Copolymerization of Ethylene/Diene with Different Metallocene Catalysts

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Z. Naturforsch. 61b, 1426 – 1432 (2006); received April 18, 2006

Copolymerizations of ethylene and 1,7-octadiene were carried out employing homogeneous catalysts \( \text{Cp}_2\text{ZrCl}_2 \), \( \text{Ph}_2\text{C(}\text{Flu,Cp}\text{)}\text{ZrCl}_2 \), and \( \text{Et(Ind)}_2\text{ZrCl}_2 \), and methylaluminoxane as cocatalyst. The polymerization characteristics, such as catalytic activity, polymerization rate, copolymer composition, and thermal properties were examined in relation to the catalyst type. Different comonomer concentrations were employed, and the reaction time was varied, ranging from 1 h up to 4 h, at 90 °C and at 0.5 bar ethylene pressure. The results showed that the catalyst \( \text{Cp}_2\text{ZrCl}_2 \) was more efficient than \( \text{Et(Ind)}_2\text{ZrCl}_2 \) in the preparation of high diene content ethylene/1,7-octadiene copolymers. On the other hand, \( \text{Et(Ind)}_2\text{ZrCl}_2 \) and \( \text{Ph}_2\text{C(}\text{Flu,Cp}\text{)}\text{ZrCl}_2 \) catalysts produced low insaturation content but possibly formed cyclic structures and crosslinking.

Key words: Ethylene Copolymer, Non-Conjugated Dienes, Metallocene Catalysts, Polyolefins, Copolymerization

Introduction

Although copolymerizations of ethylene with dienes employing heterogeneous catalysts have already been studied, little work has been reported in relation to copolymerizations of olefins with non-conjugated dienes initiated by homogeneous catalysts. Synthesis of functionalized polyolefins is very important in the development of new materials, which present tailor-made properties. The copolymerization of olefins with polar monomers would be the most effective way to obtain functionalized polymers. However, both Ziegler-Natta and metallocene catalysts are affected by poisoning, due to the interaction between polar groups and the active centers of the catalysts [1].

Another way to introduce functional groups into polyolefins is the copolymerization of olefins with \( \alpha, \omega \)-diienes, or rather with non-conjugated dienes like 1,5-hexadiene, 1,7-octadiene, dicyclopentadiene, norbornadiene etc. These comonomers could be appropriate to introduce functional groups like \( \text{C}=\text{C} \) in the branches of polymer chains, where only one double bond of the monomer reacts in the copolymerization. On the other hand, the residual double bond could be made to react with other chemicals in order to incorporate polar groups within the side chains.

However, when 1,5-hexadiene or 1,7-octadiene are used as monomers, cyclization is likely to occur, depending on the reaction conditions. Indeed, that could be the prevailing way for insertion of these comonomers.

Therefore, it is very difficult to polymerize \( \alpha, \omega \)-linear dienes, whose residual double bonds can also react producing crosslinking, which would be deleterious for the polymer properties [2, 3].

Developing ways to influence the insertion of non-conjugated dienes in the copolymerization with olefins is crucial for controlling the microstructure of the polyolefin chains and, consequently, for controlling their properties.

Some authors have reported both ethylene/1,5-hexadiene, and ethylene/1,7-octadiene copolymerizations with metallocene catalysts [4, 5]. In the copolymerization, 1,5-hexadiene was incorporated in the ethylene sequence in the cyclic structure. On the other hand, 1,7-octadiene was incorporated by cyclo-addition as much as by 1,2-addition in the copolymerization of ethylene/1,7-octadiene, forming pendant vinyl groups. These pendant groups could be used to modify the polyethylene. In the case of copolymerization of ethylene with 1,5-hexadiene, either crosslinking occurred, or 1,3-cyclopentene rings were formed, independently of the nature of the zirconocene catalyst.

