Further Studies on Homo- and Copolymerization of Styrene through Metallocenic Initiator Systems

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Summary: Binary metallocene-MAO and ternary diphenylzinc-metallocene-MAO initiator systems have been tested as initiators in the homopolymerization of styrene and also in its copolymerization with several diverse comonomers including substituted styrenes, styrene derivatives, α-olefins and dienes. Various titanocenes and zirconocenes and some exploratory experiment with hafnocene were carried out. The results indicate that titanocenes were more effective than zirconocenes in the homopolymerization of styrene while zirconocenes did better in α-olefin polymerization. It was found that titanocenes generated mainly syndiotactic polystyrene, s-PS, while zirconocenes yielded atactic polystyrene or, depending on the zirconocene, a low percentage of s-PS. For these types of initiators the polymerization process depends largely on the inductive effect of the substituents linked to the benzene ring of styrene and on its position (*ortho, meta or para*). Substituent multiplicity reduced markedly the effectiveness of these initiator systems. Styrene/isoprene polymerization was also studied using binary zirconocene-MAO initiator systems that yielded low conversions and also low molecular weight polymers.

Keywords: metallocene catalysts; styrene homopolymerization; styrene/(substituted styrene) copolymerization; styrene/(α-olefin) polymerization; tacticity

Introduction

Since Ishihara[1] and Zambelli,[2] who first synthesized syndiotactic polystyrene, numerous researchers have studied homo-and copolymers of styrene using metallocene initiators. Among them, titanocenes and zirconocenes have been used most extensively. In particular, titanocenes give good yields of syndiotactic polystyrene and styrene copolymers, with special and improved properties with respect to conventional (atactic) polystyrene.[3,4]

We have been working on styrene homo- and copolymerization using binary, metallocene-MAO, and ternary diphenylzinc-metallocene-MAO initiator systems, with the aim to improve polystyrene properties and mainly those related to thermal behavior, solubility, flexibility and mechanical resistance.

In our work we concluded that styrene copolymerization using these initiator systems is greatly influenced by electrical and steric factors. Substituents in the *para*–position having I+ inductive effect favor the polymerization efficiency, while those with I– inductive effect are less prone to polymerize. As to steric effects, it was concluded that styrene monomers with more crowding near the vinyl group made them less reactive and yielded low conversion on homopolymerization and low incorporation in their copolymer products.

In the present work it is emphasize the fact that not only inductive effects are

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important in conversion to polymer or copolymer of styrene, but also steric effects are quite significant.

The present paper report further experimental results of styrene homo- and copolymerization through these binary and ternary initiator systems, including half-sandwich titanocene cyclopentadienyltitanium trichloride, and on the other hand the truly metallocene ethylenebis(indenyl)-zirconium dichloride.

Experimental Part

Homo- and copolymerization reactions were carried out in an argon atmosphere in a 100 cm^3 Schlenk tube equipped with a magnetic stirrer. Solvent toluene (ca. 10 to 30 mL), MAO solution, Ph_2Zn, and metallocene toluene-solution were sequentially charged by syringe under argon pressure. Polymerization was initiated by injecting either the styrene or the α-olefin, or simultaneously the required amount of styrene and the second comonomer. The reactions were kept at 60 °C with stirring for the required length of time. Polymerization was terminated by adding a mixture of hydrochloric acid and methanol. The polymers, coagulated in the acidified methanol, were recovered by filtration after washing several times with methanol, and dried under vacuum at 60 °C.

Gel permeation chromatography, GPC, measurements were performed in a Waters Alliance 2000 apparatus, operated at 135 °C and equipped with three styragel HT columns (HT3, HT5, and HT6). 1,2,4-trichlorobenzene was used as solvent with a 1.0 mL/min flow, and calibration was done with polystyrene molecular weight standards.

