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Effects of trisobutylaluminium on styrene polymerization with $Ni(acac)_2$ /MAO/SiO_2 catalyst system activated by methylaluminoxane

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Summary

Styrene polymerization with $Ni(acac)_2/MAO/SiO_2$ catalytic system was carried out in the presence of methylaluminoxane (MAO), triisobutylaluminum (TIBA) or MAO and TIBA mixture as activators. The catalytic system activated only by TIBA produced polymer with 53% of isotacticity. When the catalytic system was activated by a mixture of MAO and TIBA the polymer isotacticity increases as MAO concentration increases. In this case, the maximum of isotacticity was 59%. The polymer has presented lower molecular weight than the polymer obtained by MAO as activators and the polymer microstructure was not explained by Markov first-order model. In addition, ^{13}C NMR spectra of the polymers obtained after extraction with MEK, have indicated that there are two active sites in this catalytic system.

Introduction

In the last years, the role of alkylaluminium on the type of aluminoxane cocatalyst used for coordination catalyst systems had been studied[1-7]. Alkylaluminium compounds are employed in order to improve the catalyst performance, including the control of polymer molecular weight and stereospecificity [8-10]

It is known that $Ni(acac)_2$ is inactive when combined with alkylaluminium as cocatalyst for styrene polymerization. Nevertheless, this catalyst combined with MAO is very active for this monomer [11-15]. In addition, the catalyst performance depends on the content of TMA on MAO [11].

More recently, we have investigated the $Ni(acac)_2/MAO/SiO_2$ catalyst system activated by MAO with different TMA contents [17,18]. The aim of this work is to study the TIBA effects on the catalyst performance and show some features of styrene polymerization mechanism with $Ni(acac)_2/MAO/SiO_2$ activated by MAO and TIBA.

Experimental Part

Material - Toluene was refluxed and distilled over Na/benzophenone. Styrene was dried over CaH_2 and distilled in vacuum. Ni(acac)$_2$ was purified by toluene azeotropic distillation. MAO (M_w = 1500-2000) at 10% in toluene suspension was kindly supplied by Akzo and used as received. SiO_2 (MS3070, 700m^2/g) donated by PQ Co. (USA) was employed as carrier. N_2 was purified by passing through molecular sieves (3Å) and P_2O_5 columns. Methyl-ethyl ketone (MEK) was utilized as received.

Supported Catalyst - SiO_2 was calcinated at 400ºC for 4h using inert atmosphere (N_2). To a Schlenk 2 g of SiO_2, 20 mL of toluene and 25 mmol of MAO were added. After stirring during 1 h at room temperature, the modified SiO_2 was washed with three portions of 20 mL of toluene and then 0.1 mmol of Ni(acac)$_2$ was added. After 5 min of aging, the resultant suspension was thoroughly washed with toluene and dried at 40ºC under a nitrogen flux.

Polymerization procedure - The polymerizations were carried out at 40ºC in a Schlenk flask (100 mL) fitted a magnetic stirrer. The reagents were added in the following order: toluene, MAO, TIBA and catalyst suspension. After stirring during 5 min, styrene was added to the Schlenk. After 24h, a solution of ethanol/HCl 5 % v/v was added. The polymer was thoroughly washed with ethanol and dried at 60ºC.

Characterization - Spectra of ^{13}C NMR was obtained on a Varian Mercury 200 MHz equipment operating at 75 MHz, using a polystyrene solution in $CDCl_3$. Measurements of molecular weights (M_w and M_n) and polydispersity (M_w/M_n) were obtained by gel permeation chromatography (GPC) with a Waters plus 150 equipment with trichlorobenzene as solvent. The content of Ni(acac)$_2$ adsorbed on SiO_2/MAO surface was measured with atomic absorption spectrometry (AAS). Polystyrene samples were fractionated with methyl-ethyl ketone (MEK) into Soxhlet extractor during 24h.

Results and discussion

The catalyst activities are shown in the Figure 1. The Ni(acac)$_2$/MAO/SiO_2 catalyst system was activated by TIBA for styrene polymerization. These results should be due to stabilization of Ni(acac)$_2$ ionic species through multicoordinating “crown” methylaluminoxane complexes as observed for metallocene catalysts [19].

