Polymerization and copolymerization of styrene by Ph_2Zn-Metallocene-MAO initiator systems.

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SUMMARY: Combined systems including diphenylzinc, Ph_2Zn, a metallocene, and methylaluminoxane, MAO, have been employed to initiate styrene polymerization. These initiator systems have been also used to initiate the copolymerization of styrene with p-alkylsubstituted styrenes and with α-olefins. Both polymerization and copolymerization processes depend on the nature of the metallocene included in the initiator system, the presence of Ph_2Zn, the temperature and the solvent used. Titanocenes produced syndiotactic polystyrene, s-PS, while zirconocenes gave atactic polystyrene, a-PS, with a certain content, less the 20% of s-PS. For copolymerizations the conversion to polymer was also influenced by the comonomer nature and its molar proportion in the initial feed, as well as the sort of metallocene, titanocene or zirconocene included.

Introduction

Ishihara et al.[1,2] and also Pellecchia et al.[3,4] first reported the preparation of syndiotactic polystyrene, s-PS. Since then several authors have been dealing with the synthesis of s-PS using homogeneous methylaluminoxane-based catalysts. Regarding the active species for styrene syndiotactic polymerization, Zambelli considered two classes of group IV metal compounds showing high activities: a) $CpTiX_n$ or Cp^*TiX_n (Cp^* = 1,2,3,4,5-pentamethylcyclopentadienyl), with n = 2, 3 and X = halide, alkoxide; b) TiX_n compounds with n = 2-4 and X = alkyl, alkoxide, halide.[5]

Invited lecture at 7th Latin American Symposium on Polymers, SLAP'2000, 5th Ibero American Congress on Polymers and 1st Latin American Symposium on Chitin and Chitosan, SOLAQ, 20-24 November 2000, La Habana, Cuba.

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CCC 1022-1360/00/$ 17.50+.50/0

Zambelli and Pellecchia,[6)] pointed out that the reasons of the higher activity for the catalyst based on Ti compounds in comparison with catalyst based on Zr compounds in promoting styrene polymerization are not clearly established, and taking into account the possibility of obtaining active catalyst using Ti(III) compounds it could be suggested that the active species are formed after reduction of the group 4 metal, which is easier for Ti(IV) than for Zr(IV). These authors also mentioned the weaker Lewis-acidity of Zr as compared to Ti.

Copolymerization of styrene with substituted styrenes[7,8)] and between styrene and α-olefins, mostly ethylene has also been extensively studied.[9,10)] Aaltonen and Seppälä[11)] reported that styrene with ethylene copolymerization using a $CpTiCl_3$/MAO initiator system produces a mixture of the respective homopolymer. But Longo et al.[12)] revealed by NMR the presence of ethylene-styrene sequences in the polymer produced under certain conditions. Oliva et al.,[13)] working with $Et(Ind)_2ZrCl_2$/MAO systems, reported that an almost alternating stereoregular copolymer can be obtained by its use in ethylene-styrene copolymerization at -25°C.

We have been working on S polymerization[14-16)] and S/p-alkylstyrene[17)] and S/1-alkene[18)] copolymerization using combined systems including Ph_2Zn, a metallocene and methylaluminoxane. Our findings indicate that these initiator systems are active initiators of styrene homopolymerization and of S/p-alkylstyrene and S/1-alkene copolymerization. We find that such processes depend on the temperature, the metallocene, and the Ph_2Zn/metallocene molar ratio employed. For copolymerization, the synthesis also depends on the nature of the comonomer as well as on the S/comonomer composition in the initial feed.

This paper deals with new experimental results on S polymerization and on S/p-alkylsubstituted styrene and S/1-alkene copolymerization.

Experimental

Homo- and copolymerization experiments 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 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 ended 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 the equation,20) $[\eta] = 1.12\text{x}10^{-4}\ M_v^{0.73}$, which is reported to be valid for the $7\text{-}150\text{x}10^4$ molecular weight range. For s-PS fractions and chloroform-insoluble copolymers, viscosities were measured in o-dichlorobenzene at 135°C.

DSC analyses were performed by using a Rheometrics Scientific DSC apparatus with the samples placed under a nitrogen atmosphere. Three to four 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 ^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.

Homopolymerization

In previous papers14-16) we reported on various Ph_2Zn-additive systems being active as initiators for styrene polymerization. Systems including Ph_2Zn-Metallocene-MAO were able to produce s-PS when the metallocene was a titanocene, while a-PS with a small content of stereoregular polymer was produced by zirconocenes.

