Polymer Bulletin 51, 199–208 (2003)
DOI 10.1007/s00289-003-0214-4

Polymer Bulletin

Ph_2Zn-metallocene-MAO initiator systems in the homo- and copolymerization of styrene/*p*-alkylstyrene

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Received: 27 January 2003 /Revised version: 21 October 2003 / Accepted: 22 October 2003

Summary

The homo- and copolymerization of styrene (S) with p-methylstyrene (p-MeS) and p-tert-butylstyrene (p-Bu^{t}S) has been tested using initiator systems of the Ph_2Zn-metallocene-MAO type. The metallocenes used were $CpTiCl_3$, $IndTiCl_3$, $(n\text{-}BuCp)_2TiCl_2$, Ind_2ZrCl_2 and $Et(Ind)_2ZrCl_2$. The Ph_2Zn-metallocene-MAO systems homopolymerize styrene, p-methylstyrene and p-tert-butylstyrene, producing syndiotactic polymers in the case of the titanocenes and amorphous polymers in the case of the zirconocenes. The S/p-MeS and S/p-Bu^{t}S copolymers obtained with the Ph_2Zn-titanocene-MAO systems are enriched in the comonomer with respect to the initial feed.

Introduction

Following the discovery of methylaluminoxane (MAO) by Sinn and Kaminsky (1), metallocene type catalysts started being used in the synthesis of polyolefins, and particularly of stereoregular polymers (2-4). In 1986, Ishihara (3) found that "semi-sandwich" compounds of the metallocene type together with MAO, such as the $CpTiCl_3$/MAO initiator system, for example, produced syndiotactic polystyrene (s-PS). Other authors (5-6) reported the synthesis of s-PS and of stereoregular poly(alkylstyrenes) with different catalytic systems, with the polymers obtained showing no significant decrease in their melting point (Tm) with respect to s-PS. On the other hand, there have been few researches done on the copolymerization of styrene with substituted styrenes (7-8). H. Nakatani et al. (7) reported the copolymerization of styrene with p-CH_3S, p-ClS, p-BrS and m-ClS using $Ti(OMen)_4$-MAO as the catalytic system. They determined the reactivity ratios and related them with Hammett's equation, establishing that copolymerization takes place via a cationic coordination mechanism.

From work done by our group (9-10) on the copolymerization of styrene/p-tert-butylstyrene (p-Bu^{t}S), we reported that the resulting copolymers are of a syndiotactic nature when Ph_2Zn-titanocene-MAO initiator systems are used, and are also enriched in p-Bu^{t}S with respect to the initial feed. In this paper we show the results of the homo- and copolymerization of styrene (S) with p-methylstyrene (p-MeS) and p-tert-butylstyrene (p-Bu^{t}S), with different initiator systems of the Ph_2Zn-metallocene-MAO type.

Experimental

The homo- and copolymerizations were carried out under an argon atmosphere in a 100-mL reactor equipped with a magnetic stirrer. The solvent, MAO solution, Ph_2Zn, and metallocene solution were added sequentially with a syringe under argon pressure. The homo and copolymerizations started when the required amount of styrene and the other comonomer were injected simultaneously. The reactions took place at 60 °C during the required time and were stopped by adding methanol acidified with HCl. The polymers were recovered by filtration, then washed several times with cold methanol and dried in vacuum at 50 °C. The products were characterized by intrinsic viscosity, thermal analysis and ^{1}H-NMR spectroscopy. Molecular weights were determined from the intrinsic viscosity in o-dichlorobenzene at 135 °C (11), $[\eta] = 1.38x10^{-4}Mw^{0.7}$. The DSC analyses were carried out in a Rheometric Scientific DSC apparatus in a nitrogen atmosphere. Three to four milligram samples were heated at a rate of 10 °C/min, and then cooled to room temperature and reheated at a rate of 10 °C/min. The reported Tg and Tm were those obtained in the second scan. The copolymers were fractionated by exhaustive extraction with boiling methyl ethyl ketone (MEK). Polymer composition was determined by ^{1}H-NMR, and the spectra were ran in $CDCl_3$ at 60 °C in a Bruker DRX-300 spectrometer at 300 MHz, using TMS as an internal reference. The UV-visible studies were carried out on the initiator systems at 60 °C under the polymerization conditions. $CpTiCl_3$, $IndTICl_3$, $(n\text{-}BuCp)_2TiCl_2$, Ph_2Zn, (Aldrich Chem. Co) and MAO (WITCO, Co), were used without further purification.

