

Zirconocene-Based Catalysts for the Ethylene–Styrene Copolymerization: Reactivity Ratios and Reaction Mechanism

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ABSTRACT: A kinetic study of the ethylene–styrene copolymerization in the presence of *rac*-(ethylenebis(1-indenyl)zirconium dichloride activated by MAO shows the peculiar behavior of this catalytic system that is known to produce crystalline nearly alternating copolymers. Some inferences on the monomer–metal interactions are made on the basis of this study. The parallel investigation on the catalyst based on isopropylidene(1-cyclopentadienyl)(9-fluorenyl)zirconium dichloride allows us to produce a stereoregular nearly alternating ethylene–styrene copolymer also with this catalytic system. The same main tacticity seems to characterize the copolymers obtained with the C_2 and C_s symmetric catalysts in accordance with the generally accepted mechanism of stereocontrol in the 1-alkene polymerizations.

Introduction

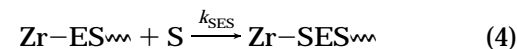
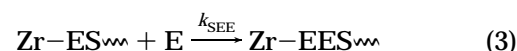
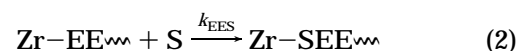
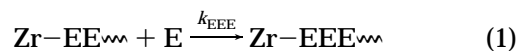
Several metallocene and half-metallocene based catalysts are known to promote the ethylene–styrene copolymerization.¹ The catalytic system constituted by *rac*-ethylenebis(1-indenyl)zirconium dichloride ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) activated by methylaluminoxane (MAO) has been recently reported² to produce at low temperature a crystalline nearly alternating copolymer with possibly isotactic structure due to the C_2 symmetry of the metallocene catalyst precursor. The occurrence that the same catalyst produces at room temperature copolymers with low styrene unit content needs to be clarified. In this kinetic investigation we have determined the reactivity rate constants at different temperatures by NMR. As a matter of fact, by using the literature assignments,^{1a,3,4} the analysis of the ^{13}C NMR spectra of the ethylene–styrene copolymers allows one to determine the triads composition of the macromolecules. The triad content can be related to the comonomer feed compositions to obtain, as a consequence, the reactivity rate constants. This study is aimed at gaining a deeper knowledge on the monomer–catalyst interactions and at describing the dependence of the behavior of the catalyst on the polymerization temperature. Attention is also focused on the comparison between the behavior of the $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst and that of isopropylidene(1-cyclopentadienyl)(9-fluorenyl)zirconium dichloride ($\text{iPr}[\text{Cp}][\text{Flu}]\text{ZrCl}_2$) activated by MAO and between the microstructures of the copolymers obtained with these catalysts.

Results and Discussion

The ^{13}C NMR spectra of two copolymers obtained with similar comonomer feed compositions at +20 and –25 °C are shown in Figure 1a,b respectively. A comparison of the alternating sequences content can be made from the relative intensity of the resonance at 23.4 ppm ($S_{\beta\beta}$) with respect to that around 28 ppm ($S_{\gamma^+\gamma^+}$).

For a kinetic analysis we have to keep in mind that in this copolymerization as in the previously described E–S copolymerizations the regioselective insertion of the styrene into the $\text{M}-\text{S}\cdots$ bond is forbidden,^{1b,3} so four propagation steps are interesting from the kinetic point of view:

Scheme 1



and two reactivity ratios,⁵ $r_{\text{E}} = k_{\text{EEE}}/k_{\text{EES}}$ and $r'_{\text{E}} = k_{\text{SEE}}/k_{\text{SES}}$, measure the preference of the zirconium–polymer bond to insert ethylene instead of styrene when the end monomer unit of the growing chain is ethylene and the penultimate one is ethylene (r_{E}) or styrene (r'_{E}).