Table 1. Polymerization of styrene by Ph_2Zn-metallocene-MAO systems in toluene after 48 hours at 60°C.[a)]

Molar ratio Met/Ph_2Zn	**$[Met]x10^4$ Mol/L**	**Yield, PS g**	**Activity[b)]**	**$\lvert\eta\rvert$ [c)] $dLxg^{-1}$**	**Insol. Fr.[d)] %**
Cp_2TiCl_2					
0.25	1.59	0.47	4.9	0.19*	59.8
0.50	1.59	0.76	7.9	0.17*	65.4
0.75	1.59	1.08	11.2	0.19*	67.5
1.00	1.59	1.60	16.5	0.28*	58.3
1.25	----	----	----	----	----
$(n\text{-}BuCp)_2TiCl_2$					
0.25	0.52	1.23	50.5	0.22*	47.8
0.50	1.04	0.64	13.1	n.d.	69.3
0.75	1.56	0.92	12.6	0.15*	90.2
1.00	2.08	1.50	15.4	0.20*	91.7
1.25	2.59	1.81	14.9	0.18*	94.3
$(BzCp)_2ZrCl_2$					
0.25	0.53	1.59	86.1	0.08	21.9
0.50	1.05	0.50	13.5	0.08*	53.2
0.75	1.58	0.17	3.1	0.19	n.d.
1.00	2.11	0.66	9.0	0.12*	58.7
1.25	2.60	0.22	2.4	n.d.	n.d.
Ind_2ZrCl_2					
0.25	2.08	----	----	----	----
0.50	4.24	0.69	4.6	0.40	3.0
0.75	6.53	0.92	4.0	0.31	3.8
1.00	9.70	1.49	4.4	0.26	3.8
1.25	14.10	0.55	1.1	0.24	8.7

[a)] Polymerization conditions: Total volume 60 mL: [S] = 2.0 mol/L; [MAO] = 0.33 mol/L; For runs with Cp_2TiCl_2: Total volume: 78.4 mL and [MAO] = 0.25 mol/L

[b)] Activity = Kg PS/(mol met*mol S*h)

[c)] Measured in chloroform at 25°C, * Measured in o-dichlorobenzene at 135°C

[d)] Boiling butanone-insoluble polymer

n.d. = not determined

Table 1 shows the results of styrene polymerization initiated by Ph_2Zn-metallocene-MAO systems for metallocenes: biscyclopentadienyltitanium dichloride, Cp_2TiCl_2, bis(nbutylcyclopentadienyl)titanium dichloride, (n-BuCp)$_2$TiCl$_2$, bis(benzylciclopentadienyl)zirconium dichloride, (BzCp)$_2$ZrCl$_2$, and bisindenylzirconium dichloride, Ind$_2$ZrCl$_2$. As can be seen from the figures in Table 1, conversion to polymer is largely affected by the metallocene employed and by the metallocene/Ph$_2$Zn molar ratio. For most of the cases included in Table 1, Ph$_2$Zn/Met molar ratio of one gave the largest conversion to polymer. On the other hand, the system which showed the highest activity was the one that included the titanocene (n-BuCp)$_2$TiCl$_2$ and the resulting polymer was almost pure s-PS.

