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Some studies on styrene polymerization using new systems prepared from coordination metal compounds

$ReBr(CO)_3$(3,3'-dimethyl-2,2'-biquinoline)-diphenylzinc with and without MAO systems[a]

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SUMMARY

The monovalent rhenium compounds ReBr $(CO)_3$ (3, 3′-dimethyl-2,2′-biquinoline) (**I**) and ReBr $(CO)_5$ (**II**) could be used as catalysts in styrene polymerization after activation with diphenylzinc (Ph_2Zn) and methylaluminoxane (MAO). The catalytic activity shown by the **I**-Ph_2Zn-MAO system was dependent on the molar ratio between the components and the temperature of polymerization. Non stereoregular polystyrene (PS) was obtained under all experimental conditions. The resulting PS gave multimodal GPC traces suggesting the presence of different species capable of polymerizing styrene, possibly species resulting from MAO alone, **I**-Ph_2Zn and **I**-Ph_2Zn-MAO systems.

INTRODUCTION

In recent years, the stereoregular polymerization of styrene has been developed principally using systems based on titanium and some zirconium complexes [1-3]. These compounds modified with aluminoxane derivatives, principally MAO, have shown to be highly syndiospecific [4-9].

The interest to expand the study toward new metals and new ligands has guided our attention to the coordination metal complexes with polypyridine ligands. These types of compounds, with Os(II), Ir(III), Ru(II) and Re(I) as center metals, have been shown to be suitable as thermal, photochemical and electrochemical catalysts in many chemical processes of industrial interest [10,11]. The coordinative role of the center metal has been suggested in the majority of these reactions.

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Considering that both the modifications of π-electronic density and changes of the structural conformations of the ligand may modulate the properties of complexes [12,13], we have designed and obtained biquinoline Re(I) derivatives [12]. Complex **I** shows pseudooctahedral structure. The more interesting contribution to asymmetric conformation in the complex arises from free rotation around the 2,2\` bond (Fig. 1). The X-ray study [14] shows distortion between the planes of both quinoline systems. ^{1}H-NMR spectra taken at room temperature in $CDCl_3$, show two quinoline systems which are not equivalent; ^{1}H-NMR preliminary studies at variable temperatures show a fast conformational equilibrium around 60°C. We believe that systems prepared from **I**, could show catalytic activity and stereospecific induction for styrene polymerization. The influence of complex geometry upon the reactivity and tactic induction has been reported [15].

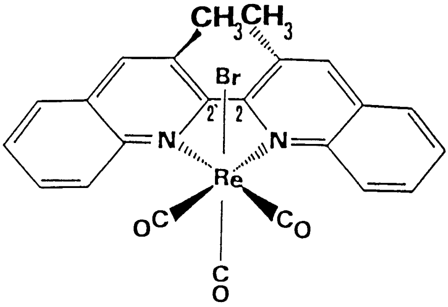

Figure 1. Structure of the rhenium compound employed in styrene polymerization. Tricarbonylbromo (3,3\`-dime\_ thyl - 2, 2\` - biquinoline) - rhenium (**I**).

Experimental

All operations were carried out under argon atmosphere using standard techniques. Toluene was dried over sodium. Styrene was dried over anhydrous Na_2SO_4, followed by CaH_2 and distilled under reduced pressure. The preparation of **I** and **II** complexes has been reported [12,16]. In 100 ml. Schlenck-type reactors equipped with magnetic stirrer, benzene solutions of **I**-Ph_2Zn and **II**-Ph_2Zn systems were aged at 60°C for 1 hour followed by adding MAO (Witco) and styrene. The reactors were then kept at polymerization temperature for 48 hours. All runs were stopped by precipitation in methanol acidified with HCl. The polymers were recovered by filtration, washed several times with methanol and dried under vacuum at 60°C. Viscosity measurements were performed at 25°C using $CHC1_3$ as solvent and intrinsic viscosities were calculated by using the Solomon-Gotesman relationship [17]. The molecular weight was estimated using the Mark-Houwink-Sakurada relationship, employing the K= $1.12x10^{-4}$ (dL/g) and a= 0.73 [18]. Gel-permeation chromatograms, GPC, were obtained at room temperature using three columns connected in series and packed with Ultastyragel: 10^3, 10^4 and 10^5 A° with THF as solvent, and the flow rate of 1 mL/min. Thermal analyses were run with a Perkin-Elmer DSC7 differential scanning calorimeter at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

We have studied styrene polymerizations using Ph_2Zn-additives systems [19-24]. Lately we have combined Ph_2Zn with metallocenes of titanium and zirconium, incorporating MAO as modifier [25,26]. We have found that the activity depended on the nature of the initiating system. Also, we have already reported the isolation of a portion of syndiotactic PS [21]. Now we are reporting results obtained by using modified catalytic systems based upon **I** and **II** complexes on styrene polymerization.