Viscosities were measured either in chloroform or in *o*-dichlorobenzene, depending on the solubility of the polymer, and intrinsic viscosities were determined by the one-point method.[5] Differential scanning calorimeter, DSC, analyses were performed by using a Rheometrics Scientific DSC apparatus with samples placed in a nitrogen atmosphere. 3 to 4 mg samples were heated at a rate of 10 °C/min, cooled to room temperature, and reheated at the same rate. The reported Tg and Tm were those obtained in the second heating scan. Nuclear magnetic resonance, NMR, spectra were recorded on a Bruker AMX-300 spectrometer at 60 °C, operating at 300.1 and 75.5 MHz for ^1H and ^{13}C, respectively. The polymers and copolymers were dissolved in deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$, 5% w/v). A total of 64 and 4000 scans with 16 K and 32 K data points and with a relaxation delay of 1 and 2 seconds were collected for ^1H and ^{13}C, respectively. Chemical shifts were calibrated with tetramethylsilane (TMS) used as internal reference.

Results and Discussion

Since Ishihara and Zambelli time, numerous researchers, from both academy and industry have devoted their efforts to the synthesis of polystyrene and mainly to the copolymerization of styrene, with the aim of preparing new materials with enhanced properties characteristics of the commonly known and thoroughly used atactic polystyrene (a-PS), and at the same time to overcome its disadvantages, mainly rigidity, brittleness, and poor thermal and chemical resistance.

In our studies on homo- and copolymerization of styrene were employed binary viz. a metallocene and MAO (metallocene-MAO), and also ternary viz. diphenylzinc, (Ph_2Zn), a metallocene and MAO (Ph_2Zn-metallocene-MAO) initiator systems. From the results it was concluded that Ph_2Zn-metallocene-MAO initiator systems were more effective than systems without Ph_2Zn. Titanocenes were the most effective in styrene polymerization, particularly when acting in the ternary systems. Furthermore, it was concluded that this homo- and copolymerization of styrene producing syndiotactic-PS, (s-PS) is initiated by coordination of a monomer with the active species which include Ti^+ resulting from the metallocene, and then the polymerization propagates by insertion of the incoming monomer unit in the growing polymer chain-metal atom link through a cationic pathway.[6,7] Regarding the efficiency of ternary systems it was postulated that since Ph_2Zn is a Lewis acid, it favors the reduction of Ti^{4+} to Ti^{3+}, as it is known that Ti^{3+} is the effective active species of these systems.[8]

Besides titanocenes it were used zirconocenes and to a lower extent hafnocenes. That also make a noticeable difference. Zirconocene are less efficient than titanocenes and produce atactic PS with a low content of s-PS, while hafnocenes were the poorest catalysts, producing only a-PS or atactic copolymers. In other words, for an specific type of metallocene: $(n\text{-}BuCp)_2MCl_2$ where $M = Ti$, Zr or Hf, the efficiency order $Ti > Zr > Hf$ was established for the homopolymerization of styrene and also for the copolymerization of S/p-Bu^tS.[9]

Our studies also allowed us to establish that substitution at the phenyl ring of styrene has a large influence on the efficiency of the polymerization, on agreement with the electrical effect of substituents. Groups with an I+ inductive effect in the *para*-position of the styrene benzene ring favor the polymerization process, while those with an I− inductive effect substantially decrease conversion to polymer or copolymer.[7,10] Furthermore, not only the substituent's electrical effect is determinant, but also the steric effect: polymerization of α-methylstyrene, or 2,4-dimethylstyrene, or 2,4,6-trimethylstyrene is far less effective than *para* monoalkyl substituted styrenes.[8,9] Our research also included studies of the polymerization of α-olefins and their copolymerization with styrene. It was established that zirconocenes were more effective than titanocenes, and also that not only the polymerization process depends on the particular zirconocene used, but also, and more critically, on the molecular size of the α-olefin. Conversion increases as the molecular size of α-olefin increases.[11–13]

As established for titanocenes, the ternary initiator systems including Ph_2Zn are more effective than the binary systems, but to a lower extent than that found for titanocenes. Another significant point is that the obtained poly(α-olefin) obtained was isotactic instead of the established syndiotactic microstructure of PS obtained with titanocene for styrene polymerization.[13]

