STYRENE/STYRENE-DERIVATIVE COPOLYMERIZATION BY Ph_2Zn -METALLOCENE-MAO SYSTEMS: HOMO- AND COPOLYMERIZATION OF α -METHYLSTYRENE WITH STYRENE

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ABSTRACT

The copolymerization of styrene with α -methylstyrene has been tested using combined metallocene-MAO initiator systems with and without diphenylzinc. The metallocenes used were biscyclopentadienyltitanium dichloride, Cp_2TiCl_2 , bis(n-butylcyclopentadienyl)titanium dichloride, $(\text{n-BuCp})_2\text{TiCl}_2$, and the half-sandwich metallocene indenyltitanium trichloride, IndTiCl_3 . The results indicate that both binary metallocene-MAO, and ternary Ph_2Zn -metallocene-MAO systems are capable of polymerizing α -methylstyrene to poly(α -methylstyrene) as well of its copolymerization with styrene. These initiator systems also show that despite the I+ inductive effect of the methyl group, which enhances electron density at the vinyl double bond of styrene, the steric consequence of vinyl substitution hinders monomer coordination to active species, causing a decrease in conversion of either α -MeS to homopolymer or S/ α -MeS to the corresponding copolymer. The nature and structure of the metallocene included in the initiator system are determinant of the initiator system's efficiency. For the metallocenes used the efficiency follows the order $\text{IndTiCl}_3 > \text{Cp}_2\text{TiCl}_2 > (\text{n-BuCp})_2\text{TiCl}_2$, with the half-sandwich metallocene IndTiCl_3 showing greater efficiency than the true metallocenes.

Keywords: Styrene copolymerization; diphenylzinc; metallocene catalysts; tacticity.

INTRODUCTION

Most of research on α -methylstyrene polymerization and of its copolymerization has been performed through ionic polymerization, particularly anionic polymerization.^{2,3} There are no examples of metallocene polymerization neither of one using diphenylzinc as ingredient of initiator systems.

Working on styrene/substituted styrene copolymerization using diphenylzinc-metallocene-MAO and metallocene-MAO initiator systems, Rabagliati et al. concluded that both the nature and position of substituents on the styrene unit have great influence on the course of the polymerization process.^{4,7}

Substituents with I+ inductive effect groups in the para position of the benzene ring of styrene favor its polymerization,^{4,5} while para-halide substituents (I- inductive effect) produce lower conversion.⁶ Conversion of p-chlorostyrene, p-ClS, to its corresponding poly(para-chlorostyrene), P(p-ClS) it is much lower than conversion of para-alkylstyrenes such as p-methyl- and p-tertbutyl styrene to their corresponding homopolymers, showing the following reactivity order: p-chlorostyrene < styrene < p-methylstyrene < p-tertbutylstyrene.^{6,7} This is in agreement with the results of Grassi et al. working with the tetrabenzyltitanium-MAO initiator system,⁸ they reported that polymerization rates decrease in the order p-methoxystyrene > bis(cyclopentadienyl) > styrene > m-methylstyrene > p-chlorostyrene > o-chlorostyrene > m-chlorostyrene. Around that time Po and Cardí⁹ published a review on the synthesis of syndiotactic polystyrene, including styrene copolymerization, and referring to alkylstyrenes and halostyrenes as the earliest studied monomers and pointing out that, according to Ishihara,¹⁰ halogenated styrenes produce stereoregular homopolymers, while stereoregularity is very poor or absent according to Grassi⁸ and Soga.¹¹ Recently we reported that p-methoxystyrene, due to its inductive effect was also more prone to polymerize through our initiator systems, but when using the ternary systems, including diphenylzinc, in contrast with the other para I+ substituents, there was no increase in conversion, probably due to interaction of Ph_2Zn -MeOS through coordination between the zinc atom and the oxygen of methoxystyrene ($\text{Ph}_2\text{Zn} \cdot \text{ether}$).¹²

Working with di- and tri-substituted alkylstyrene we established that not only the electric inductive effect is relevant toward polymer conversion, but also steric hindrance due to substituents has a critical role.^{13,14} According to our results the steric effect is predominant, so di- and trimethylsubstitution on the ring decreases the efficiency of the polymerization process, and particularly when the substituent is in the ortho position.¹¹ On the other hand, exploratory experimental work on S/ α -MeS copolymerization using either CpTiCl_3 -MAO or Ph_2Zn - CpTiCl_3 -MAO initiator systems showed that conversion to copolymer decreases as the proportion of α -MeS increases in the initial feed, in agreement with a polymerization hindrance due to methyl substitution on the vinyl carbon of styrene.¹³

The present paper reports new experimental work on S/ α -MeS copolymerization using binary metallocene-MAO and also ternary Ph_2Zn -

metallocene-MAO initiator systems including Cp_2TiCl_2 , $(\text{n-BuCp})_2\text{TiCl}_2$ metallocenes, and the half-sandwich metallocene IndTiCl_3 .