Results and discussion

I. Homopolymers of styrene, p-methylstyrene and p-tert-butylstyrene obtained with initiator systems Ph_2Zn-metallocene-MAO.

Table 1. Polystyrenes obtained with Ph2Zn, MAO and various titanium and zirconium compound initiator systems.[a]

Compound	Activity[b]	Insol. f.[c] %	$Mw*10^{-5}$[d] g/mol	Tg[e] °C	Tm[e] °C
$CpTiCl_3$	923	99.7	6.5	100.7	264.8
$IndTiCl_3$	642	93.7	5.7	97.3	263.3
$(n\text{-}BuCp)_2TiCl_2$	408	90.9	6.5	102.4	268.8
Ind_2ZrCl_2	101	n.d.[f]	3.6	107.9	n.s.[g]
$Et(Ind)_2ZrCl_2$	80	n.d.[f]	3.9	98.5	n.s.[g]

[a] Polymerization temperature (Tp) = 60 °C; polymerization time (tp) = 6 hours; total volume = 25 mL; styrene concentration = [S] = 2,0 mol/L; $[Ph_2Zn] = [Ti] = [Zr] = 2*10^{-4}$; Al/Ti = Al/Zr = 1600. [b] Activity = kilograms of PS/(mol of Ti (Zr) *mol S *h). [c] % Insoluble fraction = (grams of polymer insoluble in boiling MEK)/(grams of crude polymer) * 100. [d] Molecular weight(Mw), determined by intrinsic viscosity. [e] Tg and Tm, determined by DSC, second heating at 10 °C/min. [f] No determined, [g] No signal.

Table 1 shows the results of the homopolymerization of styrene with different initiator systems of the Ph_2Zn-metallocene-MAO type, with zirconium compounds showing considerably lower activity than titanium compounds. On the other hand, only with the Ph_2Zn-titanocene-MAO initiator systems is there a high content of boiling MEK insoluble fraction corresponding to s-PS. Also, the molecular weights are lower when the initiator system contains zirconium compounds. Table 2 shows the results achieved in the homopolymerization of p-methylstyrene using different initiator systems of the Ph_2Zn-metallocene-MAO type. These systems show an activity quite similar to that obtained in the homopolymerization of styrene, except for the Ph_2Zn-$CpTiCl_3$-MAO system, which has an activity 2.5 times greater for p-methylstyrene than for styrene. The electron donor effect of the substituent in the *para* position produce an increase in the nucleophilic character on the double bond stabilizing the active specie $[CpTiMe]^+$ $[MAO \times X_2]$ proposed by Zambelli (14) for the polymerization of styrene, for this reason is that probably becomes more important when catalysts containing only one cyclopentadienyl ring (Cp) are used. The homopolymers of p-methylstyrene did not exhibit a crystalline melting temperature. The initiator systems containing zirconium compounds show lower activities and stereoregularity, and the Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO initiator system has a quite lower activity than the Ph_2Zn-Ind_2ZrCl_2-MAO system for both the homopolymerization of styrene (Table 1) and that of p-methylstyrene (Table 2). This may be attributed to the fact that $Et(Ind)_2ZrCl_2$ has bridging groups (-CH2-CH_2-) which make the system rigid and therefore make more difficult the coordination and later insertion of the monomers in the growing chain.

Table 2. Poly(p-methylstyrene) obtained with Ph_2Zn-MAO initiator systems and various titanium and zirconium compounds a)

Compound	Activity b)	Mw*10^{-5} c) g/mol	Tg d) °C	Tm d) °C
$CpTiCl_3$	2282	5.7	114.1	n.s e)
$IndTiCl_3$	423	2.6	110.9	n.s e)
$(n\text{-}BuCp)_2TiCl_2$	386	6.9	112.1	n.s e)
Ind_2ZrCl_2	144	5.1	118.0	n.s e)
$Et(Ind)_2ZrCl_2$	52	4.1	116.3	n.s e)

a) Polymerization temperature (Tp) = 60°C; Polymerization time (tp) = 6 hours; Total volume = 25 mL; styrene concentration = [S] = 2,0 mol/L, $[Ph_2Zn]$ =[Ti] = [Zr] = $2*10^{-4}$, Al/Ti = Al/Zr = 1600.

b) Activity = Kilograms of poly(p-MeS)/(mol of Ti (Zr) *mol p-MeS *h). c) % Insoluble fraction = (grams of polymer insoluble in boiling MEK)/(grams of crude polymer) * 100. d) Molecular weight (Mw), determined from intrinsic viscosity. e) Tg and Tm, determined by DSC, second heating at 10°C/minute f) No signal.

