

Polymerization of styrene by diphenylzinc-additive systems

Part VII: $\text{Ph}_2\text{Zn}-(n\text{-BuCp})_2\text{TiCl}_2\text{-MAO}$ systems^a

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Summary

The polymerization of styrene using the combined system diphenylzinc-bis(*n*-butylcyclopentadienyl)titanium dichloride-methylaluminumoxane, $\text{Ph}_2\text{Zn}-(n\text{-BuCp})_2\text{TiCl}_2\text{-MAO}$, in toluene at 60°C, produced highly syndiotactic polystyrene, confirming that Ph_2Zn -titanocene-MAO are good initiator systems for the stereoregular polymerization of styrene. The syndiotacticity of PS was established by its insolubility in chloroform, benzene or toluene, and after continuous extraction in boiling butanone. DSC analysis showed endotherm signals corresponding to the melting temperature, T_m , of syndiotactic polystyrene.

Introduction

In previous papers we have informed about the polymerization of styrene, S, using combined diphenylzinc-additive systems, Ph_2Zn -Add. Additives such as water, butanone, zinc chloride or copper chloride produced polystyrene, PS, of high molecular weight. Conversion to the polymer is critically influenced by the molar ratio additive/ Ph_2Zn . With some Ph_2Zn -Add systems a fraction of stereoregular PS was also obtained (1). Furthermore, depending on the initiator system employed, more than one active species for S polymerization was detected.

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Several combinations of Ph_2Zn -metallocene-MAO (2-4) have proved to be effective initiator systems for S polymerization. Variable amounts of boiling butanone-insoluble polymer were separated from the crude polystyrene obtained. ^{13}C -NMR analysis as well as the thermal behavior of such fractions, together with their insolubility in benzene, toluene, chloroform, and other solvents, confirmed the syndiotactic nature of such polystyrene.

The present paper shows further results for styrene polymerization initiated by Ph_2Zn -metallocene-MAO systems, this time using $(n\text{-BuCp})_2\text{TiCl}_2$.

Experimental

Polymerizations were carried out in an argon atmosphere in a 100 cm^3 Schlenk tube equipped with a magnetic stirrer. Solvent toluene (ca., 35 cm^3), Ph_2Zn solution, and additive(s) were charged by syringe under argon pressure. Polymerization was initiated by injecting the required amount of styrene. The reactions were kept with stirring at 60 °C.

Polymerization was terminated by adding a mixture of hydrochloric acid and methanol. The polymers, coagulated in acidified methanol, were recovered by filtration after washing several times with methanol, and were dried in vacuum at 60°C. The polystyrene 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 (5):

$$[\eta] = 1.12 \times 10^{-4} M_v^{0.73}$$

valid for the molecular weight range 7-150 $\times 10^4$.

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

Results and discussion

The polymerization of styrene using combined Ph_2Zn -metallocene systems with or without MAO led to conversion into polymer which critically depends on the metallocene employed and on the molar ratio metallocene/ Ph_2Zn . Zirconocenes produced mainly amorphous PS containing a small amount, less than 15%, of stereoregular polymer, while the absence of MAO resulted in a product without any stereoregular PS (2-4).

Table 1 shows the results of styrene polymerization using the Ph_2Zn - $(n\text{-BuCp})_2\text{TiCl}_2$ -MAO combined system. It can be seen that conversion to polymer increases when the molar ratio $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn}$ increases. The same happens regarding the content of boiling butanone-insoluble fraction. Furthermore, the crude polymer obtained showed DSC melting temperature

signals in the syndiotactic PS range. These results confirm our previous findings in the sense that Ph_2Zn -metallocene-MAO systems initiate polystyrene polymerization producing highly syndiotactic PS (2-4).

