Study of the Effect of the Monomer Pressure on the Copolymerization of Ethylene with 1-Hexene

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ABSTRACT: The effect of ethylene pressure on the copolymerization of ethylene with 1-hexene was studied. The results show an increasing of productivities (g of polymer/n_{Zr} h) with pressure. This tendency was not observed for the activity (g of polymer/n_{Zr} h bar) that decreases when pressure is raised. When varing the pressure, the characteristics and properties of the formed copolymers are in accordance with the expectation for changes in the monomer concentration; increasing the pressure causes a decrease in comonomer incorporation. At higher ethylene pressure, the polymer is more crystalline due to less incorporation of 1-hexene and the molecular weight is higher. The density of the copolymers also decreases with comonomer incorporation into the copolymer © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2567–2574, 1997

INTRODUCTION

The linear low-density polyethylene (LLDPE) obtained from the copolymerization of ethylene with α-olefins is an important product in the petrochemical industry. The conventional Ziegler–Natta catalysis produces copolymers characterized by a broad distribution of composition limiting their practical use. Since the discovery of catalytic systems based on metallocene/methyl aluminoxane, copolymers with a narrow distribution of composition can be obtained. Using this catalytic system enables one to control the molecular structure of polymers and a new important field of research has been opened.[1,2] Metallocene-based polyethylene is now entering the main stream of development processes and several new applications are underway.[3]

In the last 10 years, several authors have presented studies related to new catalytic systems for the homo- and copolymerization of ethylene and propylene with α-olefins.[4,5] Many studies related to the catalytic system have also been undertaken for the stereospecific polymerization of propylene with stereorigid metallocene.[6,7] Little work has been concentrated on reaction parameters such as temperature, monomer/comonomer concentration, and monomer pressure.

Our group has been working on the effect of different parameters on the copolymerization of ethylene with α-olefins for the past 5 years. Our studies are focused on establishing correlations between the type of catalyst and the structure and properties of the products.[8–10] In the present work, we demonstrate that the monomer pressure plays an important role in the polymerization reaction indicated by the influence of pressure on the activity and properties of the produced polymers.

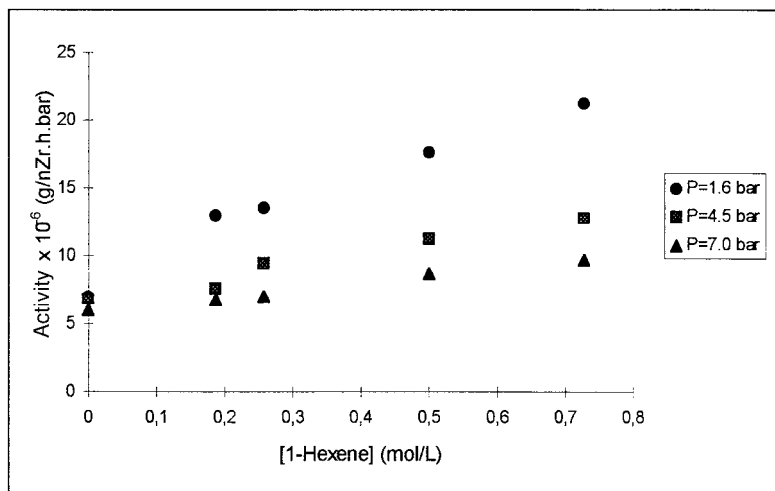**Figure 1** Effect of ethylene pressure and initial 1-hexene concentration on the activity in ethylene/1-hexene copolymerization using $Et[Ind]_2ZrCl_2$/MAO as the catalytic system. $T = 65°C$, $[Al]/[Zr] = 1750$, $n_{Zr} = 3.8 \times 10^{-6}$ mol.

EXPERIMENTAL

Polymerization

All polymerizations were carried out in an inert atmosphere. Toluene and 1-hexene were refluxed over metallic Na and freshly distilled under argon. Polymerization-grade ethylene was dried by passing through a 4 Å molecular sieve column.

