Styrene Copolymerization Using Diphenylzinc-Additive Initiator Systems: Styrene/*p*-Substituted Styrenes

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Summary: Combined systems including diphenylzinc (Ph_2Zn), a metallocene, and methylaluminoxane (MAO), have been employed to initiate the copolymerization of styrene (S) with p-alkylsubstituted styrenes and with α-olefins. The copolymerization processes depend largely on the comonomer, the nature of the metallocene included in the initiator system, the presence of Ph_2Zn, the polymerization temperature and the solvent used. Titanocenes produced true copolymers for S/p-substituted styrene, but not in S/α-olefin copolymerization. On the other hand zirconocenes either did not copolymerize S/p-substituted styrene or produced very low conversions, while they succeeded in copolymerizing S/α-olefin, depending on the particular zirconocene employed. A low p-methylstyrene (p-MeS) content in the S/p-MeS copolymer and a low p-tertbutylstyrene (p-Bu^{t}S) content in the S/p-Bu^{t}S copolymer decreased Tm, making them easier to process material than s-PS.

Introduction

Amorphous polystyrene or crystal-polystyrene, is a very important commercial polymer with many and diversified applications due to its very reliable properties. It is a good electrical insulator, has excellent optical clarity, and is easy to process. On the other hand, it presents some deficiencies: it is attacked by organic solvents, has poor weatherability, is brittle with low impact resistance, and has low upper temperature limit. With the discovery of syndiotactic polystyrene, s-PS, by Ishihara,[1,2] and by the same time Pellecchia[3] a new type of polystyrene with outstanding properties was obtained: high melting point (Tm = 270°C), high crystallinity, high solvent and thermal resistance.[4-6] Despite these excellent properties, s-PS is still a brittle material with low impact resistance, and its processing requires a rather high temperature.

With the aim to clarify the mechanism of stereospecific polymerization of styrene, and on the other hand, and in order to prepare a material with the properties s-PS but with decreased deficiencies, there have been many studies on the copolymerization of styrene.[10-14]

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Cardi et al.[15)] reported the S/p-MeS copolymerization using a $Ti(EtO)_4$-MAO initiator system obtaining the corresponding copolymer with a composition enriched in p-MeS with respect to the composition in the feed. Grassi et al.,[16)] established that the I^+ substituents on the benzene ring of styrene enhanced the reactivity to a greater extent than that observed for isotactic polymerization, and that the stereospecificity is also effected by ring substituents even when they are in the para position. They concluded that the copolymer of S with p-MeS obtained using Bz_4Ti-MAO as initiator system is cosyndiotactic, and considered that this fact seems also to confirm that the coordination of the monomer to the catalytic center is actually a determining factor in the stereoregulation.[16)]

Recently, Schwecke and Kaminsky[17)] reported on syndiotactic copolymers of styrene with p-MeS, p-Bu^tS and α-MeS obtained using a $CpTiF_3$-MAO initiator system. The authors emphasized the fact that small amounts of p-Bu^tS in S/p-Bu^tS copolymer are needed to reduce the Tm by up to 40°C with respect to that of s-PS, whereas 20% of p-MeS in the S/p-MeS copolymer S/p-MeS decreased the melting point by up 60°C. This was considered an advantage regarding the processing of these materials.

We have been working on the polymerization[18-20)] of S and its copolymerization with p-alkylstyrenes (S/p-alkylstyrene), and with α-olefins (S/α-olefin)[21-24)] initiated by combined systems including diphenylzinc, a metallocene, and methylaluminoxane. Our findings indicate that these systems are active initiators of styrene homopolymerization as well as of S/p-alkylstyrene and of S/α-olefin copolymerization. We have found that the polymerization processes depend on the temperature, the metallocene, Ph_2Zn/metallocene molar ratio, as well as on the polarity of the solvent employed. For copolymerization, the synthesis also depends on the nature of the comonomer employed and on the S/comonomer composition in the initial feed.

