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ORIGINAL PAPER

Styrene copolymerization using a metallocenic initiator. Homo- and copolymerization of styrene with isoprene through zirconocene–MAO initiating systems

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Abstract The copolymerization of styrene with isoprene (Ip) has been tested using combined zirconocene–methylaluminoxane (MAO) initiating system. Both "half-sandwich" and real zirconium-based metallocenes were used. Regardless of the metallocene employed, conversion to copolymer was much influenced by the proportion of Ip in the initial feed. As the proportion of Ip is enriched, conversion to copolymer decreases substantially. Results of NMR and DSC analyses indicate that the products obtained were truly copolymers and not a mixture of both homopolymers. The studied zirconocene–MAO initiating system produces atactic polystyrene. A small amount of Ip in the initial feed substantially diminishes the conversion and at best traces of poly(isoprene) *were* detected in the homopolymerization of Ip with these initiating systems.

Keywords Styrene copolymerization · Dienes · Metallocene catalysts · Tacticity

Introduction

A very important discovery was made by Ishihara et al. [1, 2] and at about the same time by Zambelli and coworkers [3] when they reported a new kind of polystyrene

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with a crystalline melting temperature, T_m, of the order of 270 °C obtained by using a metallocene combined with methylaluminoxane (MAO) presenting a syndiotactic microstructure (s-PS) according to its NMR spectrum. Later, numerous researchers have worked on the topic and various comonomers have been used to produce styrene copolymers with particular and improved properties with respect to polystyrene [4, 5]. More recently, Rodrigues et al. [6] and also Schellenberg [7] published very complete and important reviews of the stereospecific polymerization of styrene and of metal transition catalysts for syndiotactic polystyrene, respectively. Furthermore, last year a book on syndiotactic polystyrene, in which synthesis, characterization, processing, and applications are treated, was published by Wiley [8].

Since the early 90s styrene–isoprene (Ip) polymerization research has been done with two main goals: to clarify the mechanism of styrene polymerization and to improve the mechanical resistance of commercial polystyrene, particularly its impact resistance and flexibility as well its thermal behavior. Several of them have used $CpTiCl_3$–MAO initiating systems with good results. Pellecchia et al. [9] reported that their results confirmed a close relation between the mechanism of syndiospecific polymerization of styrene and *cis*-1,4 polymerization of conjugated diolefins. They reported that polymerization of Ip is much slower than that of styrene, while coordination of Ip would be faster and more favored than coordination of styrene, but insertion on the Ti-allyl bond would be slower than insertion on the Ti-benzyl bond. Furthermore, they considered that incorporation of the monomers occurs in two steps, both rate-determining: coordination of the monomer followed by subsequent insertion. In another paper [10], it was pointed out that a qualitative explanation of the reactivity of different monomers in homo- and copolymerization using $CpTiCl_3$–MAO is achieved by considering the nucleophilicity of the monomers and the electrophilicity of active species. An investigation by means of Extended Huckel theory (EHT) and ab initio computation indicates that the large difference in the homopolymerization rates of butadiene and Ip appears to be due to the higher reactivity of the growing chain ending with a butenyl unit [11]. Other authors, working with the same initiator system in toluene at 50 °C, reported the formation of an S–Ip copolymer in low yield (4% after 72 h) [12].

Naga and Imanishi [13] used half-sandwich titanocenes with different ligands: cyclopentadienyl, indenyl, and pentamethylcyclopentadienyl, and reported that random S/Ip copolymers were obtained. $CpTiCl_3$ gave the copolymer containing the largest amount of Ip and showed a steep melting point depression with increasing Ip content. Cugini et al. [14] using $CpTiCl_3$–MAO, studied the homopolymerization of 4-methyl-1,3-pentadiene and its copolymerization with alkenes, establishing that backbiting coordination has little influence, if any, on chemoselectivity in the polymerizations that were studied.

