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Polymerization of styrene by diphenylzinc-additive systems

Part VI: $Ph_2Zn–Cp_2TiCl_2$-MAO systems

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SUMMARY

The polymerization of styrene using combined systems of diphenylzinc-biscyclopentadienyltitanium dichloride-methylaluminoxane, $Ph_2Zn-Cp_2TiCl_2$-MAO, in toluene at 60°C produced highly syndiotactic polystyrene. The syndiotacticity was established first by polymer insolubility in chloroform, benzene or toluene, and also by continuous extraction in boiling butanone. DSC analysis confirmed this finding and showed signals corresponding to the melting temperature, T_m, of syndiotactic polystyrene.

INTRODUCTION

The synthesis of syndiotactic polystyrene, s-PS, has received much attention from both the academic and industrial fields. A considerable number of initiator systems have been employed since 1986, when Ishihara et al. (1) succeed obtaining a new polystyrene with a syndiotactic structure and a high degree of crystallinity.

In previous papers (2,3) we had commented on the diversity of systems employed to obtain s-PS, and about the possible mechanisms involved. From recent papers it can be accepted that in titanocene-MAO systems the soluble Ti compounds are the active species (4), and of these Ti(III) is responsible for s-PS (5). On the other hand, new results strongly support a polyinsertion mechanism (6). It has recently been pointed out that the (tert-butylcyclopentadienyl)titanium complex produces PS with 100% syndiotacticity (7), and that $CpTiCl_2(OPr\text{-}i)$ is more active than $CpTiCl_3$-MAO systems (8).

We have reported on the polymerization of styrene, S, using combined systems that included diphenylzinc, Ph_2Zn, and metallocenes activated by methylaluminoxane, MAO, (2,3). Several zirconocenes were explored: bis(cyclopentadienyl)zirconium dichloride, Cp_2ZrCl_2, bis(indenyl)zirconium dichloride Ind_2ZrCl_2,

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[isopropyl(cyclopentadienyl)(1-fluorenyl)]zirconium dichloride, i-Pr(Flu)(Cp)$ZrCl_2$, and the stereorigid metallocene Et$(Ind)_2ZrCl_2$. Additionally, Cp_2TiCl_2 together with Ph_2Zn and MAO was also employed for comparison.

Our results showed that Ph_2Zn-zirconocene-MAO systems are capable of inducing S polymerization. Conversion to PS and the nature of the polymer obtained are greatly influenced by both the zirconocene employed and the zirconocene/Ph_2Zn mole ratio of the initiator system. A boiling-butanone insoluble polymer fraction was separated from the crude PS. The insoluble fraction was shown to be syndiotactic PS (2,3).

The present paper gives additional results of S polymerization initiated by Ph_2Zn-metallocene-MAO systems, this time using Cp_2TiCl_2.

EXPERIMENTAL

Polymerizations were carried out under an argon atmosphere in a 100 cm^3 Schlenk tube equipped with a magnetic stirrer. Toluene (ca. 35 cm^3), a toluene solution of Ph_2Zn, and additive(s) were charged by syringe under argon pressure. Polymerizations were initiated by injecting the required amount of S. The 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 and washed several times with methanol, were recovered by filtration and dried in vacuum at 60°C. The PS samples were fractionated by exhaustive extraction with boiling butanone.

The 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 (9):

$$[\eta] = 1.12\times10^{-4}M_v^{0.73}$$

valid for molecular weights within the $7\text{-}150\times10^4$ range. The intrinsic viscosities of the butanone-insoluble polymers were measured in 1,2-dichlorobenzene at 135°C.

DSC analyses were performed by using a Rheometrics Scientific DSC apparatus in a nitrogen atmosphere at a heating rate of 10°C/min, and reheated at the same rate. Samples of 3 to 4 mg were used. The reported melting points were obtained in the second scan.

RESULTS AND DISCUSSION

Combined systems including Ph_2Zn, metallocenes and MAO have been used to initiate S polymerization (2,3). The metallocenes employed are zirconium derivatives. For comparison, bis(cyclopentadienyl)titanium dichloride was also used. Of the various zirconocenes it was established that bis(indenyl)zirconium dichloride produced the largest proportion of PS. However, according to our exploratory experiments, bis(cyclopentadienyl)titanium dichloride produced the highest proportion of PS insoluble in boiling butanone (2). This boiling-butanone insoluble fraction of PS is considered to be s-PS.

When working with Ph_2Zn-Ind_2ZrCl_2-MAO systems, the presence of a fraction of insoluble PS in the crude polymer was also established. The proportion of such insoluble fraction varies according to the Ind_2ZrCl_2/Ph_2Zn mole ratio employed (3).

The combination of Cp_2TiCl_2 with the other components, i.e. Cp_2TiCl_2-MAO, Ph_2Zn-Cp_2TiCl_2-MAO, Ph_2Zn-Cp_2TiCl_2, and H_2O/Ph_2Zn-Cp_2TiCl_2, produced initiator systems which were able to induce S polymerization. As shown in Table 1, the three-component combination Ph_2Zn-Cp_2TiCl_2-MAO produced the largest conversion to PS and also the largest proportion of PS insoluble in boiling butanone. Furthermore, the absence of MAO decreased both the conversion to polymer and the insoluble fraction content. In experiments without MAO, practically no stereoregular PS was obtained.