EXPERIMENTAL

Homo- and copolymerization experiments were carried out in an argon atmosphere in a 100 cm³ Schlenk tube equipped with a magnetic stirrer. Solvent toluene, MAO solution, Ph_2Zn , and metallocene solution in toluene were sequentially charged by syringe under argon pressure. Polymerization was initiated by injecting the styrene or simultaneously the required amount of styrene and comonomer. The reactions were kept at 60 °C with stirring for the required length of time. Polymerization was ended by adding a mixture of hydrochloric acid and methanol. The polymers, coagulated in the acidified methanol, were recovered by filtration, washed several times with methanol, and dried in vacuum at 60 °C.

Intrinsic viscosity, $[\eta]$, was measured in o-dichlorobenzene at 135 °C, and was determined by the one-point method.¹⁵

DSC analyses were performed using a Rheometrics Scientific DSC apparatus with the samples placed in a nitrogen atmosphere, at a rate of 10 °C/min and, after cooling to room temperature, reheated at the same rate. The reported Tg and Tm were those obtained in the second scan. ¹³C-NMR spectra in 1,1,2,2-tetrachloroethane-d₂ at 60 °C were recorded on a Bruker Avance-400 spectrometer operating at 100.61 MHz. Chemical shifts were calibrated to tetramethylsilane (TMS).

RESULTS AND DISCUSSION

Table 1 and Table 2, show the results of styrene/ α -methylstyrene, S/ α -MeS, copolymerization at various molar monomer/comonomer proportions using both ternary diphenylzinc-metallocene-MAO and binary metallocene-MAO initiator systems, where the metallocenes used were bis(n-butylcyclopentadienyl)titanium dichloride, bis(cyclopentadienyl) titanium dichloride, $(\text{n-BuCp})_2\text{TiCl}_2$, Cp_2TiCl_2 , and also the half-sandwich metallocene indenyltitanium trichloride, IndTiCl_3 .

Results in both Tables show that conversion to copolymer decreases as the proportion of α -MeS increases in the initial feed. Furthermore, all the initiator systems used were more effective in styrene homopolymerization than in its copolymerization with α -MeS. in agreement with previous results in the sense that the polymerization of styrene derivatives is much affected by both the nature of the substituent (I+ or I- inductive effect) and by its steric hindrance depending on its position on the styrene phenyl group and/or at the styrene vinyl group.^{12,13} "Half-sandwich" metallocene IndTiCl_3 was more effective than the proper metallocenes $(\text{n-BuCp})_2\text{TiCl}_2$, Cp_2TiCl_2 , as it was the case when using CpTiCl_3 .¹³

Table 1. Styrene/ α -methylstyrene copolymerization using ternary Ph_2Zn -metallocene-MAO initiator systems, in toluene after 6 hours at 60 °C.^a

Initial Feed S/ α -MeS mol/mol	Conversion %	$[\eta]$ dL/g	Tg °C	Tm1 °C	Tm2 °C
(n-BuCp)₂TiCl₂					
Only S	10.2	0.26	88	240	260
95/5	8.5	0.27	97	244	263
75/25	1.3	n.d.	95	237	257
50/50	0.5	n.d.	88	235	257
25/75	0.8	n.d.	n.s.	224	233
5/95	0.7	n.d.	n.d.	n.d.	n.d.
Only α -MeS	1.5	n.d.	n.d.	n.d.	n.d.
Cp₂TiCl₂					
Only S	10.5	0.19	90	243	258
95/5	22.2	0.12	83	243	258
75/25	15.3	0.16	85	234	250
50/50	2.7	0.12	92	228	242
25/75	2.4	0.16	84	216	n.s.
5/95	0.04	n.d.	n.d.	n.d.	n.d.
Only α -MeS	0.07	n.d.	n.d.	n.d.	n.d.
IndTiCl₃					
Only S	21.3	0.43	101	259	274
95/5	19.7	0.39	99	259	273
75/25	25.1	0.23	97	252	268
50/50	23.4	n.d.	n.s.	n.s.	253
25/75	15.8	n.d.	n.d.	n.d.	n.d.
5/95	4.4	n.d.	n.d.	n.d.	n.d.
Only α -MeS	11.8	n.d.	n.d.	n.d.	n.d.

