

## HOMO- AND COPOLYMERIZATION OF STYRENE AND STYRENE RELATED MONOMERS. SYNTHESIS AND CHARACTERIZATION

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### ABSTRACT

Systems including diphenylzinc, metallocene, and methylaluminoxane, at various combinations has been attempted, as initiating systems for homo- and copolymerization of styrene and various styrene related comonomers including : substituted styrenes, styrene derivatives,  $\alpha$ -olefins, dienes and more recently cyclohexenes including norbornene. The used metallocenes were those containing titanium, zirconium and for comparative reasons hafnium. The metallocene efficiency towards syndiotactic polystyrene polymerization showed the order : titanocene > zirconocene > hafnocene. While the polymerization as well the copolymerization of Styrene with related to styrene compounds resulted to be much influenced by both electrical and steric hindrance effect. For styrene substituted derivative those group or element having I+ inductive effect depending its position at styrene's its phenyl ring favours homopolymerization as well their copolymerization with styrene. The steric hindrance also showed a determinant influence on reactivity, so methyl and tert-butyl group, having a I+ effect, when at *para*-position improve activity and stereoregularity of their polymerization processes. But when placing at *ortho*-position showed a very low capacity to polymerize. The present and previous results indicate that polymerization processes are initiated by monomer coordination to active metal species either of the binary metallocene-MAO or of the ternary  $\text{Ph}_2\text{Zn}$ -metallocene-MAO.

**Keywords:** Polymer synthesis - Polymer blends – Composites Polymer based, Polymer/Pharmaceutical Blends.

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### INTRODUCTION

By 2010 “Worldwide production of plastics” (polymers) reached ca. 2,628,000 Ton/year.[1] The applications for plastics are widely recognized as essentially limitless on consequently plastics are found almost every where: Packaging, Building, and Construction Industry, Automobile Manufacture, at Home and many others applications where plastics are present. Polyethylene both low and high density, are included in most of the packaging materials. Furthermore, certain polymers (plastics) have excellent impenetrable properties acting as barriers to oxygen, water vapor, and other gases. The building (construction) industry is the second largest consumer of plastics which requires high density polyethylene, HDPE, and poly(vinyl chloride), PVC, it is found as a wide diversity of plastics uses : pipes, sheets, wifes to entire buildings, roofing materials, door and windows frames, mounding screws, and hardware. Also a variety of plastics are used in the manufacture of automobiles, trucks, buses, trains, airplanes and chips. Electronic devices it is also a wide field where plastics are used. The wifes of almost all electronic devices are encased in some type of plastic, outer casing of telephones, lighting fixture, electronic mixer housing, fans, radio cabinets, computers, clocks and many other. In any home there are plenty pieces made of plastics.

The incorporation of plastic into modern medicine has steadily increased in the last decade. Plastics have contributed to a reduction in medical costs, infectious disease and pain management. High tech polymers are used to create new and improved artificial limbs and plastic disposable delivery devices have succeeded in reducing the risk of infection to patients. Patients directly benefit from the use of plastic with more lives being saved, improved and prolonged due to its use.

Conventional or commercial polystyrene, also called General Purpose Polystyrene is one of the most employed worldwide polymer, actually one of the most employed polymer, after polyethylene, polypropylene and poly(ethylene terephthalate), according worldwide plastics production in 2011. [1] Commercial polystyrene is an inexpensive polymer with reliable properties: is a good electrical insulator, has excellent optical clarity and is easy to process. Anyhow it has some deficiencies : it is attacked by organic solvents, is a rather poor barrier to oxygen and water and has a relatively low melting point. Furthermore PS is very low to biodegrade and therefore is a focus of controversy among environmentalists.

Our group, since the early nineties has been dedicated to the synthesis and characterization of polymers mainly working with styrene and styrene related compounds. Both styrene homopolymerization and also copolymerization of styrene/(styrene derivative), styrene/alkene, styrene/diene, styrene/cycloalkene

copolymerization, through metallocenic polymerization; [5-11,13] in the last years, with incorporation of Dr. Paula Zapata, our research group has performed successfully researches in nanoparticles and nanocomposites. [12 a,b]. Finally most recent research works on polymer-pharmaceutical composites has been developed [14,15]

### EXPERIMENTAL

Homo- and copolymerization experiments were carried out in an argon atmosphere in a 100 cm<sup>3</sup> Schlenk tube equipped with a magnetic stirrer. Toluene solvent, MAO solution,  $\text{Ph}_2\text{Zn}$  solution, and metallocene solution in toluene were sequentially charged by syringe under argon pressure. Polymerization was initiated by injecting the styrene or simultaneously the required amount of S and comonomer. The reactions were kept at 60 °C with stirring for the required length of time. Polymerization was ended by adding a mixture of hydrochloric acid and methanol. The polymers, coagulated in the acidified methanol, were recovered by filtration, were washed several times with methanol, and dried under vacuum at 60 °C.