The $Ti(\eta^5\text{-}C_5H_5)\text{-}(\eta^2\text{-MBMP})Cl$ system, where MBMP = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxo) activated with MAO produces P(S–Ip), but in spite of the syndiotacticity of the styrene homosequence, the copolymers obtained were completely soluble in organic solvents and also amorphous at high styrene concentration [15].

Oliva et al. [16] reported that polymerization of butadiene and its methyl derivatives with bis(acetylacetonato)nickel or cyclopentadienyltitanium trichloride gave predominantly 1,4-polymers without stereotactic characteristics.

Recently, Rodrigues et al. [17] studied the copolymerizarion of styrene with Ip and styrene–ethylene–Ip terpolymerization and reported that the ansa-metallocene complex $(CpCMe_2Flu)Nd(C_3H_5)(THF)$ is an effective single-component catalyst for the production of syndiotactic-rich polymer materials modified by Ip and/or ethylene. The copolymers have high molecular weights ($M_n = 12.000$–91.000 g/mol) and unimodal relatively narrow molecular weight distributions ($M_w/M_n = 1.3$–2.8), and the comonomer feed can be easily manipulated to tune the respective amounts of monomers incorporated in the copolymer.

We have studied both homo- and copolymerization of styrene using titanocenes as well as zirconocenes and a couple of hafnocenes [18–22]. Copolymerization of styrene with substituted styrenes; alkylstyrenes, methoxystyrene, halostyrene, and α-methylstyrene was studied, and we concluded that titanocenes are more active than zirconocene in styrene polymerization, producing almost pure s-PS [18, 19]. The initiator effectiveness is much influenced by the inductive effect of the substituents. I+ groups favor the polymerization process, [20] while I− substituents hindered the polymerization of styrene monomer by these systems. On the other hand, these metallocene–MAO systems with and without diphenylzinc have been used in the homopolymerization of α-olefins and their copolymerization with styrene, while zirconocenes were more effective than titanocene [23–26]. More recently, we reported on the copolymerization of styrene with α-methylstyrene and with di- and trimethyl styrenes, finding that steric hindrance plays a significant role. α-Methylstyrene, despite its I+ methyl group, is less reactive than *p*-methylstyrene or styrene itself [21]. Di- and trimethyl styrene showed that *ortho*-substitution decreases reactivity substantially. These results indicated that polymerization of substituted styrene and its copolymerization with styrene is governed not only by electric effects, but also by steric effects. According to our results, the steric effect is predominant, so that di- and trimethyl substitution on the ring decreases the efficiency of the polymerization process [22].

We have used binary $CpTiCl_3$–MAO and ternary Ph_2Zn–$CpTiCl_3$–MAO to copolymerize styrene with the functionalized *p-tert*-butyldimethylsilyloxystyrene to prepare the corresponding poly(*S*-*co*-*p*-TBDMSOS) copolymer, which after acid hydrolysis yielded the corresponding poly(styrene-*co*-*p*-hydroxystyrene) which cannot be obtained in high molecular weight by direct copolymerization. The copolymers produced are semicrystalline [27].

In the present work, we report the results of styrene/Ip copolymerization using zirconocene–MAO initiating systems, for the metallocenes: $CpZrCl_3$, $(n\text{-}BuCp)_2ZrCl_2$, Ind_2ZrMe_2, and $Me_2Si(Ind)_2ZrCl_2$. Some exploratory experiments using Ph_2Zn–zirconocene–MAO ternary initiating systems were performed with metallocene: $CpZrCl_3$ and Ind_2ZrMe_2.

Experimental

Materials

Toluene (J.T. Baker) was purified by refluxing over metallic sodium, with benzophenone as indicator. Styrene monomer (Aldrich) was treated with a 5% NaOH solution, then thoroughly washed with distilled water, dried over Na_2SO_4, filtered, and dried over CaH_2, and distilled under reduced pressure. Ip was dried over CaH_2 and distilled before use. MAO (Chemtura Europe GMBH), cyclopentadienylzirconium trichloride (Aldrich), bis(*n*-butylcyclopentadienyl)zirconium dichloride, and dimethylsilyl(bisindenyl)zirconium dichloride (Boulder Scientific Company) were used without further purification. All the operations were carried out in an atmosphere of high purity Ar (99.95%), using a dry box to handle the metallocenes. Solvent, MAO, and toluene solutions of metallocenes, styrene, as well as toluene solution of comonomers were transferred by the syringe technique to Schlenk reactors.

