

Polymerization of styrene by diphenylzinc-additive systems

4. Ph₂Zn-metallocene-MAO systems *

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SUMMARY

Styrene was polymerized using combined systems of diphenylzinc, Ph₂Zn, and metallocene compounds activated by methylaluminoxane, MAO. From the various metallocenes employed bis(indenyl)zirconium dichloride, Ind₂ZrCl₂, [isopropyl(cyclopentadienyl)(1-fluorenyl)]zirconium dichloride, i-Pr(Flu)(Cp)ZrCl₂, and bis(cyclopentadienyl) titanium dichloride, Cp₂TiCl₂, produced the larger amounts of polymer. Ph₂Zn-Cp₂TiCl₂-MAO system gave polystyrene, PSt, whose DSC analysis indicated a major endotherm peak at 256°C. A butanone insoluble fraction of the polymer was separated from the crude PSt. The proportion of insoluble polymer depends on the metallocene employed and on the conversion to polymer.

INTRODUCTION

Since the discovery of Ishihara and co-workers [1] and the early works from the University of Salerno's Group [2,3], several papers have reported on the syndiotactic polymerization of styrene. Most of these workers use combined catalyst systems with methylaluminoxane as the activating ingredient [4-8].

Recently the preparation of ansa-bridged metallocenes of Ti, Zr, and Hf was reported [9]. Some of these metallocenes in the presence of MAO polymerize propene to isotactic polypropene and styrene to syndiotactic polystyrene.

We have been working with combined systems diphenylzinc-cocatalyst, Ph₂Zn-cocat, (where cocat = H₂O [10], butanols [11], butanone [12]) for the polymerization of styrene. A significant dependence of conversion on cocat/Ph₂Zn molar ratio was established.

Recently we studied styrene polymerization using Ph₂Zn-ZnCl₂ and Ph₂Zn-CuCl₂ systems [13]. With ZnCl₂ the crude polymer included a stereoregular polymer fraction which T_m varied accordingly to the ZnCl₂/Ph₂Zn molar ratio employed. At molar ratio equal unity the

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crude polymer included a portion which DSC showed a endothermic peak at 209°C suggesting the presence of isotactic polystyrene, i-PSt. Melting point at 210-220°C has been reported for i-PSt [6]. For molar ratio $ZnCl_2/Ph_2Zn = 0.78$, was separated a fraction which DSC showed the presence of two endothermic peaks centered respectively at 231.4 and at 236.6°C. Telling about the presence of stereoregular PSt.

Continuing with our studies on St polymerization we have performed exploratory experiments including MAO and/or metallocene compounds as initiator systems.

The present communication reports on the polymerization of St in solution initiated by Ph_2Zn , combined with zirconium compounds activated by MAO. For comparison, results of experiments using dicyclopentadienyl-titanium dichloride instead of the zirconocene are included.

EXPERIMENTAL

Polymerizations were carried out under argon atmosphere in a 100 cm³ Schlenk tube equipped with a magnetic stirrer. Solvent toluene (ca., 35 cm³), Ph_2Zn solution, and additive(s) were charged by syringe under pressure of argon. Polymerizations were initiated by injecting the required amount of St. Reactions were maintained with stirring at 60°C.

Polymerization was terminated by adding a mixture of hydrochloric acid and methanol. The polymers, coagulated in acidified methanol, after washing several times with methanol were recovered by filtration and dried in vacuum at 60°C.

The PSt samples were fractionated by exhaustive extraction with boiling butanone.

Intrinsic viscosities, $[\eta]$, of the amorphous polymer and of the butanone soluble fraction, were measured at 25°C in chloroform. Viscosity-average molecular weights, M_v , were calculated according to equation [14]:

$$[\eta] = 1.12 \times 10^{-5} M_v^{0.73}$$

valid for the molecular weight range 7-150x10⁴.

For the butanone insoluble polymer, intrinsic viscosity was measured in 1,2-dichlorobenzene at 135°C.