The Ph_2Zn-$CpTiCl_3$-MAO initiator system, under the experimental conditions used, shows greater activity in the homopolymerization of styrene (Table 1), p-methylstyrene (Table 2) and p-tert-butylstyrene (Table 3) than the Ph_2Zn-$IndTiCl_3$-MAO initiator system, in agreement with the results obtained by Tomotsu (13). In the case of the homopolymerization of p-tertbutylstyrene, the activity with Ph_2Zn-

$CpTiCl_3$-MAO is 6.5 times greater than that achieved using the Ph_2Zn-$IndTiCl_3$-MAO system, and this may be attributed to the structure of the indenyl group, which would make more difficult the insertion of the p-tert-butylstyrene monomer, regardless of the electron donor effect of the $-C(CH_3)_3$ group in the *para* position.

On the other hand, the Ph_2Zn-$(n\text{-}BuCp)_2TiCl_2$-MAO initiator systems used in the homopolymerization of styrene (Table 1), p-methylstyrene (Table 2) and p-tert-butylstyrene (Table 3) show lower activities than the Ph_2Zn-$CpTiCl_3$-MAO and Ph_2Zn-$IndTiCl_3$-MAO systems due to the presence of two Cp rings in the structure of the catalyst which prevent the formation of the active species $[CpTiMe]^+$ $[MAOxX_2]$ proposed by Zambelli (14) for the polymerization of styrene. These systems, however, in spite of not showing a high activity, produce syndiotactic polystyrene, confirmed by its Tm = 268.8 °C. As to the cristallinity of the p-tert-butylstyrene homopolymers, a Tm was obtained only for poly(p-tert-butylstyrene) obtained with the Ph_2Zn-$IndTiCl_3$-MAO initiator system. On the other hand, poly(p-tert-butylstyrene) obtained with Ph_2Zn-$CpTiCl_3$-MAO initiators systems present a high stereoregular content (insoluble fraction in boiling MEK) but our studies indicate that is not easily crystallizable.

Table 3. Poly(p-tert-butylstyrene) obtained with the Ph2Zn-MAO initiator systems and various titanium and zirconium compounds a)

Compound	Activity b)	Insoluble f. c) %	$Mw*10^{-5}$ d) g/mol	Tg e) °C	Tm e) °C
$CpTiCl_3$	3161	99.2	7.2	141.6	n.s. g)
$IndTiCl_3$	487	n.d. f)	9.5	138.8	312.9
$(n\text{-}BuCp)_2TiCl_2$	372	n.d. f)	6.5	144.0	n.s. g)
Ind_2ZrCl_2	281	n.d. f)	5.7	152.4	n.s. g)
$Et(Ind)_2ZrCl_2$	70	n.d. f)	4.4	156.9	n.s. g)

a) Polymerization temperature (Tp) = 60°C; polymerization time (tp) = 6 hours; total volume = 25 mL; styrene concentration = [S] = 2.0 mol/L; $[Ph_2Zn]$ = [Ti] = [Zr] = $2*10^{-4}$, Al/Ti = Al/Zr = 1600. b) Activity = Kilograms of poly(p- Bu^tS)/(mol of Ti (Zr) *mol p-MeS *h). c) % Insoluble fraction = (grams of polymer insoluble in boiling MEK)/(grams of crude polymer) * 100. d) Molecular weight (Mw), determined from intrinsic viscosity. e) Tg and Tm, determined by DSC, second heating at 10°C/minute. f) No determined, g) No signal.

In order to establish the behavior of the initiator systems, they were studied by UV-visible spectroscopy under the same polymerization conditions, and those systems that showed the highest activity and gave rise to the greatest stereoregularity in the resultant polymers were selected. The systems under study were those of the Ph_2Zn-titanocene-MAO type.

