Polymer Bulletin 46, 427–434 (2001)

Polymer Bulletin

Copolymerization of styrene by diphenylzinc-additive systems. Part II: Copolymerization of styrene/1-alkene by Ph_2Zn-metallocene-MAO systems

Franco M. Rabagliati (✉), Rodrigo A. Cancino, Francisco J. Rodríguez

Grupo Polímeros, Departamento Ciencias Químicas, Facultad Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile

Received: 17 November 2000/Revised version: 9 May 2001/Accepted: 10 May 2001

Summary

The copolymerization of styrene with 1-alkene (1-hexene, 1-decene and 1-hexadecene) has been tested using combined diphenylzinc-additive initiator systems, including diphenylzinc (Ph_2Zn), a metallocene and methylaluminoxane (MAO). The metallocene were biscyclopentadienyltitanium dichloride, bis(n-butylcyclopentadienyl)titanium dichloride, cyclopentadienyltitanium trichloride and bisindenylzirconium dichloride. For Ph_2Zn-metallocene-MAO systems, titanocenes gave mainly syndiotactic homo polystyrene irrespective of the styrene/1-alkene proportion in the initial feed. Systems including Ind_2ZrCl_2 were able to copolymerize styrene 1-alkene with the copolymers incorporating alkene in a lower proportion than the present in the initial feed.

Keywords: Styrene copolymerization; diphenylzinc; metallocene catalysts; tacticity.

Introduction

Styrene copolymerization with α-olefins or with substituted styrenes has occupied the attention of several authors due their important role from both the academic and technological standpoints, with the aim of elucidating stereoregular styrene polymerization, and on the other hand, of producing new materials with improved properties with regards to atactic polystyrene (a-PS). Great interest has been placed in the synthesis of well defined copolymers which are expected to have a unique mechanical performance.

In our group we have polymerized styrene using initiator systems including diphenylzinc a metallocene and methylaluminoxane. Our studies include ternary Ph_2Zn-metallocene-MAO systems and binary metallocene-MAO systems. Syndiotactic polystyrene (s-PS) was obtained almost pure when using a titanocene, Cp_2TiCl_2, $(n\text{-}BuCp)_2TiCl_2$ or $CpTiCl_3$, while mainly atactic polystyrene was obtained with zirconocene. Anyhow, the PS obtained with the zirconocenes always included a low content, less than 20%, of a stereoregular fraction, s-PS (1-5).

---

[a] Partly presented at World Polymer Congress, IUPAC Macro 2000, 38th Macromolecular IUPAC Symposium, Warsaw, Poland, July 9 - 14, 2000.

[*] Corresponding author

Most of the work on the copolymerization of styrene with α-olefins refers to the styrene-ethylene couple, where the incorporation of ethylene units will be a sort of spacer between styrene units as one or more ethylene units are incorporate in the S polymer chains. The products of such copolymerization depend largely on the initiator system and on the polymerization conditions employed. Longo et al. (6) concluded that $CpTiCl_3$/MAO initiator systems with a high Al/Ti mole ratio produce copolymers of ethylene and s-PS, but Zr-based catalysts do not promote copolymerization at all. Later it was reported (8) that $CpTiCl_3$/MAO produces a nonstereospecific E-S copolymer, while $Et(Ind)_2ZrCl_2$/MAO was a stereospecific catalyst for E-S copolymerization (7).

Altonen and Seppälä pointed out that in S-E copolymerization using $CpTiCl_3$/MAO systems no copolymer was produced, but rather a mixture of PS and PE (8). They obtained similar results with a trichloro(2,6-di-tert-butylphenoxy)titanium/MAO system which resulted active in E polymerization and also produces atactic PS, but was not able to form an ethylene-styrene copolymer (9).

Oliva et al., working with $Et(Ind)_2ZrCl_2$/MAO systems, reported that an almost alternating stereoregular copolymer can be obtained by its use in E-S copolymerization at −25°C. The authors considered that the unusual behavior of the two comonomers toward copolymerization, is relate to a penultimated unit effect through back biting of the aromatic ring of the next-to-last unit on the catalytic metal (10).

Other combinations of MAO with metallocenes: i-Pr(Flu)(Cp)$ZrCl_2$, (11) $CpTi(OPh)_3$, (12) $CpTi(OBz)_3$ (13) have been reported to be able to induce E-S copolymerization.

We have already published results of styrene copolymerization between S and p-tert-butylstyrene and exploratory results on S/1-hexadecene copolymerization (14, 15).

The present communication relates results of styrene/α-olefin (1-hexene, 1-decene and 1-hexadecene) copolymerization by Ph_2Zn-metallocene-MAO systems including metallocenes: Ind_2ZrCl_2, Cp_2TiCl_2, $(n\text{-}BuCp)_2TiCl_2$ and $CpTiCl_3$.