Several metallocene have been employed in our studies. Table 1 summarizes the results of various metallocenes used in styrene polymerization. It is seen that titanocenes are much more effective initiators than zirconocenes and produce syndiotactic polymers. Of the metallocene

Table 1.
Homopolymerization of styrene using binary initiator systems, metallocene-MAO and ternary systems, diphenylzinc-metallocene-MAO, including various metallocenes, in toluene at 60 °C for 48 hours.[a)]

	Metallocene – MAO		Ph_2Zn-Metallocene-MAO	
Metallocene	Conversion (%)	Tacticity	Conversion (%)	Tacticity
Cp_2TiCl_2	1.8	Syndiotactic	6.7	Syndiotactic
$(n\text{-}BuCp)_2TiCl_2$	11.0	Syndiotactic	11.4	Syndiotactic
$CpTiCl_3$	30.5[b)]	Syndiotactic	42.0[b]	Syndiotactic
Cp_2ZrCl_2	1.0	Atactic	1.1	Atactic
$(i\text{-}BuCp)_2ZrCl_2$	2.5	Atactic	2.7	Atactic
Ind_2ZrCl_2	7.8	Atactic	8,4	Atactic
$(H_4\text{-}Ind)_2ZrCl_2$	1.6	Atactic	2.1	Atactic
$Et(Ind)_2ZrCl_2$	3.1	Atactic	3.3	Atactic
$i\text{-}Pr(Flu)(Cp)ZrCl_2$	8.2	Atactic	8.5	Atactic
$(n\text{-}BuCp)_2HfCl_2$	n.p.[c]	Atactic	0.6	Atactic

[a)] Polymerization conditions: Total volume 40 mL, [S] = 2 mol/L, [metallocene] = 4.0E-04 mol/L, [MAO] = 0.33 mol/L for binary initiator systems. The same concentrations for ternary systems, but [metallocene] = $[Ph_2Zn]$ = 2.0E-04 mol/L [b)] After 6 hours polymerization. n.p = not performed.

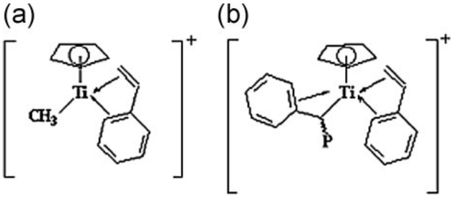

Figure 1.
Styrene polymerization initiated by ternary Ph_2Zn-$CpTiCl_3$-MAO or binary $CpTiCl_3$-MAO system. (a) styrene coordination to Ti^+ active species; (b) insertion of oncoming styrene unit in growing polymer chain.

used, it is also relevant that the "half-sandwich" $CpTiCl_3$ turned out to be the most active, yielding practically pure s-PS, more than 90%.

In Table 1 it is seen that for a specific type of metallocene: $(n\text{-}BuCp)_2MCl_2$ where M = Ti, Zr or Hf, the following order of efficiency order was found for styrene polymerization and also for S/p-Bu^tS copolymerization: Ti > Zr > Hf .[9]

The studies on styrene copolymerization using our initiator systems, like those shown in Table 2, confirm the relevance of the inductive effect of the substituent on the styrene benzene ring as well the inhibiting results when they are placed in the *ortho* position, even though they have an I+ inductive effect.

Table 2 summarizes the results of the copolymerization of styrene initiated by ternary Ph_2Zn-$CpTiCl_3$-MAO systems including monomers having substituents at the styrene phenyl group. Conversion to copolymer is much more affected by the inductive effect of substituents at the phenyl group of styrene. CH_3O-, $(CH_3)_3C-$, CH_3- and NH_2- produced more conversion to polymer while the presence of an halogen atom decreases the conversion compared to conversion for the homopolymerization of styrene. A similar effect is produced by α-methyl styrene, 2,4-dimethylstyrene and 2,4,6-trimethyl styrene. In them, despite their I + inductive effect, a lower conversion compared to styrene itself is indicative that not only electrical effect governs the polymerization process, but also steric hindrance affect its feasibility.