Intrinsic viscosity,  $[\eta]$ , was measured in o-dichlorobenzene at 135 °C, or at 25 °C in chloroform for a-PS (amorphous), and was determined by the one-point method. [16]

Differential scanning calorimetry, DSC, analyses were performed by using a Rheometric Scientific DSC apparatus with the samples placed under a nitrogen atmosphere, at a rate of 10 °C min<sup>-1</sup> and after cooling to room temperature, reheated at the same rate. The reported T<sub>g</sub> and T<sub>m</sub> were those obtained in the second scan.

<sup>13</sup>C-NMR spectra, in 1,1,2,2-tetrachloroethane-d<sub>2</sub> at 60°C, were recorded on a Bruker Avance-400 spectrometer operating at 100.61 MHz. Chemical shifts calibrated against tetra-methylsilane, TMS.

### RESULTS AND DISCUSSION

Polystyrene, PS, is a synthetic aromatic polymer made from monomer styrene. Commercial polystyrene, also called: General Purpose Polystyrene is clear, hard, and rather brittle. It is a low cost resin per unit weight. It is rather a poor barrier to oxygen and water vapor and has a relatively low melting point. The synthesis of s-PS has received much attention from academy and also from industry researchers resulting a considerable number of papers and studies having styrene as its model. By 1945 G. Natta and K. Ziegler introduce the term tacticity (atactic, isotactic, and syndiotactic polymers) to describe stereoregular polymers, as it is the case of polystyrene, polypropylene and

others, to name the possible configuration of their stereoregular polymers.

Years later, Ishihara et al. [2] published the discovery of a special type of polystyrene, s-PS. By that time Italian researcher also announced a similar success: Pellecchia et al. [3] Since then, there was much interest from both

academy and industry for this sort of PS and a considerable number of papers were produced on special synthesis of stereoregular syndiotactic polystyrene; describing new catalysts for its stereoregular synthesis. [19]

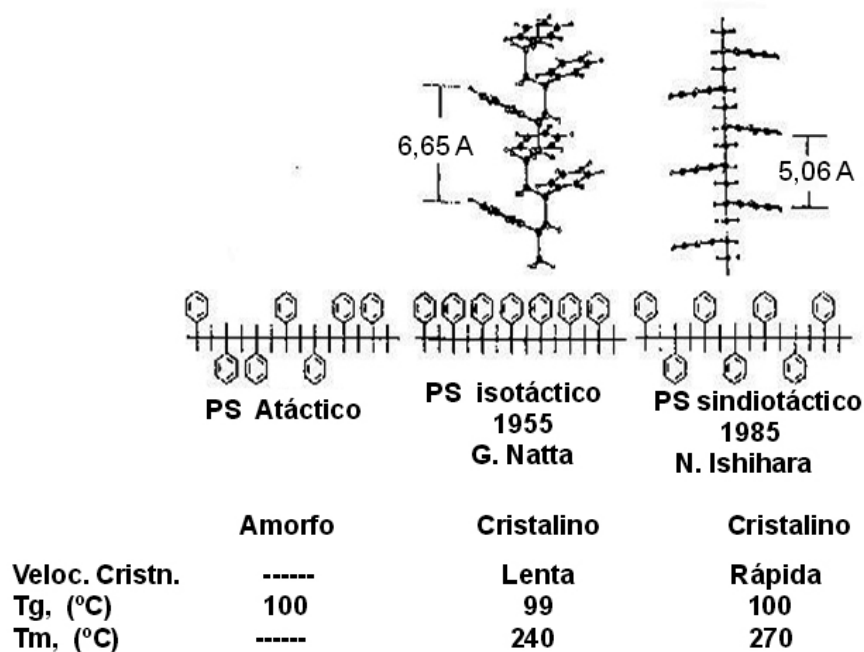


Figure 1. Structure, disposition and thermal properties of atactic, isotactic and syndiotactic-polystyrene.