This paper deals with new experimental results on S polymerization and on the copolymerization of S/para-alkylstyrenes. For comparison, some example of S/long-chain-α-olefin copolymerizations are also included.

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 (to complete 25 cm^3), MAO 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 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) $|\eta| = 1.12 \times 10^{-4} M_v^{0.73}$, which is reported to be valid for the $7\text{-}150 \times 10^4$ 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 on a Rheometrics Scientific DSC apparatus with samples placed under a nitrogen atmosphere. The samples (3 to 4 mg) were heated at a rate of 10°C/min, and after cooling to room temperature they were 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 ^1H 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 ^1H and ^{13}C respectively. Chemical shifts were calibrated to tetramethylsilane (TMS) used as internal reference.

The NMR spectra of samples soluble at room temperature were recorded on a Bruker Avance DRX-300 spectrometer operating at 300.13 MHz. Polymers were dissolved in deuterated chloroform and TMS was used as internal reference.

Results

Table 1, shows the results of S/p-MeS and of S/p-Bu^{t}S copolymerizations initiated by the $CpTiCl_3$-MAO system for various S/comonomer molar ratios as well as for the homopolymerization of S, p-MeS, and p-Bu^{t}S. These results indicate that conversion to polymer increases as the molar ratio of p-MeS or of p-Bu^{t}S increases in the initial feed. The reported activity ratio corresponds to the ratio between the activity for the particular copolymerization with respect to the activity of styrene homopolymerization, which arbitrarily was given a value of 1. The activity ratio increases with the increase of p-alkylstyrene in the initial feed. From these figures it is clear that para-alquilsubstituted styrenes are more reactive than styrene in concordance with an I^+ effect of the para-substituent, which facilitate the coordination of monomer through its π-vinyl electrons to the active species of the initiator system.

Table 1 Styrene/p-alkylstyrene copolymerization initiated by $CpTiCl_3$-MAO in toluene after 6 hours at 60 °C.[a)]

Initial Feed S/p-alkylS Mol/mol	Conversion[b)] %	Activity ratio[c)]	$\|\eta\|$ [d)] dL/g	T_g °C	T_m °C
S/p-MeS					
S only	30.4	1.0	0.25	97.5	245.7
95/5	34.3	1.1	0.26	98.1	225.1
75/25	38.7	1.3	0.23	100.6	n.s.
50/50	40,7	1.4	0.23	102.1	n.s.
25/75	49.5	1.8	0.20	104.4	n.s.
5/95	45.8	1.7	0.20	106.0	n.s.
p-MeS only	57.3	2.1	0.21	105.4	n.s.
S/p-Bu^{t}S					
S only	30.5	1.0	0.25	93.5	255.0
95/5	45.3	1.0	0.35	101.1	n.s.
75/25	73.0	1.7	0.33	110.0	n.s.
50/50	82.0	2.1	0.43	123.0	n.s.
25/75	100.0	2.9	0.40	127.4	n.s.
5/95	n.p.	-------	------	------	------
p-Bu^{t}S only	100.0	3.2	0.63	134.0	n.s.

[a)] Polymerization conditions: Total volume = 25 mL, [S] + [p-MeS] = 2.1 mol/L, [Al] = 0.33 mol/L, [$CpTiCl_3$] = 2.0E-04 mol/L.

[b)] Based on comonomers in initial feed.

[c)] Referred to that of styrene arbitrarily defined as equal to 1.

