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Control of Branch Formation in Ethylene Polymerization by a [Ni(η³-2-MeC₃H₄)(diimine)] PF₆ / DEAC Catalyst System

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A polimerização de etileno em presença do precursor catalítico [Ni(η³-2-MeC₃H₄)- {ArN=C(H)C(H)=NAr}]PF₆, Ar = 2,6-C₆H₃ⁱPr₂/DEAC sob condições reacionais brandas (temperatura de reação entre -10 ºC e 25 ºC e pressão de etileno entre 109 e 1520 kPa) conduz à formação de polietileno ramificado de alto peso molecular. A taxa de ramificação foi modulada através de uma escolha cuidadosa das condições reacionais. Assim, a 0 ºC e 109 kPa, a taxa de ramificação foi de 17 ramificações /1000 carbonos da cadeia, valor que cresce para 90 ramificações /1000 carbonos da cadeia a 25 ºC. A natureza das ramificações observadas (metilas, etilas ou longas), as quantidades e a distribuição sobre a cadeia do polímero podem ser explicadas por um mecanismo envolvendo o processo de *deslocamento sobre a cadeia* (*chain walking*) e o controle da isomerização pelo impedimento espacial da cadeia polimérica em crescimento.

The polymerization of ethylene mediated by [Ni(η³-2-MeC₃H₄){ArN=C(H)C(H)=NAr}] PF₆, Ar = 2,6-C₆H₃ⁱPr₂/DEAC catalyst precursor under mild reaction conditions (reaction temperature between -10 ºC and 25 ºC and ethylene pressure between 109 and 1520 kPa) yields high molecular weight branched polyethylene. The degree of branching was modulated by a careful choice of reaction conditions. Thus, at 0 ºC and 109 kPa, the branching degree was 17 branches/1000 backbone carbon atoms and at 25 ºC, it went up to 90 branches/1000 backbone carbon atoms. The nature of the observed branches (methyl, ethyl and longer), their quantity and distribution along the polymer backbone chain can be rationalized in terms of a *chain walking* process and control of the extend of isomerization by the steric hindrance of the growing chain.

Keywords: ethylene polymerization, nickel-diimine, branching

Introduction

Nickel-diimine complexes have been extensively described[1,2] and claimed to be catalysts in the Du Pont de Nemours's Versipol process[3]. These catalysts have a unique characteristic as they homopolymerize ethylene affording branched polymers. The scientific and technological importance of this process has led to large interest in the study of the polymeric materials that can be obtained by a polymerization / isomerization reaction. Some examples of olefin polymerization by late transition metals are known[4-7], but nickel-diimine complexes are unusual since they induce both, chain growth and chain isomerization. The high quantity of methyl and, even more importantly, long branches, has attracted much attention since it is one of the first applications of late transition metals in ethylene homopolymerization that affords high molecular weight low-density polyethylene. Functional density calculations have been independently performed by Ziegler[8,9] and Morokuma[10] in order to explain the nature of the different steps in ethylene polymerization in the presence of cationic nickel-alkyl-diimine complexes, which are proposed as active species. These calculations have provided good explanations for the isomerization process, but suffer from limited systematic experimental descriptions of the effect of the reaction conditions on the polymerization reaction.

We described previously that cationic nickel η³-allyldiimine complexes are able to polymerize ethylene even when associated with low amounts of diethylaluminum chloride (DEAC)[11]. The polyethylenes obtained in such processes have shown variable degrees of branching[12]. In this work we describe the tailoring of branching by the control of the reaction conditions, allowing access to new materials with different branch distributions along the polymer chain.

Experimental

All reactions were performed under argon using standard Schlenk tube techniques. Solids were dried under reduced pressure and liquids were distilled over adequate desiccant

