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^{13}C-NMR study of ethylene/1-hexene and ethylene/1-octene copolymers obtained using homogeneous catalysts

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SUMMARY

This study employed the^{13}C-NMR spectroscopy to investigate the influence of the increase of the comonomer concentration on the microstruture of ethylene/1-hexene and ethylene/1-octene copolymers obtained by the use of $MeSiCp_2ZrCl_2$, Cp_2ZrCl_2,, $Et[Ind]_2ZrCl_2$ and $[Ind]_2ZrCl_2$ catalysts. For both comonomers butyl or hexyl branches were isolated between ethylene blocks. As the α-olefin concentration in the copolymer increased, butyl or hexyl branches became closer, some of them, separated by only one or two ethylene units. Incorporation of α-olefin in the copolymer was higher for the bridged catalysts, $MeSiCp_2ZrCl_2$, and $Et[Ind]_2ZrCl_2$ than for the unbridged ones. The α-olefin size did not seem to effect its reactivity towards ethylene.

INTRODUCTION

Linear low density polyethylene (LLDPE) is of great interest for industry. This product can be obtained by the copolymerization of ethylene with α-olefins, such as, 1-butene, 1-hexene and 1-octene, which result in ethyl, butyl and hexyl branches, respectively.

The microstruture of the copolymers (i.e., the way the comonomers are incorporated in the polymer chain) is important because it determines the properties of the final products. Consequently, it is of interest to establish how these comonomers are incorporated, and the extent to which they exist as isolated branches or as "clusters" (such as 1,3-dialkyl branches, 1,3,5-trialkyl branches, and so forth). carbon nuclear magnetic resonance (^{13}C-NMR) is the most useful technique for analysing the comonomer's sequence. This technique also allows for the quantitative determination of the respective comonomer compositions and the average sequence lengths of the comonomers, which permits a complete determination of copolymer microstructures.[1,2]

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This work presents a study of the microstructure of ethylene/1-hexene and ethylene/1-octene copolymers obtained by the use of $MeSiCp_2ZrCl_2$[3], Cp_2ZrCl_2[4] (Cp=η^5-cyclopentadienyl), Et[Ind]$_2$ZrCl$_2$[5] and [Ind]$_2$ZrCl$_2$[6] (Ind=η^5-indenyl) homogeneous catalysts systems. It shows the microestructural effects due to the increase of comonomer concentration in the copolymer for the different catalysts.

EXPERIMENTAL

Copolymerization procedures were described elsewhere.[7]

The ^{13}C-NMR spectra were recorded at 80°C using a VARIAN XL-200 spectrometer operating at 50.309 MHz. Sample solutions of copolymers were prepared in 5 mm tubes with o-dichlorobenzene as solvent and benzene-d_6 (20% v/v) as internal lock. Chromium(III) acetylacetonate was used as the paramagnetic substance to reduce relaxation times. The spectra were taken with 70° flip angle, acquisition time, 1.5 s and a delay of 5.0 s .

RESULTS AND DISCUSSION

The conditions used for the ^{13}C-NMR analysis (flip angle=70°, pulse delay=5 s and $Cr(Acac)_3$ to reduce relaxation times) gave similar results to those obtained using quantitative ^{13}C-NMR analysis conditions as described in the literature[8] (flip angle=83° and pulse delay=3.8 x T_1). These conditions permitted the reduction of analysis time. To calculate the comonomer composition the method of Randall[1,2] was used with the following modification: the average of the T_B, T_G and T_H integrals corresponding to the carbons $T\delta\delta$, SC_2 and SC_1, respectively, was used to calculate the integral for one carbon of the branch, which was in turn, employed to derive the comonomer composition.

Figure 1 shows the spectra for three types of ethylene-1-hexene copolymers, which differ in the content of 1-hexene incorporated (a) 1.9 %, (b) 11.6 % and (c) 18.0 %. The absence of peaks at 40.18-41.40 ppm indicate that the HH diads (1,3-dibutyl branches) were absent in the three cases. Resonances at 34.9 and at 24.2-24.5 ppm due to sequences HEHE (1,5-dibutyl branches) and at 30.9 ppm due to sequences HEEH (1,7-dibutyl branches) appeared only in the spectra (b) and (c), indicating that these sequences were only present in copolymers with higher levels of 1-hexene (above 7 % of 1-hexene). These spectra show that most of the 1-hexene units were isolated in the copolymer between polyethylene blocks. As the concentration of 1-hexene in the copolymer increased, butyl branches became closer. Some of the butyl branches were separated only by one or two units of ethylene, as indicated by the presence of 1,5 and 1,7 dibutyl branches.