[d)] Measured in o-diclorobenzene at 135°C.

n.p. = not performed; n.s. = no signal

Table 2, shows the results obtained for this copolymerization when the initiator system, Ph_2Zn-$CpTiCl_3$-MAO, included diphenylzinc. The inclusion of Ph_2Zn resulted in an improved conversion to polymer while, activity ratio, intrinsic viscosity and thermal behavior remained

Table 2 Styrene/p-alkylstyrene copolymerization initiated by Ph_2Zn-$CpTiCl_3$-MAO in toluene after 6 hours at 60 °C.[a)]

Initial Feed S/p-alkylS Mol/mol	Conversion[b)] %	Activity ratio[c)]	$\lvert \eta \rvert$[d)] dL/g	T_g °C	T_m °C
S/p-MeS					
S only	32.8	1.0	0.35	97.1	254.8
95/5	39.2	1.2	0.34	95.1	231.8
75/25	44.2	1.4	0.33	98.5	n.s.
50/50	41.3	1.3	0.30	100.9	n.s.
25/75	58.4	2.0	0.26	103.9	n.s.
5/95	60.6	2.1	0.23	102.6	n.s.
p-MeS only	69.3	2.1	0.23	106.3	n.s.
S/p-BuᵗS					-----
S only	42.0	1.0	0.20	100.7	262.0
95/5	54.1	1.3	0.22	103.0	n.s.
75/25	68.2	1.8	0.23	118.9	n.s.
50/50	70.2	2.1	0.23	129.6	n.s.
25/75	n.p.	------	------	------	n.s.
5/95	n.p.	------	------	------	n.s.
p-BuᵗS only	94.0	3.5	0.22	141.6	n.s.

[a)] Polymerization conditions: Total volume = 25 mL, [S] + [p-MeS] = 2.1 mol/L, [Al] = 0.33 mol/L, [$CpTiCl_3$] = 2.0E-04 mol/L.
[b)] Based on comonomers in initial feed.
[c)] Referred to that of styrene arbitrarily defined as equal to 1.
[d)] Measured in o-diclorobenzene at 135°C.
n.p. = not performed; n.s. = no signal

almost unchanged when compared to the initiator system without Ph_2Zn, accounting for the formation of more active species than that produced in the former initiator system. The same as in the case of the $CpTiCl_3$-MAO system, the initiator system including Ph_2Zn copolymerized S/p-MeS = 95/5 producing crude copolymer which shows a crystalline nature with a Tm value lower than that of s-PS. The lowering of Tm has been pointed out recently by Schwecke and Kaminsky[17] when copolymerizing styrene with p-alkylstyrene initiated by $CpTiF_3$-MAO system.

Figure 1 shows the DSC thermograms of S and p-MeS homopolymers and of the S/p-MeS copolymers at various S/p-MeS molar ratios in the initial feed, obtained using the Ph_2Zn-$CpTiCl_3$-MAO initiator system. Only PS and S/p-MeS (95/5) copolymer showed a crystalline melting temperature.

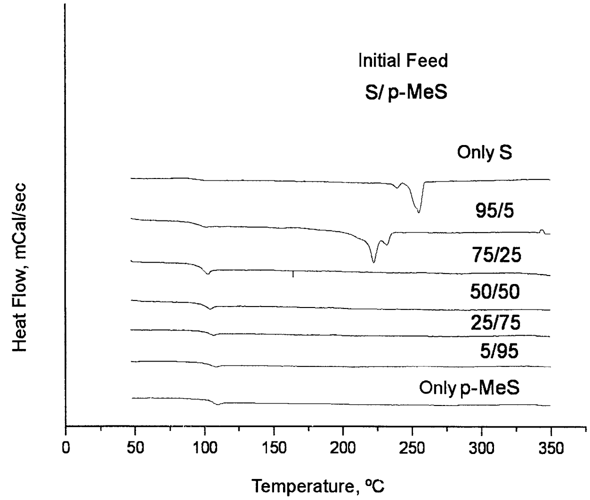

Fig. 1: DSC thermograms of S/p-MeS copolymers obtained using the Ph_2Zn-$CpTiCl_3$-MAO initiator system, in toluene after 6 hours at 60°C.