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agents, immediately prior to use. Diethylaluminum chloride (DEAC) was purchased from Aldrich and was used as supplied. The catalytic precursor nickelmethylallyl-diimine hexafluorophosphate [Ni(η^3-2-MeC$_3$H$_4$)-{ArN=C(H) C(H)=NAr}]PF$_6$, where Ar = 2,6-C$_6$H$_3^i$Pr$_2$ (**1**) was synthesized as previously described[11]. Ethylene polymerizations were carried out in a 120 mL double-walled glass reactor with magnetic stirring and constant supply of neat gaseous ethylene at atmospheric pressure (109 kPa). In a typical experiment, the reactor containing a 0.125 mol L^{-1} solution of **1** in 80 mL of chlorobenzene was purged with gaseous ethylene and the reaction temperature was controlled by an external circulation bath. When the reaction temperature was attained, the amount of DEAC solution was injected under ethylene atmosphere and the ethylene pressure was maintained constant during the reaction time. After the desired reaction time the polymer was precipitated in acidified methanol (HCl 1 vol.-%). The product was filtered off, washed twice with 100 mL of methanol and dried in a reduced pressure oven at 40ºC for 48 h (until constant weight).

Polyethylene samples obtained from different runs were analyzed by gel permeation chromatography (GPC) with a Waters 150CV system equipped with 3 columns Styragel (10^3, 10^4 and 10^6 Å) and a refraction index detector. Analyses were undertaken by using 1,2,4-trichloro-benzene as solvent at 140 ºC. Molecular weights were calculated against a calibration curve built with linear polyethylene standards. Melting temperatures were determined by differential scanning calorimetry using a TA 2010 calorimeter operating at a heating rate of 10 ºC min^{-1}. The materials were cooled down from the melt (180 ºC to 40 ºC) at a rate of 10 ºC min^{-1}. T_m was determined in the second scan. The crystallinity was calculated from the DSC thermograms from the enthalpies of fusion (the enthalpy of crystalline polyethylene used was 269.9 J g^{-1}). Branching was determined by ^{13}C NMR spectroscopy using a Varian VXR200 equipment with procedures previously described[12].

Results and Discussion

The control of branching formation during the homopolymerization of ethylene can be achieved by a careful choice of reaction conditions when using nickelmethylallyldiimine hexafluorophosphate (**1**) associated with DEAC. Table 1 shows the effects of reaction temperature and ethylene pressure on the catalytic performance and polyethylene properties.

Effect of reaction temperature

As shown in Table 1 the activity of the system increases with reaction temperature within the range –10 ºC to 20 ºC. At reaction temperatures higher than 20 ºC the activity decreases sharply and the system becomes inactive at 30 ºC.

The molecular weight (Mw) of the polyethylene samples increases from 264.10^3 g mol^{-1} at -10ºC (entry 1) up to 400.10^3 g mol^{-1} at 0 ºC (entry 2) and decreases from 236.10^3 g mol^{-1} at 10 ºC (entry 3) to 31.10^3 g mol^{-1} at 25 ºC (entry 5).

The enhancement of the molecular weight with temperature can be attributed to the increase of the reaction rate with temperature. In opposition, the rate of the termination reaction also increases with the reaction temperature, therefore leading to a drop in molecular weight at high temperatures.

The GPC traces in Figure 1 show bimodal molecular weight distributions (MWD) obtained in runs performed at temperatures between –10 ºC and 10 ºC. The formation of different molecular weight distributions and, moreover, bimodal MWD, strongly suggests the presence of more than one type of active species, as discussed further in this paper.

Effect of ethylene pressure

An increase in the ethylene pressure from 109 kPa to 1520 kPa has a small influence on the activity of the system (compare entries 2 and 9, Table 1), however it affects the molecular structure of the polyethylenes, as shown by the increase in T_m.

Table 1. Performance of nickelmethylallyldiimine hexafluorophosphate (**1**) associated with DEAC: effect of reaction temperature and ethylene pressure[a].

Entry	Pressure /kPa	Temp J ºC	Ratio [b] Al/Ni	Productivity /kg mol^{-1} h^{-1}	Mw /10^3 g mol^{-1}	Ratio Mw/Mn	T_m /ºC	Crystallinity /%
1	109	-10	100	27.8	264	2.3	128	48
2	109	0	100	106.0	400	2.5	113	31
3	109	10	100	136.6	236	3.1	110	10
4	109	20	100	277.5	112	2.1	93	11
5	109	25	100	29.2	31	1.9	67	<1
6	109	30	100	0.0	-	-	-	-
7	109	40	100	0.0	-	-	-	-
8	1520	0	10	131.5	200	2.5	133	54
9	1520	0	100	110.8	275	3.7	126	12

[a]Reaction conditions: nickel complex: **1**, 0.125 mol L^{-1} ; solvent = PhCl, 80 mL; [b]Al/Ni average molar ratio.