RESULTS AND DISCUSSION

Table 1 shows the results of St polymerization initiated by the combined systems Ph_2Zn -zirconium compound-MAO. Conversion is much influenced by the nature of the zirconium compound. Ind_2ZrCl_2 produced the largest amount of PSt. The systems including Cp_2TiCl_2 together with Ph_2Zn and MAO produced lower conversions as compared with systems including i-Pr(Flu)(Cp)ZrCl₂ and Ind_2ZrCl_2 . However, Cp_2TiCl_2 is more reactive than its homologue Cp_2ZrCl_2 in concordance with the assessment of Longo et al. [7] establishing

Table 1. Styrene polymerization initiated by Ph_2Zn -Metallocene-MAO system, in toluene solution for 48 hours at $60^\circ\text{C}^{\text{a)}$.

Metallocene	Yield ^{c)}	$[\eta]^{\text{d)}$	M_v	$M_w^{\text{e)}$
	%	$\text{dL}\cdot\text{g}^{-1}$	$\times 10^{-4}$	M_n
$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	3.29	0.12	1.45	1.20
$i\text{-Pr}(\text{Flu})(\text{Cp})\text{ZrCl}_2$	8.46	0.10	1.13	2.81
Cp_2ZrCl_2	1.04	0.17	2.33	1.20
$\text{Ind}_2\text{ZrCl}_2$	9.59	0.13	1.50	1.13
$\text{Cp}_2\text{TiCl}_2^{\text{b)}$	6.68	n.d. ^{f)}	----	n.d. ^{f)}

a) $[\text{MAO}] = 3.28 \times 10^{-1} \text{M}$, $[\text{Zr}] = 2.10 \times 10^{-4} \text{M}$, $[\text{Ph}_2\text{Zn}] = 2.10 \times 10^{-4} \text{M}$, $[\text{St}] = 2.05 \text{M}$.

b) $[\text{MAO}] = 3.37 \times 10^{-1} \text{M}$, $[\text{Ti}] = 1.57 \times 10^{-4} \text{M}$, $[\text{Ph}_2\text{Zn}] = 2.10 \times 10^{-4} \text{M}$, $[\text{S}] = 2.06 \text{M}$.

c) Based on initial styrene.

d) Measured in chloroform at 25°C .

e) SEC, THF room temperature.

f) Not determined, insoluble.

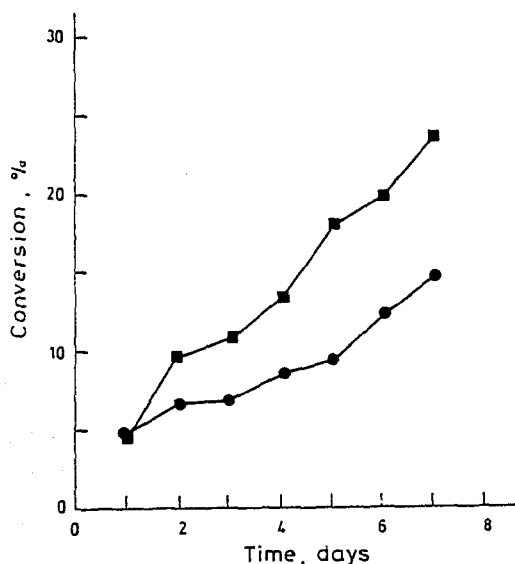


Fig. 1. Polymerization of styrene by Ph_2Zn -Metallocene-MAO systems in toluene at 60°C . (■) Ph_2Zn - $\text{Ind}_2\text{ZrCl}_2$ -MAO; (●) Ph_2Zn - Cp_2TiCl_2 -MAO. $[\text{Zn}] = 2.11 \times 10^{-4} \text{M}$; $[\text{Zr}] = 1.73 \times 10^{-4} \text{M}$; $[\text{Ti}] = 1.57 \times 10^{-4} \text{M}$; $[\text{Al}] = 3.36 \times 10^{-1} \text{M}$; $[\text{St}] = 2.0 \text{M}$.

that Zr based catalysts appear less effective than Ti based catalysts toward St polymerization.

Table 2. Polymerization of styrene initiated by combined systems Ph₂Zn-Metalocene-MAO in toluene at 60°C for 48 hours^{a)}.