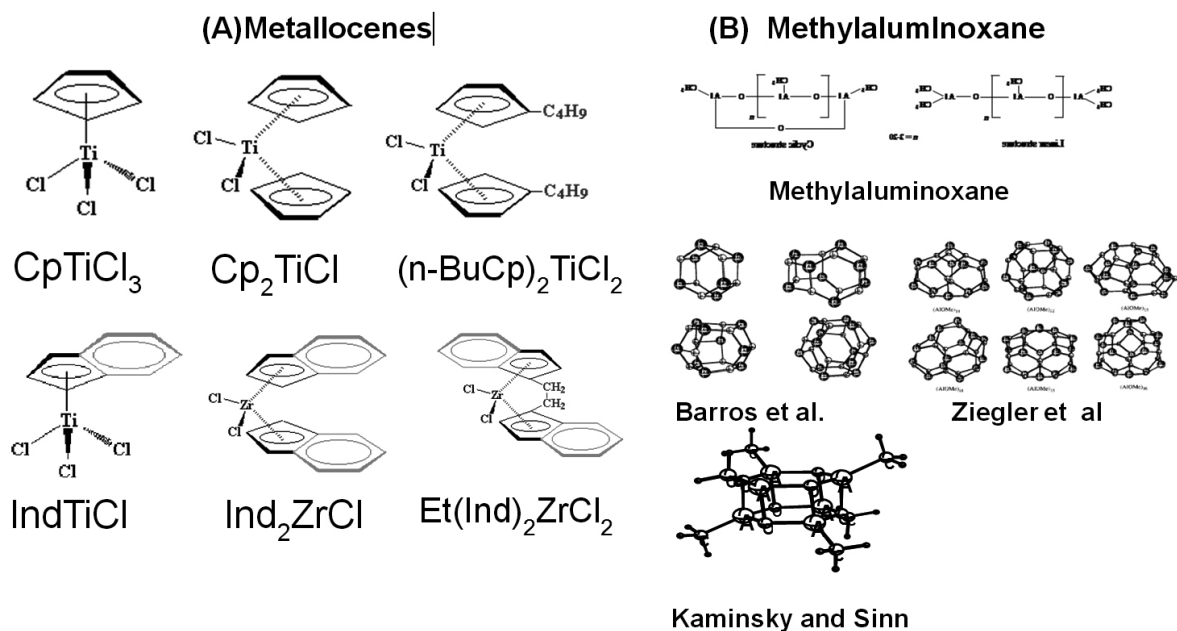


Figure 2. Structure of A) Some metallocenes and B) Methylaluminoxane and its cyclic structure postulated by Barros et al., F. Ziegler et al., and by Kaminsky and Sinn.

Figure 1 summarize the characteristics of the three known forms of polystyrene according to its stereoregularity. There, are shown their structures and some properties basically the placements of aromatic ring of styrene repeating units along the polymer chain, which geometry made the particular characteristic of each configuration (atactic, isotactic and syndiotactic). From Fig. 1 it is appreciated that all the three PS have practically the same glass temperature ( $T_g = 99-100$  °C) but quite different ceiling temperature in agreement with its capacity of crystallization. Atactic-PS being amorphous does not present  $T_m$  value, while the other two, show both:  $T_g$  and  $T_m$ . ( $T_{m,PS} = 240$  and  $T_{m,s-PS} = 270$ °C). Anyhow there is an important difference between them: i-PS has a low rate of crystallization which make it with no commercial interest.

At figure 2A are shown some metallocenes as well as its more employed cocatalyst (Fig. 2B), methylaluminoxane. For which its real structure it is not complete cleared. So as example are shown the structures suggested by various authors.

Table 1, shows a series of ternary  $Ph_2Zn$ -Metallocene-MAO styrene's polymerization initiator systems, where are included pertinent parameters of the systems studied by us in preliminary experiments. From there it is possible compare the efficiency of each ternary  $Ph_2Zn$ -Metallocene-MAO initiating system including polymerization conditions as indicate at bottom notes of this Table.

From Table 1, it is noted that PS obtained when catalyzed through zirconocene produce crude PS with none content of insoluble in boiling butanone, or at the best only low percentages (3.4 and 15.6 %) of insoluble polymer in boiling

**Table 1.** Polymerization of styrene by  $Ph_2Zn$ -Met-MAO initiator systems, in toluene after 48 h at 60 °C,<sup>a)</sup>

