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$ReBr(CO)_3$(3,3'-disubstituted-2,2'-biquinoline) modified complexes as initiating systems for styrene polymerization*

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Summary

$ReBr(CO)_3$(3,3’-disubstituted-2,2’-biquinoline) complexes modified with diphenylzinc (Ph_2Zn) and methylaluminoxane (MAO) were employed in the polymerization of styrene (St). The results show that both the initiating activity and the characteristics of the polystyrenes (PSts) are independent of the different conformational rhenium complexes. Studies made using UV-vis spectroscopy agree with a dissociation of the biquinoline ligand when MAO is added to the reaction system.

Introduction

Crystalline polystyrene, specially in its syndiotactic configuration, has great physical and mechanical advantages over commercial polystyrene (atactic configuration). This fact has given rise to much research activity which has led to the development of highly syndiospecific initiator systems. Among this research, the use of systems based upon titanium complexes (titanocenes) modified with MAO is extremely important (1-4). Usually, these complexes contain ligands with a high π-electron delocalization and sometimes they have asymmetric elements on the central atom.

We have already employed titanium and zirconium complexes combined with Ph_2Zn and MAO for styrene polymerization. These systems have shown that their initiating activity is strongly dependent on their nature and on the reaction conditions (5,7). Recently, we have reported the polymerization of styrene using monovalent rhenium compounds such as $ReBr(CO)_5$ and $ReBr(CO)_3$(3,3’-dimethyl-2,2’-biquinoline) (**I**) in which Ph_2Zn and MAO have been incorporated as modifying agents (8). No great differences were observed in the initiating activity of these systems. On the other hand, atactic PSts were obtained using different polymerization temperatures and several MAO/I and I/Ph_2Zn molar ratios (9). This showed that conformational asymmetry of the ligand was not capable of directing the stereoregular polymerization of styrene.

The present work shows the results obtained when styrene was polymerized with a series of monovalent rhenium complexes modified with Ph_2Zn and MAO. The conformational asymmetry elements and the π-electron delocalization in the rhenium

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complexes were modified by the different degree of torsion of the biquinoline ligands arising from the various substituents in the 3 and 3’ positions (Fig. 1) (9-11).

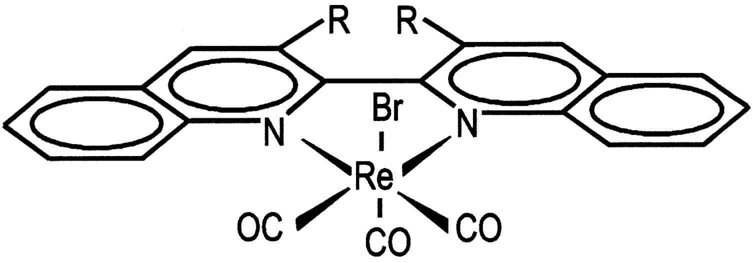

Fig. 1. Monovalent rhenium compounds used:
R= $-CH_3$ (**I**), $-CH_2CH_2CH_2-$ (bridged) (**II**), $-CH_2CH_2-$ (bridged) (**III**), -H (**IV**).

Experimental

The monovalent rhenium compounds $ReBr(CO)_3$(3,3’-dimethyl-2,2’-biquinoline) (**I**), $ReBr(CO)_3$(3,3’-trimethylene-2,2’-biquinoline) (**II**) $ReBr(CO)_3$(3,3’-dimethylene-2,2’-biquinoline) (**III**) and $ReBr(CO)_3$(2,2’-biquinoline) (**IV**) were synthesized as described in the literature (11, 12). In 100 mL Schlenck-type reactors equipped with stir bars and under an argon atmosphere, toluene solutions of the rhenium complex-Ph_2Zn were aged at 60°C for 1 hour, followed by the addition of MAO and styrene. Polymerization was carried out at 60°C during 48 hours. All runs were stopped by precipitation with HCl-acidified methanol. The polymers were recovered by filtration, washed several times with methanol and dried under vacuum at 60°C.