Figure 2 shows the spectra for three types of ethylene-1-octene copolymers with contents of 1-octene incorporated in the copolymer of (a) 4.4 %, (b) 7.3 % and (c) 11.2 %. As in the case of 1-hexene, there are no signals of octene blocks (OOO) in the these spectra. Resonances at 35.0 ppm and at 24.6 ppm due to OEO triads and resonances at 30.9 ppm due to OEEO tetrads are only present in the spectra with higher content of 1-octene, the (b) and (c) spectra. As with the ethylene-1-hexene

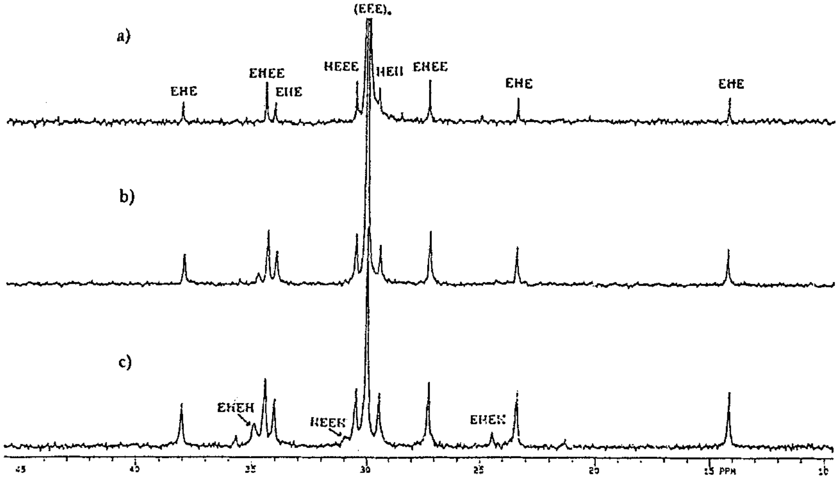

FIGURE 1: ^{13}C-NMR spectra of ethylene-1-hexene copolymer with different percentages of 1-hexene incorporated using Et[Ind]$_2$ZrCl$_2$:(a) 1.9 %, (b) 11.6 % and (c) 18.0 %.

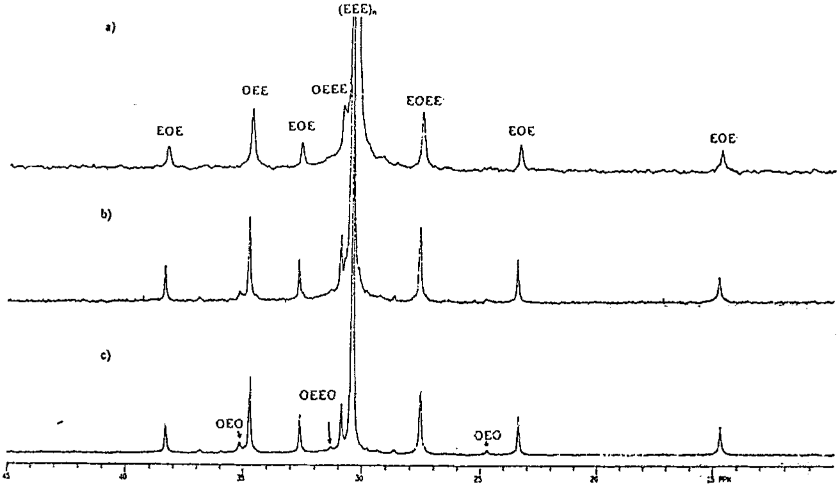

FIGURE 2: ^{13}C-NMR spectra of ethylene-1-octene copolymers with different percentages of 1-octene incorporated using Cp$_2$ZrCl$_2$:(a) 4.4 %, (b) 7.3 % and (c) 11.2 %.

copolymerization, an increase in the incorporation of 1-octene in the copolymer causes the hexyl branches to become closer, which in some cases are separated by only one or two units of ethylene.

Table 1 shows the α-olefin (1-hexene and 1-octene) incorporation in the ethylene copolymer using different metallocene catalysts for the same α-olefin concentration in the feed. As one can observe, the bridged catalysts $MeSiCp_2ZrCl_2$ and $Et[Ind]_2ZrCl_2$ add more 1- hexene to the copolymer than the unbridged catalysts. The same type of behaviour is followed by 1-octene. These results suggest that the bridge between the ligands reduce the steric hinderance caused by their mobility. The reduction of the ligand's mobility permit a better approximation of the large α-olefins to the active center, increasing their copolymer incorporation.

Table 1- Comonomer incorporation in ethylene copolymerization using different metallocenes.

Catalyst	[1-hexene] in the feed (mol/l)	[1-hexene] in the copolymer (mol%)	[1-octene] in the feed (mol/l)	[1-octene] in the copolymer (mol%)
$MeSiCp_2ZrCl_2$	0.533	13.4	0.580	14.8
Cp_2ZrCl_2	0.533	7.9	0.580	7.3
$Et[Ind]_2ZrCl_2$	0.533	11.6		
$[Ind]_2ZrCl_2$	0.533	6.3		

Polymerization: $[Zr]= 2.0x10^{-6}$, $[Al]/[Zr] = 1750$, T = 60°C, t = 30min., $P_E = 1.6$ bar.

