

Polymerization of ethylene by chromium acetylacetonate/methylaluminoxane catalyst system

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Summary

The present paper deals with polymerization of ethylene by chromium acetylacetonate - $\text{Cr}(\text{acac})_3$ - activated by alkylaluminium, e.g. $\text{Al}(\text{C}_2\text{H}_5)_3$ or $\text{Al}(\text{i-C}_5\text{H}_9)_3$, or methylaluminoxane (MAO). The influence of polymerization parameters on catalyst performance, such as Al/Cr mole ratio, temperature, aging time, type of cocatalyst, was investigated. High activities were obtained only when MAO was the cocatalyst. The polymers were characterized by size exclusion chromatography (SEC) and differential scanning calorimetry (DSC) analyses.

Introduction

The catalysts employed in polyethylene manufacturing are mainly based on only two transition metals: titanium or chromium and more recently, some group 4 metallocene-based compounds. Whereas the titanium-based catalyst is one of the components of conventional Ziegler-Natta systems (1), the chromium compounds are the basic constituents of the Phillips catalyst (2,3). Catalysts based on metallocenes can produce different kinds of polyethylene, e.g., high density polyethylene (HDPE), linear low density polyethylene (LLDPE), etc.(4).

In recent years, the polymerization of olefins with transition metal compounds activated by MAO has been investigated. Much attention has been given to the use of organometallic compounds as catalysts for ethylene and propylene polymerizations. In contrast with conventional Ziegler-Natta catalysts, some of the systems based on transition metal acetylacetonates are active toward polar monomers (5-7). Endo and co-workers have found that $\text{Cr}(\text{acac})_3/\text{MAO}$ can polymerize methyl methacrylate with low activity (6) In addition, ethylene can be polymerized by $\text{Cr}(\text{acac})_3/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ albeit with low yield (8). Studies on ethylene polymerization with $\text{Cr}(\text{acac})_3/\text{MAO}$ are not found, to our knowledge, in the literature. Since block copolymerization of ethylene with polar monomers remains an ultimate goal in polyolefin engineering, the main objective of this work was to start a study on ethylene polymerization employing $\text{Cr}(\text{acac})_3/\text{MAO}$.

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Experimental part

Materials

Chromium acetylacetonate was commercially purchased (Toyo, Japan) and used as received. Toluene (donated by Shell Química) was refluxed for 24 h over sodium-benzophenone and distilled prior to use. Methanol (donated by PROSINT) was purified according to standard method. Ethylene of petrochemical grade (donated by CENPES/PETROBRAS a Petroleum Brazilian Company) was purified by passing through columns filled with molecular sieves (3Å) and Cu-catalyst to remove water and O₂, respectively. MAO, a 30% w/w toluene suspension (donated by Witco GmbH) was used without further purification. Triisobutylaluminium (TIBA) and triethylaluminium (TEA) (donated by Polibrasil Resinas) were used as received. The other chemicals (research grade) were commercially purchased and used without further purification.

Ethylene Polymerization

To a 100 mL Schlenk flask equipped with a magnetic stirrer bar and maintained at a determined temperature under dry nitrogen atmosphere were added 30 mL of toluene (recently distilled), cocatalyst solution, catalyst solution and ethylene was then continuously fed to maintain a positive pressure of 100 mmHg during 2 h. The polymerization was terminated after 2h by adding a dilute hydrochloric acid solution in methanol. The polymer was filtered, washed with large amount of methanol and dried at 65°C until constant weight.

Polymer characterization

The molecular weight and molecular weight distributions (MWD) were determined in 1,2,4-trichlorobenzene by SEC (Waters 150CV *plus*) at 135°C calibrated with polystyrene-standards. The soluble content of the whole polymer was determined by Soxhlet extraction with n-heptane for 6 h. Entalphy of fusion (ΔH_m), crystallinity index and melting temperature (T_m) were measured by differential scanning calorimetry (DSC) at 10 K/min under nitrogen flux, using a Perkin-Elmer equipment (DSC 7).

Results and discussion

Our goal was to find best conditions to obtain linear polyethylene. It was observed that Cr(acac)₃ cannot polymerize ethylene without a cocatalyst under conditions employed in this study. Hence, the polymerization was conducted with different kinds of aluminium compounds using various Al/Cr mole ratios. The results are summarized in Table 1. The catalyst system presented the highest activity when MAO was used as cocatalyst, producing polyethylene in fairly good yields. Increasing the Al/Cr ratio provoked a decrease in catalyst activity probably due to the over-reduction of chromium species. TEA and TIBA did not contribute significantly to the catalyst activation, thus it can be concluded that MAO has an important role in the catalyst activation in ethylene polymerization.