Polymerization

Solvent (toluene), MAOs toluene solution (10 wt%), styrene, toluene solution of metallocene, comonomer and of diphenylzinc (for ternary initiating system) were added sequentially to a 50–100 mL Schlenk reactor provided with magnetic stirring. The mixture was stirred at constant temperature for the required length of time.

The reaction was stopped by addition of a solution of methanol acidified with HCl (1%). The polymer was recovered by filtration and washed several times with methanol to remove unreacted comonomer. Finally, the product was dried in vacuum at 60 °C.

Characterization

Intrinsic viscosity

Viscosities were measured either in chloroform (30 °C) or in *o*-dichlorobenzene (135 °C), depending on the solubility of the polymer, and intrinsic viscosities were determined by the one-point method [28].

Calorimetric analysis

DSC analyses were performed on a Rheometrics Scientific DSC apparatus with samples placed in a nitrogen atmosphere. The samples (3–4 mg) were heated at a rate of 10 °C/min. Crystallization of the sample was done at the same rate, and after cooling to room temperature, reheated at the same rate. The reported T_g and T_m were those obtained in the second heating scan.

NMR analysis

NMR spectra were recorded on a Bruker AMX-300 spectrometer at 60 °C, operating at 300.1 and 75.5 MHz for ^1H and ^{13}C, respectively. The polymers and copolymers were dissolved in deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$, 5% w/v). A total of 64 and 4,000 scans with 16 and 32 K data points and with relaxation delays of 1 and 2 s were collected for ^{1}H and ^{13}C, respectively. Chemical shifts were calibrated with tetramethylsilane (TMS) used as internal reference.

Results and discussion

Table 1 summarizes the comparative values for both styrene polymerization and styrene/Ip copolymerization using various zirconocenes in the metallocene–MAO initiating systems. The zirconocenes used were cyclopentadienyl zirconium trichloride, $CpZrCl_3$, bis(*n*-butylcyclopentadienyl)zirconium dichloride, $(n\text{-BuCp})_2ZrCl_2$, bis(indenyl) zirconium dimethyl, Ind_2ZrMe_2, and dimethylsilylbisindenylzirconium dichloride, $Me_2Si(Ind)_2ZrCl_2$.

Table 1 Styrene/isoprene copolymerization using binary zirconocene–MAO initiating systems, in toluene after 24 h at 40 °C

Ip in initial feed (% mol)	Convn. (%)	Activ.[a]	$\|\eta\|$[b] (dL/g)	DSC[c]		Composition[d]	
				T_g (°C)	T_m (°C)	S (% mol)	Ip (% mol)
$CpZrCl_3$							
0.0	16.8	7.1	0.08	84.1	ns	100.0	0.0
2.1	13.4	5.8	0.11	82.2	ns	99.2	0.8
4.8	12.3	5.4	0.09	76.4	ns	99.4	0.6
9.1	10.5	4.7	0.08	66.9	ns	95.2	4.8
$(n\text{-BuCp})_2ZrCl_2$							
0.0	8.6	3.7	0.07	87.1	ns	100.0	0.0
4.8	9.5	4.2	0.13	83.8	ns	99.1	0.9
9.1	9.1	4.1	0.07	71.2	ns	98.4	1.6
Ind_2ZrMe_2							
0.0	12.8	5.5	0.26	92.2	ns	100.0	0.0
2.4	2.8	1.2	nd	90.3	ns	98.9	1.1
5.0	5.9	2.6	0.33	84.8	ns	98.5	1.5
10.0	4.9	2.2	nd	75.5	ns	93.4	6.6
$Me_2Si(Ind)_2ZrCl_2$							
0.0	4.8	2.0	insol	98.9	ns	100.0	0.0
5.0	4.0	1.8	nd	81.1	ns	95.4	4.6
10.0	3.0	1.3	nd	74.1	ns	92.0	8.0