The use of the $IndTiCl_3$, Ind_2ZrCl_2 and $Et(Ind)_2ZrCl_2$ metallocenes combined with Ph_2Zn and MAO for S, p-Bu^tS and S/p-Bu^tS polymerization are presented in Table 3. From these results it can be seen that conversion to polymer or copolymer is much affected by the nature of metallocene. The metallocene included showed conversion to polymer notoriously lower than the ones produced by Ph2Zn-$CpTiCl_3$-MAO, which is in accordance with previous findings in the sense that the active species producing s-PS corresponds to species including reduced Ti^{+3}. On the other hand, we have already pointed out that zirconocene produced PS mostly amorphous with a low s-PS content.

For styrene/α-olefin copolymerizations using Ph_2Zn-metallocene-MAO systems it was found that titanocene either did not copolymerize S/α-olefin or produce very low conversions. On the other hand, when using zirconocenes such as Ind_2ZrCl_2 or better yet $Et(Ind)_2ZrCl_2$ true S/α-olefin copolymers were obtained. Figure 2 shows the ^{1}H-NMR spectra for S/1-$C_{10}H_{20}$ and S/1-$C_{16}H_{32}$ copolymers obtained using the Ph_2Zn-Ind_2ZrCl_2-MAO initiator system. In each case the corresponding CH_3-group signal at 0.9 ppm can be seen, which together with the other signals indicates the incorporation of both styrene and 1-alkene comonomers to the polymer chains. DSC analysis of such copolymers showed only one Tg signal, indicating the presence of a single product. The NMR and DSC analyses are indicative of a true copolymer

Table 3 Styrene/p-Bu^{t}S copolymerization initiated by Ph2Zn-Metallocene-MAO in toluene after 6 hours at 60 °C.[a)]

Initial Feed S/p-alkylS Mol/mol	Conversion[b)] %	Activity ratio[c)]	$\lvert\eta\rvert$[d)] dL/g	T_g °C	T_m °C
IndTiCl$_3$					
S only	1.8	1.0	0.30	100.3	n.s.
95/5	2.6	1.5	0.28	101.3	n.s.
75/25	2.7	1.7	0.32	112.7	n.s.
50/50	3.5	2.5	0.39	125.0	n.s.
25/75	4.6	3.6	0.46	132.4	n.s.
5/95	6.5	5.5	0.40	138.1	n.s.
p-Bu^{t}S only	7.3	6.2	0.42	n.p.	-----
Ind$_2$ZrCl$_2$					
S only	2.2	1.0	0.18	107.9	n.s.
95/5	4.7	2.2	0.15	113.4	n.s.
75/25	5.2	2.7	0.18	121.5	n.s.
50/50	5.3	3.1	0.17	131.5	n.s.
25/75	5.3	3.4	0.15	141.8	n.s.
5/95	6.5	4.5	0.16	151.2	n.s.
p-Bu^{t}S only	9.7	6.5	0.18	152.4	n.s.
Et(Ind)$_2$ZrCl$_2$					
S only	2.1	1.0	0.12	97.9	n.s.
95/5	0.4	0.2	0.12	103.2	n.s.
75/25	2.6	1.4	0.12	110.5	n.s.
50/50	4.8	2.8	0.12	134.9	n.s.
25/75	4.8	3.2	0.12	137.3	n.s.
5/95	5.0	3.6	0.12	154.2	n.s.
p-Bu^{t}S only	5.1	3.7	0.14	157.0	n.s.

[a)] Polymerization conditions: Total volume = 25 mL, [S] + [p-MeS] = 2.1 mol/L, [Al] = 0.33 mol/L, [CpTiCl$_3$] = 2.0E-04 mol/L.

[b)] Based on comonomers in initial feed.

[c)] Referred to that of styrene arbitrarily defined as equal to 1.

[d)] Measured in o-diclorobenzene at 135°C.

n.p. = not performed; n.s. = no signal

instead of a mixture of both PS and P(1-alkene) homopolymers.