The $Et[Ind]_2ZrCl_2$ catalyst was prepared according to the literature.[6] All the polymerizations were performed in a stainless-steel reactor from POLISUL at 65°C for 30 min. The reactor was filled with toluene (600 mL), comonomer, methylaluminoxane (MAO), and the catalyst. The [Al]/[Zr] ratio was 1750 and the amount of catalyst was kept constant at 3.8×10^{-6} mol. The monomer pressure was kept constant during the poly-
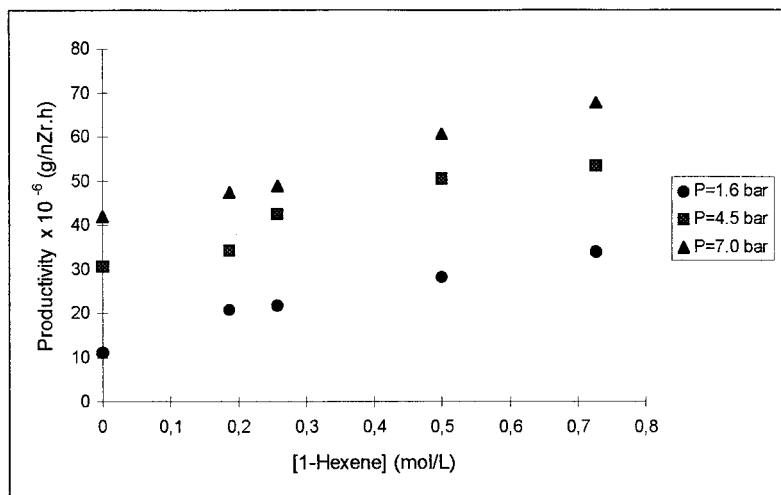

Figure 2 Effect of ethylene pressure and 1-hexene concentration on the productivity in ethylene/1-hexene copolymerization using $Et[Ind]_2ZrCl_2$/MAO as the catalytic system. $T = 65°C$, $[Al]/[Zr] = 1750$, $n_{Zr} = 3.8 \times 10^{-6}$ mol.
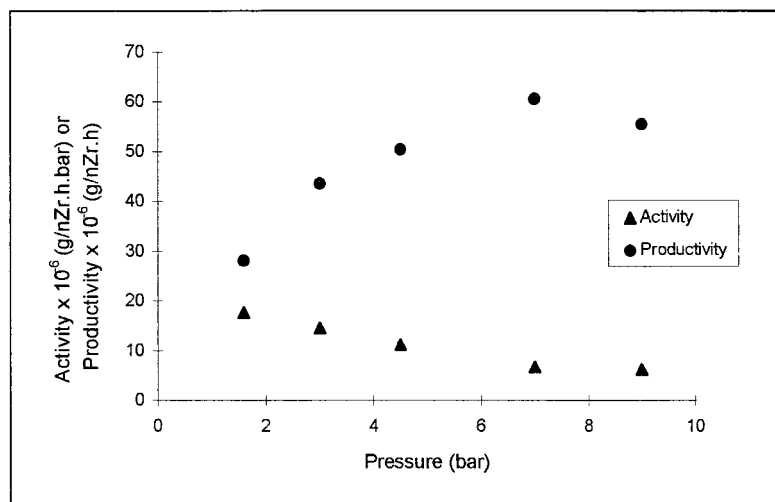
Figure 3   Effect of pressure on activity and productivity at constant 1-hexene concentration ($[H] = 0.50M$) in ethylene/1-hexene copolymerization using $Et[Ind]_2ZrCl_2/$ MAO as the catalytic system. $T = 65°C$, $[Al]/[Zr] = 1750$, $n_{Zr} = 3.8 \times 10^{-6}$ mol.

merization. After 30 min, the reaction was stopped by addition of an acidic methanol solution. The polymer was subsequently filtered, washed with methanol, and dried in a vacuum.

Characterization of the Polymers

^{13}C-NMR was employed to determine the composition of the copolymers according to the literature procedures.[11] The ^{13}C-NMR spectra were recorded at 80°C using a Varian XL-200 spectrometer operating at 50.309 MHz. Sample solutions of the copolymer were prepared in *o*-dichlorobenzene and benzene-d_6 (20% v/v) containing chromium(III) acetylacetonate as a paramagnetic substance to reduce relaxation times. Spectra were taken with a 70° flip angle, an acquisition time of 1.5 s, and a delay of 5.0 s.