Table 2 shows the results of ethylene polymerization with the Cr(acac)₃/MAO system at different Al/Cr ratios at 50°C. Increasing of the Al/Cr ratio provoked a decrease of the catalyst activity. These results could also be attributed to the over-reduction of the chromium species. Table 3 shows the results of ethylene polymerization at different Al/Cr mole ratios at 20°C. The catalyst activity at Al/Cr = 200 (mole ratio) was higher at 20°C (Table 3) than at 50°C (Table 2). This behavior confirms that the of over-reduction is preponderant at higher temperatures.

Table 1 - Effect of cocatalyst type on ethylene polymerization with chromium acetylacetonate [Cr(acac)₃]

Cocatalyst	Al/Cr mole ratio	Catalyst activity (g polyethylene/gCr.h)
MAO	50	279
	100	118
TEA	5	(a)
	10	(a)
TIBA	5	(a)
	10	3

Polymerization conditions: contact time between catalyst/cocatalyst = 3 min; Cr(acac)₃ = 0.03 mmol; 30 ml toluene; polymerization time = 2 h; temperature = 50°C. (a) It was not obtained polymer.

Table 2 - Effect of Al/Cr mole ratio on ethylene polymerization at 50°C with chromium acetylacetonate/MAO

Al/Cr molar ratio	Catalyst activity (gPE/gCr.h)	Soluble polymer (%) ^a	T _m (°C) ^b	ΔH _m (J/g) ^b	Crystallinity Index (%) ^b
50	279	3	132	212	72
100	118	2	134	176	60
150	121	16	136	215	73
200	98	10	130	81	28

Polymerization conditions: contact time between catalyst/cocatalyst = 3 min; Cr(acac)₃ = 0.03 mmol; 30 ml toluene; polymerization time = 2 h. ^a Determined by Soxhlet extraction with n-heptane during 6 hours. ^b Determined by DSC. PE - polyethylene

Table 3 - Effect of Al/Cr mole ratio on ethylene polymerization at 20°C with chromium acetylacetonate/MAO

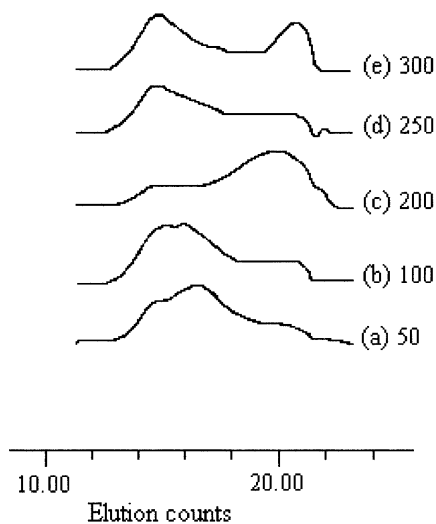
Al/Cr molar ratio	Catalyst activity (gPE/gCr.h)	Soluble polymer (%) ^a	T _m (°C) ^b	ΔH _m (J/g) ^b	Crystallinity Index (%) ^b
50	147	5	134	206	40
100	82	nd	135	184	63
200	537	42	129	186	64
250	333	14	135	168	57
300	13	nd	nd	nd	nd

Polymerization conditions: contact time between catalyst/cocatalyst = 3 min; Cr(acac)₃ = 0.03 mmol; 30 ml toluene; polymerization time = 2 h. ^a Determined by Soxhlet extraction with n-heptane during 6 hours. ^b Determined by DSC. PE - polyethylene. nd = not determined

The catalyst system became a jelly-like solid when the Al/Cr mole ratio was higher than 100 at 50°C. This feature was also described in the literature for Cr(acac)₃/Al(C₂H₅)₂Cl (8).

Figure 1 presents SEC curves of polymers listed in Table 3. The MWD's are at least bimodal, indicating the heterogeneity of the catalyst system.

Figure 1 - SEC curves of the polymers (Table 3) obtained with different Al/Cr mole ratios



These results could be confirmed by Soxhlet extraction with n-heptane of the polymer obtained at Al/Cr = 200 (Figure 2). As expected, the molecular weight of the soluble fraction (Figure 2c) was low ($M_w = 5930$) and its molecular weight distribution was narrow ($M_w/M_n = 2$) due to the presence of a single-site chromium species. On the other hand, the insoluble fraction (Figure 2b) showed bimodal molecular weight distribution of the crude polymer (Figure 2a), indicating the heterogeneity of the catalyst system.