It should be noted that the triads generated by reactions 2 and 3 are not distinguishable from each other because the dead macromolecule has forgotten its own sense of growth. As a consequence, we can only evaluate the sum of the events (2) and (3), i.e., the sum of the oriented triads SEE and EES. But if we assume that in a long chain the amount of EES is practically the same as that of SEE (their number differs at most by one), the amount of the oriented triads can be separately evaluated to be proportional to half of the area of the ^{13}C NMR resonance assigned to the $S_{\beta\delta^+}$ carbon. On the other hand the amount of the symmetric triad SES is proportional to the area of the $S_{\beta\beta}$ carbon while for the EEE triad the following relationship can be used:

$$[\text{EEE}] \propto 0.5\{A(S_{\gamma^+\gamma^+}) - 0.5(S_{\beta\delta^+})\}$$

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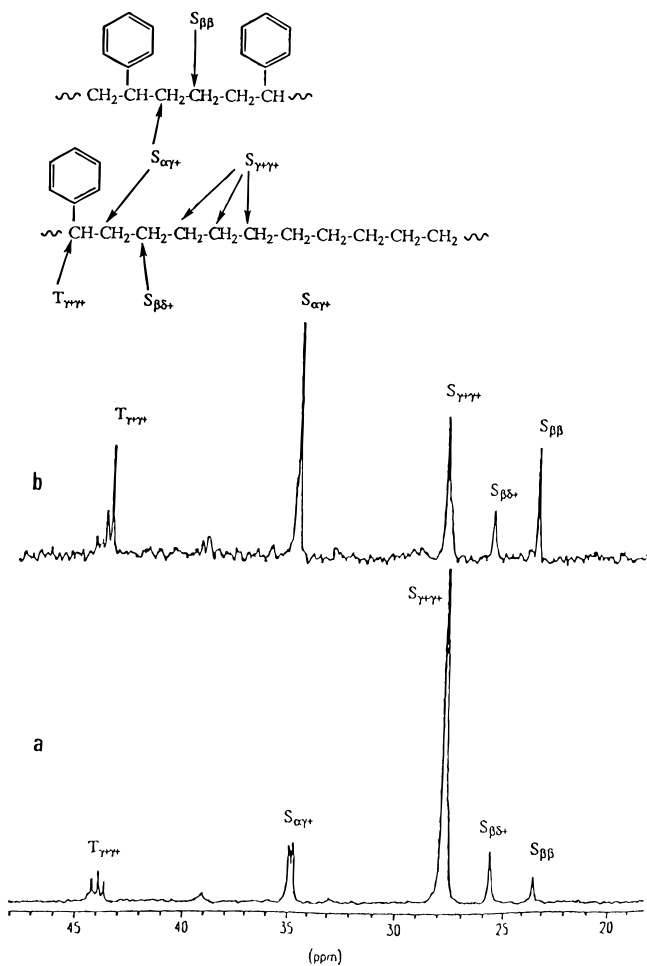


Figure 1. Aliphatic region of the ^{13}C NMR spectra of two copolymers obtained by similar comonomer feeds ($f(\text{E}) = 0.09$) at 20 °C (a) and at -25 °C (b) in the presence of the $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ -based catalyst.

The rate of formation of the above triads is related to the kinetic constants reported in Scheme 1 through the relationships

$$\frac{d[\text{EEE}]}{dt} = k_{\text{EEE}}[\text{Zr}-\text{EE}^{\sim}] [\text{E}]_{\text{feed}} \quad (5)$$

$$\frac{d[\text{EES}]}{dt} = k_{\text{EES}}[\text{Zr}-\text{EE}^{\sim}] [\text{S}]_{\text{feed}} \quad (6)$$

$$\frac{d[\text{SEE}]}{dt} = k_{\text{SEE}}[\text{Zr}-\text{ES}^{\sim}] [\text{E}]_{\text{feed}} \quad (7)$$

