Homo- and Copolymerization of Styrene Using Combined Diphenylzinc-Additive Initiator Systems

Franco M. Rabagliati, Mónica A. Pérez, Rodrigo A. Cancino,*
Francisco J. Rodríguez, Carlos J. Caro

Grupo Polímeros, Departamento Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile
E-mail: frabagli@lauca.usach.cl

Summary: Combined systems including diphenylzinc, Ph_2Zn, a metallocene, and methylaluminoxane, MAO, have been employed to initiate styrene polymerization and the copolymerization of styrene with p-alkylsubstituted styrenes and 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. S/1-alkene copolymers were obtained when the initiator systems included a zirconocene, but not when a titanocene participated.

Keywords: diphenylzinc; metallocene catalysts; styrene polymerization; tacticity

Introduction

In 1986 Ishihara[1,2] and at about the same time Pellecchia et al.[3,4] reported the synthesis of syndiotactic polystyrene, s-PS, which has a fast rate of crystallization, a Tm of 270°C, and high resistance to organic solvents. Since then many papers have been published regarding s-PS synthesis, using methylaluminoxane-based catalysts including a metallocene.[5-10] The focus has been centered on the improvements of syndioselectivity and catalytic activity with structural modifications of the catalyst.[7-10] Zambelli et al.[11] have studied styrene polymerization and postulated that Ti^{3+} is responsible for syndiotacticity when styrene is polymerized using titanocene/MAO initiator systems.

Copolymerization of styrene with substituted styrenes[5,12] and of styrene with 1-alkene[13,14] have also been extensively studied. Oliva et al.,[15] working with $Et(Ind)_2ZrCl_2$/MAO systems reported that an almost alternating stereoregular copolymer can be obtained.

We have been working on both homo- and copolymerization of S,[16-24] using combined diphenylzinc-additive initiator systems including Ph_2Zn, a metallocene and MAO. We have

CCC 1022-1360/00/$ 17,50+.50/0

investigated the binary and ternary combinations and concluded that these systems are effective initiators for the homo- and copolymerization of styrene. The effectiveness depends on the metallocene, the comonomer, the temperature and the styrene/comonomer molar ratio in the initial feed.

This paper reports the results obtained for the homopolymerization of styrene and substituted styrenes, and the copolymerization of styrene with substituted styrenes and of styrene with 1-alkenes.

Results and Discussion

In our work on homo- and copolymerization of styrene using combined diphenylzinc, Ph_2Zn, additive systems, various binary and ternary combinations were used, including Ph_2Zn, a metallocene -either a titanocene or a zirconocene- and methylaluminoxane, MAO. Table 1 shows some of our results when using Ph_2Zn-metallocene-MAO ternary initiator systems. The results show that both titanocenes and zirconocenes induce styrene polymerization. Titanocenes led to highly syndiotactic polystyrene, s-PS, while the use of a zirconocene resulted mainly in atactic polystyrene, a-PS. Anyhow, from the polystyrene obtained using a zirconocene it was possible in most cases to extract a certain content of a boiling-butanone-insoluble fraction, which was found to be s-PS according to its NMR-spectra. DSC analysis of insoluble PS confirms the syndiotactic assessment for the boiling-butanone-insoluble PS.

From the results in Table 1 it is clear that the system including $CpTiCl_3$ was the most active initiator for styrene polymerization, with 45.70 % conversion in only 6 hours

Table 1. Polymerization of styrene using various initiator systems in toluene after 48 hours at 60°C.$^{a)}$