Initiator System	[Zn] Mx10 ⁴	[Zr] Mx10 ⁴	[Al] Mx10 ²	Yield ^{b)} %	[η] ^{c)} dlxg ⁻¹	M _v x10 ⁻⁴	Insoluble Fraction ^{d)} %
--/Zr/Al	----	3.49	33.6	9.07	0.08	0.86	13.0
Zn/Zr/Al	2.11	1.75	33.6	9.59	0.125	1.50	7.0
Zn/Zr/--	4.21	3.48	----	0.56	0.70	15.82	n.d. ^{f)}
Zn/Zr/--e)	4.21	3.48	----	0.07	n.d. ^{f)}	----	n.d. ^{f)}
--/Ti/Al	----	4.08	32.9	1.75	n.d. ^{f)}	----	33.0
Zn/Ti/Al	2.09	2.11	33.8	6.68	n.d. ^{f)}	----	68.0
Zn/Ti/--	4.06	4.06	----	2.65	0.755	17.57	1.7
Zn/Ti/--e)	4.06	4.06	----	3.20	0.68	15.26	3.0

a) [St] = 2.0 M; Zn = Ph₂Zn, Zr = Ind₂ZrCl₂, Ti = Cp₂TiCl₂, Al = MAO.

b) Based on initial styrene.

c) Measured in chloroform at 25°C.

d) In boiling butanone.

e) With H₂O, H₂O/Ph₂Zn = 1.

f) Not determined.

Figure 1 shows the progress of St polymerization using $\text{Ind}_2\text{ZrCl}_2$ and Cp_2TiCl_2 systems. Conversion increases with time and the Ph_2ZnCl_2 - $\text{Ind}_2\text{ZrCl}_2$ -MAO system produced the larger amounts of polymer.

Ph_2Zn - Cp_2TiCl_2 -MAO produces PST which does not dissolve in chloroform. Furthermore, after extraction with boiling butanone, a 68 % butanone-insoluble fraction was recovered. Such insoluble PST fractions are considered essentially syndiotactic [15].

Experiment were also performed with Ph_2Zn , and MAO, combined in various ways, with $\text{Ind}_2\text{ZrCl}_2$, and also with Cp_2TiCl_2 [$\text{---}/\text{Ind}_2\text{ZrCl}_2/\text{MAO}$, $\text{Ph}_2\text{Zn}/\text{Ind}_2\text{ZrCl}_2/\text{MAO}$, $\text{Ph}_2\text{Zn}/\text{Ind}_2\text{ZrCl}_2/\text{---}$, $(\text{H}_2\text{O}/\text{Ph}_2\text{Zn})/\text{Ind}_2\text{ZrCl}_2/\text{---}$], and similar combinations with Cp_2TiCl_2 . From the data in Table 2, it is clear that the Ph_2Zn - $\text{Ind}_2\text{ZrCl}_2$ -MAO system produced the largest conversion but the Ph_2Zn - Cp_2TiCl_2 -MAO system gives the largest amount of butanone-insoluble PST. These results show the potential of Ph_2Zn -Metallocene-MAO catalyst systems to obtain syndiotactic-PST.

A similar situation resulted for systems including only metallocene and MAO without Ph_2Zn . The zirconium derivative produced the largest conversion but those with titanium gave the higher amount of butanone-insoluble PST.

Figure 2 shows typical DSC curves for crude polymer obtained using Cp_2TiCl_2 . The heating/cooling rates were $10^\circ\text{C}/\text{min}$. In the