Table 1. Polymerization of styrene by $\text{Ph}_2\text{Zn}-(n\text{-BuCp})_2\text{TiCl}_2$ -MAO systems, at various molar ratios $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn}$, in toluene after 48 hours at 60 °C^{a)}

Molar ratio $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn}$ mol/mol	Yield PS		$A \times 10^{-3}$ b)	$[\eta]$ c)	T_m d)		Insol. Fractn e)
	g	%			°C	(1)	
0.50	0.64	5.03	17.49	nd	247.9	264.6	69.25
0.75	0.92	7.27	16.85	0.15	245.0	260.1	90.21
1.00	1.50	11.82	20.51	0.20	249.4	266.0	91.69
1.25	1.81	14.30	19.89	0.18	251.2	266.1	94.30

a) Polymerization conditions: Total volume = 60 mL; $St = 2.0$ mol/L, MAO = 0.33 mol/L, $\text{Ph}_2\text{Zn} = 2.09 \times 10^{-4}$ mol/L.

b) Activity in: g PS/(molTi*molS*h)

c) Measured in o-dichlorobenzene at 135° C.

d) Melting temperature, second heating, crude polymer

e) Boiling butanone-insoluble PS.

DSC results confirm the syndiotactic nature of the obtained PS. Figure 1 shows the DSC curves of the various PS obtained when using $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn}$ molar ratios from 0.25 to 1.25. The second heating curves are split into two peaks which can be assigned to two different ways of crystallization, of the various crystal forms that s-PS can show (6,7).

The insoluble fraction content increases with the molar ratio $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn}$. It reaches a content of 90% and higher as the molar ratio moves from 0.75 to 1.00 and 1.25. This finding suggest that the active species capable of inducing stereoregular polymerization are very much influenced by the interaction between Ph_2Zn and $(n\text{-BuCp})_2\text{TiCl}_2$. Another point to be noticed is that initiator systems with a molar ratio $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn} = 1$ present an activity larger than those with molar ratios of 0.50, 0.75 or 1.25, emphasizing the interaction between the two components of the system.

The DSC analysis of the crude polymers confirmed the presence of stereoregular polystyrene. Figure 1 shows the DSC thermogram. for the complete series. From these results the presence of crystalline polystyrene is clear. The first

heating shows only one peak in the region of 262.5-267 °C (Fig. 1a). After cooling to room temperature and carrying out a second heating, the signal split into two (Fig. 1b). The double peak signal have already been observed by other authors (6,7) and are attributed to different ways of crystallizing of syndiotactic polystyrene.

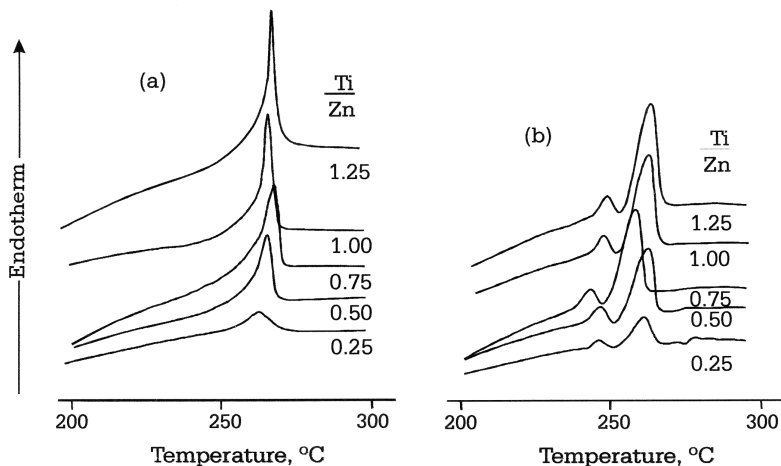


Figure 1. DSC curves for crude PS obtained using $\text{Ph}_2\text{Zn}-(n\text{-BuCp})_2\text{TiCl}_2\text{-MAO}$ in toluene at 60°C at various molar ratios $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn}$. (a) First heating at 10°C/min; (b) Second heating at 10°C/min.

Figure 2, shows polymer conversion with time. It can be seen that conversion to polymer increases with time and also, on the other hand, that the s-PS content did not change with time, pointing to the real importance of the initiator system. DSC analysis of the polymer obtained indicates that, independently of reaction time, the presence of syndiotactic polymer in the crude polymers can be detected.

