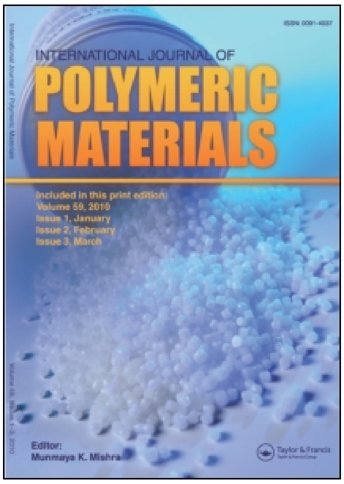

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Polymerization of Styrene by Diphenylzinc-Additive Systems. Part V: Ph_2Zn-Ind_2ZrCl_2-MAO Systems

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Polymerization of Styrene by Diphenylzinc-Additive Systems. Part V: Ph_2Zn-Ind_2ZrCl_2-MAO Systems[a]

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Styrene was polymerized using various combined systems including diphenylzinc, Ph_2Zn, bis(indenyl)zirconium dichloride, Ind_2ZrCl_2, and methylaluminoxane, MAO. Conversion to polystyrene depends on the combination used: Ph_2Zn-Ind_2ZrCl_2-MAO, Ph_2Zn-Ind_2ZrCl_2, Ind_2ZrCl_2-MAO or Ph_2Zn/H_2O-Ind_2ZrCl_2. Furthermore, for Ph_2Zn-Ind_2ZrCl_2-MAO the maximum conversion to polymer was reached for molar ratio Ph_2Zn/Ind_2ZrCl_2 equal unity. Polymers were predominantly atactic. A 5 to 10% fraction of insoluble in boiling butanone polymer was separated from the crude polystyrene. The amount of such fraction depends on the molar ratio Ph_2Zn/Ind_2ZrCl_2 used.

Keywords: Styrene polymerization; diphenylzinc; metallocene catalyst; tacticity

INTRODUCTION

We have been employing Ph_2Zn-Additive systems as initiator of styrene, St, polymerization. For most of the cases conversion to polymer was strongly influence by the nature of the additive employed: H_2O [1], butanols [2], butanone [3], zinc chloride, copper chloride [4]. With the exception of

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[a] Partly presented at XXII Congreso Latinoamericano de Química, and XXI Jornadas Chilenas de Química, Concepción, Chile. January 1996. Part IV: cf. [6].

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butanone the PSt obtained showed GPC chromatograms with more than one peak suggesting that our initiator systems produced more than one active species toward St polymerization. H^1-NMR analysis of obained PSt indicates an atactic nature for PSt but for polymers obtained by the use of initiator systems Ph_2Zn-$ZnCl_2$, up to 83% of syndiotactic triads were established planimetrically. Furthermore, DSC analysis showed a T_m peak at region higher than 230°C indicating that PSt polymerized by Ph_2Zn-$ZnCl_2$ systems contained a portion of stereoregular PSt [4]. Afterwards we have performed exploratory studies of St polymerization using combinations of Ph_2Zn with several zirconocenes [5] and also with bis(cyclopentadienyl) titanium dichloride. From these experiments we established that Ph_2Zn-Zirconocene systems by themselves and also with methylaluminoxane, MAO, are capable to induce St polymerization which conversion to PSt and nature of polymer are much influenced by both the zirconocene employed and the combination used. From the zirconocenes employed Ind_2ZrCl_2 produced the hig her conversions to polymer. On the other hand polymerizations using Cp_2TiCl_2 gave almost pure stereoregular PSt [6].

The present paper shows further results of St polymerization initiate by combinations Ph_2Zn, Ind_2ZrCl_2 and MAO.