Polymerization conditions: total volume = 21.6 mL; [S] = 2.2 mol/L; [metallocene] = 2.3*E*−04 mol/L; [MAO] = 0.37 mol/L

nd Not determined, *ns* no signal, *insol* insoluble at 30 °C

[a] Activity = (kg copolymer)(mol Met)$^{-1}$(h)$^{-1}$

[b] Measured in chloroform at 30 °C

[c] Second heating at 10 °C/min for crude copolymer

[d] Determined by ^{1}H-NMR spectroscopy

For each particular metallocene–MAO initiating system, conversion to copolymer decreases as the proportion of Ip in the initial feed increases. On the other hand, Ip incorporation in the copolymer was always lower than its proportion in the starting mixture, indicating a lower reactivity of Ip compared to styrene, in agreement with results reported by Zambelli using $CpTiCl_3$–MAO initiator system, which could result from an inhibition of the polymerization process caused by the insertion of an Ip unit. The thermal behavior of the polymers showed low T_g values for PS as well as for the copolymers obtained, regardless of the zirconocene included in the particular initiator system. Copolymer composition determined from the ^{1}H-NMR spectra showed low incorporation of Ip, always in lower percentage with respect to that in the initial feed.

The copolymers' low viscosity, and consequently their low molecular weights, suggest that these monomers are not prone to polymerize with the systems used, confirming previous considerations indicating that zirconocene–MAO initiator systems are less effective than titanocene–MAO initiator systems [21], particularly when a large excess of styrene is present in the initial feed. With respect to the S/Ip copolymerization results, a sort of competition can be considered between the incoming monomer, either styrene or Ip, and the possible coordination of the remaining C=C double bond of the last Ip unit already inserted in the growing polymer chain. Regardless of the possible ways in which Ip is incorporated (inserted), i.e., 1,4-, 1,2-, or 3,4-addition, there is always a double bond remained which will compete with an incoming monomer unit before its coordination with the active species.

Exploratory copolymerizations using ternary diphenylzinc–metallocene–MAO (Ph_2Zn–$CpZrCl_3$–MAO and Ph_2Zn–Ind_2ZrMe_2–MAO) initiating systems did not show any improvement in activity (conversion to polymer) compared with the ones when using binary initiating system, confirming previous results [18, 19, 21] which indicate that the zirconocenes did not behave like the titanocenes with Ph_2Zn participation in the initiating system. For titanocenes it was postulated that diphenylzinc, being a Lewis acid, favors the reduction of titanium to Ti^{3+}, which is considered to be responsible for syndiotactic polystyrene as well as for the higher conversion to polymer than their zirconocene homologs [18–22].

Figure 1 shows the expanded ^{1}H-NMR spectra of the copolymers obtained for each zirconocene–MAO initiator system. Each set of signals shows the spectrum of each particular S/Ip mole ratio used in the initial feed. These NMR spectra show small signals at 4.5–5.3 ppm which correspond to alkenyl protons due to the C=C double bond remaining in each inserted Ip unit in the copolymer chains. These signals, together with the signal in the aromatic region, were used to calculate the copolymer composition presented in Table 1.

Furthermore, following the work of Cuomo et al. [15] where the regioselectivity of Ip insertion in S/Ip copolymers was thoroughly analyzed by NMR, it is possible to make some comments on the ^{1}H-NMR spectra shown in Fig. 1. Signals at 4.6–4.8 ppm and 4.8–5.0 ppm are seen corresponding to 3,4-vinyl and 1,2-vinyl units, respectively, of Ip. However, no signals due to 1,4 insertion of Ip could be detected in the 5.0–5.2 ppm region. This suggests, in the present case, that the insertion of Ip units is mainly due to 1,2 and 3,4 addition. The absence of signals at