A number of papers regarding styrene polymerization initiated by metallocene-MAO systems (7-11) indicates a variety of findings depending on the particular metallocene employed. Anyhow, it is considered that the active species are complex products resulting from reaction of the titanium compound with MAO (8). On the other hand, the oxidation number of titanium has been considered to play a determinant role in the stereospecific polymerization of styrene, with the Ti(+3) species being responsible for the formation of s-PS (9-10). Therefore, the titanocene employed is critically determinant in the formation of s-PS. It has been reported that 100% s-PS can be obtained using $[\text{Ti}(\eta^5\text{-C}(5)\text{H}(4)(t)\text{Bu}(\text{Cl})\text{-3})\text{-MAO}$ (11).

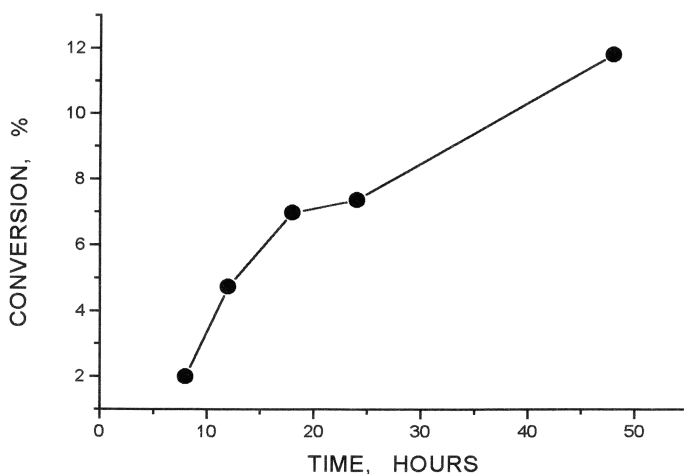


Figure 2. Polymerization of styrene $\text{Ph}_2\text{Zn}-(n\text{-BuCp})_2\text{TiCl}_2\text{-MAO}$ system in toluene at 60°C after various time periods. Polymerization conditions $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn} = 1.0$ mol/mol; $[(n\text{-BuCp})_2\text{TiCl}_2] = 2.06 \times 10^{-4}$ M; $[\text{MAO}] = 0.33$ M; $[\text{S}] = 2.03$ M. Total volume = 60 mL.

Our results indicates that $\text{Ph}_2\text{Zn}-(n\text{-BuCp})_2\text{TiCl}_2\text{-MAO}$ combinations are capable of inducing styrene polymerization. Conversion to polymer and s-PS content change depending on the molar ratio $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn}$ employed.

Recently we performed experiments of styrene polymerization initiated by Ph_2Zn -Metallocene-MAO systems using nonpolar and polar solvents and their 1:1 mixtures, where the metallocene employed were: $\text{Ind}_2\text{ZrCl}_2$, Cp_2TiCl_2 and $(n\text{-BuCp})_2\text{TiCl}_2$ (12). The conversion to polymer was much increased with solvent polarity while the content of stereoregular PS remains almost unchanged.

Polymerization of S with $\text{Ph}_2\text{Zn}-(n\text{-BuCp})_2\text{TiCl}_2\text{-MAO}$ systems with molar ratio $(n\text{-BuCp})_2\text{TiCl}_2/\text{Ph}_2\text{Zn} = 1.0$, produced conversion of 16.0; 23.9 and 31.8% for respectively chlorobenzene, toluene/o-dichlorobenzene and o-dichlorobenzene as solvents, while conversion to polymer with toluene as solvent was only 11.8%. The dielectric constant (ϵ) for these solvents are: toluene 2.38, chlorobenzene 5.69 and o-dichlorobenzene 10.12 (13). These results indicate that polymerization using $\text{Ph}_2\text{Zn}-(n\text{-BuCp})_2\text{TiCl}_2\text{-MAO}$ initiator systems are favored by polarity of the reaction media. These results support our previous assessments (12), where was postulated

that styrene polymerization by Ph_2Zn -metallocene-MAO initiator systems starts by coordination of styrene to the active species, and then polymerization propagates through an ionic pathway. Further work is under way, from which more conclusive results are expected.

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