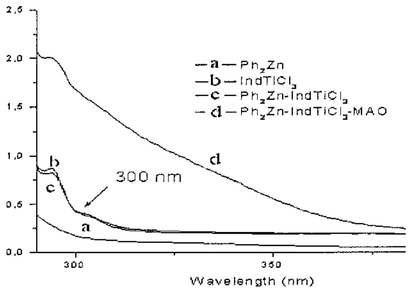

Figure 1. UV-visible spectrum of Ph_2Zn-$IndTiCl_3$-MAO, in toluene at 60°C in an argon atmosphere

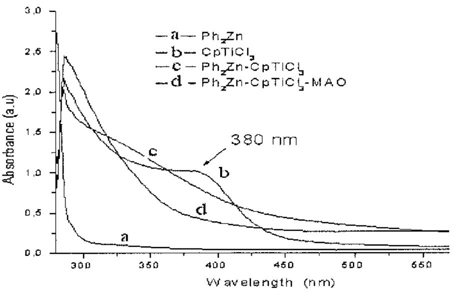

Figure 2. UV-visible spectrum of Ph_2Zn-$CpTiCl_3$-MAO, in toluene at 60°C in an argon atmosphere

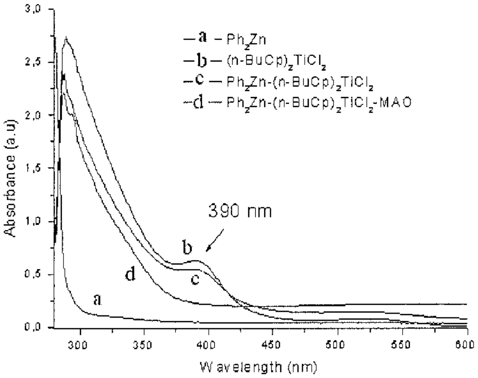

Figure 3. UV-visible spectrum of Ph_2Zn-(n-$BuCp)_2TiCl_2$-MAO in toluene at 60 °C.

Figures 1, 2 and 3 show a strong absorption band at 300, 380 and 390 nm, respectively. In all three cases this band corresponds to the delocalization of ð electrons on the cyclopentadienyl ring, coming from an interaction between the ligand (Cp) around the titanium atom. When Ph_2Zn is added to the initiator system, the absorption bands change in a very different way: in the first case there is no change in the absorption band, probably because there is no interaction between $IndTiCl_3$ and Ph_2Zn. When the metallocene used is $CpTiCl_3$, three is a hypsochromic shift and a reduction of the band. In the latter case only a decrease in the Ph_2Zn-(n-$BuCp)_2TiCl_2$ band is seen, which would explain an interaction between the components of the catalytic system. When MAO is part of the initiator system, there is an important reduction of the bands and a hypsochromic shift due to the localization of electrons on the cyclopentadienyl ring caused by the electron deficiency of the Ti atom positively charged by the MAO.

II. Copolymers of styrene/p-alkylstyrene using combined systems of the Ph_2Zn-titanocene-MAO type.

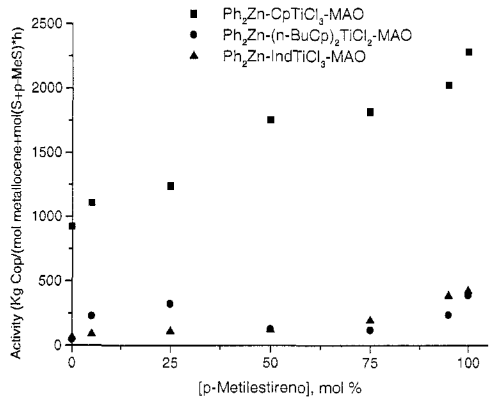

Figure 4. Copolymerization of S/p-MeS using Ph_2Zn-titanocene-MAO systems

Ph_2Zn-metallocene-MAO initiator systems were used for the copolymerization of S with p-MeS and p-Bu^tS. The results achieved for those systems which include titanocenes are reported, since the systems which contain zirconocenes produced low activities and poor stereoregularity when used for the corresponding homopolymerizations.

Figure 4 shows the results obtained for the copolymerization of S/p-MeS when Ph_2Zn-metallocene-MAO initiator systems were used, including different titanocenes. The Ph_2Zn-$CpTiCl_3$-MAO system shows the highest catalytic activity for the copolymerization of S/p-MeS, in agreement with the UV-visible study, confirming the interaction that there is between the three components of the initiator system, and stressing the influence of Ph_2Zn on the initiator system. These results allow us to deduce that Ph_2Zn produces increased activity only for initiator systems having cyclopentadienyl ligands.