Run	Initiator system	Activity	$ \eta ^b$	$M_v \times 10^{-4}$	DSC		Insoluble
		(PS-Kg/Met-mol x S-mol x hour)	dL/g	g/mol	$T_m 1$ °C	$T_m 2$ °C	Fraction %
1	$Ph_2Zn-Et_3Al$ -MAO	0.02	n.d.	n.d.	None	None	n.d.
2	$Ph_2Zn-Cp_2ZrCl_2$ -MAO	3.51	0.19 <sup>b</sup>	2.7	None	None	n.d.
3	$Ph_2Zn-(MeCp)_2ZrCl_2$ -MAO	8.74	0.14 <sup>b</sup>	1,8	None	None	n.d.
4	$Ph_2Zn-(BzCp)_2ZrCl_2$ -MAO	19.21	0.89 <sup>b</sup>	22,0	None	None	3.4
5	$Ph_2Zn-Ind_2ZrCl_2$ -MAO	14.79	0.37 <sup>b</sup>	6.6	None	None	15.6
6	$Ph_2Zn-(H_4-Ind)_2ZrCl_2$ -MAO	3.10	1.80 <sup>b</sup>	57.8	None	None	n.d.
7	$Ph_2Zn-Cp_2TiCl_2$ -MAO	11,34	0.19 <sup>c</sup>	n.d.	246.1	259.7	86.4 <sup>d</sup>
8	$Ph_2Zn-(n.BuCp)_2TiCl_2$ -MAO	15,77	0.20 <sup>c</sup>	n.d.	249.4	266.0	91.0 <sup>d</sup>

<sup>a)</sup> Polymerization conditions: Total volume = 60 mL; S = 2.0 mol/L; MAO = 0.33 mol/L;

Met = 2,0E-4 mol/L, Met/ $Ph_2Zn$  = 1/1 mol/mol. <sup>b)</sup> Measured in chloroform at 25 °C

<sup>c)</sup> Measured in o-dichlorobenzene 135 °C, <sup>d)</sup> These fractions are essentially s-PS butanone, say a low content of s-PS which it is also detected by DSC analyses.

By the other hand, when the ternary system  $Ph_2Zn$ -metallocene-MAO includes a titanocene (run 7 and 8) a high percentage of crystalline PS is produced (86.4 and 91.0 %).

**Table 2.** Ternary  $Ph_2Zn-Cp_2TiCl_2$ -MAO initiating system in toluene after 48 hours at 60 °C.<sup>a)</sup>

$Cp_2TiCl_2/Ph_2Zn$ molar ratio mol/mol	Yield %	$ \eta ^b$ dL/g	Insoluble Friction %
0.25	2.76	0.19	59.8
0.50	4.48	0.17	65.4
0.75	6.40	0.19	67.5
1.00	9.44	0.28	58.3

<sup>a)</sup> Polymerization cond it ions: Total volume = 60 mL; S = 2.0 mol/L; MAO = 0.33 mol/L;  $TiCl_2 = 2,08 E-04$  mol/L.

<sup>b)</sup> Measured in o-dichlorobenzene at 135 °C.<sup>c)</sup> s-PS, insoluble in boiling butanone.

Table 2 analyses the effectiveness of ternary initiator system at various molar ratios  $Cp_2TiCl_2$ /Diphenylzinc (Met/ $Ph_2Zn$ ) and their behavior in front to conversion (Yield %) on styrene homopolymerization catalyzed through ternary  $Ph_2Zn-Cp_2TiCl_2$ -MAO initiator systems. Results indicate that conversion to polymer increases as  $Cp_2TiCl_2$  increases reaching its major yield (9.44 %) when molar ratio Met/ $Ph_2Zn$  = 1.0. While the insoluble in boiling butanone polymer fraction, say the content of s-PS, show lower variation: 60, 65, 68, 58 % accordingly the respective molar ratio Met/ $Ph_2Zn$  = 0.25 – 0.50 – 0.75 and 1.0 mol/mol employed.

Table 3 shows the homopolymerization of styrene using some combined diphenylzinc-metallocene-MAO initiator systems where are compared a titanocene ( $Cp_2TiCl_2$ ) with a zirconocene ( $Ind_2ZrCl_2$ ) with variable molar ratio diphenylzinc / metallocene. Results indicate that conversion to polymer and content of insoluble in boiling butanone (s-PS) are affected according this ratio. Anyhow, yield resulted the same when this ratio was near to 1.0. But the percentage of insoluble in boiling butanone, say the obtaintion of s-PS was 68.0

% for the ternary system including the titanocene ( $Cp_2TiCl_2$ ). Furthermore, the obtained product was insoluble while the product obtained for the zirconocene, which was soluble in chloroform (see  $|\eta|$ ), indicate absence of s-PS or only very low percentage of s-PS. In both cases a last entry was also included: some water was incorporated at the ternary initiator system:  $H_2O/Ph_2Zn = 1.0$  mol/mol, which did not produce major changes at the parameter studied.

