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Styrene/(Styrene Derivative) and Styrene/(1-Alkene) Copolymerization using Ph_2Zn-Additive Initiator Systems

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Summary: Diphenylzinc-metallocene-MAO initiator systems have proven to be effective initiator systems for styrene and for substituted styrenes as well as for their styrene/(styrene-derivative) copolymerization. Titanocene produced almost pure syndiotactic polymers while zirconocenes gave atactic polystyrene together with a low content, less than 20%, of syndiotactic polystyrene. Systems including a zirconocene, particularly ethenyl(bisindenyl)zirconium dichloride were effective initiators of 1-alkene polymerization and of styrene/1-alkene copolymerization. Conversion to polymer increases with the molecular size of 1-alkene. Styrene derivative and styrene/(styrene derivative) polymerization was greatly influenced by the inductive effect of substituent and by steric hindrance due to the monomer.

Keywords: diphenylzinc; metallocene catalysts; styrene polymerization; tacticity

Introduction

Commercial polystyrene, an amorphous polymer, has very reliable properties: it is a good electrical insulator, has excellent optical clarity, and is easy to process making it a suitable material for many and diverse applications However, it is brittle, has poor impact resistance, has a low upper temperature limit, poor weatherability, and is attacked by organic solvents. With the aim to overcome these deficiencies, effort have been made through copolymerization with other monomers, blending with other polymers, and stereoregular polymerization. Both isotactic[1] and syndiotactic [2-4] polystyrene, with Tm = 240 and 270°C, respectively, have been obtained, raising considerably the ceiling temperature of amorphous polystyrene, which is limited by its Tg of 100°C. Isotactic polystyrene, i-PS, has a very low crystallization rate which make it of no commercial interest, while syndiotactic polystyrene, s-PS, has a fast crystallization rate. Beside its high melting temperature, s-PS has high crystallinity and high solvent and thermal resistance. However, due to its rigidity, s-PS is still a brittle material with low impact resistance, and its processing requires a rather high temperature.

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With the aim of overcoming the deficiencies of s-PS, several research groups have been working on stereoregular styrene polymerization of styrene and on its copolymerization with various monomers. Since the discovery of s-PS in 1985, many papers have been published regarding s-PS synthesis using combined systems including a metallocene and methylaluminoxane, MAO.[5-9] Zambelli et al.[10] have postulated that Ti^{3+} is responsible for syndiotacticity when styrene is polymerized using titanocene/MAO initiators. Copolymerization of styrene with substituted styrenes and of styrene with 1-alkene have also been extensively studied. Po and Cardi published a review on homo- and copolymerization of styrene covering work from the discovery of s-PS until 1994.[11] A more recent review dealing with syndiotactic polystyrene catalysts and polymerization has been published by Schellenberg and Tomotsu.[12]

We have been working on styrene polymerization,[13-17] and on styrene copolymerization including p-substituted styrenes,[18-22,24] and α-olefins. [19,22] We reported that Ph_2Zn-metallocene-MAO systems are effective initiators for the homopolymerization of styrene, and depending on the inclusion of a titanocene or a zirconocene, for copolymerization of styrene with substituted styrenes or with α-olefins. According to our results the effectiveness of the initiator system is highly dependent on the metallocene, the styrene-comonomer couple, and the styrene/comonomer mole ratio in the initial feed. The polarity of reaction media also influences the effectiveness of the homopolymerization of styrene and the copolymerization of S/p-alkylstyrene.[17]

In this paper further results on styrene/substituted-styrene and styrene/α-olefin copolymerization are reported, with the purpose to providing additional information to our previous findings regarding the polymerization process, and also with the aim to improving properties of s-PS through S/comonomer copolymerization.

Experimental

Homo- and copolymerization experiments were carried out under argon atmosphere in a 100 cm^3 Schlenk tube equipped with a magnetic stirrer. Solvent toluene (ca., 10 to 30 cm^3), MAO solution, Ph_2Zn, and metallocene toluene-solution, were sequentially charged by syringe under argon pressure. Polymerization was initiated by injecting the styrene or simultaneously the required amount of styrene and the second comonomer. The reactions were kept at 60°C under stirring for the required length of time. Polymerization was finished 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 in vacuum at 60°C.

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.19)

For chloroform soluble polymer, viscosity measurements were carried out in chloroform at 25°C and viscosity-average molecular weights, M_v, for a-PS, were calculated according to equation,[20] $[\eta] = 1.12\text{x}10^{-4}\ M_v^{0.73}$, which is reported to be valid for the 7-150x10^4 molecular weight range. For s-PS fractions and insoluble in chloroform copolymers, viscosities were measured in o-dichlorobenzene at 135°C.