Experimental

Copolymerizations were carried out in an argon atmosphere in a 100 cm^3 Schlenk tube equipped with a magnetic stirrer. Solvent toluene (ca., 20 cm^3), MAO solution, Ph_2Zn, and metallocene toluene-solution, were sequentially charged by syringe under argon pressure. Polymerization was initiated by injecting 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 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 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 (16). For a-PS, viscosity measurements were carried out in chloroform at 25°C and viscosity-average molecular weights, M_v, were calculated according to the equation, $[\eta] = 1.12 \text{x} 10^{-4} M_v^{0.73}$ (17), which is reported to be valid for the 7-150x10^4 molecular weight range of PS. For s-PS, viscosities were measured in o-dichlorobenzene at 135°C.

DSC analyses were performed on a Rheometric Scientific DSC apparatus with samples placed in a nitrogen atmosphere. The samples, 3-4 mg, were heated at a rate of 10°C/min, and after cooling to room temperature 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 MHz for ^1H and 75.5 MHz for ^{13}C. 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.

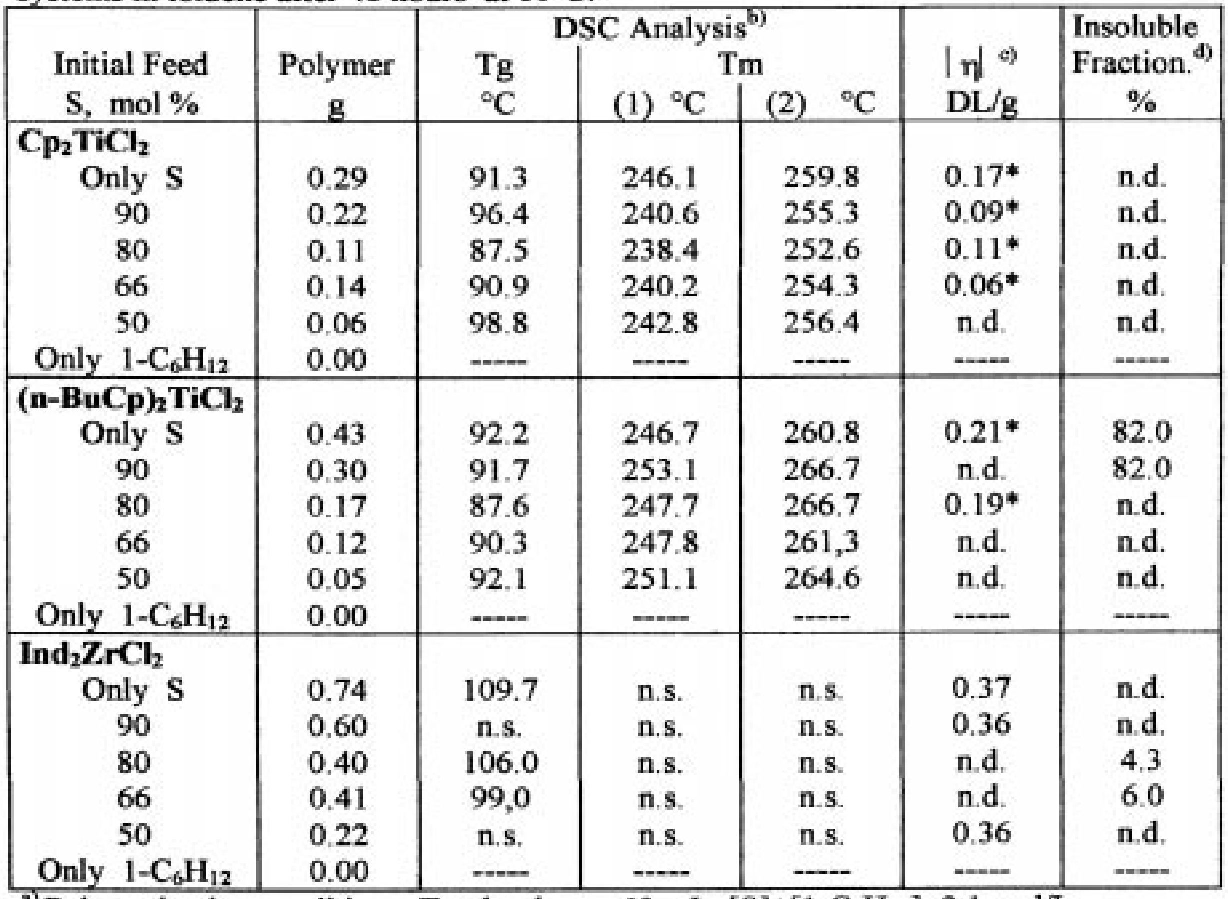
The NMR spectra of samples soluble at room temperature were recorded on a Bruker Avance DRX-300 spectrometer operating at 300.13 MHz. Polymers were dissolved in deuterated chloroform and the chemical shifts calibrated to tetramethylsilane (TMS) used as internal reference.