Table 3 shows the results for some of the previous copolymerization but using binary initiator systems. The effect due to the presence of diphenylzinc is clear. Its absence from the initiator system causes a decrease in conversion. For that reason we consider that diphenylzinc, being a Lewis acid, favors the reduction of titanium to Ti^{3+}, which is consider to be the active species who govern the polymerization process.[14]

Table 2.
Styrene copolymerization using Ph_2Zn -$CpTiCl_3$-MAO ternary initiator system in toluene at 60 °C for 6 hours. Styrene/Comonomer = 50/50 (mol/mol).[a)]

Run	Comonomer	Yield	$\lvert\eta\rvert$[b)]	DSC[c)]		Insoluble Fraction
				T_g	T_m	
		(%)	(dL/g)	(°C)	(°C)	(%)
1	Only S	42.0	0.20	100.7	262.3	99.3
2	p-MeOS	75.1	0.47	110.1	n.s.	4.6
3	p-Bu^tS	70.2	0.23	129.6	n.s.	13.5
4	p-MeS	47.3	0.18	108.8	n.s.	28.0
5	p-NH_2S	47.0	n.d.	97.6	257.6	n.d.
6	p-ClS	26.3	n.d.	92	226.8	n.d.
7	p-FS	27.0	n.d.	92.4	252.8	n.d.
8	p-BrS	7.7	n.d.	93.0	231.4	n.d.
9	α-MeS	14.4	n.d.	94.1	238.1	n.d.
10	2,4-Me_2S	6.8	n.d.	112.4	n.s	n.d.
11	2,4,6-Me_3S	3.6	n.d.	91.6	251	n.d.

[a)] Polymerization conditions: Total volume 60 mL; [S] + [comonomer] = 2 mol/L; [MAO] = 0.33 mol/L; [metallocene] = [Ph_2Zn] = 2.0E-04 mol/L, [b)] Intrinsic viscosity: measured in o-DCB at 35 °C, 1 point determination, [c)] Second heating, crude polymer.
n.d. = not determined; n.s. = no signal; * 48 h run; ** 40 °C, and 1.5 h run.

Table 3.
Styrene copolymerization using $CpTiCl_3$-MAO binary initiator system, in toluene at 60 °C for 6 hours. Styrene/Comonomer = 50/50 (mol/mol). a)

Run	Comonomer	Yield (%)	|η| b) (dL/g)	DSC c) Tg(°C)	DSC c) Tm(°)	Insoluble Fraction (%)
1	Only S	30.5	0.25	93.5	255	99.2
2	p-MeS	32.8	0.35	97.1	255	99.9
3	2,4-Me_2S	6.8	n.d.	112.4	n.s	n.d.
4	A-MeS*	25.1	0.12	91.4	239	n.d.
5	1-$C_{10}H_{20}$	3.8	0.25	96.9	261	n.d.
6	1-$C_{16}H_{32}$	11.6	0.10	n.s.	248	81.9

a) Polymerization conditions: Total volume 60 mL; [S] + [comonomer] = 2 mol/L; [MAO] = 0.33 mol/L [metallocene] = 2.0E-04 mol/L, b) Intrinsic viscosity: measured in o-DCB at 35 °C, 1 point determination, c) Second heating, crude polymer.
n.d. = not determined; n.s. = no signal; * 48 h run.

Table 4.
Styrene/(*para*-halostyrene) copolymerization initiated by ternary initiator system Ph_2Zn-$CpTiCl_3$-MAO in toluene at 60 °C during 1 hour. a)