Naga and Ymanishi [6] investigated the copolymerization of ethylene/1,7-octadiene and ethylene/1,9-
decadiene with various bridged and unbridged zirconocene catalysts, in order to relate the catalyst structure to the copolymer structure. As it is well known, the polymerization temperature deeply affects the structure of the diene incorporated in the polymer chain. In this work, the polymerization temperature used was 40 °C, the cocatalyst/catalyst molar ratio Al/Zr was 1000, and the ethylene pressure 1.0 atm. Copolymer extraction was carried out using 1,2-dichlorobenzene in order to separate the soluble and insoluble fractions. The insoluble fraction is a crosslinked polymer, originated by intermolecular reactions of the pendent double bonds. In the copolymerizations using bridged catalysts (Me₂SiCp₂ZrCl₂, Et(Ind)₂ZrCl₂ and Me₂Si(Ind)₂ZrCl₂) and an unbridged catalyst (Cp₂ZrCl₂), an increase of the soluble fraction was observed, with increasing OD content. On the other hand, copolymers obtained with unbridged catalysts (Cp²ZrCl₂ and (Ind)₂ZrCl₂), and the bridged catalyst Ph₂C(Cp)(Flu)ZrCl₂ showed an opposite trend.

The ¹³C NMR spectrum of the soluble fraction of poly(ethylene-co-octadiene) and its assignments according to Naga et al. [6] are shown in Fig. 1. This catalyst produces poly(ethylene-co-octadiene) with 1-hexenyl branches and some units of 1,3-disubstituted cyclo-heptane (signed with O in Fig. 1). The Cp²ZrCl₂ and Me₂SiCp₂ZrCl₂ catalysts, and the Cp₂ZrCl₂ catalyst produced the same type of copolymers, however, the percentages of cyclo-heptane units obtained with Cp²ZrCl₂ and Me₂SiCp₂ZrCl₂ were higher than the percentage obtained with Cp₂ZrCl₂ [6].

Sepälä et al. [7, 8] studied the effect of the polymerization temperature on ethylene/non-conjugated diene (1,5-hexadiene, 1,7-octadiene and 7-methyl-1,6-octadiene) copolymerization with the Cp₂ZrCl₂/MAO catalyst system. In the case of copolymerization with 1,5-hexadiene, crosslinking occurred at polymerization temperatures ranging from 20 to 65 °C, and the product crosslinking degree increased as the polymerization temperature was lowered. Crosslinking was also observed in the copolymerization with 1,7-octadiene in the same polymerization temperature range, however in this case the degree of crosslinking was highly independent on both the polymerization temperature and the comonomer ratio in the feed. In both cases, crosslinking did not occur when the copolymerizations were conducted at 90 °C. On the other hand, when 7-methyl-1,6-octadiene was used as comonomer, the degree of crosslinking was low, independent of the polymerization temperature.

Recently, Soga et al. [1] reported the copolymerization of ethylene and 1,9-decadiene using the Me₂Si(Flu)₂ZrMe₂/MAO catalyst system. Cyclization and crosslinking did not occur, due to the consecutive insertion of the vinyl double bond of the diene. The pendent double bond in the chain can be cohydrolyzed quantitatively with polysiloxanes in order to graft the polymer.

Hyoung-Joon et al. [9] investigated the copolymerization of ethylene with other dienes (1,5-hexadiene, 1,4-hexadiene, and 1,7-octadiene) using a bis(2-methyl-indenyl)zirconium dichloride catalyst. At low polymerization temperatures, an increase in the insoluble fraction was observed. These copolymers did not have cyclic structures and were almost insoluble in xylene at 160 °C. However, ethylene/1,4-hexadiene copolymers were completely soluble in xylenes. Catalytic activity, molecular weights and thermal properties were evaluated. Ethylene/1,5-hexadiene and ethylene/1,7-octadiene copolymers showed broad melting peaks and ethylene/1,4-hexadiene copolymers showed narrow melting peaks in the DSC analysis. The latter was due to the lack of both crosslinked and cyclic structures. Moreover, the addition of 1,4-hexadiene and 1,7-octadiene comonomers diminished both the polymerization rate and the copolymer’s molecular weight at a higher degree in comparison to the addition of 1,5-hexadiene comonomer.