$$\frac{d[\text{SES}]}{dt} = k_{\text{SES}}[\text{Zr}-\text{ES}^{\sim}] [\text{S}]_{\text{feed}} \quad (8)$$

where first-order kinetics has been assumed with respect to the monomer and to the active site. Dividing eq 5 by eq 6 and eq 7 by eq 8 yields the ratios at which the monomers enter the copolymer at different penultimate units. By using the above mentioned reactivity ratios we can write

$$[\text{EEE}]/[\text{EES}] = r_{\text{E}}f(\text{E}) \quad \text{and} \quad [\text{SEE}]/[\text{SES}] = r'_{\text{E}}f(\text{E})$$

where $f(\text{E})$ is the ratio of the concentrations of the comonomers in the feed $[\text{E}]/[\text{S}]$. The plot of $[\text{EEE}]/[\text{EES}]$ vs $f(\text{E})$ for a series of copolymerizations carried out at 20 °C with the $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ -based catalyst is reported

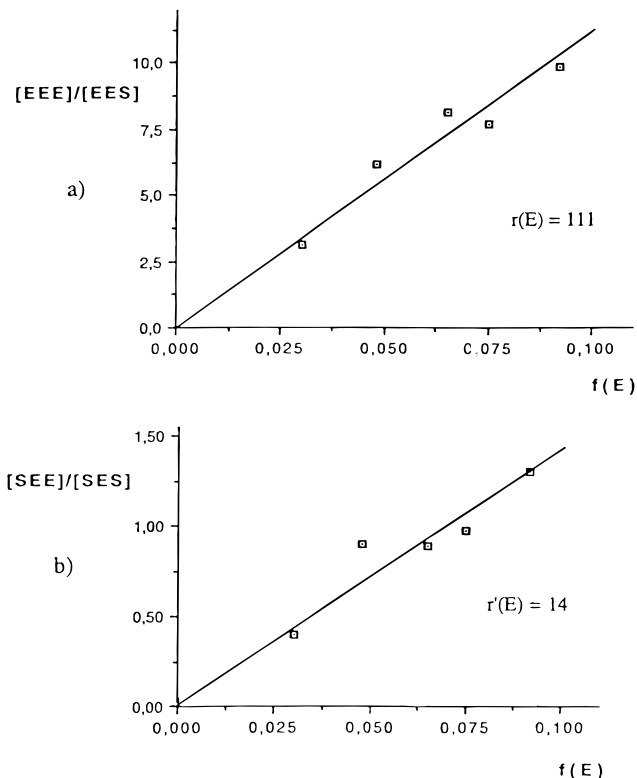


Figure 2. Dependence of the triad content ratio on the ratio between ethylene and styrene concentration in the feed for a series of copolymerizations carried out at 20 °C ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$ -based catalyst).

in Figure 2a and yields a straight line with a slope of 111 that is the value of the reactivity ratio r_{E} .

On the other hand, a value of 14 for r'_{E} is obtained from the plot of $[\text{SEE}]/[\text{SES}]$ vs $f(\text{E})$, which also yields a straight line. In this approach to the kinetics of the copolymerization, the insertion of the styrene is assumed to be regioregular. In fact, weak NMR signals for regioirregularly inserted styrene units are detected around 33 ppm from HMDS but their intensity indicates that the preferred insertion is at least 10 times faster than the other one,³ which therefore can be disregarded.

