the reaction temperature and then a solution of catalyst in 20 mL of cyclohexane was injected in the reactor with the aid of the pipette. Ethylene was continuously fed during the reaction time. After the polymerization time the reactor was vented and the polymer was washed with acidic ethanol (2 wt% HCl) and dried in a vacuum oven at 60°C for 24 h.

Results and Discussion

The system nickel-α-diimine-Cl_2 (**1**)/MAO (where α-diimine is 1,4–bis(2,6-diisopropylphenyl)-acenaphthenediimine) has been tested in the homopolymerization of ethylene under high ethylene pressure, condition that, as far as we are concerned, has no previous description in the open literature. The results reported in Table 1 show that the polymerization of ethylene with the system (**1**)/MAO at high ethylene pressure is dependent on experimental parameters such as ethylene pressure and temperature.

Table 1. Performance of the system Nickel-α-diimine-Cl_2(1)/MAO in ethylene polymerization at high ethylene pressure.

Run	Pressure (atm)	Temp. (°C)	Productivity[a] (kg/mol Ni.h)	M_w[b] (kg/mol)	M_w /M_n[c]	SCB [d] (branches/ 1000C)
1	30	40	2880	105	2.8	111
2	30	60	2126	77	4.0	-
3	30	80	1791	45	2.0	-
4	40	60	1734	65	2.5	277
5	50	60	1829	50	2.0	171
6	60	40	1783	82	3.7	-
7	60	60	1480	47	3.0	118
8	60	100	779	43	1.9	263

Polymerization conditions: time= 10 min, [Ni]= 19μmol; solvent = cyclohexane (50mL), [Al]/[Ni]=200

[a] = Productivity in kg PE/(mol_{Ni}.h);

[b] M_w = molecular weight; express in g/mol;

[c] M_w /M_n = Polydispersity;

[d] SCB= Short chain branch distribution

It has been reported previously that the system Ni (α-diimine) Cl_2 (**1**)/MAO is quite sensitive to reaction parameters [6]. The effect of the temperature on the productivity was observed comparing runs 1, 2 and 3, for 30 atm and entries 6, 7 and 8 for 60 atm, as shown in Figure 1.

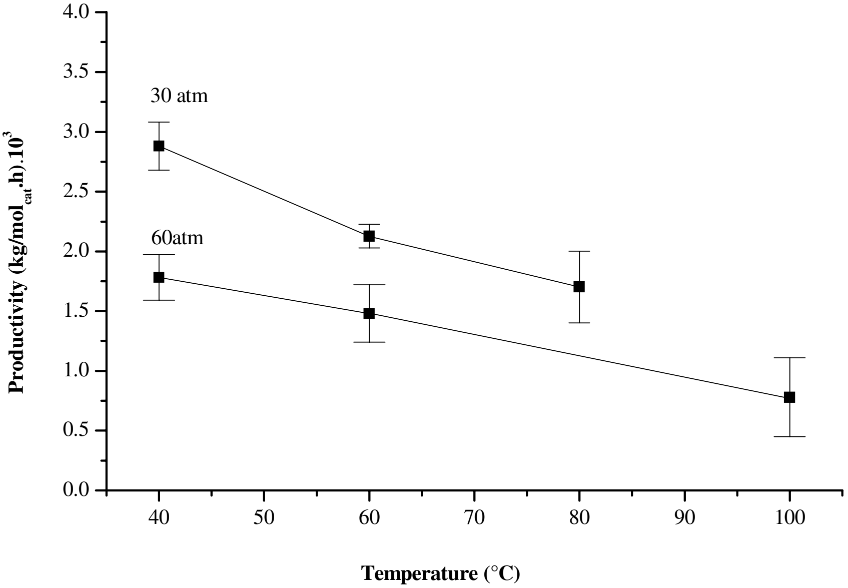

Figure 1. Dependence of productivity of the system (**1**)/MAO with the reaction temperature

It is worth pointing out that the increase of temperature decreases productivity and both at 30 atm and 60 atm. Some authors observed the same behavior for nickel complexes at lower pressures [1,6]. The reduction of the productivity with the rise of temperature is an indication of the occurrence of deactivation of the catalytic precursor with the increase of initial temperature of reaction [7].

