Polymer Bulletin 37, 469–474 (1996)

Polymer Bulletin

The effect of the ethylene pressure on its reaction with 1-hexene, 1-octene and 4-methyl-1-pentene

Raquel S. Mauler [1,*], Griselda B. Galland [1], Rosangela B. Scipioni [1], Raul Quijada [2,*]

[1] Instituto de Química, Universidade Federal do Rio Grande do Sul,
Av. Bento Gonçalves 9500, 90540 Porto Alegre, RS, Brazil
[2] Departamento de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas,
Universidad de Chile, Casilla 2777, Santiago, Chile

Received: 15 February 1996/Revised version: 21 May 1996/Accepted: 11 June 1996

SUMMARY

Copolymers of ethylene and 1-hexexe, 1-octene and 4-methyl-1-pentene were obtained using Et[In]$_2$ZrCl$_2$/MAO catalyst at various pressures. The increase of 1-hexene and 1-octene concentration in the feed increases catalyst activity(g/nZr.h.bar) and productivity(g/nZr.h). For 4-methyl-1-pentene the activity is independent on comonomer concentration. Increasing the ethylene pressure the productivity of the copolymerization increases and the activity shows a weak decay. Characterization of the copolymer shows that at higher pressure the cristallinity of the copolymers is higher due to lower comonomer incorporation.There is a good linear correlation of cristallinity with comonomer concentration in the feed for 1-hexene and 1-octene at a fixed pressure, but not for 4-methyl-1-pentene.

INTRODUCTION

Copolymers of ethylene and α-olefins obtained via metallocenes show great scientific and industrial interest. These copolymers have a narrow molecular weight distribution and well-defined microstructure, where the type and the number of branching can be controlled[1].

Polyethylene density can be controlled through incorporation of a low amount of an α-olefin, which keeps polymer chain linearity and leads to short chain branches randomly spaced in the polymer backbone. The linear α-olefins, 1-butene, 1-hexene and 1-octene, are important comercially and result in ethyl, butyl and hexyl branches in the respective copolymer[2].

The reaction parameters, i.e, 1-hexene concentration, temperature, [Al]/[Zr] ratio, for the reaction of ethylene with 1-hexene as comonomer using Et[In]$_2$ZrCl$_2$

---

* Corresponding author

catalyst system have been studied by our group[3-6]. Little has been published on the effect of the monomer pressure on these catalytic systems. The aim of this work was to study the effect of ethylene pressure on the copolymerization of ethylene with 1-hexene and 1-octene, and to investigate 4-methyl-1-pentene as comonomer in this type of polymerization.

EXPERIMENTAL PART

Polymerization

All polymerizations were conducted in a stainless steel reactor from POLISUL at 65 °C in an inert atmosphere. Toluene, 1-hexene, 1-octene and 4-methyl-1-pentene were refluxed and freshly distilled under argon from metallic Na. Polymerization-grade ethylene was dried by passage through a molecular sieves (4Å) drying tube. $Et[Ind]_2ZrCl_2$ catalyst was prepared according to the literature[7]. The reactor was filled with toluene (600 ml), comonomer, MAO, and the catalyst. The [Al]/[Zr] ratio was 1750 and the catalyst amount was kept constant (3.8×10^{-6}moles). The monomer pressure was kept constant during the polymerization. The reaction was stopped through addition of acidic metanol solution. The polymer was filtered, washed with methanol, and dried in vacuum.

Characterization of the polymers

Differencial scanning calorimetry (DSC) measurements were made with a Polymer Laboratories DSC instrument. Each sample was heated from 40 °C to 180 °C at 10 °C/min and maintained at 180 °C for 2 min, cooled down to 40 °C at 10 °C/min, and finally a DSC scan was recorded at 10 °C/min. The percentage of crystallinity was derived from ΔH_f by $X_c=\Delta H_f \times 100/64.5$[8].

RESULTS AND DISCUSSION

Figure 1 shows the copolymerization activity of ethylene/1-hexene and ethylene/1-octene for two different pressures at different comonomer concentration. As was discussed previously[3-5], at low pressures there is a clear tendency of increasing activity with increasing 1-hexene concentration, so these results confirm this tendency for ethylene/1-hexene and ethylene/1-octene at 1.6 bar.

When the ethylene pressure is increased to 7.0 bar the comonomer concentration does not have any marked influence in either systems, i.e., the activity is not independent of comonomer concentration at higher pressures.

Figure 2 shows that with 4-methyl-1-pentene comonomer, the activity is independent of the comonomer concentration at low ethylene pressure. This may be because the pendant group of this comonomer does not exert a positive effect of the linear pendant groups as butyl or hexyl branch. The linear group has a positive influence on the activity giving the so-called comonomer effect[6].