Differential scanning calorimetry (DSC) measurements were performed on a Polymer Laboratories DSC instrument. Each sample was heated from 40 to 180°C at a heating rate of 10°C/min and maintained at this temperature for 2 min, then cooled down to 40°C at 10°C/min, and, fi-
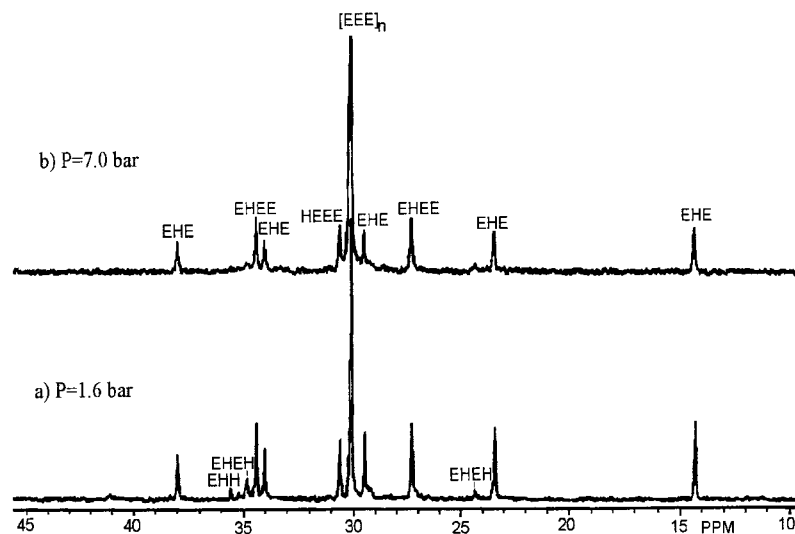

Figure 4   ^{13}C-NMR spectra for ethylene/1-hexene copolymer obtained from initial [1-hexene] = 0.727M. E: ethylene; H: 1-hexene.

Table I   Variation of 1-Hexene Concentration During the Copolymerization Reaction

[H]$_{initial}$ (mol/L)	P_E (bar)	[H] in the Copolymer (% mol)	Yield (g)	[H]$_{final}$ (mol/L)
0.19	1.6	5.4	47.85	0.055
	4.5	3.7	70.64	0.048
	7.0	4.0	90.45	~ 0
0.26	1.6	7.1	49.87	0.081
	4.5	5.0	84.43	0.039
	7.0	5.7	92.39	~ 0
0.50	1.6	10.3	55.37	0.236
	4.5	7.7	104.25	0.112
	7.0	6.9	121.9	0.056
0.73	1.6	19.3	68.93	0.210
	4.5	10.8	109.97	0.200
	7.0	11.9	128.93	0.060

The ethylene concentrations in solution were for P_E = 1.6 bar → 0.11M; P_E = 4.5 bar → 0.38M; P_E = 7.0 bar → 0.55M. Polymerization conditions were: T = 65°C, [Al]/[Zr] = 1750, [Et[Ind]$_2$ZrCl$_2$] = 3.8 × 10^{-6} mol.

nally, a DSC scan was recorded at 10°C/min. The crystallinity percentage was derived from ΔH_f by $X_c = \Delta H_f \cdot 100 / \Delta H f°$ ($\Delta H f°$ = 269.9 J/g). The density of the copolymers was measured according to the DIN 53479/76 and ASTM D792-91 standards.

Molecular weight and molecular weight distribution (M_w/M_n) of the polymers were determined by gel permeation chromatography using a Waters-150C GPC and 1,2,4-trichlorobenzene as a solvent at 140°C. The universal calibration curve of 18 polystyrene and three polyethylene monodisperse standards was necessary to calculate the molecular weights. The intrinsic viscosity ([η]) of the polymer dissolved in decalin at 135°C was measured on a Viscomatic-MS-Sofica viscosimeter.

RESULTS AND DISCUSSION

Activity and Productivity

The productivity (P) is defined as the amount of polymer (in grams) per moles of catalyst (n_{Zr}) and time of reaction (h). The activity (A) is the ratio between productivity and ethylene pressure.