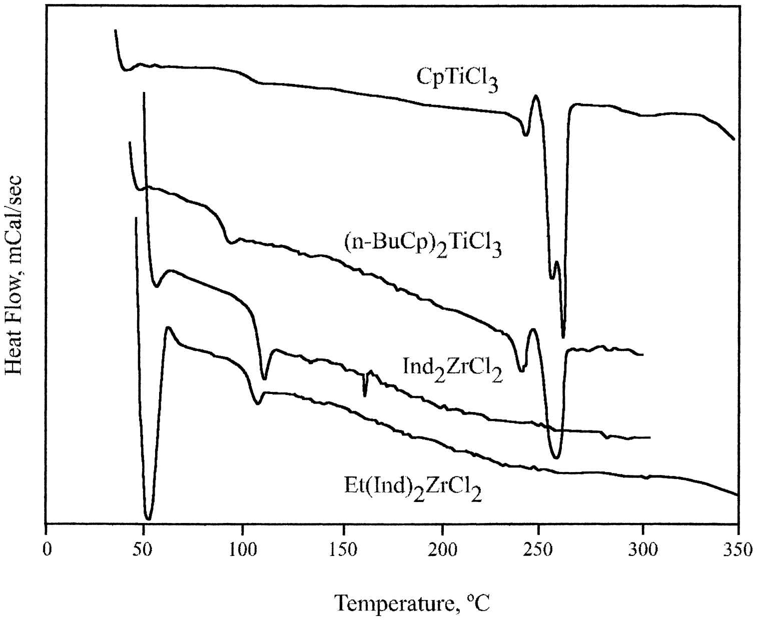

Fig. 1: DSC thermograms of crude PS obtained using Ph$_2$Zn-metallocene-MAO initiator systems, in toluene at 60°C. Second heating at 10°C/min.

Table 2 compares the behavior, as styrene polymerization initiator of various zirconocenes included in Ph$_2$Zn-metallocene-MAO systems. All of them produced PS but their activity was considerably lower than that achieved when a titanocene was included in the initiator catalyst system. Figure 1 shows the DSC thermograms of PS obtained using Ph$_2$Zn-zirconocene-MAO and Ph$_2$Zn-titanocene-MAO systems. It can be seen that the polymer obtained when using a titanocene, either (n-BuCp)$_2$TiCl$_2$ or CpTiCl$_3$, showed a Tm signal in the s-PS melting region, in agreement with the stereoregular nature of these polymers and the capacity of titanocenes in Ph$_2$Zn-metallocene-MAO initiator systems to induce stereoregular polymerization of styrene.

Table 2. Polymerization of styrene by Ph_2Zn-zirconocene-MAO systems in toluene after 48 hours at 60°C.[a]

Metallocene	**[Met]x10^4** **Mol/L**	**Yield PS, g**	**Activity**[b]	**|η|**[c] **dLxg^{-1}**	**Insol. Fr.**[d] **%**
Cp_2ZrCl_2	2.15	0.13	1.8	0.17	n.d.
$(i\text{-}BuCp)_2ZrCl_2$	2.16	0.34	4.6	0.14	n.d.
$(BzCp)_2ZrCl_2$	2.11	0.66	9.0	0.12*	58.7
Ind_2ZrCl_2	2.03	1.06	14.6	0.21	15.6
$(H_4\text{-}Ind)_2ZrCl_2$	2.12	0.26	3.7	0.09	n.d.
$i\text{-}Pr(Flu)(Cp)ZrCl_2$	2.11	1.07	14.8	0.10	28.1
$Et(Ind)_2ZrCl_2$	2.02	0.42	5.8	0.12	n.d.

[a] Polymerization conditions: Total volume 60 mL; [S] = 2.0 mol/L; [MAO] = 0.33 mol/L; Metallocene/Ph_2Zn = 1/1 mol/mol.

[b] Activity = Kg PS/(mol met*mol S*h)

[c] Measured in chloroform at 25°C, * Measured in o-dichlorobenzene at 135°C

[d] Boiling butanone-insoluble polymer

n.d. = not determined

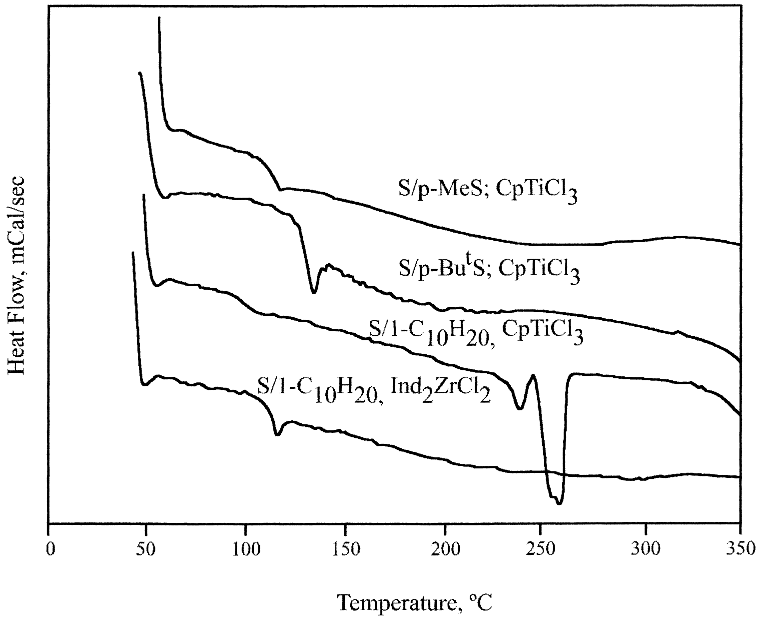

Fig.2: DSC thermograms of copolymers obtained using Ph_2Zn-metallocene-MAO initiator systems, in toluene at 60°C. Initial feed: S/comonomer = 50/50 mol/mol. Second heating at 10°C/min.