Feed	Styrene/p-Chlorostyrene					Styrene/p-Fluorostyrene					Styrene/p-Bromostyrene				
S/HaloS mol/mol	Yield (%)	Activity b)	DSC c) Tg (°C)	DSC c) Tm (°C)	M_w d) x10^{-4}	Yield (%)	Activity b)	DSC c) Tg (°C)	DSC c) Tm (°C)	M_w d) x10^{-4}	Yield (%)	Activity b)	DSC c) Tg (°C)	DSC c) Tm (°C)	M_w d) x10^{-4}
S Only	56.9	645	97.4	255	n.d.	55.0	633	97.8	n.s.	n.d.	54.5	628	n.d.	--	n.d.
95/5	48.0	594	98,5	254	3.63	50.2	581	98,6	n.s.	6.21	43.7	523	97.1	236	5.10
50/50	26.3	351	92.0	227	1.91	27.0	336	92.4	253	3.16	7.7	123	93.0	219	2.86
26/74	14.4	196	n.s.	n.s	1.15	19.7	244	86.0	245	1.60	3.6	67	98.8	n.s.	1.35
5/95	8.7	129	97.4	259	5.11	6.5	85	84.0	237	1.02	2.7	53	118.0	n.s.	0.70
HaloS	2.8	42	92.5	274	n.d.	2.7	35	n.d.	n.d.	0.72	2.0	39	127.5	n.s.	0.95

a) Polymerization conditions: Total volume 60 mL; [S] + [comonomer] =2 mol/L; [MAO] = 0.33 mol/L; [metallocene] = [Ph_2Zn] = 2.0E-04 mol/L, b) Activiry, Kg copolymer/(mol Met * h), c) Second heating, crude polymer.
n.d. = not determined; n.s. = no signal.

Table 4 reports the result reached for the copolymerization of styrene with *para*-halostyrene at various mol/mol ratios. From these results it is seen that conversion to copolymer decreases as the proportion of halostyrene increases in the initial feed in agreement with the I- inductive effect of the halides.

Our research works also included studies on the polymerization of α-olefins and their copolymerization with styrene. For such monomers our results indicate that zirconocenes are more effective than titanocenes, and also that not only polymerization process depends on the particular zirconocene used, but also, and more critically, on the molecular size of the α-olefin. Conversion increases as the molecular size of the α-olefin increases.[11–13] As established for the titanocenes the ternary initiator systems including Ph_2Zn are more effective than the binary systems, but to a lower extent than in the case of the titanocenes. It can be attributed to a lower capacity of Ph_2Zn to reduce Zr. Another significant point is that the obtained poly(α-olefin) were isotactic.[13]

Table 5 shows results on α-olefins polymerization initiated by ternary initiator systems, including ethylenebis(indenyl)zirconium dichlorure, $Et(Ind)_2ZrCl_2$. As indicated for the homo- and copolymerization of styrene using titanium-based metallocenes, the inclusion of Ph_2Zn in the zirconocene systems improves the polymerization efficiency but to a lower extent than in the case of titanocenes. This is attributed to differences between specific characteristics of both metal atoms.

Figure 2 shows comparatively the activities related to various α-olefins when

Table 5.
Homopolymerization of α-olefins using the Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO ternary initiator system in toluene at 60 °C during 6 hours.[a)]

	Yield	$\lvert\eta\rvert^{b)}$	GPC[c)]		T_m[d)]
A-Olefin	(%)	(dL/g)	M_w*10^{-4}	M_w /M_n	(°C)
1-C_6H_{12}	34.2	0.03	1.74	2.1	n.s.
1-C_8H_{16}	32.7	0.07	2.13	2.0	n.s.
1-$C_{10}H_{20}$	32.5	0.05	2.46	2.1	n.s.
1-$C_{12}H_{24}$	39.2	0.06	2.22	2.1	32.5
1-$C_{16}H_{32}$	44.5	0.06	2.28	1.9	59.3
1-$C_{18}H_{36}$	51.9	0.07	2.45	1.7	67.2

a)Polymerization conditions: total volume = 50 mL; [α-olefin] = 2.0 mol/L; [MAO] = 0.33 mol/L; [Ph_2Zn] = [metallocene] = 2.0E-04 mol/L, b)Measured in o-dichloro benzene at 135 °C, c)Measured in 1,2,4-trichlorobenzene at 135 °C, d)DSC for crude polymer. Second heating at 10 °C/min.
n.s. = no signal.

