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Regiospecificity of Ethylene–Styrene Copolymerization with a Homogeneous Zirconocene Catalyst

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ABSTRACT: Ethylene–styrene copolymers have been prepared in the presence of the catalytic system based on [(methyl)(phenyl)methylene(1-cyclopentadienyl)(9-fluorenyl)]zirconium dichloride, methylalumoxane, and $Al(^{13}CH_3)_3$. End-group analysis shows that in the initiation step the regiospecificity of styrene insertion into the $Zr-^{13}CH_3$ bonds is prevailingly secondary.

Introduction

Copolymerization of styrene (S) with ethylene (E) has been achieved only recently, by using several homogeneous catalysts, consisting of Ti or Zr compounds activated with methylalumoxane (MAO).[1–4] Kakugo *et al.*[1] reported that an alternating styrene–ethylene copolymer (together with some syndiotactic polystyrene) could be obtained by using a catalyst based on 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxy)titanium dichloride and MAO. Later on, in the patent literature[2] was reported the copolymerization of styrene and ethylene promoted by bridged amido–monocyclopentadienyl Ti or Zr complexes, such as (phenylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium dichloride and MAO. The copolymers obtained were called "pseudorandom", since no regioregularly arranged S–S sequences were detected by ^{13}C NMR and the styrene content in the copolymers was always less than 50% by mol, no matter how low the E/S ratio of the feed was. Similar copolymers, together with some homopolyethylene and/or syndiotactic polystyrene, had been previously obtained in our laboratory[3] by using the catalytic system $CpTiCl_3$–MAO. More recently, Inoue *et al.*[4] reported that analogous pseudorandom E–S copolymers can be obtained by using suitable metallocene-based catalytic systems, such as [isopropylidene(1-cyclopentadienyl)(9-fluorenyl)]zirconium dichloride–MAO.

In this paper, as a first contribution to a better understanding of the copolymerization mechanism, we investigate the regiospecificity of styrene insertion in the initiation step in the presence of a catalytic system based on the closely related metallocene [(methyl)(phenyl)methylene(1-cyclopentadienyl)(9-fluorenyl)]zirconium dichloride (**1**) and MAO.

Results and Discussion

The ^{13}C NMR spectrum of an E–S copolymer prepared at 50 °C in the presence of the catalytic system $1/MAO/Al(CH_3)_3$ (sample 1; see the Experimental Section) is displayed in Figure 1. In the aliphatic region of the spectrum, the main resonances are observed at 23.5, 25.6, 27.8, 35.0, and around 43.7–44.2 ppm from hexamethyldisiloxane. According to the literature,[3] these resonances are attributable respectively to $S_{\beta\beta}$, $S_{\beta\delta+}$, $S_{\delta+\delta+}$, $S_{\alpha\gamma+}$, and $T_{\gamma+\gamma+}$ carbons. This pattern of resonances is diagnostic of an ethylene–styrene copolymer containing EEE, EES, and ESE sequences.