Copolymerization

Copolymerization was attempted for styrene with p-alkylstyrene (p-tertbutylstyrene, p-Bu^{t}S, and p-methylstyrene, p-MeS) and for styrene with 1-alkene (1-hexene, 1-decene, 1-hexadecene), S/1-C_nH_{2n}.

Table 3 shows the results for S/p-MeS copolymerization using Ph_2Zn-$CpTiCl_3$-MAO initiator systems. These data show that the amount of copolymer increases as the starting mixture is richer in p-MeS. A similar trend was observed for the Tg values, accounting for a larger amount of the p-MeS component in the copolymer obtained, which is in agreement with the composition at the initial feed, increasing in p-MeS, from S/p-MeS = 95/5 to 5/95 mol/mol.

Table 3. Copolymerization of styrene/p-methylstyrene by Ph_2Zn-$CpTiCl_3$-MAO systems in toluene after 6 hours at 60°C.[a)]

S/p-MeS Mol/mol	Yield Copolymer g	Activity [b)]	$\|\eta\|$ [c)] dL/g	Tg [d)] °C
Only S	1.69	934	0.20*	n. s.
95/5	1.99	1120	0.22*	105.0
75/25	2.25	1251	0.22*	106.7
50/50	3.20	1773	0.18*	108.8
25/75	3.34	1482	0.20*	111.7
5/95	3.72	2048	0.18*	114.2
Only p-MeS	4.16	2308	0.18*	114.1

[a)] Polymerization conditions: Total volume 60 mL: [S] + [p-MeS] = 2.0 mol/L; [MAO] = 0.33 mol/L; Metallocene/Ph_2Zn = 1/1 mol/mol.
[b)] Activity = Kg PS/[mol met*(mol S + mol p-MeS)*h]
[c)] Measured in chloroform at 25°C, * Measured in o-dichlorobenzene at 135°C
[d)] Second heating, crude polymer
n.d. = not determined

Table 4, shows the results for S/p-Bu^{t}S copolymerization using Ph_2Zn-metallocene-MAO systems for metallocenes $CpTiCl_3$ with and without Ph_2Zn. As it was the case for S/p-MeS, the effectiveness of the initiator system is largely improved with respect to that obtained in the homopolymerization of styrene, as can be seen from the run using only S in the initial feed. This is in agreement with a higher reactivity of p-alkylstyrene when a donor substituent group, either CH_3- or $(CH_3)_3C$-, is introduced in the para position. Again, the same as with p-MeS, the thermal behavior indicates that Tg increases with the enrichment in, this time, the p-Bu^{t}S component.

Table 4. Copolymerization of styrene/p-tertbutylstyrene by CpTiCl$_3$-MAO and by Ph$_2$Zn-CpTiCl$_3$-MAO initiator systems in toluene after 6 hours at 60°C.[a]

Initial Feed S/p-MeS Mol/mol	Yield Copolymer g	Activity [b]	$\lvert\eta\rvert$ [c] dL/g	Tg [d] °C
CpTiCl$_3$-MAO				
Only S	2.62	658	0.25*	93.5
95/5	4.01	1005	0.35*	105.1
85/15	5.05	1258.	0.34*	106.1
75/25	7.06	1794	0.33*	113.1
60/40	9.02	2245	0.37*	123.9
50/50	9.01	2242	0.43*	127.0
25/75	12.34	3056	0.40*	132.2
Only p-Bu^{t}S	13.57	3345	0.63*	136.6
Ph$_2$Zn-CpTiCl$_3$-MAO				
Only S	3.62	918	0.20*	100.7
95/5	5.03	1211	0.22*	103.0
85/15	5.84	1470	0.36*	116.1
75/25	6.59	1691	0.23*	118.9
65/35	8.42	2126	0.45*	n.d.
50/50	7.72	1941	0.23*	129.6
35/65	11.06	2800	n.d.	n.d.
Only p-Bu^{t}S	12.70	3162	0.22*	141.6