The crystalline content of the PSs was determined by extraction with boiling butanone. The approximate chain configuration distributions were determined by ^{1}H-NMR spectroscopy at 20°C, using 1,2-dichlorobenzene as the solvent. Intrinsic viscosities, $[\eta]$, were measured at 25°C in chloroform. Viscosity-average molecular weights, Mv, were calculated according to equation $[\eta]=1.12\text{x}10^{-4}\ Mv^{0.73}$ valid for the molecular weight range 7-150x10^4. SEC chromatograms were obtained in a Hitachi 655A-12 chromatograph operated at 25°C and equipped with three columns connected in series and packed with “styragel” 10^3, 10^4 and 10^5 A°. THF was used as solvent and the flow rate was 1 mL/min. Previously, the instrument was calibrated with polystyrene standars. Thermal analyses were performed in a Perkin-Elmer DSC7 differential scanning calorimeter at a heating rate of 10°C/min. The UV spectra were recorded in a silica cell at 60°C using a Shimatzu UV-160 spectrophotometer and 1X10^{-4} mol/L solutions in toluene under the same conditions of the polymerization studies. The molar conductivity analyses were carried out in toluene at 60°C in an argon atmosphere using a Cole-Parmer 01481 conductivity meter.

Results and discussion

All polymerizations were carried out under similar reaction conditions. The results of the polymerization of styrene using rhenium compounds-Ph_2Zn-MAO systems are shown in Table 1. These systems show a moderate initiating activity which has no relationship with the conformational asymmetry of the complexes.

Table 1. Polymerization of styrene using monovalent rhenium compounds modified with Ph_2Zn and MAO[a].

Rhenium Compound	PSt Yield g	Activity[b] x 10^{-3}	Rotation X-axis degree[c]	Bending Y-axis degree[c]
I	0.70	59.1	33.4	14.1
II	0.59	48.5	21.8	21.5
III	0.65	53.9	3.2	18.9
IV	0.65	53.9	n.d.	n.d.

[a] Polymerization conditions: 60°C, 48 hours in toluene, total volume= 30 mL, C_S= 2.03 mol/L, C_{Re}= 1.84×10^{-4} mol/L, n_{Re}/n_{Zn}= 0.75 mol/mol, n_{Al}/n_{Re}= 2400 mol/mol, [b] Activity in $m_{PSt}(g)(n_{Re}(mol)n_S(mol)t(hour))^{-1}$, [c] Values obtained using X-ray techniques (9,10), n.d.= Not determined.

SEC chromatograms showed that all the PSts obtained have bimodal distributions, suggesting the presence of two species capable of polymerizing styrene (Fig. 2). The low crystalline contents obtained from exhaustive extraction with boiling butanone (approximately 1%) and DSC analyses showed that all the PSts are amorphous. The ^{1}H-NMR spectra showed a syndiotactic abundance close to 82% and a similar molecular weight distribution in all the PSts (Tab. 2).

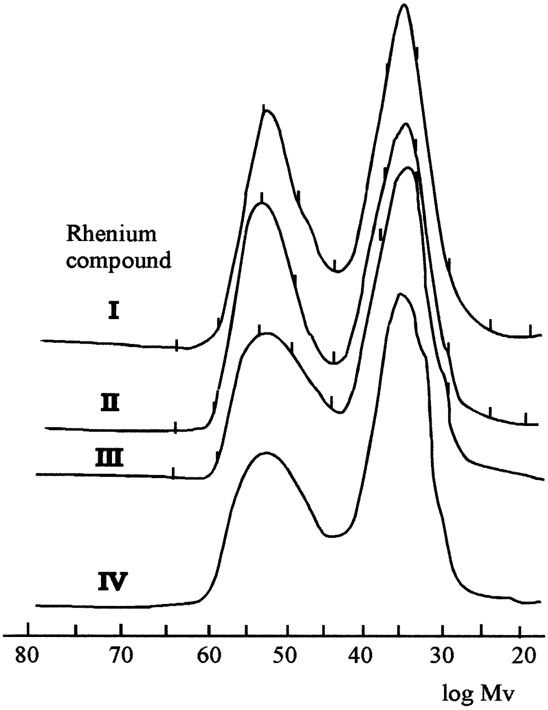

Fig. 2. SEC chromatograms of PSts obtained using, as indicated, various initiator systems based on monovalent rhenium compound-Ph_2Zn-MAO combinations.

Table 2. Characterization of PSts obtained with monovalent rhenium compound-Ph_2Zn-MAO systems[a].