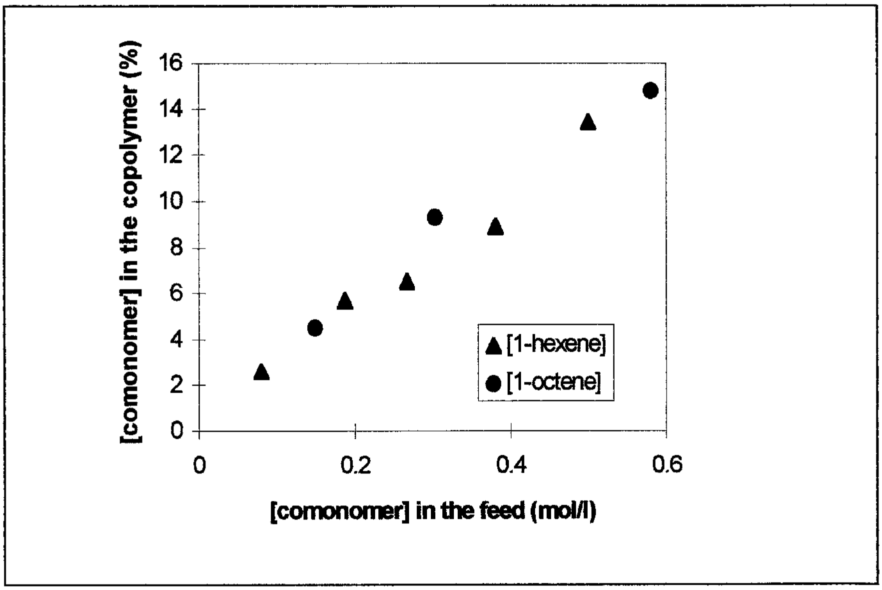

FIGURE 3: Comonomer incorporation in the ethylene copolymerization using $Me_2SiCp_2ZrCl_2$ as catalyst.

The analysis of Figures 3 and 4, shows that the reactivity of the α-olefin towards ethylene is probably not effected by its size. These curves also demonstrate a linear trend between the concentration of the comonomer in the copolymer and its concentration in the feed. This pattern of behaviour is particularly interesting because it allows for the prediction of the amount of the α-olefin in the copolymer when a specific concentration of the α-olefin in the feed is used.

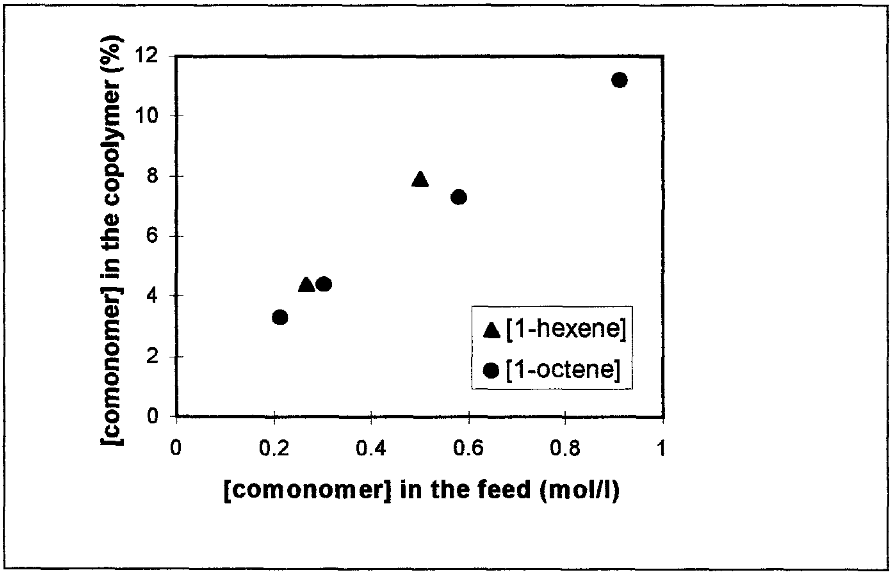

FIGURE 4 : Comonomer incorporation in the ethylene copolymerization using Cp_2ZrCl_2 as catalyst.

CONCLUSION

- The analysis of copolymer microstructure showed that the comonomer units (1-hexene or 1-octene) were isolated between ethylene blocks.
- As the concentration of the α-olefin increased some sequences of the type CEEC and CECE were obtained (C= comonomer).
- Bridged catalysts such as $Et[Ind]_2ZrCl_2$ and $MeSiCp_2ZrCl_2$ added a higher content of α-olefin to the copolymer than the unbridged ones.
- α-olefin size had no influence on the comonomer incorporation in the copolymer.

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