In the present work the behavior of three metallocenic catalytic systems in ethylene/1,7-octadiene copolymerization was studied, using different reaction conditions, in order to optimize the properties of the obtained copolymers.
Results and Discussion

Ethylene was both homopolymerized and copolymerized with 1,7-octadiene (in the range from 0 to 1.007 mol/L), in toluene solution, using three different catalyst systems (Cp₂ZrCl₂/MAO, Ph₂C(Flu,Cp)ZrCl₂/MAO, and Et(Ind)₂ZrCl₂/MAO), at [Zr] = 5.10⁻⁵ M and an Al/Zr ratio = 1000. The reaction time was kept between 1 and 4 h, at 90 °C to prevent crosslinking. Ethylene pressure was 0.5 bar.

Evaluation of the Cp₂ZrCl₂/MAO catalytic system

Results of ethylene/1,7-octadiene copolymerizations under different conditions are shown in Table 1.

The results related to the 1 h reactions using Cp₂ZrCl₂ as a catalyst showed an increase in unsaturation content from 0.27 to 13.0%, as the addition of 1,7-octadiene went from 0 to 0.47 mol/L. This means that the ethylene homopolymer obtained with this catalyst contains a small amount of unsaturations, due to chain transfer reactions, and this amount is increased in the copolymers upon addition of diene units. The copolymers showed neither Tₘ nor Tₓ, being rather amorphous, due to the high diene incorporation.

As shown in Table 1, with the increment on reaction time, the catalyst activity decreased. However, the total amount of unsaturations tends to decrease with the increment of reaction time, probably due to crosslinking. This can be confirmed by the analysis of the 1,2-dichlorobenzene extractable fractions. The copolymers obtained after 4 h reaction time presented lower extractable fractions than those obtained after 1 h (with 100% extractable, meaning the absence of crosslinking bonds).

The kinetic profiles of the polymerizations for 1 h (Fig. 2) showed a decrease of the polymerization rate, according to the increase of 1,7-octadiene concentration in the reaction medium.

Evaluation of the Et(Ind)₂ZrCl₂/MAO catalytic system

The results of ethylene/1,7-octadiene copolymerizations under different conditions are shown in Table 2.

The 1 h reactions using Et(Ind)₂ZrCl₂ as a catalyst showed the same behavior as with the Cp₂ZrCl₂ catalyst. However, diene incorporation was less than that obtained with Cp₂ZrCl₂. In other words, the Cp₂Zr Cl₂ catalyst is more efficient than the Et(Ind)₂ZrCl₂ catalyst for the preparation of ethylene/1,7-octadiene copolymers possessing high diene content. Et(Ind)₂Zr Cl₂/MAO produced a low unsaturation content, and possibly higher molecular weights.

For the 4 h reactions the catalytic activity increased in relation to the ethylene homopolymerization. How-
Table 2. Ethylene/1,7-octadiene copolymerizations using Et(Ind)2ZrCl2 as a catalyst.

Table 3. Ethylene/1,7-octadiene copolymerizations using Ph2C(Flu,Cp)ZrCl2 as a catalyst.

Fig. 3. Ethylene polymerization rate as a function of time for reactions 14 to 17. Reactions were performed with Et(Ind)2ZrCl2 as a catalyst. Concentration of 1,7-octadiene (reaction 14 = 0 mol/L, 15 = 0.336 mol/L, 16 = 0.470 mol/L and 17 = 1.007 mol/L).

However, the melting points of the products were constant, even with high diene contents. The degree of crystallinity decreased with the addition of diene in the copolymerization. Moreover, the unsaturation content increased drastically only with the addition of large amounts of diene. These copolymers did not show any crosslinked fraction.

Fig. 3 presents the kinetic profiles of the polymerizations in 4 h, showing that the polymerization rate also decreases with the increase of the 1,7-octadiene concentration.

Evaluation of the Ph2C(Flu,Cp)ZrCl2/MAO catalytic system

The results of ethylene/1,7-octadiene copolymerizations under different conditions are shown in Table 3.

For the sake of comparison, Fig. 4 shows the kinetic profile of an ethylene homopolymerization using Ph2C(Flu,Cp)ZrCl2, demonstrating that this catalyst is more active than the other two evaluated in this work.

Reactions in 1 h showed an increase in catalytic activity with the addition of the diene in the copolymerization. The melting temperatures of these copoly-
Fig. 5. Catalytic activity as a function of diene concentration in reaction times of (a) 1 h and (b) 4 h.