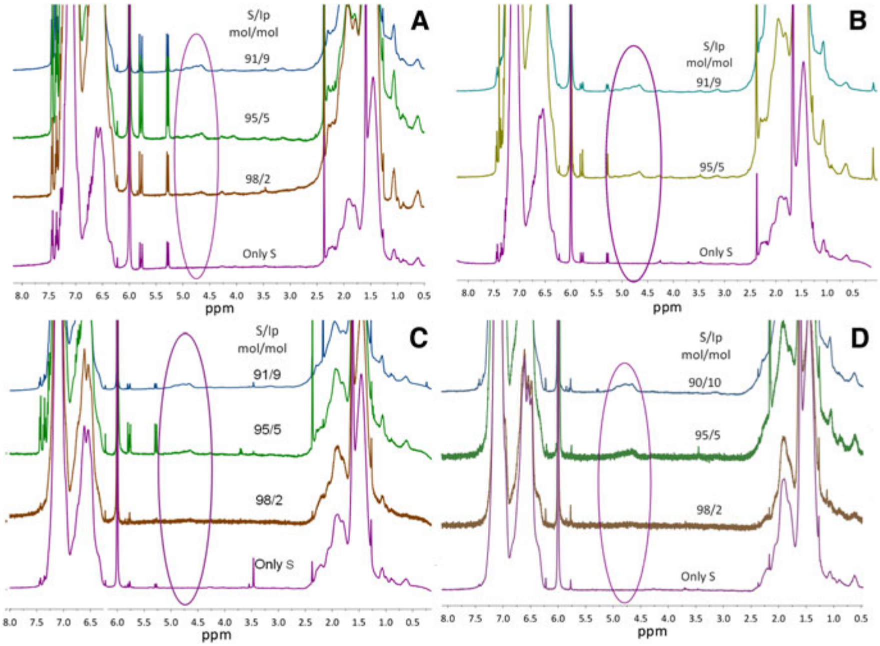


Fig. 1 Expanded ^{1}H-NMR spectra of the products obtained in S/Ip copolymerization initiated by metallocene–MAO initiator systems in toluene at 40 °C for 24 h. Metallocene **A** $CpZrCl_3$, **B** $(n\text{-}BuCp)_2ZrCl_2$, **C** Ind_2ZrMe_2, and **D** $Me_2Si(Ind)_2ZrCl_2$

5.0–5.2 ppm, in case of some 1,4 incorporation, if any, can be explained considering the small amount of Ip units in copolymer chains. According to these considerations, it can be concluded that the initiating system used favors 1,2 and 3,4 Ip incorporation in the copolymerization of styrene and Ip.

Figure 2 shows examples of the DSC thermograms of some of the S–Ip copolymers initiated by zirconocene–MAO systems. The absence of crystalline melting temperature signals, and the copolymer's solubility in chloroform at room temperature are indicative of the amorphous nature of the copolymers obtained. Figure 2 also shows a decrease of T_g as the amount of Ip in the initial feed increases, indicating a slowdown of the polymerization process or perhaps its stoppage due to the low reactivity of the "regenerated" active species after the insertion of an Ip unit. Furthermore, the decrease of T_g may also suggest that the copolymer formed, as it incorporates Ip, becomes more flexible.

According to Table 1, the effectiveness of the zirconocenes used follows the order $CpZrCl_2 > Ind_2ZrMe_2 > (n\text{-}BuCp)_2ZrCl_2 > Me_2Si(Ind)_2ZrCl_2$, with the "half-sandwich" metallocene giving better conversion for styrene homopolymerization as well as for S/Ip copolymerization. In the initiator systems, there was always a marked decrease in conversion as Ip was included in the reaction mixture. The presence of 2–5 mol% of Ip in the reaction mixture produced a high conversion drop.