Table 1. Polymerization of styrene initiated by Ph_2Zn-Cp_2TiCl_2-MAO combined systems in toluene at 60°C for 48 hours[a)].

Initiator System	[Zn] $M\times10^4$	[Ti] $M\times10^4$	[Al] $M\times10^2$	Yield[b)] %	$[\eta]$[c)] $dL\times g^{-1}$	M_v $\times10^{-5}$	Insoluble Fraction[d)] %
--/Ti/Al	----	3.28	33.8	1.71	nd[f)]	----	32.91
Zn/Ti/Al	2.12	1.64	33.7	6.68	nd[f)]	----	67.67
Zn/Ti/--	4.22	3.27	----	2.65	0.76	1.76	1.68
Zn/Ti/--[e)]	4.22	3.27	----	3.20	0.68	1.53	3.03

a) [S] = 2.0 M; Zn = Ph_2Zn, Ti = Cp_2TiCl_2, Al = MAO.
b) Based on initial styrene.
c) Measured in chloroform at 25°C.
d) In boiling butanone.
e) With H_2O, $H_2O/Ph_2Zn = 1$.
f) Not determined. Polymer insoluble in chloroform at 25°C.

Table 2 shows the results obtained for the Ph_2Zn-Cp_2TiCl_2-MAO initiator system at various Cp_2TiCl_2/Ph_2Zn mole ratios. From these results it is clear that the Cp_2TiCl_2/Ph_2Zn mole ratio critically influences the polymerization. The largest amount of PS was obtained with a mole ratio equal to unity. The insoluble fraction increases as the Cp_2TiCl_2/Ph_2Zn mole ratio increases, but for a mole ratio equal to one it decreases, while the molecular weight increases. We think that with increasing chain length it is possible that more non-stereoregular events occur, decreasing the syndiotacticity of the complete crude polymer.

Table 2. Polymerization of styrene by Ph_2Zn-Cp_2TiCl_2-MAO systems in toluene after 48 hours at 60°C[a].

Cp_2TiCl_2/Ph_2Zn Mole ratio mol/mol	Yield %	$[\eta]$[b] $dL\times g^{-1}$	Insoluble Fraction[c] %
0.25	2.76	0.19	59.8
0.50	4.48	0.17	65.4
0.75	6.40	0.19	67.5
1.00	9.44	0.28	58.3

[a] Polymerization conditions: Total volume = 60 mL; St = 2.0 mol/L, MAO = 0.33 mol/L, Cp_2TiCl_2 = 2.08×10^{-4} mol/L.

[b] Measured in o-dichlorobenzene at 135°C.

[c] PS insoluble in boiling butanone.

Figure 1 shows the progress of S polymerization using Ph_2Zn-Cp_2TiCl_2-MAO systems at Cp_2TiCl_2/Ph_2Zn mole ratios of 0.75 and 1.00. Conversion increases with time, and a mole ratio of one produces a larger amount of polymer in a given time period.

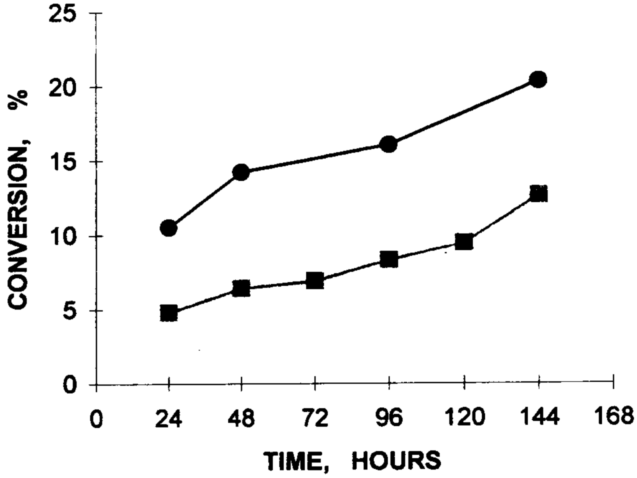

Figure 1. Polymerization of styrene by a Ph_2Zn-Cp_2TiCl_2-MAO system in toluene at 60°C after various time periods.
(●) Cp_2TiCl_2/Ph_2Zn = 1.00 mol/mol; $[Cp_2TiCl_2]$ = 1.59×10^{-4}M $[MAO]$ = 2.54×10^{-1}M, [S] = 2.08M. Total volume = 78 mL.
(■) Cp_2TiCl_2/Ph_2Zn = 0.75 mol/mol; $[Cp_2TiCl_2]$ = 1.57×10^{-4}M $[MAO]$ = 3.36×10^{-1}M, [St] = 2.06M. Total volume = 118 mL.