Results and discussion

The copolymerization of styrene with 1-alkene (1-hexene, 1-decene, and 1-hexadecene) has been attempted with Ph_2Zn-metallocene-MAO systems and also with metallocene-MAO systems. The metallocenes employed were: Ind_2ZrCl_2, Cp_2TiCl_2, $(n\text{-}BuCp)_2TiCl_2$, and $CpTiCl_3$.

In our work of styrene homopolymerization using Ph_2Zn-metallocene-MAO initiator systems we have established that titanocene produces almost pure syndiotactic polystyrene while zirconocene produces mainly atactic PS with some s-PS content (2-

Table 1 : Styrene/1-hexene copolymerization initiated by Ph_2Zn-Metallocene-MAO systems in toluene after 48 hours at 60°C.[a]



Initial Feed S, mol %	Polymer g	DSC Analysis[b] Tg °C	Tm (1) °C	Tm (2) °C	$\lvert\eta\rvert$ [c] DL/g	Insoluble Fraction.[d] %
Cp_2TiCl_2						
Only S	0.29	91.3	246.1	259.8	0.17*	n.d.
90	0.22	96.4	240.6	255.3	0.09*	n.d.
80	0.11	87.5	238.4	252.6	0.11*	n.d.
66	0.14	90.9	240.2	254.3	0.06*	n.d.
50	0.06	98.8	242.8	256.4	n.d.	n.d.
Only 1-C_6H_{12}	0.00	-----	-----	-----	-----	-----
$(n\text{-}BuCp)_2TiCl_2$						
Only S	0.43	92.2	246.7	260.8	0.21*	82.0
90	0.30	91.7	253.1	266.7	n.d.	82.0
80	0.17	87.6	247.7	266.7	0.19*	n.d.
66	0.12	90.3	247.8	261,3	n.d.	n.d.
50	0.05	92.1	251.1	264.6	n.d.	n.d.
Only 1-C_6H_{12}	0.00	-----	-----	-----	-----	-----
Ind_2ZrCl_2						
Only S	0.74	109.7	n.s.	n.s.	0.37	n.d.
90	0,60	n.s.	n.s.	n.s.	0.36	n.d.
80	0.40	106.0	n.s.	n.s.	n.d.	4.3
66	0.41	99,0	n.s.	n.s.	n.d.	6.0
50	0.22	n.s.	n.s.	n.s.	0.36	n.d.
Only 1-C_6H_{12}	0.00	-----	-----	-----	-----	-----

[a] Polymerization conditions: Total volume=60 mL, $[S]+[1\text{-}C_6H_{12}]=2.1$ mol/L, $[Al]=0.33$ mol/L, $[Ph_2Zn]=[Met]=2.0E\text{-}04$ mol/L

[b] Second heating, crude polymer.