Surprisingly the molecular weights of the products obtained at 1520 kPa are lower than those obtained at 109 kPa, dropping from 400.10^3 g mol^{-1} to 275.10^3 g mol^{-1}.

Figure 2 shows that at 1520 kPa a more symmetric distribution is obtained, with an increase of the peak corresponding to the low molecular weight fraction of the bimodal distribution obtained at 109 kPa. This result suggests that, at high ethylene pressures, one type of active site is predominant, which produces linear polyethylene.
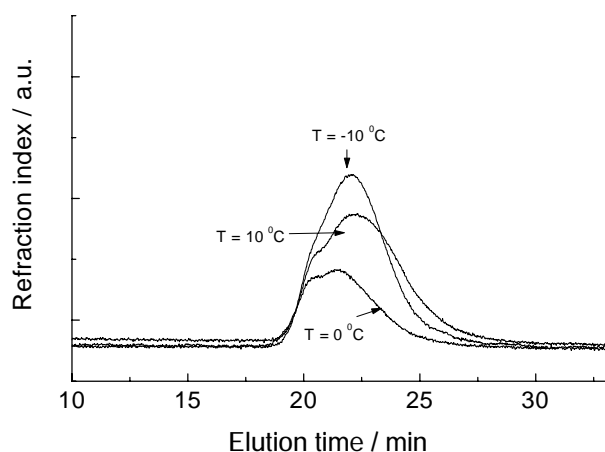
Figure 1. Effect of the reaction temperature on the MWD of polyethylenes obtained with **1**/DEAC (corresponding to reaction conditions of entries 1, 2 and 3 of Table 1)
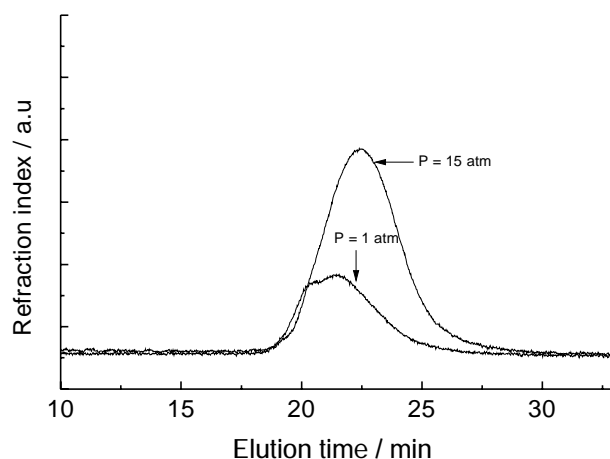

Figure 2. Effect of the ethylene pressure on the MWD of polyethylenes obtained with **1**/DEAC (corresponding to reaction conditions of entries 2 and 9 of Table 1)

Branching: amount and distribution

Reaction conditions, such as temperature and ethylene pressure, strongly affect the structure of the polyethylenes obtained with **1**/DEAC. An analysis of the $^{13}C\{^1H\}$ NMR spectra shown in Figure 3 enabled the identification of different types of branches formed during the ethylene polymerization process.
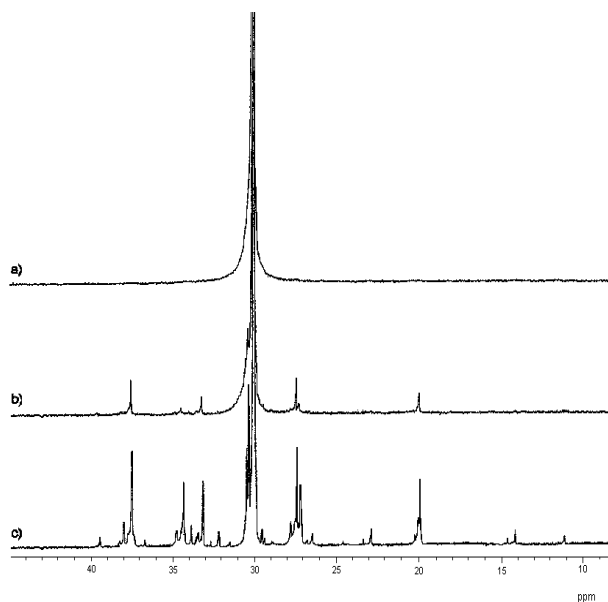

Figure 3. $^{13}C\{^1H\}$ NMR spectra of polyethylenes obtained with **1** / DEAC system: (a) sample obtained from entry 8 (b) sample obtained from entry 2 (c) sample obtained from entry 4.