^a Polymerization conditions: Total volume = 25 mL; [S] + [α -MeS] = 2.0 mol/L; [MAO] = 0.33 mol/L;
 $[\text{Ph}_2\text{Zn}] = [\text{metallocene}] = 2.0\text{E-}04$ mol/L.
 n.d. = not determined; n.s. = no signal

Figure 1 compares the DSC thermograms of PS with the various S/(α -MeS) copolymers obtained using (n-BuCp)₂TiCl₂-MAO and Ph_2Zn -(n-BuCp)₂TiCl₂-MAO initiator systems. These results indicate that the incorporation of α -MeS produces a decrease in crystallinity, particularly for those copolymer obtained from the initial feed with the larger amount of α -MeS. For the initial feed with S/ α -MeS molar ratio, with larger than 50% of α -MeS content, practically no crystalline melting temperature was detected in the copolymers obtained.

Figure 1. DSC thermograms of poly[styrene-co-(α -methylstyrene)] obtained using (A) (n-BuCp)₂TiCl₂-MAO and (B) Ph_2Zn -(n-BuCp)₂TiCl₂-MAO initiator systems in toluene after 6 hours at 60 °C. Initial S/(α -MeS) mol/mol, as indicated.

Figure 2. DSC thermograms of poly[styrene-co-(α -methylstyrene)] obtained using (A) Cp_2TiCl_2 -MAO and (B) $\text{Ph}_2\text{Zn-Cp}_2\text{TiCl}_2$ -MAO initiator systems in toluene after 6 hours at 60 °C. Initial S/(α -MeS) mol/mol, as indicated.

When using Cp_2TiCl_2 metallocene, a similar situation was detected, confirming our previous results in the sense that styrene/(styrene derivative) copolymerization was highly influenced by steric hindrance and the position of the substituent in the styrene molecule.¹³ In other words, we have found inductive effects which favor conversion to polymer, and steric hindrance which make difficult the incorporation of the incoming monomer unit. On the other hand, as α -MeS unit were incorporated to the growing copolymer chains, crystallinity decreases, and the copolymer resulting from an initial feed with S/(α -MeS) higher than 50% of α -MeS did not show any T_m signal in DSC.

Table 2. Styrene/ α -methylstyrene copolymerization using binary metallocene-MAO initiator systems, in toluene after 6 hours at 60 °C.^a

Initial Feed					
S/ α -MeS	Conversion	$[\eta]$	Tg	Tm1	Tm2
mol/mol	%	dL/g	° C	° C	° C
(n-BuCp)₂TiCl₂					
Only S	14.1	0.28	95	250	267
95/5	12.2	0.29	89	243	264
75/25	3.4	0.17	90	n.s.	259
50/50	2.0	n.d.	92	n.s.	257
25/75	0.04	n.d.	80	n.s.	233
5/95	trace	n.d.	n.d.	n.d.	n.d.
Only α -MeS	trace	n.d.	n.d.	n.d.	n.d.
Cp₂TiCl₂					
Only S	25.6	0.11	88	240	256
95/5	22.2	0.13	87	243	259
75/25	5.5	0.16	93	240	255
50/50	7.0	0.12	97	228	246
25/75	3.3	0.16	86	216	n.s.
5/95	10.7	n.d.	n.d.	n.d.	n.d.
Only α -MeS	0.03	n.d.	n.d.	n.d.	n.d.
IndTiCl₃					
Only S	29.3	0.47	103	261	274
95/5	13.3	0.27	99	260	273
75/25	22.0	n.d.	n.s.	257	269
50/50	13.0	n.d.	n.s.	n.s.	255
25/75	1.7	n.d.	n.s.	n.s.	213
5/95	0.13	n.d.	n.d.	n.d.	n.d.
Only α -MeS	1.7	n.d.	n.d.	n.d.	n.d.

^a Polymerization conditions: Total volume = 25 mL; [S] + [α -MeS] = 2.0 mol/L; [MAO] = 0.33 mol/L;

[Ph_2Zn] = [metallocene] = 2.0E-04 mol/L.