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

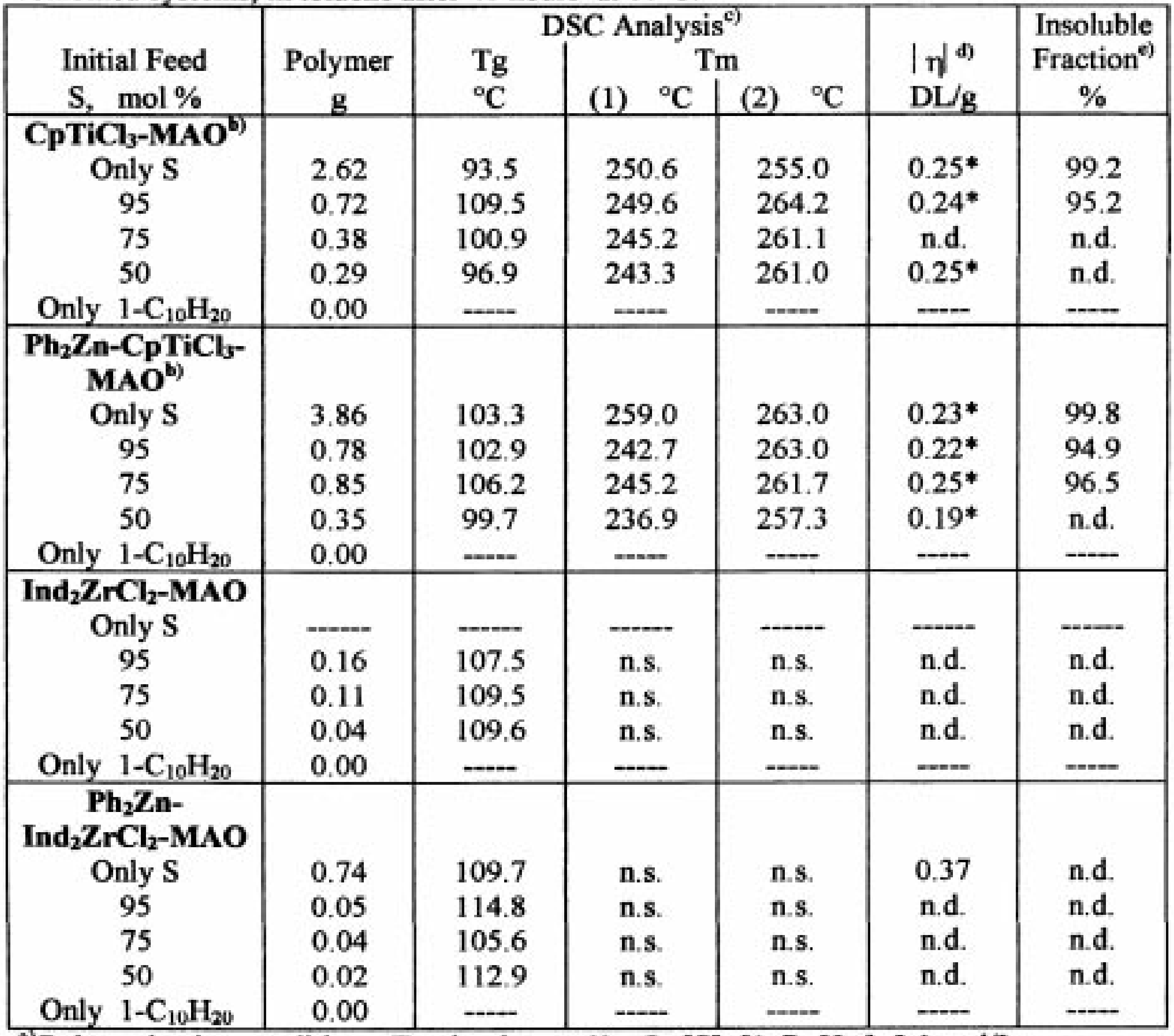
[d] Boiling butanone insoluble polymer.

n.d. = not determined; n.s. = no signal

4). However, we have not yet established the exact role of Ph_2Zn. We have postulated that Ph_2Zn favors the formation of Ti^{+3} species by reduction of Ti^{+4} species (14, 15). It is known that complexes of Ti^{+3} are the active species responsible for stereoregular polymerization of styrene, and more precisely for syndiotactic polystyrene (18). Conversely, the largest amounts of polymer for styrene polymerization were obtained when Ph_2Zn was included as can be noted from the results in Tables 2 and 3, when using initiator systems with and without Ph_2Zn. The results also indicate that the polymer obtained is practically pure s-PS.

Polymerization were carried out in toluene at 60°C during 48 hours, except for metallocene $CpTiCl_3$, with which only a 6 hours polymerization was performed. The experimental results are summarized in Tables 1 through 3.

Table 2 : Styrene/1-decene copolymerization initiated by Ph_2Zn, Metallocene, MAO combined systems, in toluene after 48 hours at 60°C.*



Initial Feed S, mol %	Polymer g	DSC Analysis[c)] Tg °C	Tm (1) °C	Tm (2) °C	$\lvert\eta\rvert$ [d)] DL/g	Insoluble Fraction[e)] %
$CpTiCl_3$-MAO[b)]						
Only S	2.62	93.5	250.6	255.0	0.25*	99.2
95	0.72	109.5	249.6	264.2	0.24*	95.2
75	0.38	100.9	245.2	261.1	n.d.	n.d.
50	0.29	96.9	243.3	261.0	0.25*	n.d.
Only $1\text{-}C_{10}H_{20}$	0.00	-----	-----	-----	-----	-----
Ph_2Zn-$CpTiCl_3$-MAO[b)]						
Only S	3.86	103.3	259.0	263.0	0.23*	99.8
95	0.78	102.9	242.7	263.0	0.22*	94.9
75	0.85	106.2	245.2	261.7	0.25*	96.5
50	0.35	99.7	236.9	257.3	0.19*	n.d.
Only $1\text{-}C_{10}H_{20}$	0.00	-----	-----	-----	-----	-----
Ind_2ZrCl_2-MAO						
Only S	------	------	------	------	------	------
95	0.16	107.5	n.s.	n.s.	n.d.	n.d.
75	0.11	109.5	n.s.	n.s.	n.d.	n.d.
50	0.04	109.6	n.s.	n.s.	n.d.	n.d.
Only $1\text{-}C_{10}H_{20}$	0.00	-----	-----	-----	-----	-----
Ph_2Zn-Ind_2ZrCl_2-MAO						
Only S	0.74	109.7	n.s.	n.s.	0.37	n.d.
95	0.05	114.8	n.s.	n.s.	n.d.	n.d.
75	0.04	105.6	n.s.	n.s.	n.d.	n.d.
50	0.02	112.9	n.s.	n.s.	n.d.	n.d.
Only $1\text{-}C_{10}H_{20}$	0.00	-----	-----	-----	-----	-----

