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Isospecific polymerization of styrene with supported nickel acetylacetonate/methylaluniinoxane catalysts

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Summary

The polymerization of styrene with catalysts based on Ni(acac)$_2$ supported on SiO$_2$ and A1$_2$O$_3$ was investigated. Using catalysts based on MAO supported on silica, a highly isotactic polystyrene was obtained. Nevertheless, the A$_1$20$_3$-supported catalyst can promote isospecific polymerization activated by common. alkyl aluminum compounds even by any prior support treatment with MAO.

1. Introduction

Catalyst systems formed by Ni(acac)$_2$ (acac = acetylacetonate) and common alkyl aluminum compounds do not polymerize styrene. However, methylaluminoxane (MAO)- activated Ni(acac)$_2$ catalysts are very active in the polymerization of this monomer, generally giving rise to moderate isotactic polystyrene (1,2). The formation of high isotactic polymer was reported to be possible by addition of an amine to the polymerization system (1) or by varying the type of MAO and the ratio Al/Ni used (2). In order to try to improve the stereospecificity of catalysts based on Ni(acac)$_2$ and MAO, we have supported the Ni compound on silica and alumina. This communication presents data on the polymerization of styrene with these supported catalysts.

2. Experimental

Materials

Ni(acac)$_2$ (TCI, Japan) was purified by azeotropic distillation. Two types of silica were employed: Type I SiO$_2$ (Fuji Co.) was treated at 400'C for 8 h under argon atmosphere; Type II was a 958-600 (Davidson Co.), 0.65 mmol OH/g used as received. γ-A1$_2$0$_3$ (Petrobrás Co.) (3) was calcinated at 400°C for 3 h under argon atmosphere. MAO (30 wt % toluene solution) kindly supplied by Witco was used without further purification. Styrene was distilled over calcium hydride. Solvents were purified by standard methods.

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Support procedure

SiO_2/ $Ni(acac)_2$: To a 100 mL glass reactor equipped with a magnetic stirrer were added 2 g of silica Type I, 40 mL of toluene and 5 mmol of $Ni(acac)_2$. The mixture was kept stirring for 24 h at room temperature. A pale green solid was separated from the liquid phase, washed four times with hot toluene and dried under vacuum (Ni content : 1.65 mmol/g).

SiO_2/MAO/ $Ni(acac)_2$: To a 100 mL glass reactor were added 2 g of silica Type I, 40 mL of toluene and 10 mmol of MAO. After 12 h of stirring at room temperature, the mixture was washed several times with hot toluene and then 5 mmol of $Ni(acac)_2$ was added. After 24h under stirring, the brown solid phase was treated as above (Ni content: 0.59 mmol/g).

SiO_2/MAO: To a 250 mL glass reactor equipped with a magnetic stirrer were added 100 mL of toluene, 6g of silica Type II and 4 g of solid MAO. After 24h of stirring at room temperature, the liquid phase was separated. The solid phase was then whashed 3 times with toluene and vacuum dried (Al content: 6.74 mmol/g).

$A1_2O_3$/$Ni(acac)_2$: To a suspension of 40 mL of toluene and 1 g of calcinated $A1_2O_3$was added 2.5 mmol of $Ni(acac)_2$. After 24 h of stirring, the solid phase was separated and washed with hot toluene. The catalyst was finally vacuum dried (Ni content: 0.365 mmol/g).

The contents of nickel on the SiO_2 - and $A1_2O_3$-supported catalysts and aluminum on SiO_2-supported MAO were measured by atomic absorption spectrophotometry. Catalyst toluene suspensions with known transition metal concentration were prepared and kept under inert atmosphere prior to use.

Polymerization

Polymerizations were performed in a 100 mL Schlenk flask equipped with a magnetic stirrer. To the flask were added a prescribed amount of fresh toluene recently distilled, Aluminum compound and Ni-containing catalyst. Styrene was then added and the temperature maintained constant for the reaction time. The polymerization was terminated by adding a dilute hydrochloric acid methanol solution and precipitated by pouring into a large amount of methanol. The resulting polymer was washed with methanol and vacuum dried. In some runs, instead of MAO solution the heterogeneous cocatalyst SiO_2/MAO was used to activate $Ni(acac)_{2.}$ In those cases, a toluene dispersion of SiO_2/MAO and a prescribed amount of $Ni(acac)_2$ toluene solution was added into the flask containing the solvent. After 5 min, styrene was added. The polymerization products were worked up as described above.

Polymers characterization

Polymer samples were fractionated by hot extraction with methylethylketone (MEK) or toluene. Molecular weights (M_W and M_n) and molecular weight distributions (M_W/M_n) were determined by size exclusion chromatography (SEC) using a Waters 610 system equipped with a refractive index detector at 25°C in THF. Monodisperse polystyrenes were used as calibrating standards. The stereoregularity of PS samples was evaluated by ^{13}C NMR measurements in a Varian Gemini 300 or Bruker AM 270 instrument (o-dichlorobenzene/benzene-d$_6$, polymer concentration ca. 10%, TMS as internal standard, 60°C).