DSC analyses were performed by using a Rheometrics Scientific DSC apparatus with samples placed under a nitrogen atmosphere. 3 to 4 mg samples were heated at a rate of 10°C/min, and after cooling to room temperature, reheated at the same rate. The reported Tg and Tm were those obtained in the second scan.

NMR spectra were recorded on a Bruker AMX-300 spectrometer at 70°C, operating at 300.1 and 75.5 MHz for ^{1}H and ^{13}C respectively. The polymers and copolymers were dissolved in deuterated benzene (C_6D_6, 5% w/v). A total of 64 and 4000 scans with 16K and 32K data points and with a relaxation delay of 1 and 2 seconds were collected for ^{1}H and ^{13}C respectively. Chemical shifts were calibrated to tetramethylsilane (TMS) used as internal reference.

Results and Discussion

For the homopolymerization of styrene we have employed various metallocene combined with MAO and diphenylzinc, Ph_2Zn. In our experiments we have tried both binary, metallocene-MAO, and ternary, Ph_2Zn-metallocene-MAO, initiator systems. Table 1 shows the results of polymerization in which s-PS was obtained when a titanocene was included in the initiator system, while the use of a zirconocene produced atactic polystyrene, a-PS. Anyhow, the crude polystyrene obtained with Ph_2Zn-zirconocene-MAO systems included some s-PS content, less than 20%, established by fractionation in boiling butanone and by NMR analysis. Anyhow DSC thermograms did not show any Tm signal for the PS obtained when using a zirconocene (Figure 1).

As can be seen in Table 1, binary or ternary initiator systems including a titanocene produced s-PS while with zirconocenes or the hafnocene, $(n\text{-}Bu)_2HfCl_2$ mainly a-PS was obtained. We find that efficiency of the initiator systems follows the sequence titanocene > zirconocene > hafnocene.

We have already reported that conversion to polymer increases with p-alkylstyrenes compared with styrene itself. On the other hand, for S/p-halostyrenes copolymerization a substantial decrease in conversion was found, indicating that styrene derivative monomers including I-substituent groups were less reactive than styrene.

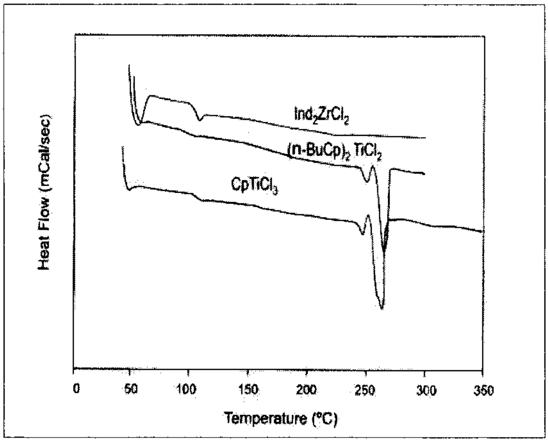

Figure 1. DSC thermograms of crude PS obtained using Ph_2Zn-metallocene-MAO initiator systems in toluene at 60°C. For Ind_2ZrCl_2 and $(n\text{-}BuCp)_2TiCl_2$ metallocenes, 48-hours polymerization. For $CpTiCl_3$, 6-hours polymerization. Second heating at 10°C/min. From Ref.: 22.

Figure 2, shows the results obtained for S/halostyrene copolymerization with the p-chloro-, p-fluoro- and p-bromostyrene. Almost no homo poly(p-halostyrene) was obtained after one hour of polymerization. These results support our previous statement regarding the influence of substitutuents in styrene in terms of copolymer conversion and of the cationic character of the propagation stage. Homopolymerization of p-halostyrene yielded very small amounts of each poly(p-halostyrene).

Table 1. Styrene polymerization using metallocene-MAO and Ph_2Zn-metallocene-MAO initiator systems, in toluene after 48 hours at 60°C.[a]

Metallocene	**Metallocene-MAO**		**Ph_2Zn-Metallocene-MAO**	
	Convn. %	**Tacticity**	**Convn. %**	**Tacticity**
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]	--------	0.6[b]	Atactic
Cp_2TiCl_2	1.8	Syndiotactic	6.7	Syndiotactic
$(n\text{-}BuCp)_2TiCl_2$	11.0	Syndiotactic	17.4	Syndiotactic
$CpTiCl_3$	30.5[b]	Syndiotactic	42.0[b]	Syndiotactic

[a] Polymerization conditions: Total volume = 40 mL, [S] = 2.0 mol/LO, [MAO] = 0.33 mol/L; [metallocene] = 4.0E-04 mol/L for metallocene-MAO systems; [Ph_2Zn] = [metallocene] = 2.0E-04 mol/L for Ph_2Zn-metallocene-MAO systems. [b] After 6 hours polymerization period. [c] not performed.