[a)] Polymerization conditions: Total volume=60 mL, $[S]+[1\text{-}C_{10}H_{20}]=2.1$ mol/L, $[Al]=0.33$ mol/L, $[Ph_2Zn]=[Met]=2.0E\text{-}04$ mol/L

[b)] Only 6 hours polymerization.

[c)] Second heating, crude polymer.

[d)] Measured in chloroform at 25°C. * Measured in o-dichlorobenzene at 135°C.

[e)] Boiling butanone insoluble polymer.

n.d. = not determined; n.s. = no signal

Table 1 shows the results obtained for S/1-hexene copolymerization using Ph_2Zn-metallocene-MAO systems for various S/1-hexene molar ratios in the initial feed. Runs including only one of the monomers were carried out to compare them with the copolymerizations. For homopolymerization with 1-alkene no polymer was obtained, but an oily fraction was separated as the polymerization product. According to H-

Table 3: Styrene/1-hexadecene copolymerization initiated by Ph_2Zn, Metallocene, MAO combined systems in toluene after 48 hours at 60°C.[a]

Initial Feed S, mole %	Polymer g	DSC Analysis[c)] Tg °C	Tm (1) °C	Tm (2) °C	$\lvert\eta\rvert$ [d)] dL/g	Insoluble Fraction %
$CpTiCl_3$-MAO[b)]						
Only S	2.63	93.5	250.8	255.0	0.25*	99.2
95	0.86	87.5	246.4	253.5	0.25*	85.9
60	1.10	63.1	235.5	235.5	0.13*	88.8
50	1.65	70.8	238.1	238.1	0.10*	81.9
25	2.20	n.s	236.9	236.9	0.03*	95.3
Only $1\text{-}C_{16}H_{32}$	0.00	-----	-----	-----	-----	-----
Ph_2Zn-$CpTiCl_3$-MAO[b)]						
Only S	3.86	103.3	259.0	263.0	0.23*	99.8
95	1.07	90.9	250.9	257.2	0.20*	99.5
60	-----	-----	-----	-----	-----	-----
50	0.69	98.0	256.0	260.4	0.21*	96.8
25	-----	-----	-----	-----	-----	-----
Only $1\text{-}C_{16}H_{32}$	0.00	-----	-----	-----	-----	-----
Ph_2Zn-$(n\text{-}BuCp)_2TiCl_2$-MAO						
Only S	0.43	86.0	235.7	249.3	0.08*	44.0
95	-----	-----	-----	-----	-----	-----
60	0.56	n.s.	241.2	252.0	0.04*	79.5
50	1.70	n.s.	239.5	251.0	0.03*	92.6
25	1.66	n.s.	n.s.	n.s.	n.d.	98.9
Only $1\text{-}C_{16}H_{32}$	0.00	-----	-----	-----	-----	-----
Ph_2Zn-Ind_2ZrCl_2-MAO						
Only S	0.74	109.7	n.s.	n.s.	0.37	n.d.
95	-----	-----	-----	-----	-----	-----
60	0.47	100.6	n.s.	n.s.	0.64	n.d.
50	0.49	n.d.	n.d.	n.d.	n.d.	n.d.
25	0.64	n.d.	n.d.	n.d.	n.d.	n.d.
Only $1\text{-}C_{16}H_{32}$	0.00	-----	-----	-----	-----	-----

[a)] Polymerization conditions: Total volume=60 mL, $[S]+[1\text{-}C_{16}H_{32}]=2.1$ mol/L, $[Al]=0.33$ mol/L, $[Ph_2Zn]=[Met]=2.0E\text{-}04$ mol/L

[b)] Only 6 hours polymerization.

[c)] Second heating, crude polymer.

[d)] Measured in chloroforn at 25°C. * Measured in o-dichlorobenzene at 135°C.