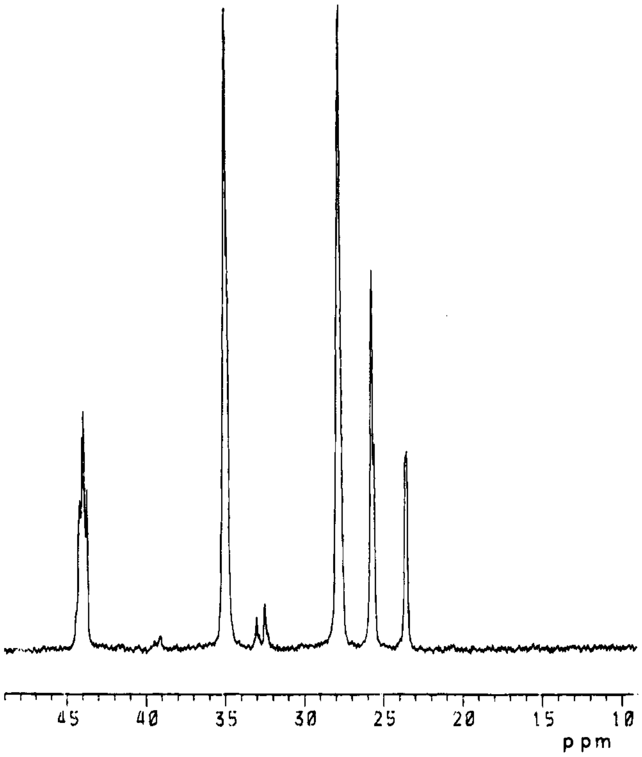

Figure 1. Aliphatic region of the ^{13}C NMR spectrum of an E–S copolymer prepared with $1/MAO/Al(CH_3)_3$ at 50 °C (sample 1). Hexamethyldisiloxane scale.

The lower intensity resonances detected at 32.2 and 32.9 ppm are diagnostic of the sequence $\cdots CH_2CH(C_6H_5)CH_2CH_2CH(C_6H_5)CH_2\cdots$, that can arise either from tail-to-tail arranged S units or from an ethylene unit bridging head-to-head arranged S units. In any case, the presence of such a sequence shows that the insertion of styrene is not completely regioregular.

The negligible amount of regioregularly arranged SS sequences can be appreciated from the very low intensity of the resonances at 39 ppm and around 42–44 ppm, expected for the secondary and tertiary carbons of the styrene homosequences. These resonances are probably due to traces of atactic polystyrene produced together with the copolymer.

The composition of the copolymer can be evaluated, e.g., from the areas of the methylene carbon resonances (see Table 1) by using the equation $x_S = \{A(S_{\alpha\gamma+}) + A(S_{\alpha\beta})\}/\{A(S_{\delta+\delta+}) + A(S_{\beta\beta}) + A(S_{\beta\delta+}) + 1.5A(S_{\alpha\gamma+}) + 1.5A(S_{\alpha\beta})\}$. For sample 1, the mole fraction of styrene is 0.32.

The average length of the methylene sequences can be similarly evaluated from the equation L_{CH_2} =

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Table 1. Observed Chemical Shifts and Relative Abundance of the Aliphatic Carbon Atoms in the E–S Copolymers

		area of the resonances[b]	
δ, ppm from HMDS	carbon[a]	sample 1	sample 2
23.5	$\beta\beta$ CH_2	0.071	0.083
25.6	$\beta\delta^+$ CH_2	0.15	0.15
27.8	$\delta^+\delta^+$ CH_2	0.30	0.26
32.2 and 32.9	$\alpha\beta$ CH_2	0.024	0.036
35.0	$\alpha\gamma^+$ CH_2	0.30	0.30
43.7–44.2	$\gamma^+\gamma^+$ CH	0.16	0.17

[a] The greek letters indicate the nearest tertiary carbon atom. [b] The areas are normalized to unity.