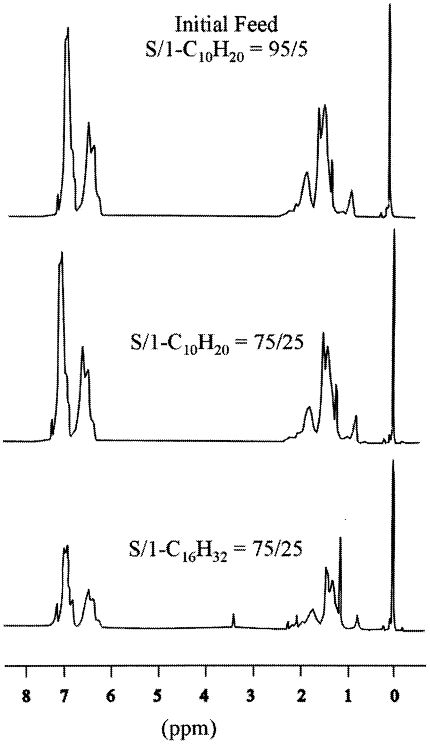

Fig. 2: ^{1}H-NMR in $CDCl_3$ at 25°C of S/1-$C_{10}H_{20}$ and S/1-$C_{16}H_{32}$ copolymers obtained using Ph_2Zn-Ind_2ZrCl_2-MAO system. Taken from reference 22.

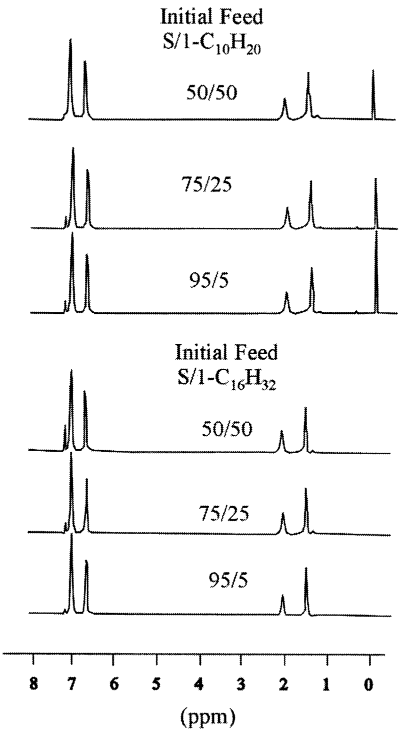

Fig. 3: ^{1}H-NMR in C_6D_6 at 70°C of S/1-$C_{10}H_{20}$ and S/1-$C_{16}H_{32}$ polymerization products obtained using Ph_2Zn-$CpTiCl_3$-MAO system. Taken from reference 22.

Figure 3 shows the ^{1}H-NMR spectra of the crude products obtained after S/1-$C_{10}H_{20}$ and S/1-$C_{16}H_{32}$ were polymerized using the Ph_2Zn-$CpTiCl_3$-MAO initiator system. No CH_3-group signal was detected, only those corresponding to PS and particularly those of s-PS in concordance with $CpTiCl_3$ behavior.

Table 4 shows the results obtained for S/α-olefin copolymerization initiated by Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO at an initial S/α-olefin molar ratio = 75/25 in the feed. It is seen that this initiator system is more effective for S/α-olefin than for S/p-alkylS copolymerization, in accordance with the activity of zirconocenes towards olefin homopolymerization. In these results it is also important to note the lower Tg values with regard to the Tg of s-PS. This behavior can be attributed to a weaker phenyl-phenyl group interaction due to a spacer effect when α-olefin incorporate between styrene units along the polymer chains.

Table 4 Styrene/α-olefin (75/25) copolymerization initiated by Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO in toluene after 6 hours at 60°C.[a)]

α-Olefin	Conversion[b)] %	Activity ratio[c)]	|η|[d)] dL/g	Tg °C	Tm °C
1-$C_{10}H_{20}$	1.00	2.1	n.d.	81.8	n.s.
1-$C_{16}H_{32}$	2.51	2.0	0.09	81.2	n.s.
1-$C_{18}H_{36}$	2.35	2.0	n.d.	81.8	n.s.