Branches of different lengths (methyl, ethyl, propyl, amyl and longer) and their distribution have been identified in the spectra of Figure 3 and quantitatively determined[12]. Figure 4 shows the distribution of branches, classified according to their lengths, in polyethylene samples obtained at different temperatures.
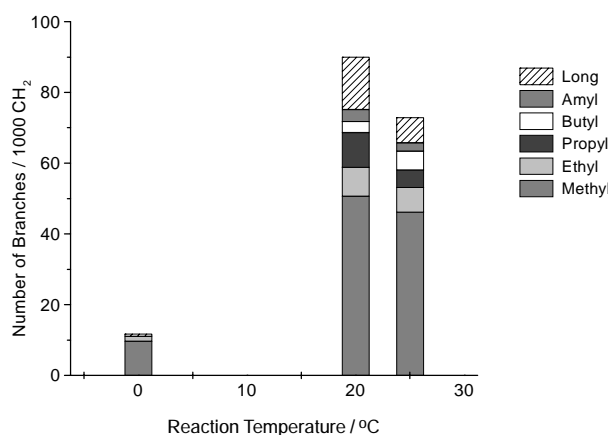

Figure 4. Influence of the reaction temperature on the quantity of branches on the polyethylene chain obtained with **1**/DEAC. (Corresponding to reaction conditions for entries 1, 2 and 3 of Table 1).

The increase in the amount of branches formed at different reaction temperatures is remarkable. At 0 °C, 12 branches/1000 backbone chain carbon atoms have been observed. This quantity enhances dramatically with the reaction temperature, attaining 90 branches/1000 backbone chain carbon atoms at 20 °C. This result is in agreement with previous descriptions of Brookhart and co-workers[1] for polyethylenes obtained with similar catalysts. It should

be pointed out that the high quantity of branches containing more than one carbon atom points to the mobility of the nickel atom along the polymer chain, a process similar to that previously proposed for other nickel systems[4,5].

Figure 5 shows the methyl branches distribution along the polymer chains obtained at different temperatures.
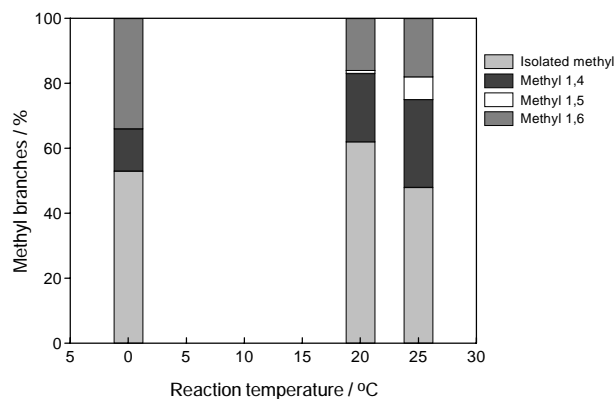

Figure 5. Influence of the reaction temperature on the distribution of methyl branches on the polyethylene chain obtained with **1**/DEAC (corresponding to reaction conditions for entries 1, 2 and 3 of Table 1).

This distribution shows that the system obtained by the association of **1** and DEAC does not generate a random distribution of methyl branches along the polymer chain. At 0 °C, 53 % of the methyl branches appear as isolated units, 13 % are separated by two methylenic units and 34 % by four methylenic units. At 20 °C, these quantities become 62 %, 21 % and 16 %, and at 25 °C, 48 %, 27 % and 18 %, respectively, with the appearance of 7 % of methyl groups separated by 3 methylenic units. This specific pattern of methyl branch distribution, *i.e.* separation of methyl branches by an odd number of methylenic units, shows that the isomerization is not a simple free migration of the nickel moiety along the polymer chain that which would produce a random distribution, but it is dependent on the sequence of the ethylene insertion and is controlled by the steric hindrance on the α-carbon atom of the growing chain (see mechanism).