Initiator System	Polymer Convn.$^{b)}$	$\lvert\eta\rvert^{c)}$ dL/g	M_v $*10^{-5}$	Tg °C	Tm(1) °C	Tm(2)	Insol. Fractn^{d}
Ph_2Zn	0.53	2.13	7.25	108.9	n.s.	n.s.	n.d.
Ph_2Zn-MAO	8.60	0.21	0.31	99.2	n.s.	n.s.	n.d.
Ph_2Zn-Cp_2ZrCl_2-MAO	1.04	0.17	0.23	n.d.	----	----	n.d.
Ph_2Zn-Ind_2ZrCl_2-MAO	8.30	0.19	0.37	102.9	n.s.	n.s.	15.6
Ph_2Zn-$(H_4$-$Ind)_2ZrCl_2$-MAO	2,06	0,09	0,09	n.d.	-----	-----	n.d.
Ph_2Zn-$(Bu^iCp)_2ZrCl_2$-MAO	2.68	0.14	0.17	n.d.	-----	-----	n.d.
Ph_2Zn-$Pr^i(Flu)(Cp)ZrCl_2$-	8.46	0.10	0.11	n.d.	-----	-----	n.d.
Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO	3.29	0.12	0.15	n.d.	-----	.....	13.8

Table 1. continued Polymerization of styrene using various initiator systems in toluene after 48 hours at 60°C.[a)]

Ph_2Zn-Cp_2TiCl_2-MAO		9.44	0.28*	----	89.0	241.4	256.6	58.3
Ph_2Zn-(n-BuCp)$_2TiCl_2$-		7.11	0.20*	----	97.4	249.4	266.0	91.7
Ph_2Zn-$CpTiCl_3$-MAO	(6	45.70	0.23*	----	101.1	259.0	263.0	99.8

---

a) Polymerization conditions: Total volume = 60 mL, [S] = 2.1 mol/L, [MAO] = 0.33 mol/L, [Ph_2Zn] = [Metallocene] = 2.0E-04 mol/L.

b) Based on initial styrene.

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

d) Boiling-butanone-insoluble PS

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

of polymerization. Furthermore, it was also the one that produced almost pure s-PS, 99.8% of the boiling-butanone-insoluble fraction. The binary $CpTiCl_3$-MAO system was also a very effective initiator for styrene polymerization: 30.4% conversion after 6 hours of polymerization, and 99.8% of the boiling-butanone-insoluble fraction.

Various para-substituted styrenes have been polymerized by $CpTiCl_3$-MAO and Ph_2Zn-$CpTiCl_3$-MAO initiator systems. As seen in Figure 1, conversion to polymer increases with the +I effect of the substituent, pointing to the higher electron availability of the π-electrons at the C=C double bond of the monomers, which facilitates coordination of the monomer to the initiator active species and the subsequent insertion in the growing polymer chain. On the other hand, the inclusion of Ph_2Zn in the initiator system led to increased conversion when compared with the $CpTiCl_3$-MAO binary system. p-Methoxystyrene behaves differently, since there was no such increase in conversion

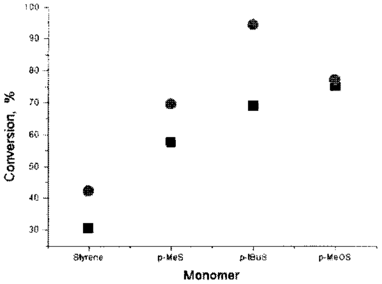

Figure 1. Homopolymerization of styrene and of p-substituted styrene in toluene after 6 hours at 60 °C using $CpTiCl_3$-MAO (■) and Ph_2Zn-$CpTiCl_3$-MAO (•) initiator systems.

when the system included Ph_2Zn. We think this may be due to an early coordination between the oxygen atom of MeOS and the zinc atom of diphenylzinc. It is known that Ph_2Zn has the capacity to form dietherates.[25] Ph_2Zn could be trapped by p-MeOS and consequently, and under these circumstances, should have a very low effect or none at all on the initiator system.