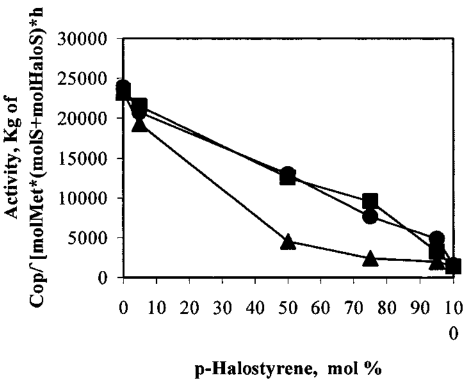

Figure 2. S/p-halostyrene copolymerization using Ph_2Zn-$CpTiCl_3$-MAO initiator system in toluene after 1 hour at 60°C, (●) p-chlorostyrene, (■) p-fluorostyrene, (▲) p-bromostyrene.

In our works we have also tested other substituted styrenes, both on the benzene ring and on the vinyl group. For styrene/α-methylstyrene, S/α-MeS, copolymerization it was found that conversion to polymer decreases as the proportion of α-MeS in the initial feed increases. Table 2 shows the results obtained for S/α-MeS copolymerization using Ph_2Zn-metallocene-MAO initiator systems. Both metallocenes, $CpTiCl_3$ and $(n\text{-}BuCp)_2TiCl_2$, gave lower conversion to copolymer as the proportion of α-MeS in the initial feed increased. We think that these results are in accordance with a steric hindrance effect at the vinyl bond of the monomer, making coordination of the monomer with the active species more difficult.

Table 2. S/α-MeS copolymerization initiated by Ph_2Zn-metallocene-MAO in toluene after 6 hours at 60°C.[a]

Initial Feed S/α-MeS	**$CpTiCl_3$**			**$(n\text{-}BuCp)_2TiCl_2$**		
mol/mol	**Convn. %**	**Tg °C**	**Tm °C**	**Convn. %**	**Tg °C**	**Tm °C**
S only	59.9	97.8	258.5	10.1	87.8	260.6
95/5	51.7	101.7	257.9	8.3	91.3	263.0
85/15	42.4	98.7	255.9	n.p.	------	------
75/25	34.6	97.8	253.1	1.3	n.p.	n.p.
50/50	23.9	96.1	240.1	0.5	n.p.	n.p.
25/75	6.3	n.p.[b]	n.p.	0.8	n.p.	n.p.
5/95	0.3	n.p.	n.p.	0.6	n.p.	n.p.
α-MeS	none	------	------	0.3	n.p.	n.p.

a) Polymerization conditions: Total volume = 25 mL, [S] + [α-MeS] = 2.0 mol/L, [MAO] = 0.33 mol/L, [metallocene] = 2.0E-04 mol/L. b) n.p. = not performed

Figure 3, shows the results of S/substituted styrene copolymerization initiated by the Ph_2Zn-$CpTiCl_3$-MAO system for comonomers: 2,4-dimethylstyrene, 2,4-Me_2S, 2,4,6-trimethylstyrene, 2,4,6-Me_3S, α-methylstyrene, α-MeS. For comparison, the results of S/p-MeS copolymerization are also included. From these results it is seen that crowded comonomers are less prone to being incorporated into the copolymer, and conversion to copolymer decreases. These results suggest that steric effects, and not only electric inductive effects, are important in terms of the efficiency of the initiator systems under study.

These results indicate that not only the electric inductive effects influence the copolymerization process of S/substituted-styrene using Ph_2Zn-metallocene-MAO initiator systems, but also steric hindrance by the incoming monomer has a substantial role in the process.

For styrene/α-olefin copolymerization using Ph_2Zn-metallocene-MAO initiator systems we have used various metallocenes, including titanocenes and zirconocenes. Initiator titanocene systems produced almost pure syndiotactic polystyrene regardless of the S/α-olefin molar ratio in the initial feed. On the other hand, initiator systems including a zirconocene, and particularly $Et(Ind)_2ZrCl_2$, were able to produce true S/α-olefin copolymer.

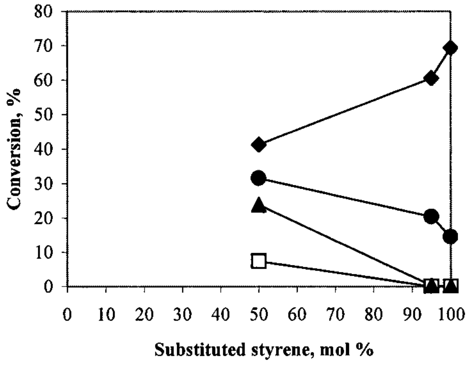

Figure 3. Copolymerization of S/substituted styrene, at various molar ratio S/SubtdS, using Ph_2Zn-$CpTiCl_3$-MAO initiator system in toluene after 6 hours at 60°C. (◆) p-methylstyrene, (●) 2,4-dimethylstyrene, (□) 2,4,6-trimethylstyrene, (▲) α-methylstyrene.