[e)] Boiling butanone insoluble polymer.

n.d. = not determined; n.s. = no signal

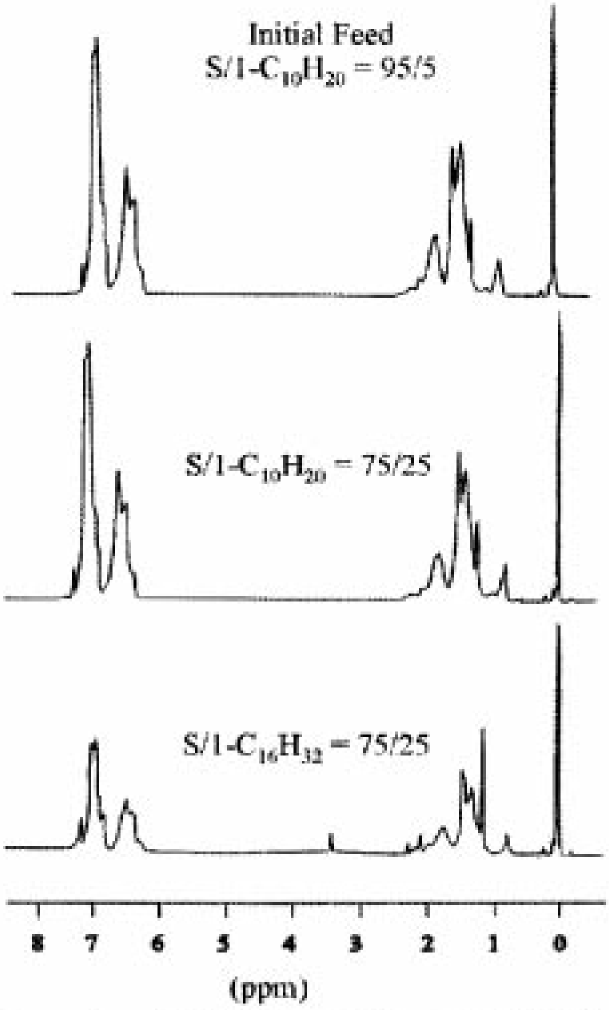


Figure 1. ^{1}H-NMR in $CDCl_3$ at 25°C of S/1-$C_{10}H_{20}$ and S/1-$C_{16}H_{32}$ copolymers obtained using Ph_2Zn-Ind_2ZrCl_2-MAO system.

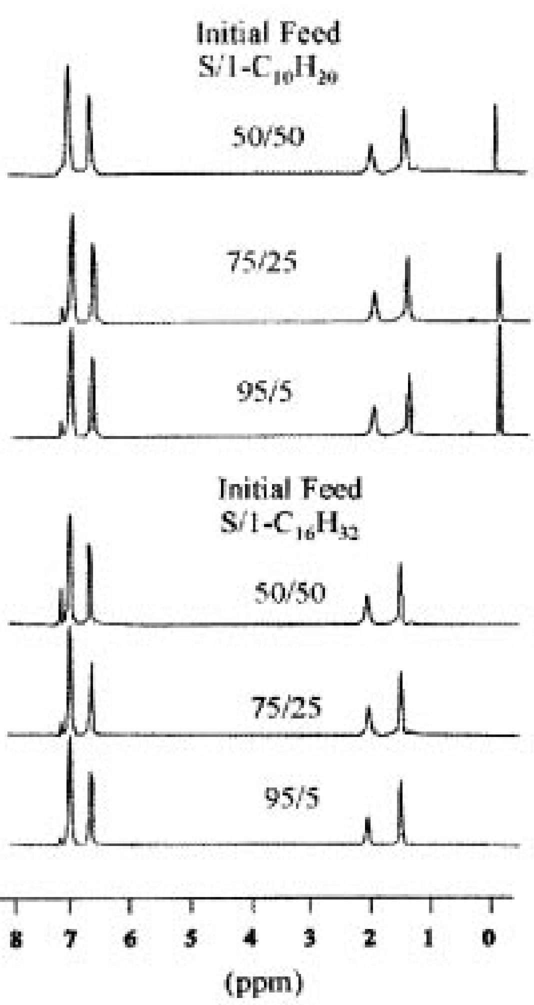


Figure 2. ^{1}H-NMR in C_6D_6 at 70°C of S/1-$C_{10}H_{20}$ and S/1-$C_{16}H_{32}$ polymerization products obtained using Ph_2Zn-$CpTiCl_3$-MAO system.

NMR analysis, it turned to be the corresponding monomer. From results in Table 1, it can be seen that the larger amounts of polymer are obtained when using the metallocene Ind_2ZrCl_2.

On the other hand, the polymer produced when using a titanocene, Cp_2TiCl_2 or $(n\text{-}BuCp)_2TiCl_2$, showed a crystalline melting temperature, Tm, in the range of syndiotactic polystyrene. No Tm was detected for polymer obtained when using Ind_2ZrCl_2.