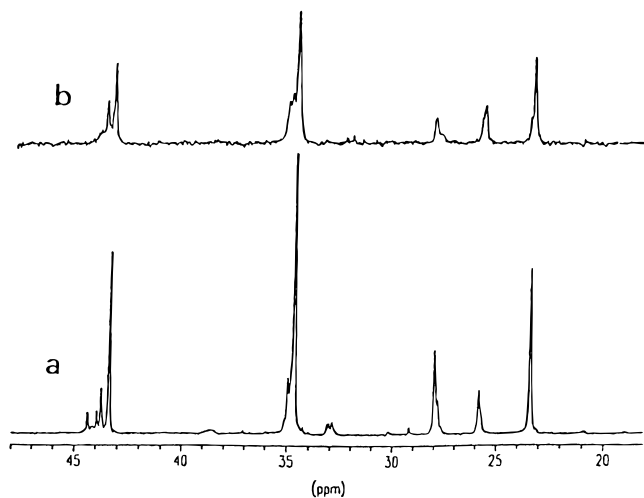
The reactivity ratios have also been determined in a more usual way, by simulating the growth of the copolymer chain by computer through the Monte Carlo method.⁶ By assuming a Markovian chain of the second order, there is a conditional probability of forming each triad in the copolymer. The sum of the conditional probabilities of insertion into the $\text{Zr}-\text{EE}^{\sim}$ and into the $\text{Zr}-\text{ES}^{\sim}$ bond are each separately equal to 1 ($P_{\text{EES}} + P_{\text{EEE}} = 1$ and $P_{\text{SES}} + P_{\text{SEE}} = 1$). This approach works also in the hypothesis of a first-order Markovian chain (P_{EES} should have the same value of P_{SES} , and P_{EEE} , the same value of P_{SEE}). The probability terms are refined to give a copolymer with an NMR spectrum as similar as possible to the experimental one, and the reactivity ratios can be calculated by using the relationships

$$r_{\text{E}} = P_{\text{EEE}}/(P_{\text{EES}}f(\text{E})) \quad \text{and} \quad r'_{\text{E}} = P_{\text{SEE}}/(P_{\text{SES}}f(\text{E}))$$

In Table 1 are reported the values of r_{E} and r'_{E} for copolymerizations carried out at different temperatures with the $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ -based catalyst and, for comparison purposes, with $\text{iPr}[\text{Cp}][\text{Flu}]\text{ZrCl}_2$ - and CpTiCl_3 -based catalysts. Upon inspection of this table one can observe that for the catalytic system based on $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ the preference for the insertion of ethylene

Table 1. Reactivity Ratios for the Ethylene–Styrene Copolymerization Carried out in the Presence of Different Catalysts

catalyst	T (°C)	triad analysis		simulation method	
		r_E	r'_E	r_E	r'_E
Et(Ind) ₂ ZrCl ₂	50	149	48		
Et(Ind) ₂ ZrCl ₂	20	111	14	106	14
Et(Ind) ₂ ZrCl ₂	0	60	9.5	60	9.0
Et(Ind) ₂ ZrCl ₂	-25	43	4.7	42	4.2
iPr[Cp][Flu]ZrCl ₂	40	14	10		
iPr[Cp][Flu]ZrCl ₂	0	13	4.7		
CpTiCl ₃ ^a	20	≤10	5.8		

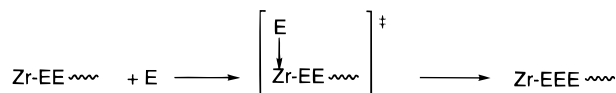
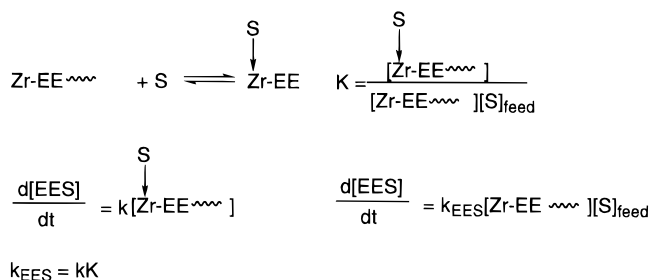
^a Reference 3.**Figure 3.** Aliphatic region of the ¹³C NMR spectra of nearly alternating copolymers obtained in the presence of the Et(Ind)₂ZrCl₂-based catalyst (a) and of the iPr[Cp][Flu]ZrCl₂-based catalyst (b). The chemical shifts of the main peaks are respectively 23.35, 25.79, 27.95, 34.65, and 43.32 ppm (a) and 23.36, 25.65, 27.98, 34.64, and 43.30 ppm (b) (HMDS scale).