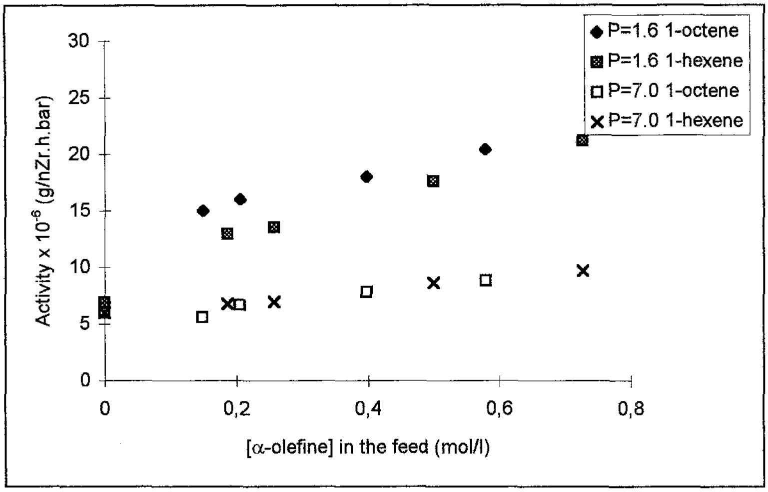

Fig.1- Copolymerization of ethylene with 1-hexene and 1-octene using $Et[In]_2ZrCl_2/MAO$ catalyst system (pressure=1.6 bar,. T=65°C, [Al]/[Zr]=1750, n_{Zr}=3.8 x 10^{-6} moles).

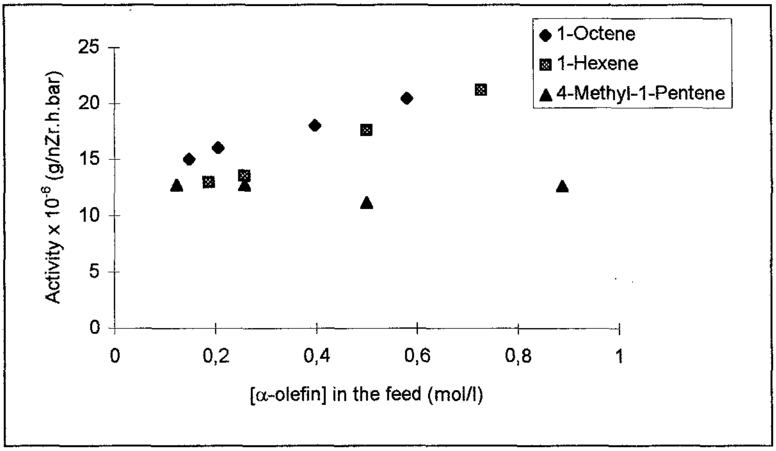

Fig. 2 --Copolymerization of ethylene with α-olefin using $Et[In]_2ZrCl_2/MAO$ catalyst system (T=65°C, [Al]/[Zr]=1750, n_{Zr}=3.8 x 10^{-6} moles, pressure=1.6 or 7.0 bar).

When the activity(g/Zr.h.bar) and produtivity(g/nZr.h) are plotted at different pressures (Figure 3), it is observed that the change in ethylene pressure affects the copolymerization of ethylene with 1-hexene or 1-octene.

The activity shows a small decrease when the pressure increases. This could be due to some concentration change of the monomer and comonomer in the reaction medium (i.e., when the pressure increases, the overall ethylene concentration increases in the medium and consequently, the comonomer concentration decreases).

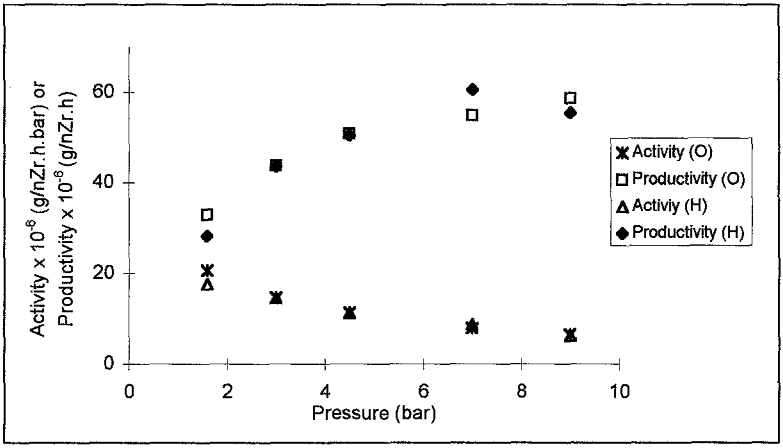

Fig 3 - Effect of pressure on the activity and productivity of copolymerization of ethylene with 1-octene (0.398 M) and 1-hexene (0.500 M). T=65°C, [Al]/[Zr]=1750, n_{Zr}=3.8 x 10^{-6} moles).

Figure 4 shows the effect of comonomer concentration on the cristallinity of copolymer formed with 1-hexene or 1-octene at the different pressures. Cristallinity is higher for both copolymers obtined at higher pressure (7.0 bar) due to a lower incorporation of comonomer.