Rhenium Compound	$Mv \times 10^{-5}$ [b] g/mol	$Mn \times 10^{-3}$ [c] g/mol	Mw/Mn[c]	Tacticity[d]		
				ii	is	ss
I	0.80	7.7	15.4	5	12	83
II	1.54	13.2	13.4	8	11	81
III	0.42	2.1	14.5	5	13	82
IV	0.58	5.2	14.2	6	13	81

[a] Polymerization conditions: 60°C, 48 hours in toluene, total volume= 30 mL, C_S= 2.03 mol/L, C_{Re}= 1.84×10^{-4} mol/L, n_{Re}/n_{Zn}= 0.75 mol/mol, n_{Al}/n_{Re}= 2400 mol/mol, [b] From intrinsic viscosity, [c] From SEC, [d] Calculated from ^{1}H-NMR spectra.

On the other hand, we have already reported the existence in the **I**-Ph_2Zn interaction of a species which has a very low initiating activity in the polymerization of

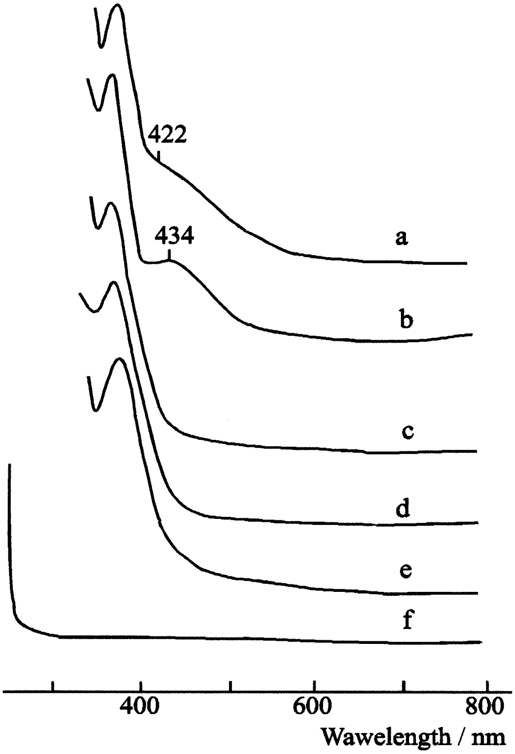

Fig. 3. UV-spectra for different systems tested as catalysts for the polymerization of styrene: a) (**I**-Ph_2Zn)* using n_{Re}/n_{Zn}=0.75 mol/mol, b) (**I**)* alone, c)(**I**-Ph_2Zn)*-MAO using n_{Re}/n_{Zn}=0.75 mol/mol and n_{Al}/n_{Re}=2400 mol/mol, d) (3,3`-dimethyl-2,2`-biquinoline ligand)* alone, e) (**I**)*-MAO using n_{Al}/n_{Re}=2400 mol/mol and f) (Ph_2Zn)* alone.
* Aged during 24 hours at 60°C.

styrene (8). The conductivity studies of the **I**-Ph_2Zn interaction system are in agreemen with a nonelectrolyte species (0-0.2 µS).

Using UV-vis spectroscopy, we have studied some alterations of the rhenium complexes in the catalyst systems. The metal ligand charge transfer band (MLCT) (d_{Re}-$\pi^*_{biquinoline}$) at 434 nm was used as reference. Figure 3 shows the UV-vis spectra of **I** and **I**-Ph_2Zn solutions, where a small displacement of the MLCT band is observed. In both cases, the absorption associated to intraligand π-π^* electron transfer is not changed. The disappearance of the MLCT band when MAO is added to the aged system is in agreement with a dissociation of the polypyridine ligand from the rhenium complex (Fig. 3). Similar results were obtained with the **II**, **III** and **IV** complexes.

The effect of MAO upon the aged system would explain the results in relation to similar initiating activity observed when different monovalent rhenium complexes were used combined with Ph_2Zn and MAO including $ReBr(CO)_5$ (8) in the styrene polymerization. In the same way, this fact would explain the absence of the conformational effects of the complexes upon the stereoregulating ability of the systems.

Further works are now in progress from which conclusive results about the nature of Ph_2Zn-rhenium complexe interaction, are expected.

Acknowledgments

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