3. Results and discussion

3. 1. Systems based on silica

Ni(acac)$_2$ seems to form a very stable linkage with the silica surface. After some days in contact with toluene the solvent remained colorless. Table 1 shows the results of styrene polymerization with SiO$_2$/ Ni(acac)$_2$ catalyst using MAO, AI(Et)$_3$ and Al(iBu)$_3$ as cocatalysts. The catalyst can be activated by all these compounds, but the activity is very low for the activation with A1(Et)$_3$ and Al(iBu)$_3$. As expected, activities increased as increasing amounts of MAO were employed. At very high Al/Ni molar ratios (e.g. Al/Ni=500) almost 100 % yield was obtained in 24 h. Nevertheless, in all cases the PS presented an oligomer-like aspect, being completely soluble in hot MEK, indicating low degree of regularity. The molecular weight, M_w, was relatively low and the polydispersity was very narrow as it is in the case of a Ni(acac)$_2$-MAO soluble system (2), suggesting that propagation proceeds by only one type of active center. Using MAO as cocatalyst a brown solution was observed indicating that the polymerization proceeds by homogeneous active sites. High yields were also obtained when isooctane was used as polymerization solvent instead of toluene, but in this case the polydispersity was slightly broader.

Table 1. Polymerization of styrene with SiO$_2$ supported Ni catalysts *a)*

Catalyst	Cocatalyst Type	Cocatalyst (mmol)	Al/Ni molar ratio	Yield (g)	M_w (x 10^{-4})	M_w/M_n
SiO$_2$/Ni(acac)$_2$	MAO	1.6	64	1.95	2.69	1.8
	MAO	2.6	104	2.72	2.38	1.7
	MAO	12.9	516	4.22	3.27	1.8
	MAO *b)*	12.9	516	4.44	2.55	2.9
	Al(Et)$_3$ *b)*	2.6	104	0.45	0.86	1.7
	Al(iBu)$_3$ *b)*	2.6	104	0.36	-	-
SiO$_2$/MAO/Ni(acac)$_2$	MAO	12.9	500	3.58	2.96	1.8
	Al(Et)$_3$	1.3	50	0.14	-	-
	Al(Et)$_3$	2.6	100	0	-	-

a) Polymerization conditions: 20 mL of toluene, 5 mL (43.5 mmol) of styrene, 0.025 mmol of Ni, 35 °C, 24 h.

b) Polymerization solvent: isooctane

The influence of SiO$_2$ treatment with MAO before the impregnation with Ni(acac)$_2$ was also investigated. The results of styrene polymerization with SiO$_2$/MAO/ Ni(acac)$_2$ are presented in Table 1. Interruption of stirring after the addition of cocatalysts like A1(Et)$_3$ in a suspension of this catalyst resulted in the decantation of brown catalyst particles and clean colorless supernatant. The same behavior was not observed when MAO was added to the catalyst suspension, suggesting that in the first case the catalyst system is heterogeneous while in the last one it is homogeneous.

A similar catalyst activity behavior described for the SiO_2/ $Ni(acac)_2$ catalyst was verified for SiO_2/MAO/ $Ni(acac)_2$; although MAO and $A1(Et)_3$ are able to activate the catalyst, the activation with MAO gives better yields. Nevertheless, the polymer is completely soluble in hot MEK when MAO was used. The polydispersity is narrow and suggests that MAO probably causes the extraction of Ni compound from the SiO_2 surface producing soluble active centers. Activation with $A1(Et)_3$ gave less than 10% yields. Increasing the A1/Ni ratio to 100, no polymer was obtained probably due to the formation of species which are inactive to the polymerization. On the other hand, the polymer obtained by $A1(Et)_3$ activation at Al/Ni 50 showed a fibrous appearance in contrast with that obtained in the polymerization activated by MAO. That polymer was highly insoluble in hot MEK (>80%) and the ^{13}C NMR spectrum revealed that it is highly isotactic (T_m = 214°C).

In order to confirm the influence of heterogenization of Ni active sites on the formation of isotactic polystyrene, the activation of $Ni(acac)_2$ with immobilized MAO cocatalyst was also investigated. Styrene polymerization using a $Ni(acac)_2$ solution activated by the heterogeneous cocatalyst SiO_2/MAO produced highly isotactic polymers in higher yields. The i-PS obtained was extracted with hot toluene in order to separate the polymer from SiO_2 ; the toluene soluble polymer was then analyzed by ^{13}C NMR. Figure 1 shows the quaternary carbon region of the ^{13}C NMR spectra of PS obtained by activation of $Ni(acac)_2$ with SiO_2/MAO. An intense peak at 146.3 ppm characteristic of isotactic pentad (4) was observed. Increasing A1/Ni ratio from 10 to 60 did not affect the stereospecificity and only a small increase in the polymer productivity was noticed as disclosed in Table 2. The results indicate that the active sites are located on the support surface resulting predominantly in the formation of stereoregular polymer.