**Table 3.** Homo-Polymerization of styrene initiated by combined system  $\text{Ph}_2\text{Zn}$ -Metalocene -MAO including  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Ind}_2\text{ZrCl}_2$ , in toluene at 60 °C after 48 hours at 60 °C.<sup>a)</sup>

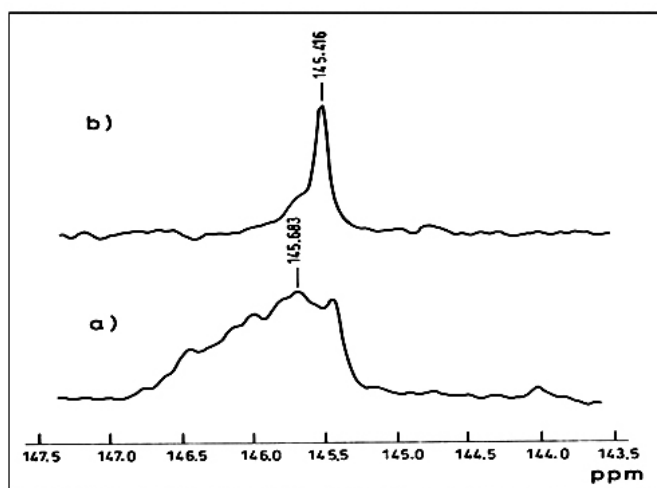
Initiator System	$[\text{Ph}_2\text{Zn}]$ $\text{Mx}10^4$	$[\text{Ind}_2\text{ZrCl}_2]$ $\text{Mx}10^4$	$[\text{Cp}_2\text{TiCl}_2]$ $\text{Mx}10^4$	$[\text{MAO}]$ $\text{Mx}10^2$	Yield %	$[\eta]$ dL/g	$M_v$ g/mol	Insoluble <sup>d</sup> Fraction in Boiling MeCOEt.%
---/Zr//MAO	None	3.44	None	33.6	9.07	0.08 <sup>b</sup>	0.86	13-0
Zn/Zr/MAO	2.11	1.75	None	33.6	9.59	0.13 <sup>b</sup>	1.50	7.0
Zn/ Zn/Zr/MAO	4.21	3.48	None	----	0.56	0.70 <sup>b</sup>	15.82	n.d. <sup>f</sup>
Zn/ Zn/Zr/ MAO <sup>e)</sup>	4.21	8.48	None	----	0.07	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>
--/Ti// MAO	None	None	4.08	32.9	1,75	n.d. <sup>f</sup>	n.d. <sup>f</sup>	33.1
Zn/Ti/MAO	2.09	None	2.11	33.8	6.68	n.d. <sup>f</sup>	n.d. <sup>f</sup>	68.0
Zn/Ti/MAO	4.96	None	4.06	----	2.65	0.76 <sup>c</sup>	17.57	1.7
Zn/Ti/MAO <sup>e)</sup>	4.06	None	4.06	----	3.20	0.68 <sup>c</sup>	15.26	3.0

<sup>a)</sup>  $[\text{S}] = 2.0 \text{ M}$ ;  $\text{Zn} = \text{Ph}_2\text{Zn}$ ;  $\text{Zr} = \text{Ind}_2\text{ZrCl}_2$ ;  $\text{Ti} = \text{Cp}_2\text{TiCl}_2$ ; Based on initial S, <sup>b)</sup> Measured in chloroform at 25 °C, <sup>c)</sup> Measured in o-dichlorobenzene at 135 °C <sup>d)</sup> insoluble in boiling butanone,

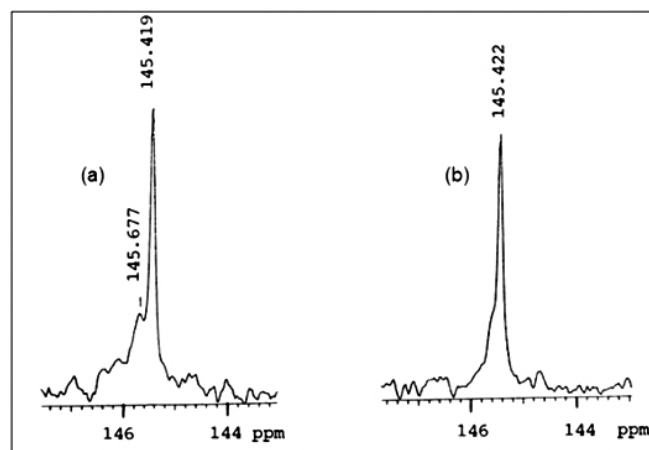
<sup>e)</sup> With  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}/\text{Ph}_2\text{Zn} = 1,0$ , <sup>f)</sup> Not determined,