Table 2, shows the results obtained for S/1-decene copolymerization using Ph_2Zn-metallocene-MAO systems, this time using metallocenes Ind_2ZrCl_2 and $CpTiCl_3$. The same as in the case of 1-hexene with Ind_2ZrCl_2, the polymer obtained did not show any Tm signal, indicating the absence of a stereoregular polymer, while DSC analysis of the polymers obtained using Ph_2Zn-$CpTiCl_3$-MAO and $CpTiCl_3$-MAO systems showed Tm(s) in the s-PS range, independently of S/1-$C_{10}H_{20}$ molar ratio employed in the initial feed. These results confirmed the ability of such systems for producing stereoregular polymers. Furthermore the conversion achieved for homopolymerization was almost four to five times greater than that obtained when there was a small percentage (ca. 5%), of the α-olefin present. Another result to point out is that titanocenes produced a large amount of polymer insoluble in boiling-butanone.

The results for S/1-hexadecene copolymerization using Ph_2Zn-metallocene-MAO systems for metallocenes: $CpTiCl_3$, $(n\text{-}BuCp)_2TiCl_2$ and Ind_2ZrCl_2, are presented in Table 3. As was the case with the other 1-alkenes, the $CpTiCl_3$ produced the larger amount of polymer, increased when Ph_2Zn was also included, and a very high percentage of boiling-butanone insoluble polymer, pointing to the stereoregularity of the product. For zirconocene, Ind_2ZrCl_2, again polymerization occurred but not sign of crystalline melting temperature was detected.

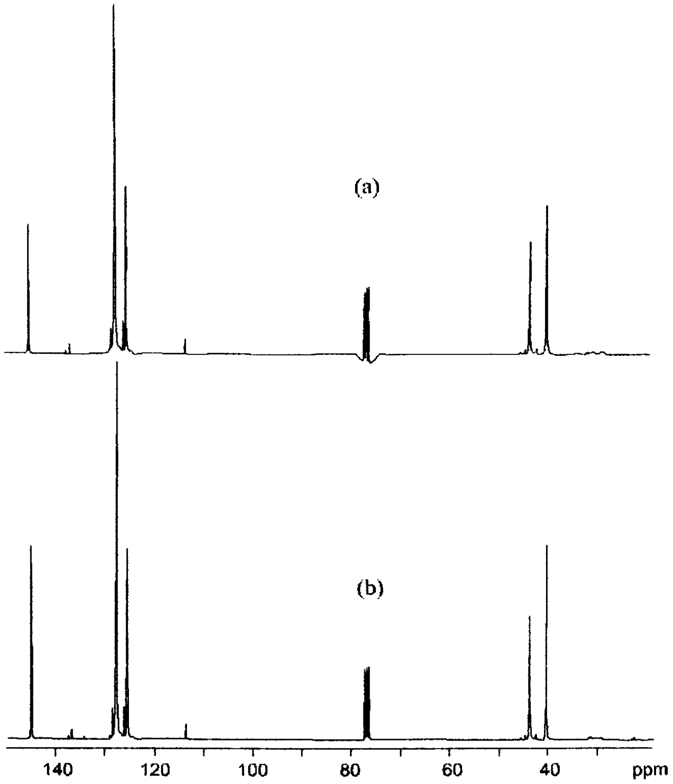


Figure 3. ^{13}C-NMR of $S/C_{10}H_{20}$ polymerization products obtained using: (a) Ph_2Zn-$CpTiCl_3$-MAO and (b) $CpTiCl_3$-MAO initiator system. Initial Feed: $S/1\text{-}C_{10}H_{20}$ = 75/25.

The polymerization products obtained using Ph_2Zn-metallocene-MAO initiator systems including metallocenes $CpTiCl_3$ and Ind_2ZrCl_2 were analyzed by ^1H-NMR and ^{13}C-NMR spectroscopy. Figure 1, shows the ^1H-NMR spectra of products obtained using Ph_2Zn-Ind_2ZrCl_2-MAO to polymerize the $S/1\text{-}C_{10}H_{20}$ mixture and the $S/1\text{-}C_{16}H_{32}$ mixture. The resulting spectra show similar patterns and indicate the presence of both, the units resulting from styrene and from the 1-alkene incorporation. The DSC thermograms show only one Tg signal indicating the presence of a single product, allowing us to conclude that they are true S/1-alkene copolymers. Furthermore, the H-NMR spectra (Fig. 1) do not show any signal in the H-vinyl region indicating the absence of any non-polymerized remaining alkene. Together with that, and taking into account the signal at ca. δ 0.9 ppm, corresponding to CH_3-groups, we concluded that these products are respectively copolymers of $S/1\text{-}C_{10}H_{20}$ and $S/1\text{-}C_{16}H_{32}$. Copolymer compositions were calculated by integration of the ^1H-NMR signals corresponding to CH, CH_2 and C_6H_5 protons. Table 4, shows the copolymer compositions.