As shown in recent work,[8,9] at low ethylene pressure (1.6 bar), there is a tendency of the activity to increase with increasing comonomer (1-hexene) concentration in the reaction medium. At higher ethylene pressures, this tendency persists as can be seen from Figure 1, but the activity decreases at higher pressures. On the other hand, productivity increases similarly for all the pressures studied (Fig. 2).
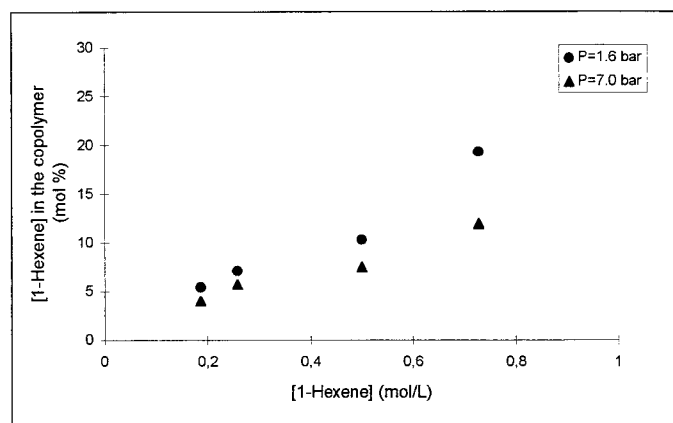

Figure 5   Comonomer incorporated in the copolymer against initial comonomer concentration for the ethylene/1-hexene copolymerization at pressure = 1.6 and 7.0 bar.
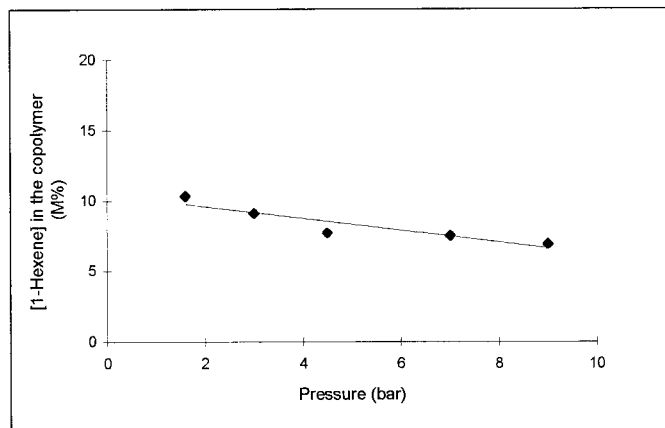
Figure 6   Effect of pressure in the incorporation of 1-hexene in the ethylene/1-hexene copolymer using $Et[In]_2ZrCl_2/MAO$ as the catalytic system. $T = 65°C$, $[Al]/[Zr] = 1750$, $n_{Zr} = 3.8 \times 10^{-6}$ mol.

The influence of the ethylene pressure on the activity and productivity can be seen more clearly in Figure 3 at a constant comonomer concentration. To explain the behavior of productivity and activity with the ethylene pressure and 1-hexene concentration, we utilize the kinetic equations. Productivity is proportional to the polymerization rate (R_p) which is related to the ethylene concentration $[E]$ and the 1-hexene concentration $[H]$ by the following equation[12]:

Table II   Influence of the Ethylene Pressure on the Viscosity and Molecular Weight Distribution of the Ethylene/1-Hexene Copolymers

Ethylene Pressure (bar)	$[1\text{-hexene}]_{initial}$ (M)	$[\eta]$ (dL/g)	M_w/M_n
1.6	0.19	1.31	2.2
	0.26	1.13	2.3
	0.50	0.93	2.2
	0.73	0.81	1.9
4.5	0.19	1.69	2.4
	0.26	1.36	2.5
	0.50	1.27	2.4
	0.73	1.02	2.5
7.0	0.19	2.35	3.1
	0.26	2.18	2.8
	0.50	1.63	2.8
	0.73	1.03	2.3

$$R_p = k_{11}[C_E^*][E] + k_{21}[C_H^*][E]$$
$$+ k_{12}[C_E^*][H] + k_{22}[C_H^*][H] \quad (1)$$

As shown by the ^{13}C-NMR spectra (Fig. 4), the amount of 1-hexene-1-hexene (HH) sequences is very low; thus, we can neglect the last term in eq. (1):

$$R_p = k_{11}[C_E^*][E] + k_{21}[C_H^*][E] + k_{12}[C_E^*][H] \quad (2)$$

At the steady state, the active center concentrations ($[C_E^*]$ and $[C_H^*]$) are constant. Thus,

$$k_{21}[C_H^*][E] = k_{12}[C_E^*][H] \quad (3)$$

Substituting the term containg $[H]$ in eq. (2) leads to

$$R_p = k_{11}[C_E^*][E] + 2 k_{21}[C_H^*][E] = [E] K \quad (4)$$

with $K = k_{11}[C_E^*] + 2 k_{21}[C_h^*]$.