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

For both ternary and binary systems (Table 1 and Table 2), the initiator systems including the “half-sandwich” metallocene IndTiCl_3 showed higher conversion to polymer than the other metallocenes studied, viz. $(n\text{-BuCp})_2\text{TiCl}_2$ and Cp_2TiCl_2 , indicating better efficiency. Furthermore, in the present work the highest T_m values were obtained for copolymers resulting from initiator systems including IndTiCl_3 in both binary and ternary initiator systems. This situation can also be focused in relation to steric hindrance around Ti^{3+} , due respectively to the two Cp- and $n\text{-BuCp}$ - groups bonded to titanium, which

hinder the approach and further coordination of the incoming monomer unit.

Figure 3(B) shows the DSC thermograms of the copolymers obtained when using the ternary initiator system $\text{Ph}_2\text{Zn-IndTiCl}_3\text{-MAO}$. It is seen that well defined signals indicate the crystalline nature of the resulting copolymer obtained from $S/\alpha\text{-MeS} = 95/5$ and $75/25$ initial feeds, but less intense and sharp for $50/50$ and $25/75$ mixtures, and finally no crystalline melting temperature appears for the $5/95$ initial mixture.

Figure 3. DSC thermograms of the poly[styrene-co-(α -methylstyrene)] obtained using (A) $\text{IndTiCl}_3\text{-MAO}$ and (B) $\text{Ph}_2\text{Zn-IndTiCl}_3\text{-MAO}$ initiator systems, in toluene after 6 hours at 60°C . Initial $S/\alpha\text{-MeS}$ (mol/mol) feed as indicated.

Figure 3(A) shows a similar situation found for the copolymer obtained using the binary $\text{IndTiCl}_3\text{-MAO}$ initiator system, indicating that copolymerization proceeds the same as for the ternary initiator system, but with slightly lower yield, in agreement with previous reports in the sense that diphenylzinc favors the reduction of Ti(IV) to Ti^{3+} , which is considered to be responsible for its efficiency as initiator of the polymerization process and the stereoregularity of the resulting polymer.

The NMR analyses of obtained products showed, as repeating units in copolymer chains, the corresponding signals of both styrene and α -methylstyrene comonomers,:

$^1\text{H-NMR}$ (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 80°C) δ 0.9 (s, $\alpha\text{-CH}_3$), 1.2 (t, CH_2), 1.8 (q, CH), 6.5 (m, $o\text{-ArH}$), 7.0 (m, $m\text{-} + p\text{-ArH}$).

$^{13}\text{C-NMR}$ (100 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 80°C) δ 22.5 ($\alpha\text{-CH}_3$), 40.5 (CH), 43.5 (CH_2), 125 ($p\text{-ArC}$), 127.5 ($o\text{-} + m\text{-ArC}$), 145.0 ($ipso\text{-ArC}$).

These spectra are in accordance with the incorporation of styrene and α -methyl styrene units along copolymer chains. Furthermore, single signals in the aromatic $^{13}\text{C-NMR}$ spectrum indicates the stereoregularity of copolymers and more precisely their syndiotactic sequence, as it was also the case for $^1\text{H-NMR}$ spectrum, where the methylene signal appears as a triplet confirming their syndiotactic nature. The very small signals at 0.9 ppm ($^1\text{H-NMR}$) and at 23 ppm ($^{13}\text{C-NMR}$) denote the presence of α -methylstyrene units incorporated in the copolymer chains; as we referred for $S/(\alpha\text{-MeS})$ copolymerization using CpTiCl_3 half metallocene,¹⁰ in agreement with the work of Elgert et al.¹⁶ for poly($\alpha\text{-MeS}$).

CONCLUSIONS

The metallocenes Cp_2TiCl_2 , $(n\text{-BuCp})_2\text{TiCl}_2$, and IndTiCl_3 combined with MAO (binary systems) and with MAO plus Ph_2Zn (ternary systems) induce the homopolymerization of styrene and its copolymerization with α -methylstyrene. By the other hand these initiator systems produced only traces of poly(α -methylstyrene) in homopolymerization of α -methylstyrene. The effectiveness of the initiator systems decreases as the proportion of $\alpha\text{-MeS}$ increases in the reaction mixture, showing lower reactivity of α -methylstyrene compared to styrene, in agreement with steric hindrance due the presence of a methyl substituent on the vinyl group of styrene.

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