into the metal–polymer bond is smaller when the penultimate unit is styrene ($r'_E < r_E$). This behavior could be explained with an interaction of the aromatic ring of the styrene penultimate unit with the catalytic metal. A similar interaction has been recently observed in a half-zirconocene compound.⁷ Also, the presence of two sites (one of them a homopolymerizing ethylene) could justify this occurrence, but such a hypothesis seems less probable because there are neither calorimetric nor diffractometric evidences for the presence of polyethylene chains. On the other hand, a second-order Markovian chain has also been observed by Fink et al.⁸ for the ethylene–1-alkene copolymerizations with *ansa*-metallocene catalysts.

On the contrary, with the iPr[Cp][Flu]ZrCl₂-based system the penultimate unit effect seems to be small at 40 °C while it increases at 0 °C.

The second observation that one can draw from Table 1 is that the preference for the insertion of ethylene decreases with decreasing temperature. This fact is the key for the alternating copolymerization at -25 °C and is surprising; in fact, one should expect an increase of the reactivity ratios with decreasing temperature since the smaller rate constant (larger activation energy) should decrease faster with decreasing temperature than the larger rate constant (smaller activation energy). The fact that the experimental trend is opposite can be justified by assuming that for styrene incorporation the monomer coordination step is an equilibrium step while for the incorporation of ethylene the coordination should be the rate-determining step, the subse-

quent insertion having a low activation energy, as generally assumed for Ziegler–Natta catalysis.

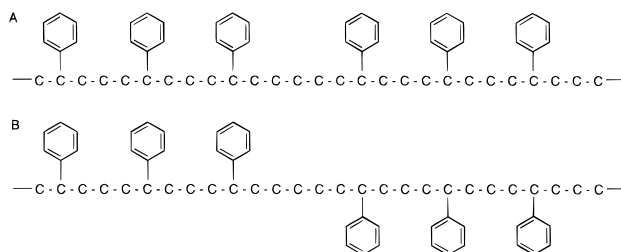


So the kinetic constants k_{EES} and k_{SES} as above defined should be the product of a kinetic constant and an equilibrium constant. The decreasing r_E and r'_E with decreasing temperature should be related to the increase of the stability constant for the active site–styrene complex.

The value of r_E and r'_E for the copolymerization in the presence of iPr[Cp][Flu]ZrCl₂/MAO catalyst at 0 °C is small enough to allow the synthesis of a nearly alternating copolymer ($x_S = 0.44$) that does not crystallize easily.

The comparison of the ¹³C NMR spectra (Figure 3) of the nearly alternating copolymers obtained with the C₂ symmetric Et(Ind)₂ZrCl₂/MAO (spectrum a) and with the C_s symmetric iPr[Cp][Flu]ZrCl₂/MAO catalysts (spectrum b) seems to indicate the same tacticity (chemical shift of the S_{ββ} carbon at 23.4 ppm, Figure 3).

This fact is not surprising because, on the basis of the stereocontrol mechanism proposed in the literature for the syndiospecific propene homopolymerization,⁹ we can suppose that in the strictly alternating copolymerization the prochiral monomer (styrene) always enters the same side of the C_s symmetric complex and, as a consequence, always has the same enantiofacial orientation, the other side being entered by the ethylene. But, in light of this picture, a difference in the microstructure appears, as a consequence of a defect in the alternation. In fact, in the neighboring of a sequence of two ethylene units we can hypothesize microstructure A for copolymer obtained with the Et(Ind)₂ZrCl₂-based catalyst and microstructure B for the copolymer obtained with the iPr[Cp][Flu]ZrCl₂-based catalyst. Such a microstructural difference should account for the little difference in the chemical shifts of the S_{ββ}⁺ signals (0.14 ppm, Figure 3) and for the different crystallization behaviors of the two copolymers.