Table 2. Homopolymerization of styrene and some substituted styrenes in toluene after 6 hours at 60 °C using the Ph_2Zn-$CpTiCl_3$-MAO initiator system.a)

Monomer	Monomer Amount mol	Polymer Yield g	Relative Reactivitiesb)
S	0,0862	3,62	1,0
p-MeS	0,0607	4,16	1,6
p-Bu^{t}S	0,0841	12,69	3,6
p-MeOS	0,0196	1,99	2,4
p-ClSb)	0,0250	0,15	0,14

a) Polymerization. Conditions: [monomer] = 2.0 mol/L, MAO] = 0.33 mol/L, $[Ph_2Zn] = [CpTiCl_3]$ = 2.0E-04 mol/L.

b) The reactivities are referred to that of S arbitrarily defined as equal to 1.

Table 2, reports the results of a series of homopolymerizations of para substituted styrene monomers compared with styrene homopolymerization. Substituted styrenes including electron-donor substituents largely improved the efficiency of the polymerization process regarding styrene polymerization. For p-chlorostyrene polymerization a very low conversionwas achieved, in agreement with electron-withdrawing character of chlorine. On the other hand, lower conversions to polymer were obtained when a zirconocene such as Ind_2ZrCl_2, or $Et(Ind)_2ZrCl_2$ was used instead of $CpTiCl_3$. Yet for these zirconocenes the pattern of substituent inductive effect is maintained, with conversion increasing in the order S < p-MeS < p-Bu^{t}S.

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

Initial	$CpTiCl_3$			$IndTiCl_3$			$IndZrCl_2$			$Et(Ind)_2ZrCl_2$		
S/p-MeS	Yield	Act.[b)]	Tg	Yield	Act.[b)]	Tg	Yield	Act.[b)]	Tg	Yield	Act.[b)]	Tg
Mol/mol	g		°C	G		°C	g		°C	g		°C
95/5	2.10	1361	95.1	0.13	90.2	98.8	0.26	170.2	106.7	0.19	121.7	100.7
75/25	2.40	1578	98.5	0.17	110.4	101.5	0.28	180.6	111.0	0.23	150.6	107.0
50/50	2.35	1521	100.9	0.18	122.8	105.4	0.33	217.2	114.1	0.38	250.2	109.5
25/75	3.36	2220	103.9	0.29	193.7	107.6	0.50	321.7	117.3	0.40	262.1	112.8
5/95	3.59	2355	102.6	0.57	384.5	107.4	n.p.	-----	-----	0.44	286.1	114.8

[a)] Polymerization conditions: Total volume = 25 mL; [S] + [p-MeS] = 2.0 mol/L; [MAO] = 0.33 mol/L, $[Ph_2Zn]$ = [Metallocene] = 2.0E-04 mol/L

[b)] Activity = Kg Copolymer/[mol met*(mol S + mol p-MeS)*h]

n.p. = not performed.

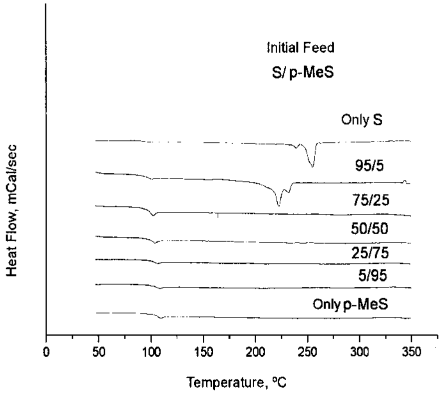

Figure 2. DSC thermograms of copolymers S/p-MeS obtained using Ph_2Zn-$CpTiCl_3$-MAO initiator system, in toluene after 6 hours at 60°C. For various S/p-MeS mol/mol ratios in the initial feed.