DSC results showed (Tables 2 and 3) that almost all polymers present very high crystallinities and melting temperatures indicating that the polyethylenes produced by this catalyst system are linear.

Catalyst homogeneity is affected by temperature (Table 4) as well as by the Al/Cr mole ratio (Tables 2, 3). The catalyst activity was the highest at 50°C. Above this temperature (65°C and 80°C), the catalyst system became heterogeneous and no polymer was produced. Probably, at higher than 50°C, the chromium species undergoes over-reduction, producing insoluble species (Cr^{+1} , Cr^0). Table 4 also shows that low soluble contents (compared to the results listed in Tables 2 and 3) were obtained, and all polymers exhibited high crystallinities and melting temperatures, indicating that the large amount of MAO cocatalyst provoked a catalyst heterogeneity (jelly-like solid).

Table 5 shows that catalyst performance was sensitive to aging time. The catalyst activity decreased when the aging time increased. The reaction between the catalyst components is instantaneous, changing from a purple solution to green after adding the cocatalyst. It was also noted that the colour of catalyst solution became light brown after monomer addition.

Figure 2 - SEC curves of fractions of the polymer produced at 20°C (Al/Cr molar ratio = 200, Table 3)

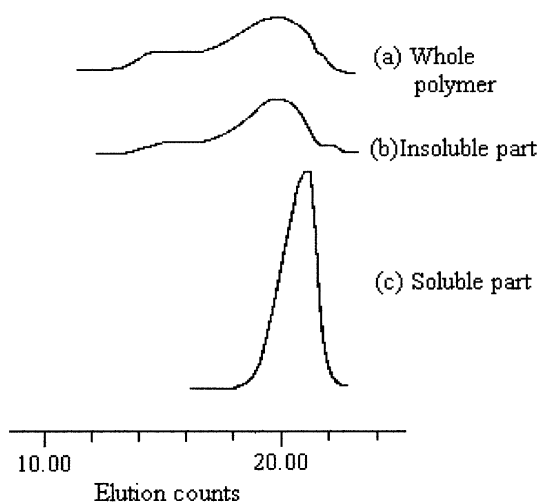


Table 4 - Influence of temperature on ethylene polymerization with chromium acetylacetonate/MAO catalyst system

Temperature (°C)	Catalyst activity (gPE/gCr.h)	Soluble polymer (%) ^a	T _m (°C) ^b	ΔH _m (J/g) ^b	Crystallinity Index (%) ^b
20	118	5	134	206	70
35	108	5	140	248	85
50	279	3	132	212	72
65	13	nd	135	201	68
80	(c)	(c)	(c)	(c)	(c)

Polymerization conditions: contact time between catalyst/cocatalyst = 3 min; Cr(acac)₃ = 0.03 mmol; 30 ml toluene; polymerization time = 2 h; Al/Cr molar ratio = 50. ^a Determined by Soxhlet extraction with n-heptane during 6 hours. ^b Determined by DSC. ^c It was not obtained polymer. PE - polyethylene. nd = not determined

This colour change can be attributed to monomer coordination with catalyst site. Strangely, the brown colour appeared even before the monomer addition at long aging times (15 and 25 minutes). In both cases, the brown colour disappears during the polymerization. During the polymerization, it is also possible that chromium species have undergone over-reduction.

Table 5 - Effect of contact time between chromium acetylacetonate and MAO on ethylene polymerization

Contact time (min)	Catalyst activity (gPE/gCr.h)
0.5	382
3	117
15	107
25	42

Polymerization conditions: 30 ml toluene; polymerization time = 2 h; Al/Cr molar ratio = 50; temperature = 20°C; Cr(acac)₃ = 0.03mmol

As already reported (6), this catalyst system is also able to polymerize methyl methacrylate. Thus, we are now investigating the copolymerization of ethylene and polar monomers and the results will be reported elsewhere.

Conclusions

The results presented in this paper have led to the following conclusions:

- (1) The catalyst based on Cr(acac)₃ was active with MAO as cocatalyst.
- (2) The homogeneity of this catalyst system is dependent on the cocatalyst concentration and polymerization temperature.
- (3) The catalyst activity is dependent on the contact time between Cr(acac)₃ and MAO, decreasing at long aging times.
- (4) The Cr(acac)₃/MAO was an effective catalyst system for polymerizing ethylene producing a linear polymer with high melting temperature and crystallinity with fairly good activity.

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