When a constant amount of TIBA was employed, the polymer yield increases as the Al(MAO)/Ni mole ratio increases. In comparison to analogous catalyst activated by MAO alone [18], this behavior was greatly different. In this case, an exchange between the TIBA and “associated” TMA on MAO [20] or the twisting of the alkyl substituents on the aluminum centers of MAO and TIBA [21] could produce an aluminoxane bearing methyl and isobutyl groups, affecting the MAO structure. These differences in its structure may have some influence on the alkylation ability and stability of the anionic species [22]. It is important to note that isobutylaluminoxane (IBAO) has a different cocatalytic activity compared to MAO.

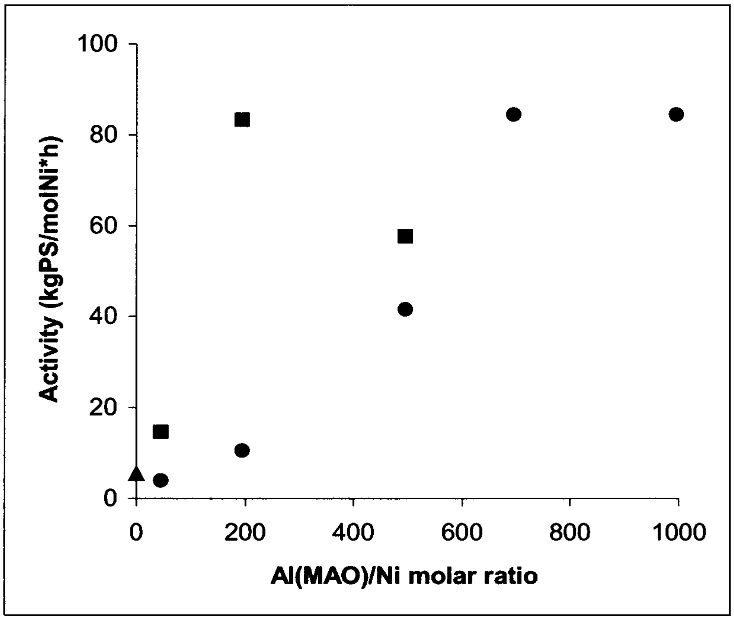

Figure 1. Evaluation of catalyst activity as a function of Al(MAO)/Ni at temperature = 40^0C, polymerization time = 24h, [Ni] = 10^{-4} mol/L, [styrene] = 2.15 mol/L; TIBA/Ni mole ratio = 5; (▲) catalyst activated with TIBA; (■) catalyst system activated by MAO lone; (•) catalyst system activated by MAO combined with TIBA

Polymer molecular weights obtained by this catalyst system activated by MAO combined with TIBA (see runs 5-9, Table 1) are lower than those obtained with the system activated by MAO alone (see runs 1-3, Table 1). These data suggest that TIBA could act as chain transfer agent. It was also observed that the polymer molecular weight decreases as the MAO concentration increases (see runs 5-9, Table 1). Other authors have reported different trends of polymer molecular weight, which is dependent on the catalyst system [7-10]. Our results could be explained by chain transfer to MAO. At the same time, the polydispersity decreases with the increasing of MAO concentration. Hence, the excess of MAO leads to single active sites.

The ^{13}C-NMR spectra of the polymers obtained with $Ni(acac)_2/MAO/SiO_2$ activated by MAO combined with TIBA show that the polymer isotacticity increases as MAO concentration increases (see runs 5-9, Table 1). Comparing to analogous system activated by MAO lone, different behavior was obtained (see runs 1-3, Table 1). Other authors describe that TIBA affects the polymer stereoregularity because of the bulky isobutyl group, which can affect the steric crowding of propagating active sites [8,10]. These results suggest that at high TIBA/MAO mole ratio the bulky isobutyl groups inhibit the formation of η^3-benzyl group that controls the stereoselective insertion [18,23,24]. In addition, it was verified that the Markov first-order model does not explain the polymer structures and that the styrene insertion occurs randomly [25].