The results of exploratory experiments on styrene polymerization employing **I** and **II** complexes are shown in Table 1. In absence of additives both **I** and **II** are inactive. Rhenium compounds show low catalyst activity when they are combined with diphenylzinc or MAO. The higher activity is obtained when MAO is added to the aged rhenium compounds-Ph_2Zn systems. Nevertheless, it is clear that structural and electronic effects of the polypyridine ligand does not influence catalytic activity.

The GPC trace of PS obtained with the three component system: **I**-Ph_2Zn-MAO shows bimodal molecular weight distribution (MWD). This may indicate that there are two different species capable of polymerizing styrene (Fig. 2). The peak detected in the low molecular weight region is due to polymerization initiated with MAO alone, while the peak appearing in the high molecular weight region, not present in the chromatograms of the

Table 1. Results of the polymerization of styrene[a].

Catalyst system	Activity[b] x 10^{-3}	Mv x10^{-5} g/mol	Mn x10^{-3} g/mol	Mw/Mn
I	0	--	--	--
I-Ph_2Zn	1.9	n.d.	4.8	7.6
I-MAO	7.4	0.80	12.8	6.8
I-Ph_2Zn-MAO	60.3	0.77	7.7	15.0
II	0	--	--	--
II-Ph_2Zn	0.6	n.d.	n.d.	n.d.
II-MAO	17.9	0.70	7.7	7.8
II-Ph_2Zn-MAO	65.0	0.44	3.0	15.5

[a] Polymerization conditions: 60°C, 48 hours in toluene, total volume= 30 mL, [S]= 2.03 mol/L, [Re]= $1.38x10^{-4}$ mol/L, Re/Zn= 0.75 mol/mol, Al/Re= 2400 mol/mol, [b] Activity in g PS (mol Re mol S h)$^{-1}$, n.d.= Not determined.

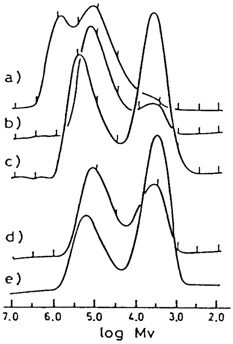

Figure 2. GPC traces of polystyrene obtained using different catalytic systems based on rhenium compounds: a) **I**-Ph$_2$Zn, b) **I**-MAO, C) **I**-Ph$_2$Zn-MAO, d) **II**-MAO, e) **II**-Ph$_2$Zn-MAO. Polymerization conditions are given in Table 1.

PS obtained with **I**-Ph$_2$Zn and **I**-MAO systems, would be associated with a species characteristic for this combination. DSC analysis of PS obtained with rhenium compound-MAO and rhenium compound-Ph$_2$Zn-MAO systems indicate atactic material.

The effect of molar ratio of MAO to rhenium on the activity of the **I**-Ph$_2$Zn-MAO combination was investigated (Tab. 2). The catalytic activity of these systems are strongly dependent on the Al/Re mole ratio employed. The activity increases with increasing MAO concentration, in accordance with the activating role established for aged **I**-Ph$_2$Zn systems. For Al/Re mole ratios higher than 2400, the yield of PS decreases. On the other hand, the GPC traces keep the same patterns shown in Figure 2c, but with decreasing intensity. Apparently, high MAO concentrations decompose the catalyst leading to inactive species. Such species could include modification of the central metal, its oxidation state, or both.

Table 2. Styrene polymerization using the **I**-Ph$_2$Zn-MAO[a] system at different Al/Re mole ratios.

Al/Re	Activity[b] x 10^{-3}	Mv x10^{-5} g/mol	Mn x10^{-3} g/mol	Mw/Mn
3600	24.0	0.49	4.2	11.4
2400	60.3	0.77	4.7	15.0
1800	49.5	0.39	5.9	9.6
900	25.9	0.29	4.6	7.9
450	7.1	0.20	4.2	7.4
Without MAO	1.9	n.d.	4.8	7.6

[a] Polymerization conditions: 60°C, 48 hours in toluene, total volume= 30 mL, [S]= 2.03 mol/L, [Zn]= 1.82×10^{-4} mol/L, [Re]= 1.38×10^{-4} mol/L. [b] Activity in g PS (mol Re mol S h)$^{-1}$, n.d.= Not determined.