Copolymers were a little lower in comparison to ethylene homopolymers. However, the degree of crystallinity drastically decreased. These copolymers contained low unsaturation contents, as well as low extractable fractions in 1,2-dichlorobenzene, showing a high degree of branching and crosslinking.

In 4 h copolymerizations, using the Ph₂C(Flu,Cp)ZrCl₂/MAO catalysts, the melting temperatures decreased (from 128.1 to 119.3 °C) with the addition of 1,7-octadiene, and the degree of crystallinity drastically diminished from 62 to 4.6%, showing high reactivity of the residual unsaturations present in 1,7-octadiene. It was also found that the residual unsaturation content slightly increased (from 0.01 to 3.0%). With a diene content of 0.336 mol/L, the polymer yield was found constant for both reaction times. A low extractable fraction in 1,2-dichlorobenzene also indicated a high degree of crosslinking.

A comparison of the catalyst activity for ethylene/1,7-octadiene copolymerizations using the three different systems and two reaction times (1 h and 4 h) is given in Fig. 5. This picture clearly illustrates the decrease of catalyst activity with the increase of reaction time. The increase of the catalyst activity with the increase on 1,7-octadiene concentration was observed in 4 h reaction time for Cp₂ZrCl₂ and Et(Ind)₂ZrCl₂ as catalysts.

Nuclear magnetic resonance spectra (¹³C NMR) for the copolymers synthesized using the three catalysts are shown in Fig. 6. The peaks were assigned in agreement with Naga [12].

It is noticeable that the Cp₂ZrCl₂ catalyst formed fewer cyclic structures in comparison to the other systems, and that copolymers using the Ph₂C(Flu,Cp)ZrCl₂ catalyst showed a higher content of cycloheptane. Moreover, all spectra showed...
branching evidence. The reactions that resulted in copolymers with higher diene incorporation followed the order: 17 (Table 2) > 25 (Table 3) > 7 (Table 1).

Conclusions

The Cp₂ZrCl₂ catalyst was more efficient than Et(Ind)₂ZrCl₂ for the preparation of ethylene/1,7-octadiene copolymers having a high diene content. On the other hand, Et(Ind)₂ZrCl₂ and Ph₁C(Flu,Cp)₂ZrCl₂ catalysts produced low unsaturation content but possibly formed cyclic structures and crosslinks.

Experimental Section

Materials

Bis(cyclopentadienyl)zirconium dichloride, (Cp₂ZrCl₂), (P. A.), from Wako Pure Chemical Industries; diphenylmethylenefluorenylcyclopentadienylzirconium dichloride, (Ph₂C(Flu,Cp)ZrCl₂), (P. A.), from Boulder Scientific; and ethyldiene-bis(indenyl)zirconium dichloride, (Et(Ind)₂ZrCl₂), from Crompton GmbH, and 10% w/w methylaluminoxane (MAO) in toluene, granted by Crompton GmbH, Germany, were all used as received. Before use, toluene was dried over sodium/benzophenone and distillation under nitrogen. Ethylene (PG) and nitrogen (PG) came both from White Martins Gases Industrials S. A., Brazil, and were used after passing through columns of molecular sieve and copper catalyst. 1,7-Octadiene from Acros Organics (98.5%) was dried over molecular sieve (3 Å).

Polymerization procedure

Copolymerizations of ethylene/1,7-octadiene were carried out using one of the three catalysts Cp₂ZrCl₂ (1), Ph₂C(Flu,Cp)ZrCl₂ (2), and Et(Ind)₂ZrCl₂ (3), all at 90 °C to prevent crosslinking. These copolymerizations were attempted to verify catalyst performance and to relate it to the obtained copolymer characteristics.

Polymerization in a glass flask: Some polymerizations were carried out first in a 250 mL glass flask with mechanical stirrer at 200 rpm. The copolymerization runs were carried out, under nitrogen atmosphere, by introducing sequentially 100 mL of toluene, MAO solution (5.8 mL) and diene. After saturation with ethylene monomer (1.3 bar), copolymerization was initiated by injection of the catalyst solution (0.005 mmol Zr). The copolymerizations were carried out under a continuous flow of ethylene for alternatively 1 h or 4 h, the temperature being maintained at 100 ± 10 °C. After the different reaction times of 1 h or 4 h, the polymer was precipitated with acidified ethanol (5% HCl), and then recovered by filtration, followed by washing and drying under vacuum.