The productivity P may be obtained by $P = R_p/n_{Zr}$, and the activity A, by $A = P/[E] = C$, where the constant C is given by K/n_{Zr}.

By eq. (4), productivity should increase with ethylene concentration. As $[E]$ is proportional to the ethylene pressure, productivity should increase with ethylene pressure, as was observed (Fig. 2). The activity, on the other hand, should be constant for all the ethylene pressures. However, Figure 3 shows a decrease. This behavior can be
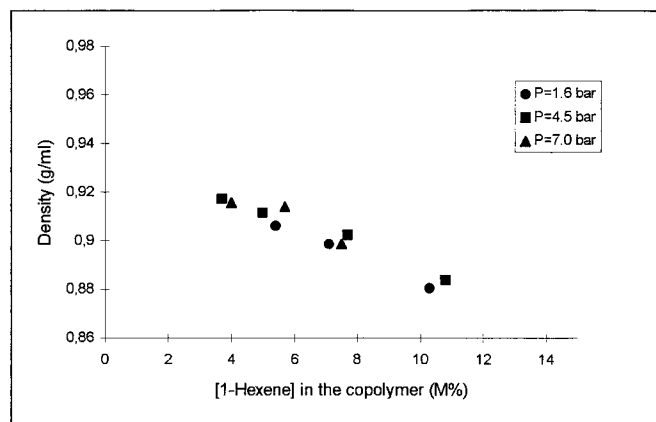
Figure 7 Density of the ethylene/1-hexene copolymers against comonomer incorporated at different pressures.

attributed to the variation of the comonomer concentration during the reaction (Table I).

Table I shows the initial and the final 1-hexene concentration. The later was calculated taking into account the initial comonomer concentration in the reaction medium, the comonomer incorporated in the copolymer, and the reaction yield. Another parameter that can influence the activity is the change in solubility of ethylene due to the growing polymer during the reaction (productivity) at higher ethylene pressures.

Copolymerization

Figure 5 shows the tendency of the copolymerization curve for a low and a high ethylene pressure,

giving almost linear relations between the incorporated 1-hexene and the concentration of ethylene. It can be seen that at lower ethylene pressures more 1-hexene is incorporated into the copolymer.

The ^{13}C-NMR spectra (Fig. 4) for two ethylene/1-hexene copolymers obtained from the same initial concentration of 1-hexene ($[H] = 0.73M$) show also this effect. The copolymer obtained from an ethylene pressure of 1.6 bar (a) has 19.3% of 1-hexene and the one obtained with an ethylene pressure of 7.0 bar (b) has 11.9% of 1-hexene incorporated. This means that the incorporation of the comonomer is favored at low ethylene pressures. This fact is expected since at higher ethylene pressures the concentration of ethylene in the

Table III   Influence of the Ethylene Pressure on the Crystallinity for Ethylene/1-Hexene Copolymers

Ethylene Pressure (bar)	[1-Hexene] Incorporated (%)	mp[a] (°C)	X_c by DSC (%)	Density (g/ml)	X_c by Density (%)
1.6	0	132.1	55	—	—
	5.4	95.8	27.7	0.9059	34.1
	7.1	98.1	20.4	0.8985	29.6
	10.1	92.8	8.5	0.8804	18.5
4.5	3.7	109.5	41.9	0.9172	40.9
	5.0	103.4	36.7	0.9114	37.4
	7.7	99.8	20.6	0.9023	31.9
	10.8	66.2	7.1	0.8838	20.6
7.0	4.0	116.7	40.0	0.9156	40.0
	5.7	112.6	39.8	0.9138	38.9
	7.5	103.4	26.9	0.8985	29.6
	11.9	86.9	14.2	0.9226	44.3