Table 3. Styrene polymerization using the I-Ph_2Zn-MAO[a] system at different Re/Zn mole ratios.

Re/Zn mole ratio	Activiy[b] x 10^{-3}	Mv x10^{-5} g/mol	Mw/Mn
0.25	53.2	0.33	7.3
0.50	36.1	0.59	13.7
0.75	60.3	0.77	15.0
1.00	46.5	0.43	9.7
1.50	13.5	0.92	8.0

[a] Polymerization conditions: 60°C, 48 hours in toluene, total volume= 30 mL, [S]= 2.03 mol/L, [Re]= $1.38x10^{-4}$ mol/L, Al/Re= 2400 mol/mol, [b] Activity in g PS (mol Re mol S $h)^{-1}$.

This could adversely affect both catalytic activity and molecular weight. MAO may also compete for vacant coordination sites [27]. In all cases, non-stereoregular PSs with broad MWDs were obtained.

Styrene polymerizations with different Re/Zn were also carried out with the **I**-Ph_2Zn-MAO system at 2400 Al/Re (Table 3). The effect of Ph_2Zn concentration on the catalytic activity is not clear. However, the highest PS yield and molecular weight was obtained with Re/Zn $\approx$ 0.75.

The GPC curves of the PSs obtained with the **I**-Ph_2Zn-MAO system at different Al/Re and Re/Zn mole ratios present similar patterns, as shown in Figure 2c. This suggests that at different additive concentrations, the amount of active species was varied while their nature remained the same.

As the polypyridine ligand exhibits conformational motion in solution due to distortion between the planes of the quinoline ring [14], symmetry elements would be thermally modulated. Therefore, the catalytic activity and stereoregular capability of the **I**-Ph_2Zn-MAO system at several polymerization temperatures was investigated. The polymerizations between 25°C and 100°C show that the activity is very sensitive to temperature (Table 4). Both catalytic activity and molecular weight shown highest values at 100°C.

Figure 3 shows GPC curves of PSs obtained with the **I**-Ph_2Zn-MAO system with Al/Re=2400 and Re/Zn=0.75 at several temperatures. The modality of GPC traces changes with the temperature. At 25°C the GPC trace was unimodal which correspond to PS obtained by MAO activation. Bimodality was observed in different proportions when polymerizations were carried out at 40°C or 60°C. However, with polymerizations at 100°C, the GPC trace was unimodal which could be due to active species generated. The dependence of the catalytic activity with the

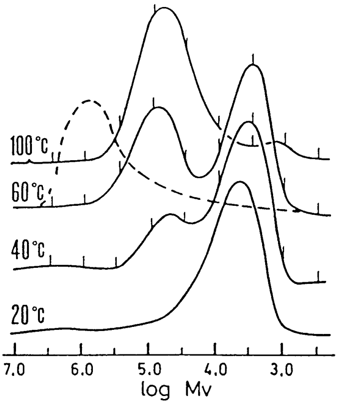

Figure 3. GPC traces of PSs obtained using **I**-Ph_2Zn-MAO system (Al/Re= 2400 mol/mol and Re/Zn= 0.75 mol/mol) at different polymerization temperatures. Polymerization conditions are given in Table 4.

(.....) Styrene autopolymerization at 60°C.

temperature suggests that around 100°C, the species generated by MAO and aged **I**-Ph_2Zn system are kinetically favorable, while at 20°C either the initiaton rate is very low, or these species can't be generated. We also observed that styrene auto-polymerization does not compete with the polymerization induced by the **I**-Ph_2Zn-MAO system (Fig. 3). PS samples obtained at different temperatures, were amorphous. This could indicate that the conformational asymmetry of compound **I** in the active systems, was not able for stereospecific induction. Currently we are studying the nature of species generated from the **I**-Ph_2Zn and **I**-Ph_2Zn-MAO combinations, and modifications of the structural symmetry of the ligand and its stereoregulating capability.

Table 4. Styrene polymerization using the I-Ph_2Zn-MAO[a] system at different temperatures.

Polymerization temperature /°C	Activity[b] x 10^{-3}	Mv x10^{-5} g/mol	Mw/Mn
25	26.8	0.16	3.5
40	45.2	0.24	5.8
60	60.3	0.77	15.0
100	152.3	0.69	4.9

[a] Polymerization conditions: 48 hours in toluene, total volume= 30 mL, [S]= 2.03 mol/L, [Re]= 1.38x10^{-4} mol/L, Re/Zn= 0.75 mol/mol, Al/Re= 2400 mol/mol, [b] Activity in g PS (mol Re mol S h)$^{-1}$.

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