Mechanism

The selectivity in the distribution of methyl branches separated by one or two ethylene units and the formation
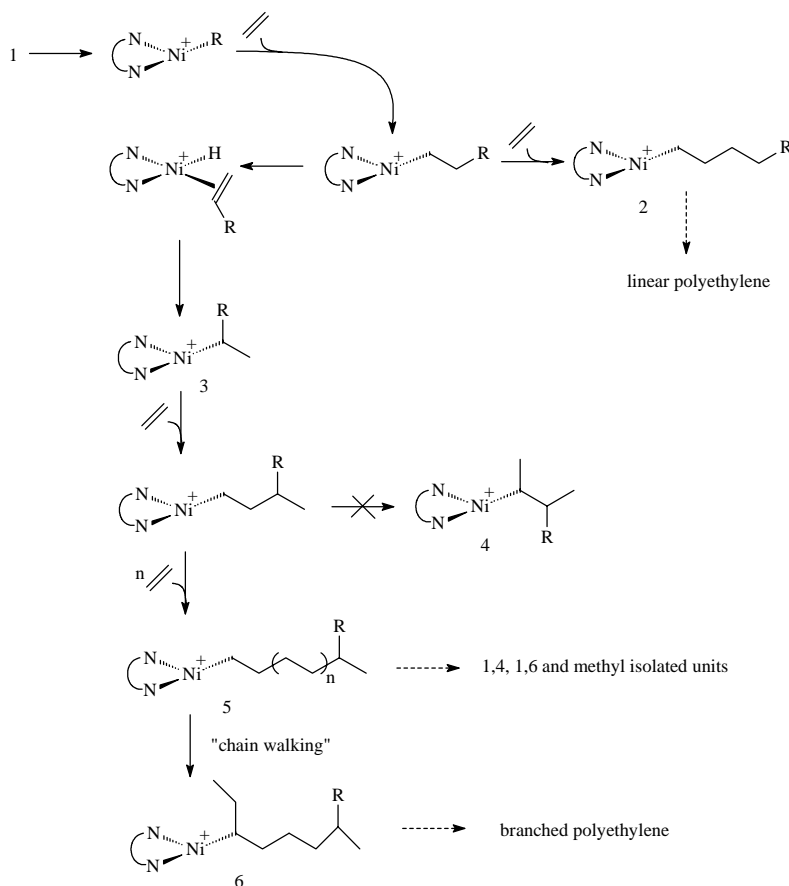

Figure 6. Mechanism of ethylene polymerization with **1**/DEAC.

of bimodal molecular weight distributions should be included in a mechanism that describes the ethylene polymerization in the presence of cationic nickel-diimine complexes. Figure 6 shows a possible mechanism which explains the formation of linear and branched polyethylenes, as previously proposed by Okuda[13], taking into account the *chain walking* process.

The intermediate species **2** to **6** would be better described as containing an ethylene molecule coordinated to the nickel center, and are four coordinated, 16 electron complexes. The ethylene molecules have been omitted for the sake of clarity.

Species such as **2** are responsible for the formation of linear chains and species such as **3** for branched chains. In the presence of excess ethylene, the formation of **3** is suppressed due to the steric hindrance on the α-carbon atom of the growing chain, precluding the α-elimination process and determining the formation of linear polyethylene predominantly.

The methyl branch distribution is controlled by the steric hindrance at the metal center. Species such as **4** are reluctant to undergo α-elimination, thus precluding neighboring methyl branching; ethylene insertion which enables the formation of 1,4 methyl units, and consecutively of 1,6 methyl units and isolated units is therefore favoured in this case.

The formation of lateral chains with more than one carbon atom shows that the nickel at the end of a polymer chain is mobile, through a *chain walking* mechanism, previously described by Fink[5] for other nickel systems. This mobility generates branches of different lengths.

Conclusions

The degree of branching in the polyethylenes obtained with the association of nickelmethylallyldiimine hexafluorophosphate and DEAC showed large variations with reaction temperature (ranging from 0 to 25 °C) and with ethylene pressure (between 109 kPa and 1520 kPa.). Polyolefins with over 90 branches per 1000 backbone carbon atoms have been obtained, with high productivity, under very mild reaction conditions, enabling these systems to be competitive to the production of low density polyethylene (LDPE).

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