[a] Polymerization conditions: Total volume 40 mL; [S] + [p-Bu^{t}S] = 2.0 mol/L; [MAO] = 0.33 mol/L; [Metallocene] = 2.0E-04; Metallocene/Ph$_2$Zn = 1/1 mol/mol.
[b] Activity = Kg PS/[mol met*(mol S + mol p-Bu^{t}S)*h]
[c] Measured in chloroform at 25°C, * Measured in o-dichlorobenzene at 135°C
[d] Second heating, crude polymer
n.d. = not determined

Table 5 shows the results for S/1-alkene copolymerization. It can be seen that conversion to copolymer was less effective than that achieved for p-alkylstyrenes, either the 1-alkene, 1-hexene through 1-hexadecene .

Figure 2 shows the DSC thermograms obtained for the polymerization products of S/p-MeS, S/p-Bu^{t}S and S/1-$C_{10}H_{20}$ mixtures. The curve patterns indicate the absence of melting temperature for all of them except those resulting from S/1-$C_{10}H_{20}$ polymerization initiated by Ph_2Zn-$CpTiCl_3$-MAO system. This polymer did not correspond to a S/1-$C_{10}H_{20}$ copolymer but a syndiotactic PS.

Table 5. Copolymerization of styrene/1-alkene by Ph_2Zn-Ind_2ZrCl_2-MAO initiator systems in toluene after 48 hours at 60°C.[a)]

Initial Feed S/p-MeS Mol/mol	Yield Copolymer g	Activity [b)]	$\mid\eta\mid$ [c)] dL/g	Tg [d)] °C
1-Hexene				
Only S	0.74	10.1	0.37	109.7
90/10	0.60	8.0	0.36	106.7
80/20	0.40	5.4	n.d.	106.0
66/34	0.41	5.3	n.d.	99.0
50/50	0.22	3.0	0.36	n.d.
Only 1-C_6H_{12}	0.03	0.6	n.d.	n.d.
1-Decene				
Only S	0.45	10.2	0.37	109.7
95/5	0.05	1.9	n.d.	114.8
75/25	0.04	1.4	n.d.	105.6
50/50	0.02	0.7	n.d.	112.9
Only 1-$C_{10}H_{20}$	0.00	----	----	----
1-Hexadecene				
Only S	0.74	10.1	0.37	109.7
60/40	0.47	6.6	0.64	100.6
50/50	0.49	6.9	n.d.	101.7
25/75	0.64	8.9	n.d.	103.9
Only 1-$C_{16}H_{32}$	Traces	----	n.d.	n.d.

[a)] Polymerization conditions: Total volume 60 mL; [S] + [1-alkene] = 2.0 mol/L; [MAO] = 0.33 mol/L; [Metallocene] = 2.0E-04; Metallocene/Ph_2Zn = 1/1 mol/mol. For 1-decene: Total volume; 25 mL

[b)] Activity = Kg PS/[mol met*(mol S + mol 1-alkene)*h]

[c)] Measured in chloroform at 25°C, * Measured in o-dichlorobenzene at 135°C

[d)] Second heating, crude polymer

n.d. = not determined

Accordingly to the ^{13}C-NMR analysis (Fig. 3) the S/p-Bu^{t}S copolymers obtained using Ph_2Zn-$CpTiCl_3$-MAO are true S/p-Bu^{t}S copolymers. Although their DSC thermograms did not show any Tm, they are stereoregular, and more precisely syndiotactic in nature.