When this initiator system was used there was increasing activity as the p-methylstyrene concentration in the initial load increased, in agreement with the electron donor effect of the methyl substituent in the para position. In the case of the Ph_2Zn-$IndTiCl_3$-MAO and Ph_2Zn-$(n\text{-}BuCp)_2TiCl_2$-MAO systems used for copolymerizing styrene with p-methylstyrene, the activities were quite lower, and as [p-MeS] increased there was a substantial increase in activity. We think that this is due to the structure of these two "metallocenes," which may hinder the formation of the active species and the insertion of the monomer units.

Table 4 shows the result in terms of copolymer composition for styrene/p-methylstyrene copolymerization using Ph_2Zn-titanocene-MAO initiator systems.

Table 4. Copolymer composition of S-co-(p-MeS) obtained by means of Ph_2Zn-titanocene-MAO systems.[a)]

Copolymer composition							
Initial Composition		$CpTiCl_3$		$IndTiCl_3$		$(n\text{-}BuCp)_2TiCl_2$	
$[S]_0$ mol%	$[p\text{-}MeS]_0$ mol%	$[S]_o$ mol%	$[p\text{-}MeS]_o$ mol%	$[S]_o$ mol%	$[p\text{-}MeS]_o$ mol%	$[S]_o$ mol%	$[p\text{-}MeS]_o$ mol%
95	5	86.5	13.5	50.4	49.6	75.6	24.4
50	50	39.5	60.5	21.1	78.9	26.0	74.0
5	95	2.6	97.4	3.6	96.4	2.8	97.2

a)Obtained by integration of the main chain CH and CH_2 and the side chain CH_3 proton signals.

Table 4 shows that, regardless of the initiator system used, the copolymers are enriched in p-MeS with respect to the initial feed.

Table 5. Thermal behavior of S/p-MeS copolymers using Ph_2Zn-titanocene-MAO initiator systems

Initial composition p-MeS	$CpTiCl_3$ Tg (°C)	$CpTiCl_3$ Tm (°C)	$IndTiCl_3$ Tg (°C)	$IndTiCl_3$ Tm (°C)	$(n\text{-}BuCp)_2TiCl_2$ Tg (°C)	$(n\text{-}BuCp)_2TiCl_2$ Tm (°C)
0	100	264	97	262	101	267
5	105	225	96	229	101	233
25	107	n.s.[a)]	100	n.s.[a)]	106	n.s.[a)]
50	109	n.s.[a)]	105	n.s.[a)]	111	n.s.[a)]
75	112	n.s.[a)]	108	n.s.[a)]	111	n.s.[a)]
95	114	n.s.[a)]	108	n.s.[a)]	112	n.s.[a)]
100	114	n.s.[a)]	111	n.s.[a)]	116	n.s.[a)]

[a)]No signal.

The S/p-MeS (95/5) copolymers obtained (Table 5), regardless of the initiator system used, had a crystalline melting temperature that was up to 40 °C lower than that of s-PS, making S/p-MeS copolymers easier to process than syndiotactic polystyrene. The vitreous transition temperature of all types of polystyrene is 100 °C, while the incorporation of p-methylstyrene increases Tg gradually to 114°C.

Copolymerization of S/p-Bu^tS by Ph2Zn-titanocene-MAO initiator systems led to the results shown in Figure 5, where it is seen that, as the proportion of p-Bu^tS in the initial feed increases, so does the system's effectiveness for all the titanocenes used. These results agree with the electron donor effect of the substituent group in the para position of p-Bu^tS.

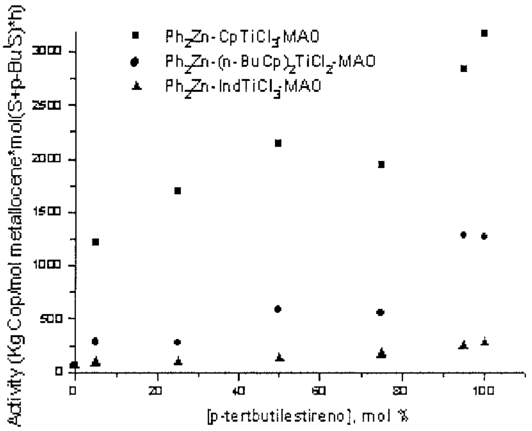

Figure 5. S/p-ButS copolymerization using Ph_2Zn-titanocene-MAO initiator systems

Now, when the different titanocenes used are compared, it is seen that the order of activity of the systems is: Ph_2Zn-$CpTiCl_3$-MAO > Ph_2Zn-$(n$-$BuCp)_2TiCl_2$-MAO > Ph_2Zn-$IndTiCl_3$-MAO. It should also be noted that when [p-Bu^{t}S] is increased, activity also increases. This effect is quite marked when the Ph_2Zn-$CpTiCl_3$-MAO initiator system is used.