[a)] Polymerization conditions: Total volume = 25 mL, [S] + [comonomer] = 2.1 mol/L, [Al] = 0.33 mol/L, $[Et(Ind)_2ZrCl_2]$ = 2.0E-04 mol/L.
[b)] Based on comonomers in initial feed.
[c)] Referred to that of styrene arbitrarily defined as equal to 1.
[d)] Measured in o-diclorobenzene at 135°C.
n.p. = not performed; n.s. = no signal

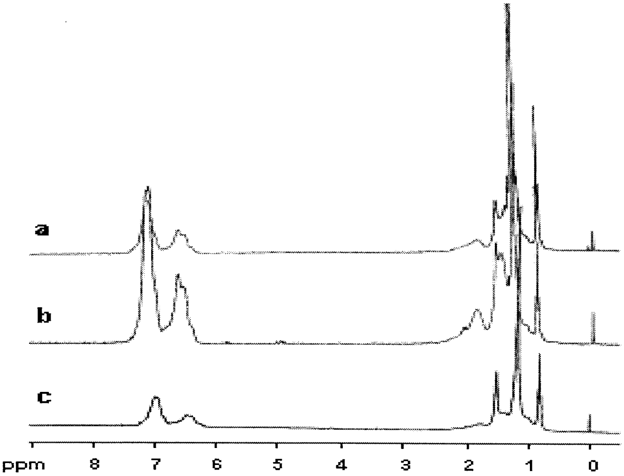

Fig. 4: ^{1}H-NMR of copolymers S/1-alkene (75/25) obtained in toluene after 6 hours at 60°C: a) S/1-$C_{18}H_{36}$, initiator system: $Et(Ind)_2ZrCl_2$-MAO, b) S/1-$C_{16}H_{32}$, initiator system: $Et(Ind)_2ZrCl_2$-MAO, c) S/1-$C_{10}H_{20}$, initiator system: Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO.

Figure 4 shows the ^{1}H-NMR spectra of copolymers obtained using the Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO initiator system included in Table 4. As in cases shown in Figure 2, there is the typical signal at ca. 0.9 ppm, which indicates the presence of a CH_3-group together with those corresponding to styrene. Again, these NMR spectra and the DSC thermograms indicate the presence of true styrene/α-olefin copolymers.

Conclusions

We can conclude from the present results that systems $CpTiCl_3$-MAO and Ph_2Zn-$CpTiCl_3$-MAO are effective initiators for styrene and p-methylstyrene homopolymerization as well as for S/p-MeS copolymerization at various S/p-MeS molar ratios in the initial feed. Furthermore, these initiator systems did not lead to S/α-olefin copolymerization nor did they initiate the homopolymerization of the corresponding α-olefin, but only to very low conversion to PS.

From our results we can conclude that systems including a zirconocene copolymerize S/α-olefin, and conversion to copolymer increases as the proportion of α-olefin in the initial feed increases. This difference with titanocenes can be attributed to zirconium atom, which is smaller than titanium and also has a lower tendency to form cationic species.

Furthermore these results also confirm the cationic pathway in the homo- and the copolymerization of styrene with p-alkylsubstituted styrene when a titanocene participates in the initiator system. The presence of electron-donating substituent group at the para position of the styrene phenyl ring enhance the nucleophilicity of para-alkylsubstituted styrene, making it a more reactive monomer as compared to styrene itself.

The present results are in agreement with previous conclusions in the sense that styrene polymerization through Ph_2Zn-Titanocene-MAO proceeds by coordination of monomer to active species followed by insertion of the monomer in the growing polymer chain-metal atom link, in a cationic pathway for chain propagation.

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

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