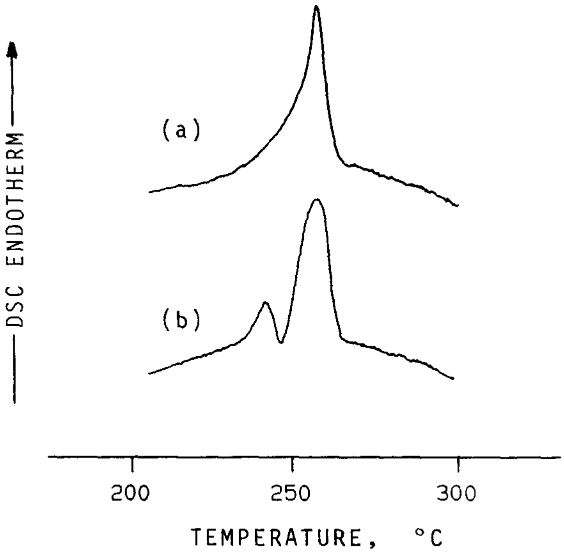

Figure 2. DSC curves for crude PS obtained using Ph_2Zn-Cp_2TiCl_2-MAO systems in toluene after 48 hours at 60°C. (a) First heating at 10°C/min, (b) Second heating at 10°C/min.

The thermal behaviour of the polymers was analyzed by differential scanning calorimetry, DSC. Figure 2, shows typical DSC curves for crude PS obtained using the Ph_2Zn-Cp_2TiCl_2-MAO initiator system at a mole ratio of Cp_2TiCl_2/Ph_2Zn = 1.00. DSC curves were measured at a heating rate of 10 °C/min, allowed to cool down to room temperature, and then reheated at the same rate. In the first heating scan only a single signal appears at 257.5 °C. When the sample was reheated for the second time, the endotherm was resolved into two melting signals at 241.4 and 257.9 °C. These same melting characteristic were observed for crude PS obtained when a mole ratio of Cp_2TiCl_2/Ph_2Zn = 0.75 was used. Changing the initiator systems to Ph_2Zn-$(n\text{-}BuCp)_2TiCl_2$-MAO produced a slight increase in the melting temperature, while maintaining the same pattern. However, when the Ph_2Zn-Ind_2ZrCl_2-MAO system was used, the DSC of the crude PS obtained did not show any sign of melting, suggesting a very low content or the absence of crystalline PS (10).

Figure 3, shows the ^{13}C-MNR spectra of crude PS and of the insoluble portion of PS obtained using the Ph_2Zn-Cp_2TiCl_2-MAO system at a mole ratio of Cp_2TiCl_2/Ph_2Zn = 1.00. The spectrum of crude PS (Fig. 3a) shows two peaks centered at 145,677 and at 145,419 ppm, while the spectrum of the insoluble portion (Fig. 3b) shows only a single signal at 145,422 ppm. These results, together with the fractionation of crude PS, are indicative of the presence of two kinds of PS, and suggest the possibility of the existence of at least two kinds of active species in S polymerization.

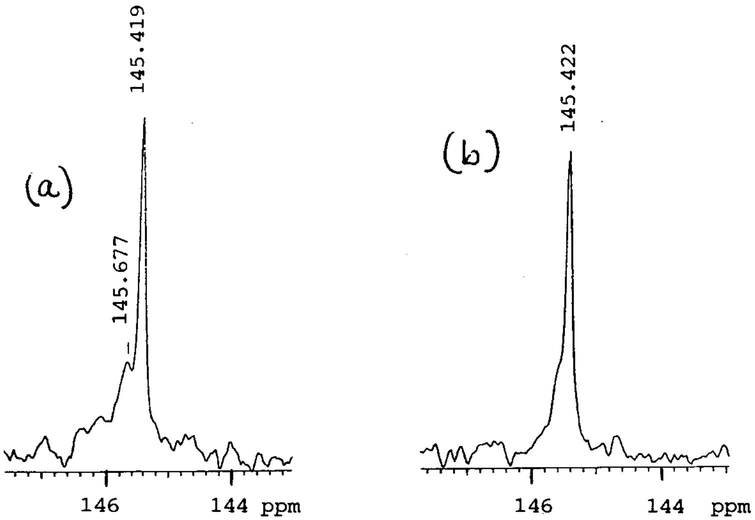

Figure 3. ^{13}C-MNR spectra of polystyrene obtained using a Ph_2Zn-Cp_2TiCl_2-MAO system (Cp_2TiCl_2/Ph_2Zn = 1.00 mol/mol). (a) crude polymer; (b) fraction insoluble in boiling butanone.

A number of authors (11-14) have considered that the reactions between titanocenes and MAO produce Ti complexes with different oxidation states which are responsible for the stereospecific polymerization of S. On the other hand, Soga et al.(15) have pointed out that systems composed of Cp_2MCl_2 (M = Ti, Zr) and MAO do not produce s-PS. However, since all the PS we obtained using Ph_2Zn-Cp_2TiCl_2-MAO systems contained a portion of s-PS, we think that our combination of Ph_2Zn with Cp_2TiCl_2 and MAO produces a rather complex system with more than one active species, yielding mixtures of atactic and s-PS. More work is in progress, from which more conclusive results are expected.

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