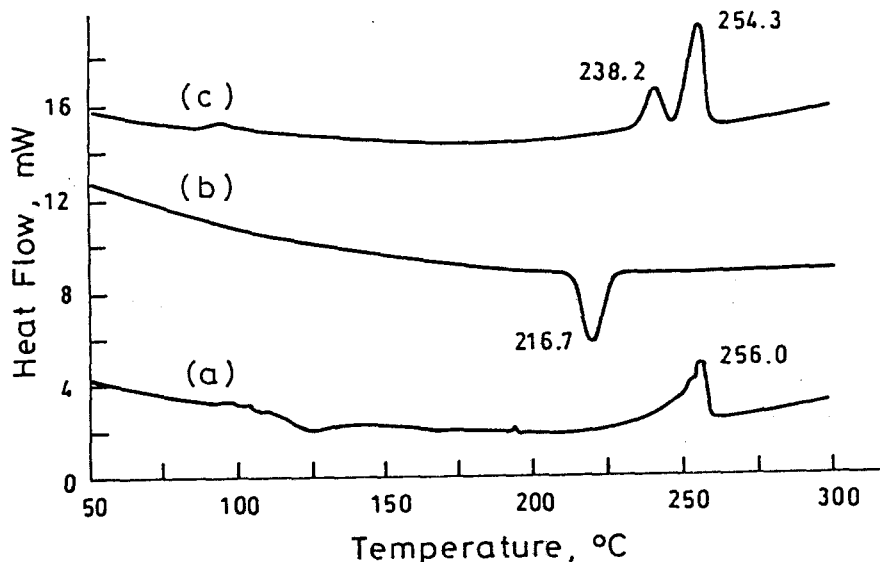


Fig. 2. DSC curves for crude PST obtained using Ph_2Zn - Cp_2TiCl_2 -MAO system. (a) first heating at $10^\circ\text{C}/\text{min}$, (b) cooling scan at $10^\circ\text{C}/\text{min}$, (c) second heating at $10^\circ\text{C}/\text{min}$.

first heating scan, there are two maxima for the major endotherm at 256°C (Fig. 2a), which is very close to the values obtained by Chien and Salajka [16]. They reported, for the first scan, T_m of 259.1, 250.0, and 242.9°C for polymerizations at 45, 75 and 90°C, respectively. Our polymerizations were performed at 60°C.

Only a single exotherm was observed at 216.7°C (Fig. 2b) during the subsequent cooling scan. When the specimen was reheated for the second time, the major endotherm resolved into two melting peaks at 238.2 and 254.3°C, (Fig. 2c). These results indicate the presence of stereoregular polymer which crystallizes in more than one form. Furthermore, these DSC results indicate the presence of syndiotactic-PSt as discussed by Chien et al. [15,16].

In conclusion, we think that our catalyst systems comprizing organozinc compounds together with metallocene and MAO produce initiator systems for syndiotactic St polymerization. Further work with these and other metallocenes, including the complete characterization of the obtained PSTs, are in progress.

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REFERENCES

1. N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, **Macromolecules** **19**, 2464 (1986).
2. C. Pellecchia, P. Longo, A. Grassi, P. Ammendola, A. Zambelli, **Makromol. Chem., Rapid Commun.** **8**, 277 (1987).
3. P. Ammendola, C. Pellecchia, P. Longo, A. Zambelli. **Gazz.Chim. Ital.** **117**, 65 (1987).
4. T. Dall'Occo, F. Sartori, G. Vecellio, U. Zucchini, **Makromol. Chem.** **194**, 151 (1993).
5. A. Kucht, H. Kucht, S. Barry, J.C.W. Chien, M.D. Rausch, **Organometallics** **12**, 3075 (1993).
6. M.L. Dias, A. Giarrusso, L. Porri, **Macromolecules** **26**, 6664 (1993).
7. P. Longo, A. Proto, L. Oliva, **Macromol. Rapid Commun.** **15**, 151 (1994).
8. N. Ishihara, M. Kuramoto, in "**Catalyst Design for Tailor-Made Polyolefins**". Kodansha (Tokyo)-Elsevier, (K.Soga and M. Terano, Eds.), 339 (1994).
9. M.L.H. Green, N. Ishihara, **J. Chem. Soc., Dalton Trans.** 657 (1994).
10. F.M. Rabagliati, C.A. Terraza, **Polym. Bull.**, **28**, 511 (1992).

11. F.M. Rabagliati, C.A. Terraza, L.A. Ramírez, J.M. Contreras, **Macromol. Symp.** **84**, 103 (1994).
12. J.M. Contreras, H.A. Ayal, F.M. Rabagliati, **Polym. Bull.**, **32**, 367 (1994).
13. F.M. Rabagliati, C.A. Terraza, H.A. Ayal, **Bol. Soc. Chil. Quím.**, **40**, 241 (1995).
14. Polymer Handbook; J. Brandrup, E.H. Immergut, Ed., Wiley-Interscience, 2nd edition, 1975, p. IV-17.
15. J.C.W. Chien, Z. Salajka, **J. Polym. Sci., A: Polym. Chem.** **29**, 1243 (1991).
16. J.C.W. Chien, Z. Salajka, **J. Polym. Sci., A: Polym. Chem.** **29**, 1253 (1991).