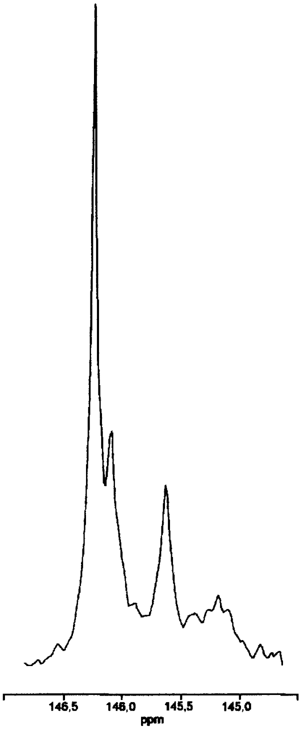

Fig. 1. Quaternary carbon region of the ^{13}C NMR spectra of PS obtained by activation of $Ni(acac)_2$ with SiO_2/MAO (hot toluene soluble fraction).

Table 2. Polymerization of styrene with $Ni(acac)_2$ activated by the heterogeneous cocatalyst SiO_2/MAO [a)]

$Ni(acac)_2$ (mmol)	Al/Ni molar ratio	Productivity (g PS/mmol Ni.h)
0.048	10	5.06
0.016	30	5.90
0.008	60	7.80

a) Polymerization conditions: 20 mL of toluene, 5 mL (43.5 mmol) of styrene, 0.48 mmol of Al, 4 h, 25°C

3.2. Systems based on alumina

The main data concerning the polymerizations using Al_2O_3/ $Ni(acac)_2$ catalyst are summarized in Table 3. As in the case of the SiO_2-supported catalysts, activation with MAO resulted in better yields, however the polymer obtained was completely soluble in hot MEK. Common alkyl aluminum compounds were also able to activate the catalyst producing high molecular weight PS, but in these cases higher amounts of MEK-insoluble polymer were produced. DSC and ^{13}C NMR analysis of these insoluble fractions confirmed the presence of highly isotactic PS. It is interesting to note that these catalyst systems did not contain any MAO. Thus, if isospecific polymerization of styrene with Ni compounds takes place by a cationic species, this may be generated by the contact of $Ni(acac)_2$ with the Al_2O_3 solid surface in presence of a common alkyl aluminum. A similar result was also obtained on the syndiospecific polymerization of styrene with $A1_2O_3$-supported titanium catalysts (5).

Table 3. Polymerization of styrene with Al_2O_3 / $Ni(acac)_2$ [a)]

Cocatalyst		Al/Ni molar ratio	Yield	Insoluble fraction[b)]		Soluble fraction[b)]	
Type	(mmol)		(g)	(%)	T_m (°C)	M_w x 10^{-4}	M_w/M_n
MAO	1.25	50	3.82	0	-	3.57	1.9
$Al(iBu)_3$	0.25	10	0.58	22	219	7.06	5.3
$Al(iBu)_3$ [c)]	1.25	57	0.14	49	218	-	-
$Al(Et)_3$	0.25	10	0.38	22	217	6.88	7.0

a) Polymerization conditions: 20 mL of toluene, 5 mL (43.5 mmol) of styrene, 0.025 mmol of Ni, 30°C, 20 h.
b) MEK extraction
c) 0.022 mmol of Ni.

It was estabilished by Ascenso et al (6,7) that the highly isospecific oligomerization of styrene by the complex [η^3-methallyl)(η^4-cycloocta-1,5-diene)-nickel(II)] hexafluorophosphate modified by tricyclohexylphosphine occurs through a

2,1-insertions. Moreover, the isotactic oligostyrene grows on a Ni catalyst complex containing an η^3-benzylic ligand between the metal center and the propagating chain. High molecular weight highly isotactic PS was also isolated by Longo et al (1) from the polymer obtained by the catalyst system $Ni(acac)_2$ /MAO/$N(Et)_3$; in the absence of the amine, the catalyst system generated only a moderately isotactic polymer. Also in that case a 2-1 insertion was identified. The high molecular weight of our samples did not permit us to identify this type of insertion by end group analysis. However, it is possible that the propagation step of the isospecific polymerization with the SiO_2- and $A1_2O_3$-supported catalyst occurs through 2-1 insertion also.

It has been observed that the nature of the ligands of Ti based catalysts (8) for the syndiospecific polymerization of styrene does not change the type of PS tacticity. In the contrary, the presence of a crowded environment seems to increase the amount of i-PS.

The presence of π-benzyl-Ni species in a square-planar coordinated complex structure has been suggested to play an important role in the isotactic propagation of styrene polymerization with soluble Ni catalysts (9). It is possible that this type of species is also present in the supported catalysts investigated.

As a conclusion, we reported that a SiO_2-supported catalyst promotes isospecific polymerization of styrene if, before impregnation with a transition metal compound, the silica is treated with MAO. The use of an excess of common alkylaluminum as cocatalyst completely deactivates these catalytic systems; further addition of MAO highly increases the polymer productivity and lowers the polymer stereoregularity. Ni catalysts supported on Al_2O_3 without any pretreatment with MAO are activated by common alkylaluminum and polymerize styrene giving highly isotactic PS. Work is in progress in order to have more information on the nature of the active isospecific sites on this supported catalyst systems.

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