Table 1. Evaluation of the Al/Ni mole ratio on the catalyst system $Ni(acac)_2/MAO/SiO_2$ activated by MAO combined with TIBA or by MAO lone

Runs	Al(MAO)/Ni molar ratio	mm (%)	mr (%)	rr (%)	M_w (10^{-4})	M_n (10^{-4})	M_w/M_n
Catalyst activated by MAO lone							
1	50	55	36	9	49	3.6	13.4
2	200	47	48	5	6.5	3.5	1.8
3	500	nd	nd	nd	8.1	1.8	4.4
Catalyst activated by MAO combined with TIBA							
4	0[a]	53	43	4	11.7	4.5	2.6
5	45	32	61	7	15.1	2.1	7.2
6	195	46	50	4	5.4	1.3	4.0
7	495	58	39	3	3.8	1.4	1.8
8	695	59	38	3	3.3	1.5	2.5
9	995	59	38	3	3.8	1.5	2.5

Reaction conditions: [Ni] = 10^{-4} mol/L, [styrene] = 2.15 mol/L;
TIBA/Ni mole ratio = 5; (a) catalyst activated with TIBA; nd – not determined

Due to the low molecular weight polymer obtained in run-9 (Table 1), this polymer was chosen to evaluate the mechanism on heterogeneous system. Initially, five types of end-chain structure were possible and two possible styrene insertions occur at Ni – H and Ni – CH_3 bonds. The chemical shifts in the aliphatic regions (47.61; 29.78 and 12.12 ppm) and (42.45; 36.56 and 33.57ppm) are absent. Therefore, the $-Ph^{1}CH-^{2}CH_2-^{3}CH_3$ and $-CH_2-Ph^{1}CH-^{2}CH_2-^{3}CH_2Ph$ chain-end groups do not occur significantly. The resonance in the aromatic region at 143 and 113.7 ppm are absent. This result shows that 1,2 insertion does not occur with the last monomeric unit. Two close peaks are present in the methyne region at 37.00 and 36.50 ppm and two others in methyl region at 20.77 and 20.99 ppm. They arise from the same end-group, which can assume the erythro or the threo configuration (Table 2).

Table 2. Chemical shifts of polystyrene chain-end structures

Chain-end	^{1}C (ppm)	^{2}C (ppm)	^{3}C (ppm)
$-PhCH-CH_2-Ph^{1}CH-^{2}CH_3$	(37.23) Erithro–37.00 Threo – 36.50	(22.43) Erithro–20.77 Threo – 20.99	
$-CH_2-Ph^{1}CH-^{2}CH=^{3}CH\,Ph$	(38.7)	(133.49) 134.68	(128.23) 128.53
$-CH_2-Ph^{1}CH-^{2}CH_2-^{3}CH_2Ph$	(42.45)	(36.56)	(33.57)
$-CH_2-PhCH-Ph^{1}CH=^{2}CH_2$	(143.00)	(113.70)	
$-Ph\,^{1}CH-^{2}CH_2-^{3}CH_3$	(47.61)	(29.78)	(12.12)

Calculated shifts are in parentheses

This ^{13}C NMR study suggests that the mechanism of heterogeneous system has a similar feature as homogenous ones [18]. In this mechanism, the main chain termination reaction is the β_2 – hydride elimination that causes the chain-end group ($-CH_2-PhCH-$ $Ph^1C={}^2CH_2$). A predominantly 2,1 monomer$_2$ insertion occurs at Ni – H bond, which forms the chain-end group ($-Ph^1CH-{}^2CH_3$) and this type of insertion is essential to the formation of η^3 species.

Figure 2 shows the C^{13} NMR spectrum of two samples of polystyrene obtained with $Ni(acac)_2/MAO/SiO_2$ in the following conditions: (a) MEK soluble fraction obtained with MAO combined with TIBA as cocatalyst at temperature of 40ºC; (b) MEK insoluble fraction obtained with MAO as cocatalyst at temperature of 30ºC. Predominantly isotactic polymer was obtained in the condition (b), however, the crude polymer has 65% of isotactic triads. The shift at 146.5 ppm on the spectrum (a) shows the isotactic pentads (mmmm). This spectrum (a) shows 16% of isotactic triads and the crude polymer has 25% of isotactic triads. These behaviors could be attributed to the presence of two active species with different stereospecificty.