For polymerization products of S/1-alkene initiated by Ph_2Zn-titanocene-MAO

Table 4. Copolymer composition calculated from ^{1}H-NMR data (Figure 1).

Copolymer	Initial Feed S/1-alkene mol/mol	Crude Copolymer	
		S units % mol	1-alkene units % mol
S/1-$C_{10}H_{20}$	95/5	95.5	4.5
S/1-$C_{10}H_{20}$	75/25	93.7	6.3
S/1-$C_{16}H_{32}$	75/25	89.1	10.9

systems neither the ^{1}H-NMR (Fig. 2) nor the ^{13}C-NMR (Fig. 3) spectra showed a copolymer nature but only signals corresponding to s-PS. Figure 2, shows the ^{1}H-NMR spectra of the products obtained using Ph_2Zn-$CpTiCl_3$-MAO to polymerize the S/1-$C_{10}H_{20}$ mixture and the S/1-$C_{16}H_{32}$ mixture. Figure 3, shows the ^{13}C-NMR spectra of the products obtained.

We can conclude that Ph_2Zn-metallocene-MAO performs differently as compared to styrene/1-alkene copolymerization. Titanocenes produce almost pure s-PS, while Ind_2ZrCl_2 gave copolymers whose composition which is enriched in styrene with respect to composition of the mixture in the feed.

Further work is under development from which conclusive results are expected.

Acknowledgements

Financial support by the Departamento de Investigaciones Científicas y Tecnológicas, Universidad de Santiago de Chile, DICYT-USACH, Grant 05-9741-RC, and by the Fondo Nacional de Desarrollo Científico y Tecnológico,FONDECYT, Grant 198-1135 is gratefully acknowledged. We thank Witco, for donation of MAO. We thank Prof. Sebastián Muñoz-Guerra, from Universidat Politècnica de Catalunya, Barcelona, Spain, and Prof. Griselda Barrera-Galland from Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil, for the NMR measurements and to Miss Ana M. Cavieres for the DSC measurements and her skillful assistance in experimental work..

References

1) F.M. Rabagliati, R. Quijada, M.V.Cuevas, C. Terraza, Polym. Bull. **37,** 13 (1996).
2) F.M. Rabagliati, C.A. Terraza, R. Quijada, Intern. J. Polymeric. Mater., **34,** 163 (1996).
3) F.M. Rabagliati, M. Pérez, H.A. Ayal, C. Terraza, R. Quijada, Polym. Bull., **39,** 693 (1997)
4) F.M. Rabagliati, M.A. Pérez, R. Quijada, Polym. Bull., **41,** 441 (1998).
5) F.M. Rabagliati, M. Pérez, R. Cancino, R. Quijada, Polym. Int. **48,** 681 (1999).
6) P. Longo, A. Grassi, L. Oliva, Makromol. Chem., **191,** 2387 (1990).
7) V. Venditto, G. De Tullio, L. Izzo, L. Oliva, Macromolecules **31,** 4027 (1998).
8) P.Aaltonen, J. Seppälä, a) Eur. Polym. J., **30,** 683 (1994); b) Eur. Polym. J., **31,** 79 (1995).
9) P.Aaltonen, J. Seppälä, L. Matilainen, M. Leskelä, Macromolecules, **27,** 3136 (1994).
10) a) L. Oliva, L. Izzo, P. Longo, Macromol. Rapid Commun. **17,** 745 (1996);
b) L. Oliva, P. Longo, L. Izzo, Macromolecules **30,** 5616 (1997).
11) J. Ren, G.L. Hatfield, Macromolecules, **28,** 2588 (1995).
12) G. Xu, S. Lin, Macromolecules, **30,** 685 (1997).
13) Q. Wu, Z. Ye, Q. Gao, S. Lin, Macromol. Chem. Phys., **199,** 1715 (1998).
14) F.M. Rabagliati, M.A. Pérez, R.A. Cancino, M.A. Soto, F.J. Rodríguez, A.G. León, H.A. Ayal, R. Quijada, Bol. Soc. Chil. Quím. **45,** 219 (2000).
15) F.M. Rabagliati, M.A. Pérez, M.A. Soto, A. Matínez de Ilarduya, S. Muñoz-Guerra, Eur. Polym. J., **37,** 1001 (2001).
16) O.F. Solomon, B.S. Gotesman, Macromol. Chem., **104,** 177 (1967).
17) J. Brandrup, E.H. Immergut, Polymer Handbook, 2nd ed., New York: Wiley Interscience, p. iv-17 (1975).
18) A. Zambelli, C. Pellecchia, L. Oliva, P. Longo, A. Grassi, Makromol. Chem. , **192,** 223 (1991). A. Zambelli, C. Pellecchia, L. Oliva, Macromol. Symp., **48/49,** 297 (1991).