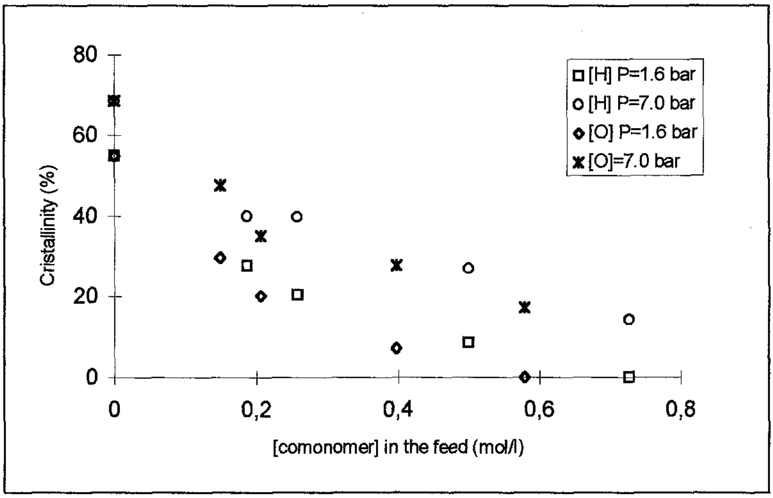

Fig. 4 - Effect of pressure and comonomer concentration on the crystallinity of the copolymer of ethylene and 1-hexene or 1-octene (T=65°C, [Al]/[Zr]=1750, n_{Zr}=3.8 x 10^{-6} moles).

Figure 5 shows the effect of concentration and the type of comonomer on cristallinity. At low comonomer concentrations all the systems behave similars.

This means that the incorporated comonomer is well separated between ethylene sequences which reduces the cristallinity.

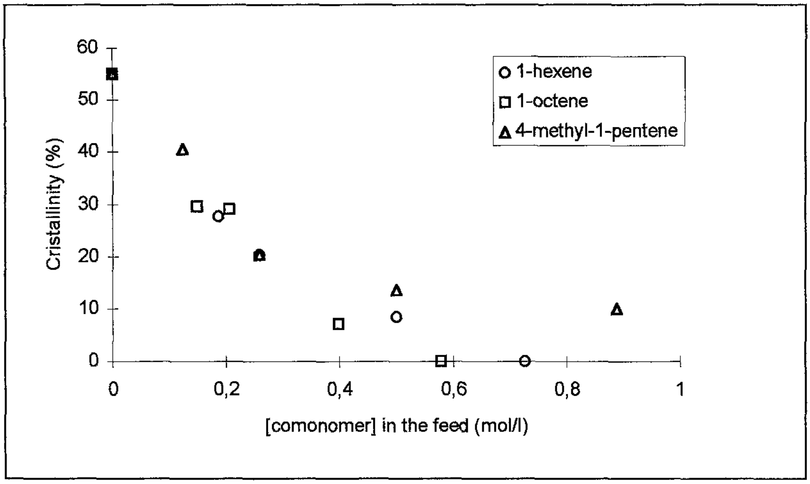

Fig 5 - Effect of comonomer concentration on the cristallinity of the copolymer of ethylene and α-olefin (pressure=1.6 bar, T=65°C, [Al]/[Zr]=1750, n_{Zr}=3.8 x 10^{-6} moles).

At higher comonomer concentration the incorporation increases and the pendent group decreases the cristallinity. The copolymer with 1-octene, compared with 1-hexene, shows lower cristallinty, probably due to the larger size of the pendant group as its incoporation is lower than the 1-hexene[6]. For these two systems there is a good linear correlation with comonomer concentration in the feed.

The results obtained for 4-methyl-1-pentene copolymer show different behaviour, indicating that as the comonomer concentration in the feed increases, the cristallinity is not affected. We elucidate this assumption in the future.

ACKNOWLEDGMENT

The authors would like to thank COPESUL, WITCO and ETHYL for the supply of raw materials; POLISUL for the laboratory facilities; CNPq and FAPERGS for financial support.

REFERENCES

1. J. Chowdhury, S. Moore, *Chem. Eng. News*, April, 34-9 (1993).
2. W. Kaminsky, K. Kulper, H. H. Bintzinger and S. Wild, *Angew. Chem.* **97**, 507(1985).
3. Raul Quijada, Rosangela B. Scipioni, Raquel S. Mauler, Griselda B. Galland, Marcia L. Miranda, *Polym. Bull.*, **35**, 299(1995)
4. R. Quijada, J. Dupont, M. L. Miranda, R. B. Scipioni, G. B. Galland, *Macromol. Chem. Phys.* **196**, 3991(1995).
5. G. B. Galland, R. S. Mauler, S. Menezes and R. Quijada, *Polym. Bull.*, 34, 599 (1995).
6. R. Quijada, G. B. Galland, R. S. Mauler -*Macromol. Chem. Phys.*, in press.
7. J. C. Chien, T. Nozaki, *J. Polym. Sci., Polym. Chem. ed.*, **31**, 227 (1993).
8. K. Soga, *Makromol. Chem.*, **190**, 995(1989).