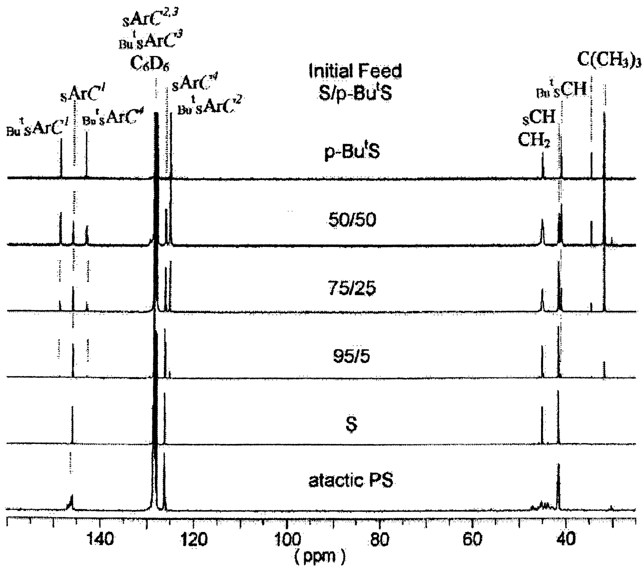

Fig. 3: ^{13}C-NMR spectra in C_6D_6 at 70°C of S/p-Bu^{t}S copolymers obtained using Ph_2Zn-$CpTiCl_3$-MAO initiator system, in toluene after 6 hors at 60°C. Taken from ref.: 17.

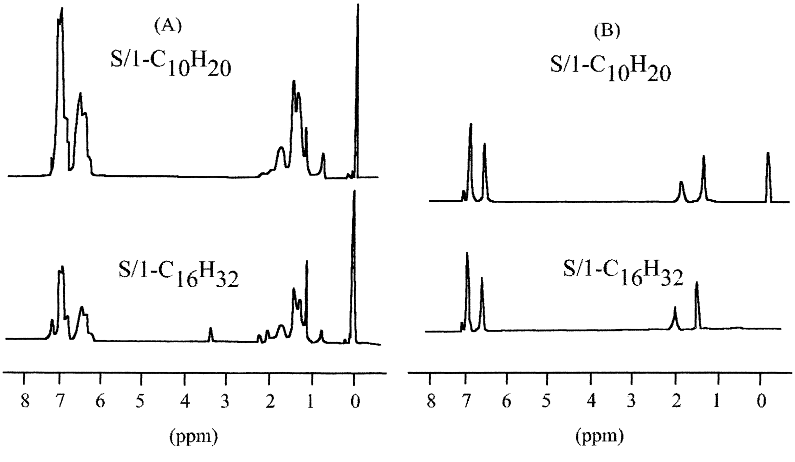

Fig. 4: Fig. 4: ^{1}H-NMR spectra of polymerization products obtained from S/1-alkene (75/25 mol/mol) mixtures using Ph_2Zn-metallocene-MAO systems. (A) Ph_2Zn-Ind_2ZrCl_2-MAO initiator system, measured in $CDCl_3$ at 27°C. (B) Ph_2Zn-$CpTiCl_3$-MAO initiator system, measured in C_6D_6 at 70°C.

^{1}H-NMR analysis of polymerization products from S/1-alkene mixture initiated by Ph_2Zn-metallocene-MAO indicates that for metallocene $CpTiCl_3$ no copolymer was produced, but only s-PS. On the other hand, zirconocene Ind_2ZrCl_2, in Ph_2Zn-metallocene-MAO initiator system produce S/1-$C_{10}H_{20}$ as well as S/1-$C_{16}H_{32}$. From the ^{1}H-NMR integrals, the composition of the resulting copolymers was calculated, showing that they contained fewer 1-alkene units than expected from the initial feed mixture.

Conclusions

From the present and previous results it can be concluded that Ph_2Zn-metallocene-MAO initiator systems including either a titanocene or a zirconocene induce the styrene polymerization. The PS obtained was highly syndiotactic when a titanocene was included, and atactic, but containing a certain amount of s-PS (less than 20%), when using a zirconocene was used.

Regarding copolymerization, it can be concluded that $CpTiCl_3$ behave differently. When starting from a S/p-alkylstyrene mixture, the corresponding copolymer enriched in p-alkylstyrene was obtained, while only s-PS was produce when the initial mixture had an S/1-alkene composition.

Thirdly, zirconoces also have the capacity to induce S polymerization, but they are less effective than titanocenes. On the other hand, Ph_2Zn-Ind_2ZrCl_2-MAO was able to produce true S/1-alkene copolymers with a lower incorporation of 1-alkene than the composition at the initial feed.

Acknowledgements

Financial support from the Departamento de Investigaciones Científicas y Tecnológicas, Universidad de Santiago de Chile, DICYT-USACH, Grant 05-9741-RC, and from the Fondo Nacional de Desarrollo Científico y Tecnológico, FONDECYT, Grant 198-1135, is gratefully acknowledged. We thank Witco, Polymerchemikalien & Kunstharze, Bergkamen, Germany, for donation of methylaluminoxane. We also thank Miss Ana M. Cavieres for the DSC measurements and her skillful assistance in experimental work.

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