At Figures 3 and 4 are shown the  $^{13}\text{C}$ -NMR spectra of PS obtained with ternary initiator systems including the metallocene  $\text{Ind}_2\text{ZnCl}_2$  at Fig.3 and  $\text{Cp}_2\text{TiCl}_2$  at Fig.4. the spectrum of the crude PS (Fig. 3a) shows several peaks in the range 145.2-146.9 ppm, while the spectrum of the insoluble in boiling butanone (Fig. 3b) shows a single peak at 145.416 ppm. These spectra showed a very good concordance with the spectra shown by Ishihara et al. [17] According to spectra crude PS is mainly atactic PS and insoluble fraction in boiling butanone is s-PS. Figure 4 shows DSC spectra

for PS obtained including the  $\text{Cp}_2\text{TiCl}_2$  metallocene, as it is noted the spectrum of crude PS (Fig. 4a) shows two peaks at 145.577 and at 145.419 ppm while the insoluble in boiling butanone sample shows only a single signal at 145.422 ppm. These DSC analyses are indicative of the presence of two kinds of PS and suggest the possibility of the presence of at least two kinds of active species in the course of polymerization process or two form of crystallization for s-PS



**Figure 3.**  $^{13}\text{C}$ -NMR spectra of PS obtained with  $\text{Ph}_2\text{Zn}$ - $\text{Ind}_2\text{ZnCl}_2$ -MAO initiating system a) crude polymer; b) insoluble in boiling butanone fraction.



**Figure 4.**  $^{13}\text{C}$ -NMR spectra of PS obtained with  $\text{Ph}_2\text{Zn}$ - $\text{Cp}_2\text{TiCl}_2$ -MAO initiating system, a) crude polymer; b) insoluble in boiling butanone Fraction

Table 4 shows the homopolymerization of styrene using various  $\text{Ph}_2\text{Zn}$ -metallocene-MAO initiator systems where are compared zirconocenes and titanocenes. Bis-cyclopentadienyl titanium dichloride :  $\text{Cp}_2\text{TiCl}_2$  and bis(n-butylcyclopentadienyl)titanium dichloride :  $(n\text{-BuCp})_2\text{TiCl}_2$  (run: 10 and 11) showed conversion to PS in an order near to zirconocene (runs: 4 and 7) which can be considered the result of a possible sort of steric influence due to a similar cyclopentadienyl-metal-cyclopentadienyl angle (two cyclic organic ligand bonded at metal titanium or zirconium) particularly when indenyls are the ligand. On the other hand the initiator  $\text{Ph}_2\text{Zn}$ - $\text{CpTiCl}_3$ -MAO (run 12, only one cyclopentadienyl link) turned out to be the most effective of the series (45,7 % conversion) which yield more than 5 times higher than the zirconocene (run 4), say a similar situation for metallocene based on bis-indenyl zirconium dichloride) or the run, with two ligand (Pr- and Flu-) at zirconium dichloride (run 7). On the other hand, the initiator system  $\text{Ph}_2\text{Zn}$ - $\text{CpTiCl}_3$ -MAO (run 12), only one cyclopentadienyl metal-link, Cp-Ti) turned out to be the most effective of the series (45,7 % conversion) which yield is more than 5 times higher than the zirconocene  $\text{Ph}_2\text{Zn}$ - $\text{Ind}_2\text{ZnCl}_2$ -MAO (run 4), with 8,3 % conversion, approximately similar to the mentioned titanocene. A similar situation it is also present at run 7 with two ligand at metal.

**Table 4.** Initiator systems used in metallocenic polymerization of styrene in toluene at 60 °C after 48 hours. <sup>a)</sup>