[a] mp = melting point; X_c = crystallinity.
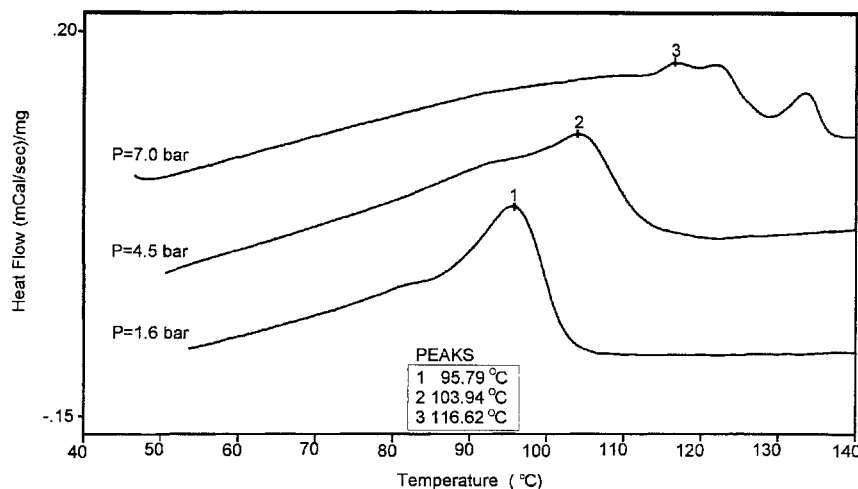
Figure 8 Thermograms of ethylene/1-hexene copolymer using $Et[Ind]_2ZrCl_2/MAO$ as the catalytic system. $T = 65°C$, $[Al]/[Zr] = 1750$, $n_{Zr} = 3.8 \times 10^{-6}$ mol. (1) Ethylene pressure = 1.6 bar, initial [1-hexene] = 0.258M, [1-hexene] in the copolymer 7.1%; (2) ethylene pressure = 4.5 bar, initial [1-hexene] = 0.5M, [1-hexene] incorporated = 7.7%; (3) ethylene pressure = 7.0 bar, initial [1-hexene] = 0.5M, [1-hexene] incorporated = 7.5%.

solution is higher and favors the reaction of ethylene with ethylene in the reaction mixture.

The spectra also show that 1-hexene units are isolated between ethylene blocks, and as 1-hexene incorporation increases, some sequences of the type EHEH and EHH appear. Figure 6 shows a linear decrease of 1-hexene incorporated into the copolymer with ethylene pressure for the same initial comonomer concentration in the reaction medium.

Properties of the Copolymers

Viscosity and Molecular Weight Distribution

Table II shows how the monomer pressure and the initial comonomer concentration influence the intrinsic viscosity and the molecular weight distribution. There is a clear tendency for the viscosity to increase with higher ethylene pressures and to decrease with the comonomer concentration. These effects are caused by termination reactions due to β-elimination as the comonomer increases, lowering the molecular weight. At higher pressures, the 1-hexene concentration is lower with respect to the ethylene concentration, so the termination reactions are less frequent. This phenomenon has already been reported.[9]

The molecular weight distribution does not show any marked effect for the changes in the initial comonomer concentration at different pressures. The values found are expected for copolymers obtained with this type of homogeneous catalyst.

Density

The correlation between density of the polymers and the percentage of 1-hexene incorporated is shown in Figure 7 for three different pressures. A linear relation was obtained and the density, apparently, is only a function of comonomer incorporation.

Crystallinity

Table III presents the influence of ethylene pressure on the crystallinity of the copolymers obtained by the DSC and density techniques. Both measurements present the same tendency of crystallinity values for the different copolymers. As expected, the cystallinity decreases with the percentage of the incorporated comonomer. The differences in crystallinities detected by the two techniques, especially at low crystallinities, are due mainly to difficulties in determining the base line in the DSC thermograms.

The DSC thermogram (Fig. 8) shows the traces corresponding to the second heating of three copolymers obtained from different ethylene pressures. It can be seen that more than one peak appears for copolymers prepared at higher pressure, indicating the presence of species with a higher melting point. This is in agreement with

the results presented in Table I. At higher ethylene pressures, the 1-hexene is almost completely consumed.

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