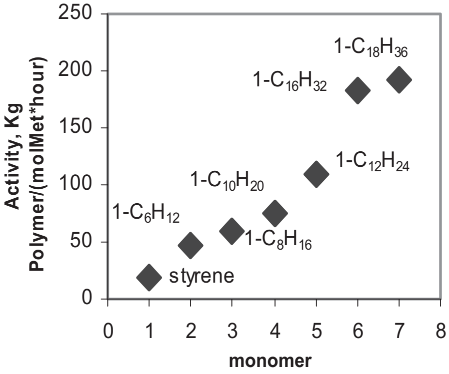

Figure 2.
Homopolymerization of α-olefins using Ph_2Zn-$Et(Ind)_2ZrCl_2$ –MAO initiator system in toluene after 6 hours at 60 °C. Polymerization conditions as indicated in Table 3.

polymerized through ternary-based initiator systems. As the molecular size of the olefin increases more effective is the polymerization process

Continuing with our studies on styrene copolymerization through metallocenic initiator systems, we performed exploratory copolymerization experiments with styrene and isoprene at various S/Ip mol/mol ratios. This time with half-sandwich zirconium metallocene, $CpZrCl_3$.

Table 6 shows the results of styrene/isoprene copolymerization using binary $CpZrCl_3$- MAO initiator systems. Low conversions to copolymer are seen with low incorporation of diene. The expanded ^{1}H-NMR spectra are shown in Figure 3, where a small signal at 4.5-5.3 ppm is seen, corresponding to alkenyl protons belonging to the remaining carbon double bond of each isoprene unit incorporated in the polymer chains. From these signals and the signal at the aromatic region the composition of these S/Ip copolymers was calculated.

Conclusion

- From these and previous results it was concluded that both binary metallocene-MAO and ternary diphenylzinc-metallocene-MAO initiator systems are capable of inducing styrene polymerization as well its copolymerization with various comonomers.

Table 6.
Styrene/isoprene copolymerization using binary $CpZrCl_3$-MAO initiator systems, in toluene after 24 hours at 40 °C.[a)]

S/Ip				DSC[d)]		Composition[e)]	
Feed (mol/mol)	Convn. (%)	Activ.[b)]	$\lvert\eta\rvert^{c)}$ (dL/g)	Tg (°C)	Tm (°C)	S (mol-%)	Ip (mol-%)
S only	16.8	7.1	0.08	84.1	Ns	100.0	0.0
98/2	13.4	5.8	0.11	82.2	Ns	99.2	0.8
95/5	12.3	5.4	0.09	76.4	Ns	99.4	0.6
90/10	10.5	4.7	0.08	66.9	Ns	95.2	4.8

a)Polymerization conditions: Total volume = 21.6 mL; [S] = 2.2 mol/L; [metallocene] = 2.3E-04 mol/L;[MAO] = 0.37 mol/L. b)Activity = (kg copolymer)(mol Met)$^{-1}$(h)$^{-1}$, c)Measured in chloroform at 30 °C, d)Second heating at 10 °C/min for crude copolymer, e)Determined by ^{1}H-NMR spectroscopy.
nd = not determined; ns = no signal.

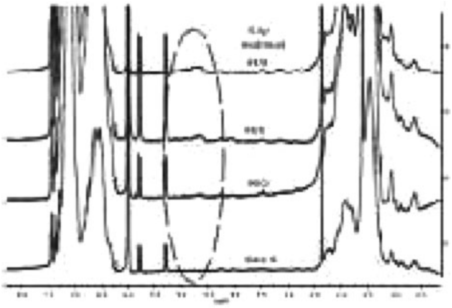

Figure 3.

Expanded ^{1}H-NMR spectra of styrene/isoprene copolymers obtained at various ratios S/Ip (mol/mol) using a $CpZrCl_3$ – MAO, initiator system in toluene, after 24 hours at 40 °C.

- The effectiveness of polymerization processes much depends largely on electronic effects and steric hindrance caused by the comonomers
- The free carbon double bond of isoprene, particularly the unit linked to the active species, whether it is linked by 1,2-, 3,4- or 1,4- addition, competes with the coordination of an incoming monomer unit necessary for polymer propagation, according the scheme shown in Figure 1.

New experimental work are in progress from which conclusive results are expected.

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