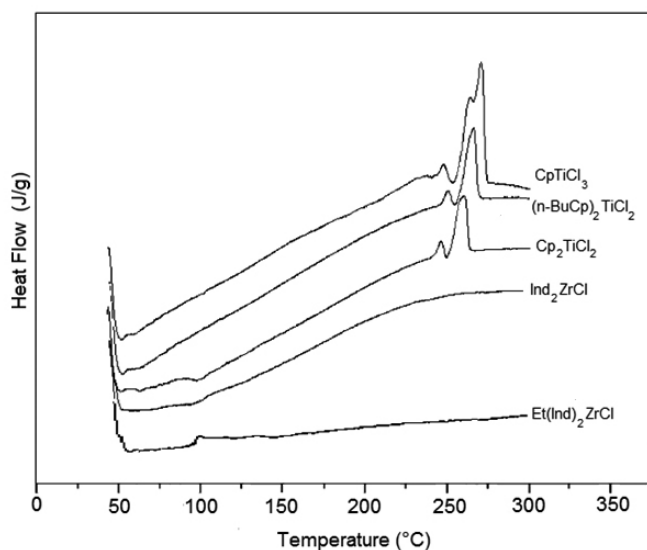
Run	Initiator System	Polymer Convn <sup>b)</sup> %	$ \eta ^{(c)}$ dL/g	$M_v \times 10^{-5}$ g/mol	$T_g$ °C	$T_m(1)$ °C	$T_m(2)$ °C	Insol. Fractn <sup>d)</sup>
1	Ph <sub>2</sub> Zn	0.53	2.13	7.25	108.9	n.s.	n.s.	n.d.
2	Ph <sub>2</sub> Zn-MAO	8.60	0.21	0.31	99.2	n.s.	n.s.	n.d.
3	Ph <sub>2</sub> Zn-Cp <sub>2</sub> ZrCl <sub>2</sub> -MAO	1.04	0.17	0.23	n.d.	n.d.	n.d.	n.d.
4	Ph <sub>2</sub> Zn-Ind <sub>2</sub> ZrCl <sub>2</sub> -MAO	8.30	0.19	0.32	102.9	n.s.	n.s.	15.6
5	Ph <sub>2</sub> Zn-(H <sub>4</sub> -Ind) <sub>2</sub> ZrCl <sub>2</sub> -MAO	2.06	0.09	0.09	n.d.	n.d.	n.d.	n.d.
6	Ph <sub>2</sub> Zn-(Bu <sup>c</sup> Cp) <sub>2</sub> ZrCl <sub>2</sub> -MAO	2.68	0.14	0.17	n.d.	n.d.	n.d.	n.d.
7	Ph <sub>2</sub> Zn-Pr(Flu)(Cp)ZrCl <sub>2</sub> -MAO	8.46	0.10	0.11	n.d.	n.d.	n.d.	n.d.
8	Ph <sub>2</sub> Zn-Et(Ind) <sub>2</sub> ZrCl <sub>2</sub> -MAO	3.29	0.12	0.15	n.d.	n.d.	n.d.	13.8
9	Ph <sub>2</sub> Zn-(n-BuCp) <sub>2</sub> HfCl <sub>2</sub> -MAO	0.50 <sup>e</sup>	n.d.	n.d.	94.5	n.d.	n.d.	n.d.
10	Ph <sub>2</sub> Zn-Cp <sub>2</sub> TiCl <sub>2</sub> -MAO	9.44	0.28 <sup>f</sup>	n.d.	n.d.	241.4	256.6	58.3
11	Ph <sub>2</sub> Zn-(n-BuCp) <sub>2</sub> TiCl <sub>2</sub> -MAO	7.11	0.20 <sup>f</sup>	n.d.	n.d.	249.4	266.0	91.7
12	Ph <sub>2</sub> Zn-CpTiCl <sub>3</sub> -MAO	45.70 <sup>e</sup>	0.23 <sup>f</sup>	n.d.	n.d.	259.0	263.0	99.8

<sup>a)</sup>Polymerization conditions: Total volume = 60 mL, [S] = 2,1 mol/L, [MAO] = 0,33 mol/L, [Ph<sub>2</sub>Zn] = [Metallocene] = 2.0E-04 mol/L <sup>b)</sup>Based on initial styrene

<sup>c)</sup> Measured in chloroform at 25 °C, \* Measured in o-dichlorobenzene at 135 °C.

<sup>d)</sup>Boiling-butanoneinsoluble butanone, <sup>e)</sup>After only 6 hours at 60 °C, <sup>f)</sup>n.d. = not determined

Figure 5, Show the DSC chromatograms of polystyrene obtained using various ternary Ph<sub>2</sub>Zn-titanocene-MAO initiator systems, which compare them with zirconocenes ternary initiator systems: Ph<sub>2</sub>Zn-Et(Ind)<sub>2</sub>Cl<sub>2</sub>. From there it is note that the polystyrene obtained from titanocene initiator systems are all crystalline with a  $T_m$  ca., 250 °C, while when using a zirconocene based initiator system, resulted amorphous polystyrenes (a-PS).