All polyethylenes produced with the system (**1**)/MAO showed no T_m (melting point) and, consequently, did not shows crystalinity, characteristics of completely amorphous materials.

The results of Table 1 also show that the molecular weight decreases with the increase of the temperature. At a pressure of 30 atm, the M_w decreases from 105,000 to 45,000 g/mol when the reaction temperature is increased from 40 to 80°C (Runs 1 and 3 – Table 1). At 60 atm the Mw decreases from 82,000 to 43,000 g/mol when the reaction temperature is increased from 60 to 100°C (Runs 6 and 8- Table 1). This can be explained by the fact that the temperature affects the competition between propagation and termination differently. This means that the termination rate, probably by β−elimination, grows more quickly than the chain growth rate, by 1, 2-shift, due to the differences in the activation energies of these reactions.

The polydispersity values at 60 atm (runs 6, 7 and 8) drops from 3.7 until 1.9 with the increase of the temperature. At 30 atm the situation is less straightforward.

The products obtained under different reaction conditions have different SCB distributions as shown in Table 1. The degree of branching increases with the polymerization temperature, from 118 to 263 branches/1000 atoms of carbon when the reaction temperature is increased from 60 to 100°C (Runs 7 and 8). This is the most remarkable characteristic of these polyethylenes, in which the branches are generated by the well accepted "*chain walking*" mechanism [3,8,9]. Table 2 shows the distribution of the chain branches determined by ^{13}C NMR.

Table 2. Branch distribution in the polyethylenes produced with 1,4–bis(2,6-diisopropylphenyl)-acenaphthenediimine-dichloronickel(II)(**1**)and methylaluminoxane

Sample	1	4	5	7	8
Methyl (total)	73	151	113	82	141
Methyl-1,4	30	44	18	33	49
Methyl-1,5	11	24	35	14	25
Methyl-1,6	32	83	60	35	67
Ethyl	10	23	12	10	22
Propyl	5	0	6	3	10
Butyl	8	12	22	10	14
Amyl	4	43	6	3	43
Hexyl and longer	12	47	10	10	32
longer -1,4	7	22	8	10	32
longer isolated	5	24	2	0	0
Degree of Branching	111	277	171	118	263

All Branching indexes are numbers of branches per 1000 backbone carbon atoms

The polyethylenes synthesized with Ni(α-diimine)Cl_2(**1**)/MAO shows almost no isolated methyl groups but a great amount of 1,4, 1,5 and 1,6 methyl patterns, in agreement with previous reports of highly branched polyethylenes obtained with nickel-α-diimine complexes [10, 11]. It is worth observing that the branching degree enhances with the rise of temperature and decreases with increase of the pressure. The degree of branching decreases with the increase of the pressure from 277 to 118 branches/1000C when the ethylene pressure is increased from 40 to 60 atm (Runs 4 and 7 - Table 1). This behavior can be explained by a classic "chain walking" mechanism, with a competition between isomerization and chain growth [12, 13].

It has been shown that the combination of the effect of the temperature and the effect of the pressure on the degree of branching enables the obtention of materials with almost 1 branch each 3 carbon atoms of the main chain, which is a characteristic of hyperbranched polyethylene and close to a 1:1 ethylene-propylene copolymer and this including a non negligible amount of longer branches.

Conclusions

The catalytic system formed by 1,4-bis(2,6-diisopropyphenyl)acenaphthenediimine-dichloro-nickel(II) (**1**) combined with methylaluminoxane (MAO) was highly active in ethylene polymerization under high pressure and temperature. This system allowed the production of highly branched ethylene homopolymers with *ca.* 277 branches by 1000 backbone carbon atoms in the absence of any α–olefin as comonomer. These branches are generated by a chain-walking mechanism. It was verified by DSC that these polyethylenes have no T_m and no crystallinity, *i.e* these are completely amorphous hyper-ramified polyolefins. The polyethylenes produced with this system have molecular weight between 43,000 and 105,000 Daltons, depending on reaction conditions. The reaction temperatures have strong influence on productivity values, molecular weight and branching number. With the increase of the temperature the values of Mw and productivity decreased, however the values of branchings increased. Otherwise the enhancement of the ethylene pressure increases the values of Mw and decreases the branching degree.

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