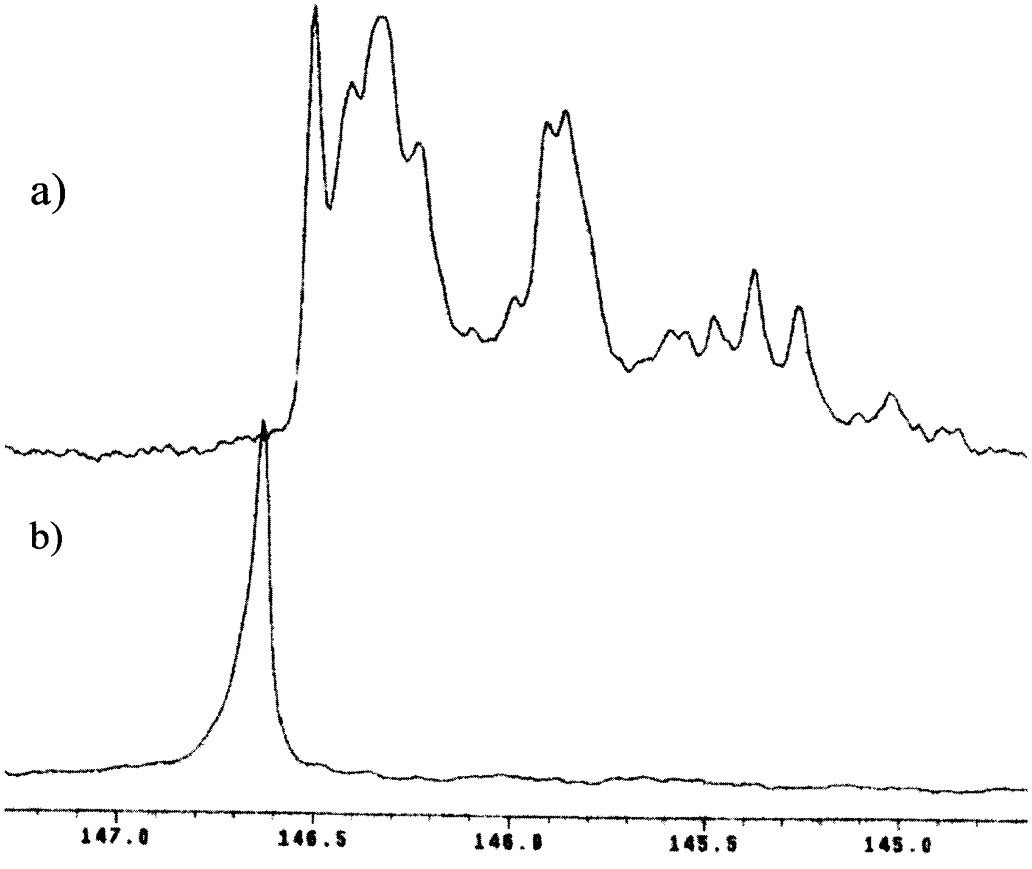

Figure 2 – ^{13}C NMR spectrums in quaternary carbono region of polystyrene obtained with $Ni(acac)_2/MAO/SiO_2$ in the following condition: (a) MEK soluble fraction obtained with MAO combined with TIBA as cocatalyst at temperature of 40°C; (b) MEK insoluble fraction obtained with MAO as cocatalyst at temperature of 30°C.

In conclusion, the presence of TIBA on the Ni(acac)$_2$/MAO/SiO$_2$ catalyst system activated by MAO promotes a strong influence on the catalyst performance. This influence could be due to a MAO modification structure by bulky isobutyl group. The isobutyl group probably affects the steric crowding of propagating active site affecting the polymer stereoregularity. It was observed that at a constant amount of TIBA, the increase of MAO concentration has produced a decrease on polymer molecular weight and has narrowed the molecular weight distribution. Futhermore, the ^{13}C NMR study suggests that the polymerization mechanism of heterogeneous system is similar to the homogeneous ones.

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