**Figure 5.** DSC chromatograms of polystyrene obtained using ternary Ph<sub>2</sub>Zn-metallocene-MAO initiator System.

From results of Table 5, it become clear that the capacity of Ph<sub>2</sub>Zn-metallocene-MAO initiator systems to induce S/p-BuS copolymerization increases in the order IndZrCl<sub>2</sub> < (n-BuCp)<sub>2</sub>TiCl<sub>2</sub> < CpTiCl<sub>3</sub>. Furthermore, values reported in Table 5 correspond to a 48 hours period of reaction for the first two systems and only to a 6 hours period for the Ph<sub>2</sub>Zn-CpTiCl<sub>3</sub>-MAO

initiator system, emphasizing the higher activity of CpTiCl<sub>3</sub> when compared with Ind<sub>2</sub>ZrCl<sub>2</sub> and (n-BuCp)<sub>2</sub>TiCl<sub>2</sub>.

Zambelli et al., [18 b] have established that syndiotactic S polymerization, using titanocenes-MAO systems, Initiates through coordination of the S monomer to metal active species. Furthermore, they demonstrated that propagation result from poly-insertion of a S monomer via secondary insertion.

Taking account these achievement and in concordance of our previous results [10-14] and the present ones, we think that syndiotactic S polymerization catalyzed by our Ph<sub>2</sub>Zn-CpTiCl<sub>3</sub>-MAO initiator system, conversely with Zambelli [3b, 18b] and other authors, proceed through coordination of S monomer to the active species followed by the insertion of the monomer into the growing chain, propagation goes throughout an ionic pathway. [12, 14]

## CONCLUSIONS

- From present and previous results: We can conclude that the binary Metallocene-MAO and the ternary Ph<sub>2</sub>Zn-Metallocene-MAO initiators systems induce the homo- and the copolymerization of styrene, substituted styrene, and styrene derivatives
- When included a titanocene, these systems generate syndiotactic polystyrene. While zirconocenes produced at the best traces or low percentage of stereoregular PS.
- The molecular weight distribution of polymers, obtained using the present initiator systems, shows values between 1 and 2, in agreement with a metallocenic polymerization process.
- The I+ inductive effect of substituent at aromatic ring of styrene and on styrene related monomer, when at para-position (phenyl) favors its polymerization through the studied initiator systems, depending their substitution-position at aromatic ring or at carbon double bond of vinyl group of styrene, or the number of substituent, as the polymerization it is affected by electrical and steric hindrance of the vinyl's styrene bond, through which the incoming monomer coordinates to the active species
- The metallocene's efficiency of initiator systems studied follows the order Titanocene > Zirconocene > Hafnocene.

**Table 5.** Styrene / p-tert-butylstyrene copolymerization initiated by various ternary Ph<sub>2</sub>Zn-metallocene-MAO initiator systems, in toluene at 60 °C after 48 hours. <sup>a)</sup>

Feed	Ind <sub>2</sub> ZrCl <sub>2</sub> <sup>b)</sup>			(n-BuCp) <sub>2</sub> TiCl <sub>2</sub> <sup>b)</sup>			CpTiCl <sub>3</sub> <sup>c)</sup>		
	Conv <sup>d)</sup>	η  <sup>d)</sup>	T <sub>g</sub> <sup>e)</sup>	Conv <sup>d)</sup>	η  <sup>d)</sup>	T <sub>g</sub>	Conv <sup>d)</sup>	η  <sup>d)</sup>	T <sub>g</sub>
mol/mol	%	dL/g	°C	%	dL/g	°C	%	dL/g	°C
S only	8,4	0.50	102.6	17.4	0.15*	100.6	42.0	0.20*	100.7
96/5	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	54.1	0.22*	103.0
75/25	5,0	0,52	116,9	12.6	0.36*	116.8	68,2	0.23*	118.9
60/40	4,7	0.58	123,2	8.3	0.39*	122.3	n.p.	n.p.	n.p.
50/50	6,3	0.52	126.8	7.5	0.46*	127.4	70.2	0.23*	129.6
25/75	13,3	0.28	134,0	12.0	0.80*	133.3	n.p.	n.p.	n.p.
Bu'S only	19,6	0.29	139.2	12,4	0.80	135.4	94,0	0.22*	141.6

<sup>a)</sup> Total volume = 40 mL, [S] + [Bu'S] = 2.0 mol/L, [MAO] = 0.33 mol/L, [Ph<sub>2</sub>Zn] = metallocene = 2.0x10<sup>-4</sup> mol/L Polymerization carried in toluene at 60 °C; <sup>b)</sup> Reaction Time 48 h., <sup>c)</sup> Reaction Time 6 h., <sup>d)</sup> Conversion based on initial feed, <sup>e)</sup> Measured in chloroform at 25 °C or in o-dichlorobenzene (\*) at 135 °C.

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