Styrene polymerization initiated by Ph_2Zn-metallocene-MAO systems, with Cp_2TiCl_2, $(n\text{-}BuCp)_2TiCl_2$, and Ind_2ZrCl_2 as metallocenes, is greatly affected by the polarity of the reaction medium, and there is a noticeable increase in conversion to polymer when the solvent is changed from toluene to dichlorobenzene, in agreement with an ionic pathway for polymer propagation.[18]

Studies have been made of styrene/p-substituted styrene (Table 3) and styrene/α-olefin copolymerization.[19-24] Ph_2Zn-titanocene-MAO initiator systems produced truly S/p-substituted styrene copolymers, with conversion to polymer increasing as the proportion of p- alkylstyrene increases in the initial feed.[20,22,24] Both $CpTiCl_3$-MAO and Ph_2Zn-$CpTiCl_3$- MAO initiator systems did not produce any S/α-olefin copolymer but only s-PS.[20,21,24] On the other hand, Ph_2Zn-zirconocene-MAO initiator systems were able to copolymerize S/α-olefin, with conversion depending largely on the zirconocene and on the α-olefin.[21,24]

Figure 2 includes the DSC thermograms of a series of S/p-MeS copolymers obtained using the Ph_2Zn-$CpTiCl_3$-MAO initiator system, showing a crystalline melting signal for runs of S-only and for S/p-MeS = 95/5. The Tm of S/p-MeS = 95/5 copolymer is 38 °C lower than that of s-PS. A similar situation was recently pointed out by Schwecke and Kaminsky for copolymerization of S/alkylstyrenes initiated by the $CpTiF_3$/MAO system.[7] They point out the situation of having a polymer with the characteristic of s-PS and at the same time a material easier to process than s-PS.

Experiments for S/p-MeS and for S/p-Bu^{t}S copolymerization using both $CpTiCl_3$-MAO and Ph_2Zn-$CpTiCl_3$-MAO and various solvents from toluene to dichlorobenzene, as was the case for homopolymerization, showed a significant increase in conversion as the polarity of the reaction medium increased.[23]

Binary and ternary combined systems including Ph_2Zn, a zirconocene, Ind_2ZrCl_2 or $Et(Ind)_2ZrCl_2$, and MAO, were used to copolymerize syrene with α-olefins, including 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-hexadecene and 1-octadecene. Conversion to copolymer depends largely on the zirconocene included in the initiator system and on the α- olefin. Table 4 shows the results obtained when using Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO initiator system in S/1-alkene = 75/25 for the copolymerization with the α-olefins 1-decene, 1-hexadecene and 1-octadecene.

The ^{1}H-NMR of products obtained for S/1-decene, S/1-hexadecene and S/1-octadecene copolymerization using Ph_2Zn-$Et(Ind)_2ZrCl_2$-MAO initiator systems as shown in Table 4 showed the signals corresponding to both styrene and 1-alkene. In all cases the typical signal at ca. 0.9 ppm is present, showing the presence of the terminal $-CH_3$ groups of each 1-alkene.

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

α-olefin	Yield g	Relative Reactivity[b)]	Tg °C	Tm °C
1-decene	0.060	2.05	81.8	n.s.
1-hexadecene	0.170	1.97	81.2	n.s.
1-octadecene	0.168	2.87	81.8	n.s.

[a)] Polymerization conditions: Total volume = 25 mL; [S] + [p-MeS] = 2.0 mol/L; [MAO] = 0.33 mol/L, [Ph_2Zn] = [$Et(Ind)_2ZrCl_2$] = 2.0E-04 mol/L

[b)] The reactivities are referred to that of S arbitrary defined as equal to 1. n.s. = no signal.

From present and previous results we can conclude that combined systems including diphenylzinc, a metallocene and methylaluminoxane are capable of inducing the polymerization of styrene and p-substituted styrenes. Diphenylzinc contributes to the improvment of the efficiency of the initiator systems, increasing both the activity of the initiator system and the stereoregularity of the PS produced. In the polymerization of p-substituted styrenes, conversion depends largely on the inductive effect of the substituent group. Electron donor groups improved conversion, while electron withdrawing groups decrease conversion as compared to styrene polymerization. Furthermore, increased polarity of the reaction medium increases conversion to the polymer.