Figure 4 shows the results of α-olefin homopolymerization using Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO as initiator system. 1-C_nH_{2n} with n = 6, 8, 10, 12, 16 and 18 were tested. Conversion to polymer increases with molecular size of olefin. This result suggest that the length of the hydrocarbon chain of the α-olefin affects the efficiency of the initiator system. The higher conversions were obtained for the homopolymerization of 1-hexadecene and for 1-octadecene, with more than 80% conversion after only three hours polymerization.

When the copolymerization of S/α-olefin was carried out using Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO as initiator system, true S/α-olefin copolymers were obtained. Figure 5 shows the results obtained for S/α-olefin copolymerization initiated by Ph_2Zn-$Et(Ind)_2ZrCl_2$- MAO initiator system. The highest conversion was obtained for the S/1-$C_{18}H_{36}$ couple, confirming that the molecular size of α-olefin has a marked role in S/α-olefin copolymerization when using Ph_2Zn-Et(Ind)$_2$$ZrCl_2$-MAO as initiator system.

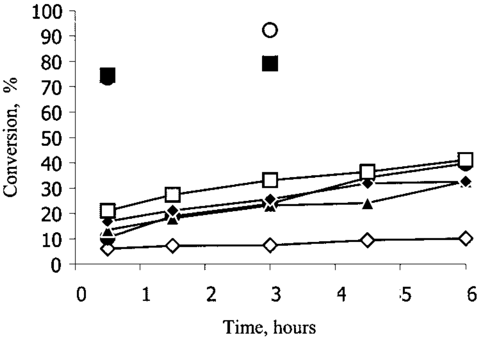

Figure 4. Homopolymerization of α-olefins using Ph_2Zn-Et(Ind)$_2$$ZrCl_2$- MAO initiator system in toluene, after various reaction times, at 60°C. (◊) styrene, (♦) 1-C_6H_{12}, (▲) 1-C_8H_{16}, (●) 1-$C_{10}H_{20}$, (□) 1-$C_{12}H_{24}$, (O) 1-$C_{16}H_{32}$, (■) 1-$C_{18}H_{36}$.

Conclusions

From these and previous results we can conclude that combined systems including diphenylzinc, a metallocene, and methylaluminoxane, Ph_2Zn-metallocene-MAO, depending on the metallocene included, induce the homopolymerization of styrene, substituted styrenes and of α-olefins, as well the copolymerization of S/substituted styrenes and of S/α-olefin.

For substituted styrene, conversion to homo- and copolymer with styrene depends largely on the inductive effect of substituent group and on the steric hindrance due to the incoming monomer.

Ph_2Zn-zirconocene-MAO systems, particularly when including Et(Ind)$_2$$ZrCl_2$, are effective initiators of homopolymerization of α-olefins and of their copolymerization with styrene.

Conversion to polymer is influenced by the molecular size of the α-olefin, increasing as the length of the olefin's hydrocarbon chain increases.

Further experimental work is in progress from which conclusive results are expected.

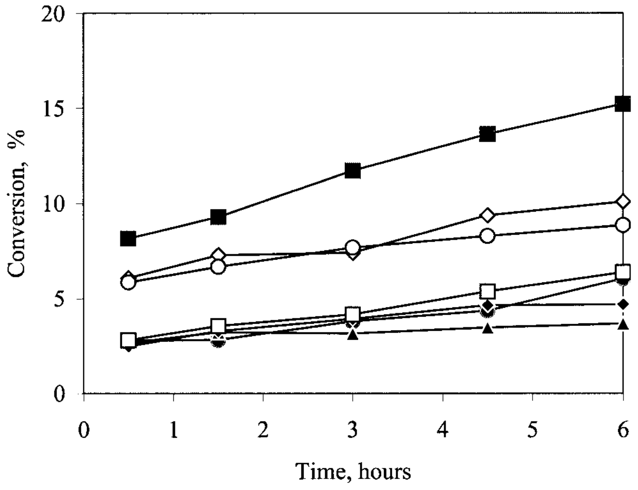

Figure 5. Copolymerization of S/α-olefin (50/50, mol/mol) using Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO initiator system in toluene, after various reaction times at 60°C. (◊) styrene, (♦) 1-C_6H_{12}, (▲) 1-C_8H_{16}, (●) 1-$C_{10}H_{20}$, (□) 1-$C_{12}H_{24}$, (O) 1-$C_{16}H_{32}$, (■) 1-$C_{18}H_{36}$.

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