Table 6 shows the values with respect to the composition of the copolymers obtained when Ph2Zn-titanocene-MAO initiator systems are used.

Table 6. Composition of the S-co-(p-MeS)copolymer obtained using Ph_2Zn-titanocene-MAO systems.[a)]

		Copolymer composition					
Initial Composition		$CpTiCl_3$		$IndTiCl_3$		$(n$-$BuCp)_2TiCl_2$	
$[S]_0$ mol%	$[p$-$Bu^tS]_0$ mol%	$[S]_o$ mol%	$[p$-$Bu^tS]_o$ mol%	$[S]_o$ mol%	$[p$-$Bu^tS]_o$ mol%	$[S]_o$ mol%	$[p$-$Bu^tS]_o$ mol%
95	5	93.2	6.8	71.1	28.9	87.5	12.5
50	50	42.2	57.8	46.5	53.5	32.4	67.6
5	95	n.d.[b)]	n.d.[b)]	2.5	97.5	3.2	96.7

a)Obtained by integration of the main chain CH and CH_2 and the side chain CH_3 proton signals, [b)] Not determined.

Table 7 shows the thermal behavior of the S/p-Bu^{t}S copolymers obtained with Ph_2Zn-titanocene-MAO initiator systems, regardless of the initiator system used, the copolymers are enriched in p-Bu^{t}S with respect to the initial feed. However, comonomer incorporation is less than in the case of p-methylstyrene (Table 4).

Table 7. Thermal behavior of S/p-Bu^{t}S copolymers using Ph_2Zn-titanocene-MAO initiator systems

Initial composition p-Bu^{t}S	$CpTiCl_3$ Tg	$CpTiCl_3$ Tm (°C)	$IndTiCl_3$ Tg	$IndTiCl_3$ Tm (°C)	$(n\text{-}BuCp)_2TiCl_2$ Tg	$(n\text{-}BuCp)_2TiCl_2$ Tm (°C)
0	101	262	101	263	102	269
5	103	n.s.[a]	102	n.s.[a]	106	n.s.[a]
25	119	n.s.[a]	113	n.s.[a]	120	n.s.[a]
50	130	n.s.[a]	124	n.s.[a]	131	n.s.[a]
75	139	n.s.[a]	132	n.s.[a]	n.s.[a]	n.s.[a]
95	140	n.s.[a]	138	n.s.[a]	144	n.s.[a]
100	142	n.s.[a]	n.s.[a]	n.s.[a]	146	n.s.[a]

[a] No signal.

Table 7 it is seen that only polystyrenes show crystalline melting, while it is not seen in the crude copolymers. With respect to Tg, they increase noticeably with p-Bu^{t}S content.

Conclusions

Ph_2Zn-Metallocene-MAO initiator systems, where Metallocene = $CpTiCl_3$, $(n\text{-}BuCp)_2TiCl_2$, $IndTiCl_3$, Ind_2ZrCl_2 and $Et(Ind)_2ZrCl_2$, induce the homopolymerization of S, p-MeS and p-Bu^{t}S, producing syndiotactic polymers in the case of the titanocenes, and amorphous polymers, or polymers having low stereoregular content, in the case of the zirconocenes. The highest catalytic activities in the homopolymerization of S, p-MeS and p-Bu^{t}S occur with the Ph_2Zn-$CpTiCl_3$-MAO system, where the UV-visible study confirms that there is a strong interaction between the components of the initiator system, substantially increasing the catalytic activity. The copolymers obtained with Ph2Zn-titanocene-MAO systems are enriched in the comonomer with respect to the initial load regardless of the initiator system used, confirming the electron donor effect of the p-methyl and p-tert-butyl substituents. The Tg of the copolymers increases with comonomer incorporation, favoring thermal stability with respect to conventional polystyrene.

Acknowledgements: The authors acknowledge the partial financial support of the Departamento de Investigaciones Científicas y Tecnológicas, Universidad de Santiago de Chile, DICYT-USACH, Project No. 05-9741-RC, and of the Fondo Nacional de Desarrollo Científico y Tecnológico, FONDECYT, Grant 101-0036, 2000054 and 2010027. M.A.P. wishes to thank CONICYT for a Doctoral Scholarship. The authors thank M.A. Cerda for the DSC determinations.

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