EXPERIMENTAL

Polymerizations were carried out under 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 pressure of argon. Polymerizations were initiated by injecting the required amount of styrene. 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, were recovered after washing several times with methanol by filtration and 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 [7]:

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

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

For initiator systems Ph_2Zn-In_2ZrCl_2-MAO we established [5] a higher effectiveness toward styrene polymerization when compared with the systems Ph_2Zn-Cp_2TiCl_2-MAO. Both initiator systems increased conversion with time but the ones including zirconium complex was more effective. As it was for other additives, molar ratio organometallic compound/Ph_2Zn was determinant prior to conversion.

Table I shows the experimental results for polymerization of St initiated by Ph_2Zn-In_2ZrCl_2-MAO systems at molar ratios In_2ZrCl_2/ Ph_2Zn of 0.50, 0.75, 1.00 and 1.25, during 48 hours at 60°C in toluene. Capacity of initiator systems increased as molar ratio In_2ZrCl_2/Ph_2Zn moved from 0.5 to 1.0 and then diminishes. The largest conversion to polymer was reached for molar ratio equal unity. We have already established similar situation for other additives used together with Ph_2Zn [1–3].

From values in Table I, it can also be appreciated that a fraction of insoluble PSt separated from the crude polymer. The amount of the insoluble fraction also varies according to the molar ratio In_2ZrCl_2/ Ph_2Zn employed. The largest amount of insoluble PSt was separated from polymer obtained using a molar ratio In_2ZrCl_2/Ph_2Zn of 1.25.

Molecular weights of the obtained PSt diminishes with increase of molar ratio In_2ZrCl_2/Ph_2Zn. On the other hand, when moving from molar ratio

TABLE I Polymerization of styrene by Ph_2Zn-In_2ZrCl_2-MAO systems in toluene after 48 hours at 60°C[a]

Molar ratio In_2ZrCl_2/Ph_2Zn mol/mol	*Yield PSt g*	*$A \times 10^{-3}$ g PSt molZr.molSt.h*	*$[\eta]$[b] $dl \times g^{-1}$*	*M_v $\times 10^{-4}$*	*Insoluble Fraction[c] %*
0.50	0.69	9.51	0.40	7.31	3.01
0.75	0.92	12.75	0.31	5.26	3.81
1.00	1.49	20.52	0.26	4.10	3.75
1.25	0.55	7.62	0.24	3.70	8.70

[a] Polymerization conditions: Total volume = 60 mL; St = 2.0 mol/L, MAO = 0.33 mol/L, $In_2ZrCl_2 = 2.06 \times 10^{-4}$ mol/L.

[b] Measured in chloroform at 25°C.

[c] Insoluble PSt in boiling butanone.

0.50 to 1.25 there is also a variation of molar ratio MAO/ Ph_2Zn, say 800, 1200, 1600 and 2000. It is well known that MAO by itself is a transfer agent in St polymerization and the diminishing of molecular weights can be attributed to the increase of MAO in the initiator system.

Figure 1 shows ^{13}C-NMR spectra of the phenyl C-1 of both crude PSt and the PSt insoluble in boiling butanone. The spectrum of the crude PSt (Fig. 1a) shows several peaks in the range 145.2–146.9 ppm while the spectrum corresponding to the insoluble PSt (Fig. 1b) shows a single peak at 145.416 ppm. These spectra showed a very good concordance with the spectra shown by Ishihara *et al.* [8]. According to the spectra crude PSt is mainly atactic PSt which PSt insoluble in boiling butanone is syndiotactic PSt.

DSC analysis of insoluble PSt corroborates the syndiotactic assessment for butanone insoluble PSt.

Figure 2, shows the SEC analysis of the various crude-PSt obtained by the Ph_2Zn-In_2ZrCl_2-MAO systems employed. It is clear from the bimodal pattern obtained for all the systems employed, that there are more than one active species capable to induce St polymerization.