These behaviors suggest a lower reactivity of Ip and/or some sort of inhibition in the propagation stage. As is well known, metallocenic polymerization of styrene

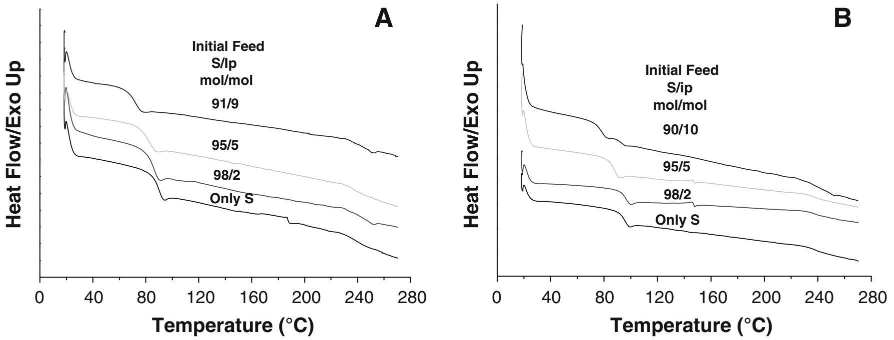
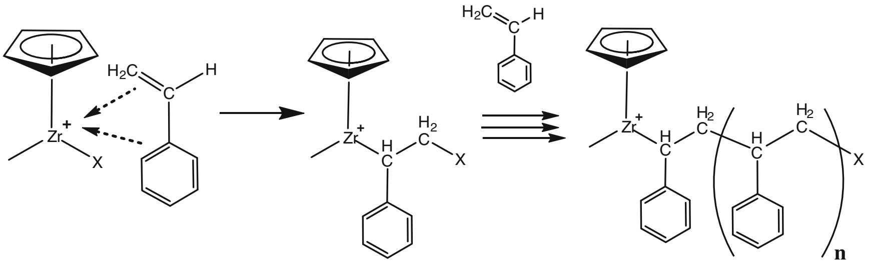


Fig. 2 DSC thermograms of products obtained in S/Ip copolymerization using metallocene–MAO initiating systems. Toluene, 40 °C, 24 h. Metallocenes: **A** $CpZrCl_3$ and **B** Ind_2ZrCl_2

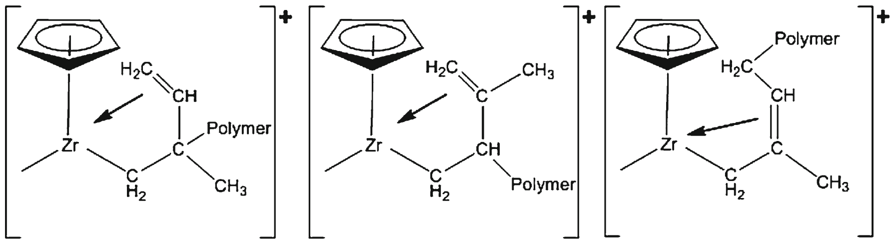
proceeds through coordination of a monomer with the initiator active species, forming a complex that leads to its incorporation and the regeneration of the active species, and then the propagation stage is followed by the sequential incorporation of monomer units:

(i) Styrene insertion:



A styrene monomer unit coordinates with the active species bonded to the polymer's growing chain, inserts itself, and regenerates the active species.

(ii) Isoprene insertion:



1,2-insertion **3,4-insertion** **1,4-insertion**

The insertion of an Ip monomer would follow a similar pathway, ending with regeneration of the active species, but here it will be more crowded, making more difficult the entry of a new monomer unit.

Hence, in each case, regardless of the resulting insertion (1,2-, 3,4-, or 1,4-), a C=C double bond remains which interacts (coordinates) with the active zirconium species, blocking, or competing with, the entry of another monomer unit necessary to continue propagation. This will lead to low conversion and low molecular weight copolymers.

Conclusions

From present and previous results, we can conclude that the zirconocene–MAO initiating systems studied are capable of homopolymerizing styrene and to a smaller extent copolymerizing styrene with Ip, provided the initial feed has a low proportion of Ip. The PS and the P(S/Ip) copolymers obtained are amorphous. According to ^{1}H-NMR analyses, it can be concluded that the initiating systems used favors 1,2 and 3,4 Ip incorporation, in the copolymerization of styrene and Ip studied. On the other hand, the lower T_g values of P(S/Ip) compared to those of PS suggest a less rigid material.

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