Conclusion

The simple evaluation of the triad composition of the copolymers prepared at different comonomer feeds al-

lows one to determine the reactivity ratios for the E–S copolymerization. The kinetic study on this copolymerization with the catalytic systems able to produce the alternating crystalline copolymer shows the difference between the pathways for the incorporation of the two monomers into the metal–polymer bond. Due to its more nucleophilic character, the styrene strongly coordinates the catalytic site, and due to the steric hindrance, its insertion is slow.

In accordance with our picture, the catalytic site spends longer times with styrene coordinated at lower temperature and so at $-25\text{ }^{\circ}\text{C}$ it is less prone to the coordination–insertion of the ethylene. On the other hand, a strong penultimate unit effect has been observed due possibly to the back-biting of the aromatic ring of the next-to-last unit of the growing chain.

In our opinion, three features of the catalyst make it able to produce at low temperature the crystalline nearly alternating copolymer: (1) the inability to insert the styrene into a metal–polymer bond when the end unit of the growing chain is styrene, (2) the coordination of the styrene to the active site as an equilibrium step, and (3) the back-biting of the aromatic ring of the next-to-last unit that promotes the formation of SES sequences.

The stereochemistry of the copolymerization with metallocene catalysts with C_2 and C_s symmetry seems to obey the same rules as for the 1-alkene homopolymerizations.

Experimental Part

Materials. Polymerization grade ethylene was purchased from Società Ossigeno Napoli and used without further purification. Toluene was refluxed for 48 h over metallic sodium and distilled under a nitrogen atmosphere. Styrene was stirred 1 h with CaH_2 and distilled under a reduced pressure of nitrogen. Methylaluminoxane (MAO) was purchased as a 30% toluene solution from Witco. Ethylenebis(1-indenyl)zirconium dichloride and isopropylidene(1-cyclopentadienyl)(9-fluorenyl)zirconium dichloride were synthesized according to the literature.^{9,10}

Copolymerizations. Copolymerizations were carried out in a 100 mL glass flask charged under a nitrogen atmosphere sequentially with toluene, styrene, and 3 mL of a 30% MAO solution by weight. The mixture was magnetically stirred, and the glass flask was thermostated at the desired temperature ($+50$, $+40$, $+20$, 0 , or $-25\text{ }^{\circ}\text{C}$). The inert atmosphere was removed and replaced with ethylene, and then 6 mL of a toluene solution of the zirconocene compound (2.4 mM) was introduced ($\text{Al/Zr} = 1000$). In all runs the total volume in the glass flask was kept constant at about 35 mL. The flask was fed with the gaseous monomer at atmospheric pressure for 2 h. Then the reaction mixture was poured in 100 mL of acidified methanol. The copolymerization product recovered

by filtration was washed with boiling acetone and dried in vacuo. The yields range between 4.8 and 0.3 g for $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ catalyst and between 3.5 and 0.1 g for $\text{iPr}[\text{Cp}][\text{Flu}]\text{ZrCl}_2$.

In the comonomer feed composition $f(\text{E}) = [\text{E}]_{\text{feed}}/[\text{S}]_{\text{feed}}$, the ethylene composition in the liquid phase was calculated by Lewis and Luke's equation^{11a} in conjunction with the fugacity function chart of ethylene as reported in literature.^{11b} A series of at least three copolymerizations at different comonomer feed compositions have been performed for each temperature.

¹³C NMR Analysis. The spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode and at a temperature of $20\text{ }^{\circ}\text{C}$. The samples were prepared by introducing 30 mg of polymer with 0.5 mL of tetrachloro-1,2-dideuterioethane into a tube (0.5 mm outer diameter). Hexamethyldisiloxane (HMDS) was used as an internal reference.

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