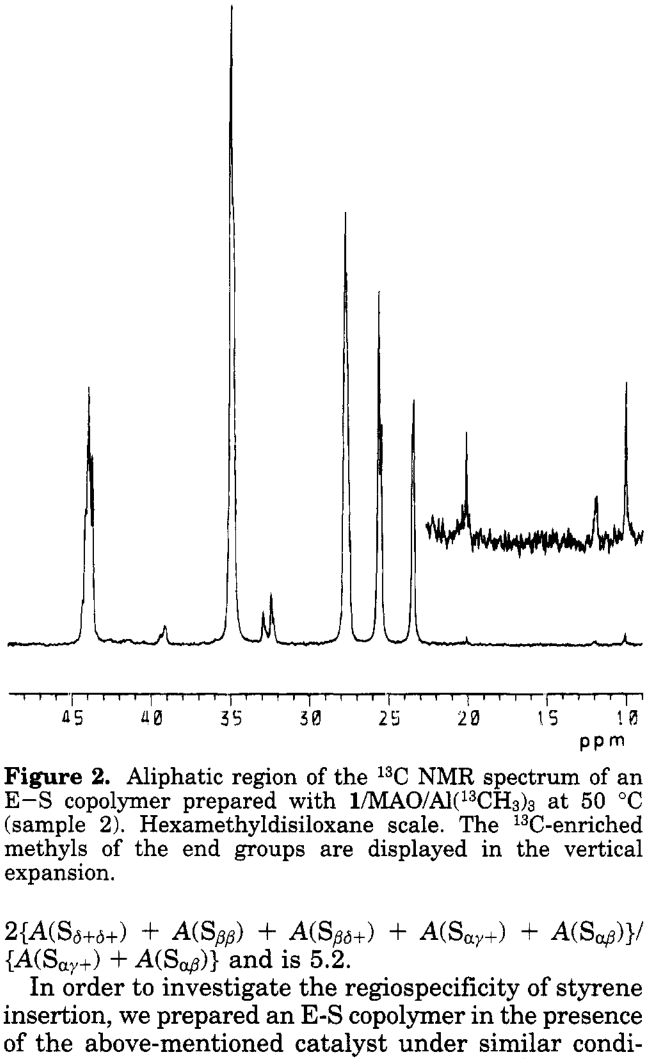

Figure 2. Aliphatic region of the ^{13}C NMR spectrum of an E–S copolymer prepared with **1**/MAO/Al($^{13}CH_3$)$_3$ at 50 °C (sample 2). Hexamethyldisiloxane scale. The ^{13}C-enriched methyls of the end groups are displayed in the vertical expansion.

$2\{A(S_{\delta+\delta+}) + A(S_{\beta\beta}) + A(S_{\beta\delta+}) + A(S_{\alpha\gamma+}) + A(S_{\alpha\beta})\}/\{A(S_{\alpha\gamma+}) + A(S_{\alpha\beta})\}$ and is 5.2.

In order to investigate the regiospecificity of styrene insertion, we prepared an E-S copolymer in the presence of the above-mentioned catalyst under similar conditions, but using $Al(CH_3)_3$ 75% enriched with ^{13}C (sample 2). In the ^{13}C NMR spectrum of sample 2 ($x_S = 0.34$), three additional resonances are observed, in comparison with the spectrum of sample 1, at 10.0, 12.0, and 20.1 ppm (see Figure 2).

Of course, these resonances arise from the enriched methyls coming from $Al(^{13}CH_3)_3$. On the basis of the chemical shifts, they are attributed to the following end groups:

$$\cdots CH(C_6H_5)CH_2{}^{13}CH_3 \qquad 10.0 \text{ ppm} \qquad (a)$$

$$\cdots CH_2CH_2{}^{13}CH_3 \qquad 12.0 \text{ ppm} \qquad (b)$$

$$\cdots CH_2CH(C_6H_5){}^{13}CH_3 \qquad 20.1 \text{ ppm} \qquad (c)$$

arising respectively from the following insertions on the $Zr-{}^{13}CH_3$ bonds of the methylated active species:

$$Zr-{}^{13}CH_3 + C_8H_8 \xrightarrow{\text{2,1 insertion}} Zr-CH(C_6H_5)CH_2{}^{13}CH_3 \quad (1)$$

$$Zr-{}^{13}CH_3 + C_2H_4 \rightarrow Zr-CH_2CH_2{}^{13}CH_3 \quad (2)$$

$$Zr-{}^{13}CH_3 + C_8H_8 \xrightarrow{\text{1,2 insertion}} Zr-CH_2CH(C_6H_5){}^{13}CH_3 \quad (3)$$

These findings suggest that (i) this polymerization is actually a polyinsertion on metal–carbon bonds, (ii) the insertion of styrene is not highly regiospecific, and (iii) at least in the initiation step, secondary insertion of styrene into the $Zr-CH_3$ bonds (eq 1) is favored (~2.3:1) in comparison with primary insertion (eq 3).