Polymerization in a reactor: Most copolymerizations were carried out in a 250 mL glass reactor (Buchi). The reactor was coupled with a flowmeter (model 5850d from Brook Instruments).

Toluene (100 mL) was introduced into the reactor. For the copolymerizations runs, MAO solution (5.8 mL) with Al/Zr = 1000, and the desired amount of 1,7-octadiene (0 to 1.007 mol) were also introduced. The reactor was pressurized with ethylene to the needed pressure of 0.5 bar and the catalyst solution was injected (0.005 mmol Zr). The pressure was maintained during the reaction and the instantaneous consumption of ethylene was measured.

The produced polymer was poured into a solution of ethanol/HCl (40%) in water and stirred for 24 h. After that, the polymer was washed with ethanol, and then poured into a solution of ethanol (30%) in water, and left stirring overnight. After the second filtration, the polymer was dried at 60 °C under vacuum until achieving constant weight.

Polymer characterization

Differential Scanning Calorimetry (DSC) was performed on a Perkin Elmer DSC-7. The specimens (4.0 to 5.0 mg) were heated up to 150 °C (10 °C/min), and afterwards cooled to 40 °C (10 °C/min) to destroy any thermal history. Finally, the specimens were heated to 150 °C (10 °C/min). The reported melting point is the peak value obtained during the last heating. Besides, the degree of crystallinity (Xc) was determined through both the melting heat value of the polymer (∆Hm), and the theoretical melting heat for 100% crystalline polyethylene, using the equation [10, 11]

\[ Xc(\%) = \left(\frac{\Delta H_m}{\Delta H_{m100}}\right) \times 100\% , \]

where ∆Hm100 (polyethylene) = 293 J/g.

Nuclear magnetic resonance (¹³C NMR) was performed only on three samples of ethylene/1,7-octadiene copolymers. Diene incorporation and polymer microstructure were thus determined. Sample solutions were prepared in both 1,2,4-trichlorobenzene and deuterated benzene (25 vol.%) in 10 mL sample tubes. The deuterated solvent was used to provide the internal lock signal. Spectra were taken with a 90° flip angle, an acquisition time of 1.5 s, a delay of 10 s, at a temperature probe of 90 °C, and with a full spectral window.

Fourier transform infrared (FTIR) spectra were used to determine the incorporation of 1,7-octadiene into the copolymers. It was considered that all unsaturated carbon atoms in the copolymer were related to the comonomer, minimizing other reactions like diene cyclization, crosslinking, or branching. Those reactions were minimized by the use of a high polymerization temperature [6]. Moreover, unsaturations owing to chain transfer reactions would happen to a comparatively lower degree in comparison to the incorporation of octadiene. In this method, the polymers can be tested...
in the solid state, preventing oxidation caused by solvents or heating. The specimens were pressed into films and pellets, and the spectra were obtained in the range between 400 and 4000 cm$^{-1}$, using 40 scans. The ratio between absorptivities at 910 and at 720 cm$^{-1}$ ($A_{910}/A_{720}$) was used to determine the comonomer incorporation, using the equation [11]

$$1,7\text{-octadiene content} = \frac{200(A_{910}/A_{720})}{31.89 - 3(A_{910}/A_{720})},$$ (2)

where 1,7-octadiene content = percentage of 1,7-octadiene in the polymer and $A_{910}/A_{720}$ = ratio between absorptivities at 910 and 720 cm$^{-1}$.

**Extraction:** Copolymer extraction was carried out with 1,2-dichlorobenzene in a Soxhlet extractor glass system. The specimens (500 mg) were extracted for 24 h. This was needed to determine the insoluble polymer percentage, that is, the percentage of crosslinking formed in the copolymer.

**Acknowledgements**

The financial support was obtained from Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq, and Fundação Carlos Chagas Filho de Amparo à Pesquisa no Estado do Rio de Janeiro – FAPERJ.