In S/p-substituted styrene and of S/α-olefin copolymerization, Ph_2Zn-metallocene-MAO initiator systems behave differently. Those including a titanocene were effective initiators of S/p-substituted styrene copolymerization, while those including a zirconocene were able to induce S/α-olefin copolymerization.

Acknowledgments

Financial support from Universidad de Santiago de Chile, DICYT-USACH, and from the Fondo Nacional de Desarrollo Científico y Tecnológico, FONDECYT, Grant 101-0036, are gratefully acknowledged. The authors also thank Maricel P. Cerda for the DSC measurements.

[1] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi. Macromolecules, **19**, 2464 (1986).

[2] N. Ishihara, M. Kuramoto, M. Uoi, Macromolecules, **21**, 3356 (1988). Rapid Commun. **8**, 277 (1987).

[3] C. Pellecchia, P.Longo, A. Grassi, P. Ammendola, A. Zambelli, Makromol. Chem. Rapid commun **8**, 227 (1987).

[4] P. Ammendola, C. Pellecchia, P. Longo, A. Zambelli, Gazz. Chim. Ital. **117**, 65 (1987).

[5] R. Pó, N. Cardi, Prog. Polym. Sci. **21,** 47 (1996).

[6] W. Kaminsky, Catalalysis Today, **62,** 23 (2000).

[7] C. Schwecke, W. Kaminsky, Macromol. Rapid Commun. **22,** 508 (2001).

[8] T. E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. **Xx,** 21 (1996).

[9] W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, Macromolecules **30,** 7647 (1997).

[10] N. Tomutso, N. Ishihara, T.H. Newman, M.T. Malanga, J. Mol. Cat. A, Chem. **128,** 167 (1998).

[11] A. Zambelli and C. Pellecchia, in "Catalyst Design for Tailor-Made Polyolefins". Kodansha (Tokyo)-Elsevier , K. Soga and M. Terano, Eds., 209 (1994).

[12] K. Soga, H. Nakatani, T. Monoi, Macromolecules, **23,** 953 (1990).

[13] P. Longo, A. Grassi, L. Oliva, Makromol. Chem., **191,** 2387 (1990).

[14] V. Venditto, G. De Tullio, L. Izzo, L. Oliva, Macromolecules, **31,** 4027 (1998).

[15] L. Oliva, P. Longo, L. Izzo, Macromolecules **30,** 5616 (1997).

[16] F.M. Rabagliati, C.A. Terraza, R. Quijada, Intern. J. Polymeric Mater., **34,** 163 (1996).

[17] F.M. Rabagliati, M.A. Pérez, R. Quijada, Polym. Bull., **41,** 441 (1998).

[18] F.M. Rabagliati, M. Pérez, R. Cancino, R. Quijada, Polym. Int. **48,** 681 (1999).

[19] 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).

[20] F.M. Rabagliati, M.A. Pérez, M.A. Soto, A. Matínez de Ilarduya, S. Muñoz-Guerra, Eur. Polym. J., **37,** 1001 (2001).

[21] F.M. Rabagliati, R.A. Cancino, F.J. Rodríguez, Polym. Bull., **46,** 427 (2001).

[22] F.M. Rabagliati, M.A. Pérez, R.A. Cancino, M.A. Soto, F.J. Rodríguez, C.J. Caro, A.G. León, H.A. Ayal, R. Quijada, Macromol. Symp., **168,** 31 (2001).

[23] F.M. Rabagliati, C.J. Caro, M.A. Pérez, Bol. Soc. Chil. Quím. **47,** 137 (2002)

[24] F.M. Rabagliati, M. Pérez, R.A. Cancino, M.A. Soto, F. Rodríguez, C.J. Caro, Macromol. Symp., submitted

[25] G. Allen, J.M. Bruce, F.G. Hutchinson, J. Chem. Soc. 5476 (1965); J.M. Bruce, F.M. Rabagliati, Polymer **8,** 361 (1967).