The low intensity of the resonances due to the enriched methyls, even considering the dilution due to the rapid exchange between $Al(^{13}CH_3)_3$ and MAO, suggests that chain transfer with aluminum is not very fast, at least under our conditions. The ratio between the areas of the resonances of the enriched methyls at 10.0 and 20.1 ppm (a and c end groups), and the area of the resonance of the enriched methyl at 12.0 ppm (b end group) is ~1.5. This value could give an estimate of the rate of the insertion of styrene relative to ethylene into the active $Zr-{}^{13}CH_3$ bonds. However, one should consider also that the polymerization run was initiated by allowing the catalytic system and styrene to contact before feeding ethylene (see the Experimental Section). If chain transfer is frequent enough to render this effect negligible, the larger frequency of styrene insertion in the initiation step in comparison with the S/E ratio in the copolymer (0.5) can be explained by considering that the reactivity ratios of the two comonomers should be comparable for the insertion on either $Zr-CH_3$ or $Zr-CH_2CH_2\cdots$ bonds and that, on the contrary, the reactivity of styrene appears extremely lower than that of ethylene for the insertion on either $Zr-CH(C_6H_5)CH_2\cdots$ or $Zr-CH_2CH(C_6H_5)\cdots$ bonds, according to the observed pseudorandom comonomer distribution.

In conclusion, from the results reported in this paper one can state that the copolymerization of ethylene and styrene is actually a polyinsertion reaction and that the regiospecificity of styrene insertion into the $Zr-CH_3$ bonds is prevailingly secondary.

Work is in progress to ascertain if the same regiospecificity is prevailing in the propagation steps, e.g., by analyzing copolymers of styrene and perdeuterated ethylene.[5]

Experimental Section

Materials. Polymerization-grade ethylene was purchased from Società Ossigeno Napoli and used without further purification. Toluene was refluxed over metallic sodium and distilled under a nitrogen atmosphere. Styrene was purified by distillation under reduced pressure over CaH_2. Methylalumoxane (MAO) was prepared by reaction of $Al(CH_3)_3$ with $FeSO_4 \cdot 7H_2O$ in toluene.[6] [(Me)(Ph)C(Cp)(Flu)]$ZrCl_2$ (**1**) and $Al(^{13}CH_3)_3$ were prepared according to published procedures.[7,8]

Copolymerizations. The copolymerization runs were carried out at atmospheric pressure in a 100-mL glass flask provided with a magnetic stirrer and thermostated at 50 °C in an oil bath. The reactor was charged under nitrogen sequentially with toluene (20 mL), MAO, $Al(CH_3)_3$, styrene (10 mL), and **1**; the inert gas was removed, and the polymerization mixture was saturated with ethylene. The flask was continuously fed with ethylene to keep the monomer concentration constant. The copolymerizations were stopped after 2 h by injecting acidified methanol. The mixtures were quenched in methanol and the polymers recovered by filtration, washed with fresh methanol, and dried in vacuo. In run 1 were used MAO (1.6 mmol), $Al(CH_3)_3$ (0.08 mmol), **1** (12 μmol); the yield was 0.9 g (sample 1). In run 2 were used MAO (2.6 mmol), 75% ^{13}C-enriched $Al(CH_3)_3$ (0.18 mmol), **1** (18 μmol); the yield was 0.65 g (sample 2). The raw polymers were washed with boiling acetone with the aim of removing traces of atactic polystyrene.

^{13}C NMR Analysis. ^{13}C NMR spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode and at a temperature of 413 K. The samples were prepared by dissolving 50 mg of polymer in 0.5 mL of tetrachloro-1,2-dideuterioethane. Hexamethyldisiloxane (HMDS) was used as the internal chemical shift reference. The resonances of the chain-end methyls have been assigned by comparison with the resonances of 2-phenylbutane and with those of long-chain *n*-alkanes.[9]

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