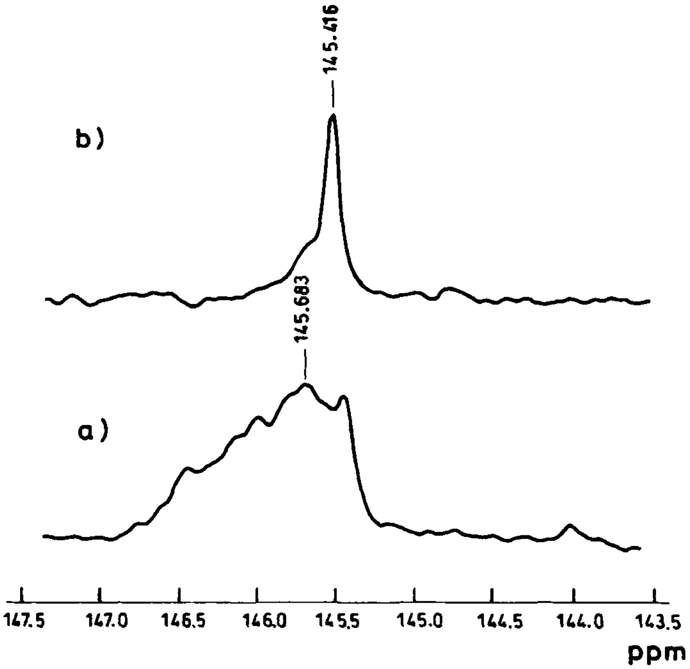

FIGURE 1 ^{13}C-NMR spectra of polystyrene obtained using Ph_2Zn-In_2ZrCl_2-MAO systems: (a) crude; (b) insoluble in boiling butanone fraction.

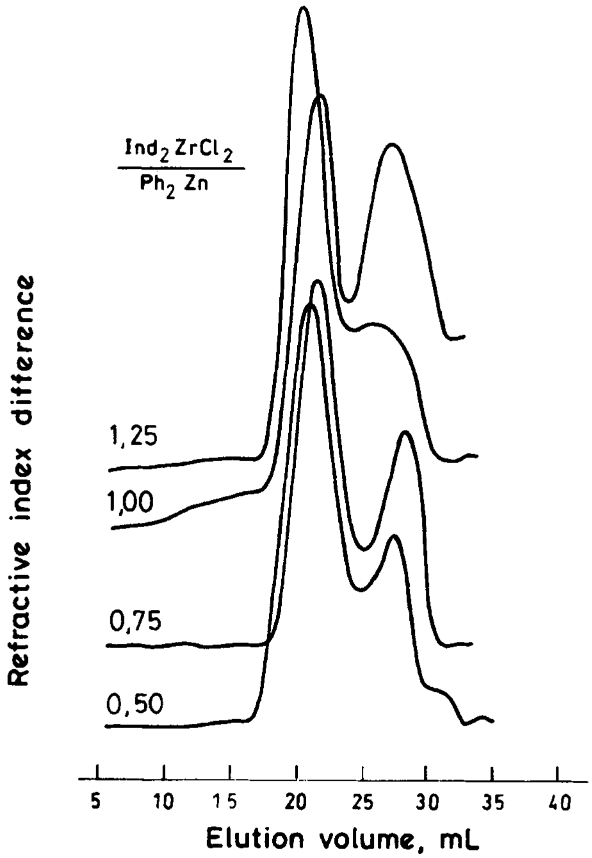

FIGURE 2 SEC chromatograms of PSts obtained using Ph_2Zn-In_2ZrCl_2-MAO systems at various molar ratios In_2ZrCl_2/Ph_2Zn in toluene at 60°C during 48 hours.

Further works are now in progress from which conclusive results are expected.

CONCLUSIONS

Accordingly with these and previous results we conclude:

1. Initiator systems including diphenylzinc, bis(indenyl)zirconium dichloride and methylaluminoxane are capable to induce styrene polymerization.
2. PSt produced by these systems included a portion of syndiotactic polystyrene whose amount varies accordingly with the molar ratio In_2ZrCl_2/Ph_2Zn employed.

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