Notes

Ethene/1,3-Butadiene Copolymerization in the Presence of *rac*-(CH_2-(3-*tert*-butyl-1-indenyl)$_2$)$ZrCl_2$/MAO Catalytic System: Study of the Polymerization Mechanism by Using ^{13}C-Labeled 1,3-Butadiene

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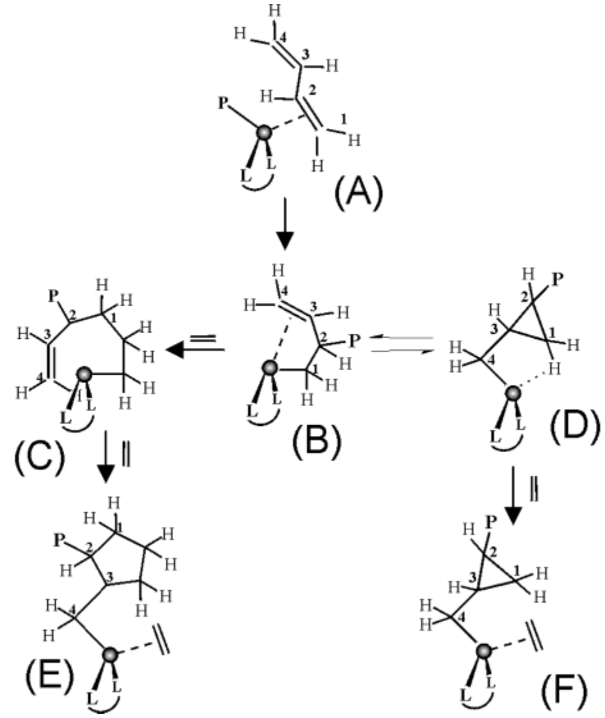
Homogeneous stereospecific olefin polymerization catalysts have enabled the preparation of novel polyolefins derived from common feedstocks.[1,2] Mechanistic studies have widely contributed to obtain polyolefins controlled microstructures by choosing appropriate catalytic systems.[3−5]

Recently, we have shown that copolymerization of 1,3-butadiene with ethene, catalyzed by the isospecific catalytic system based on the C_2 symmetric zirconocene *rac*-[CH_2-(3-*tert*-butyl-1-indenyl)$_2$]$ZrCl_2$ (**1**),[6] activated by MAO, leads to ethene copolymers only containing methylene-1,2-cyclopropane units together with methylene-1,2-cyclopentane units, both with high trans selectivity.[7] Copolymerization of the same monomers with the same catalytic system, when conducted at high temperature and low ethene concentration, leads to ethene copolymers containing only the unprecedented 1,1- and 1,3-constitutional units from 1,3-butadiene, both presenting only the *E* configuration of the double bond.[8] The microstructures of the copolymers were fully determined by ^{13}C NMR analysis.[8]

On the basis of experimental and modeling studies,[7,8] the formation of 1,2-cyclopentane and 1,2-cyclopropane units has been rationalized by the mechanism sketched in Scheme 1.[8]

According to this reaction scheme, a primary butadiene coordination (**1(A)**) would give rise, through a 1,2-insertion into the σ metal−polymer bond, to a primary growing chain, which is bound to the metal by a methylene group (**1(B)**). The resulting 1,2-inserted butadiene unit would be bonded to the metal also by a backbiting coordination of the closest double bond of the chain. This four carbon atoms backbiting chain (**1(B)**) could give rise to a six carbon atoms backbiting chain (**1(C)**) through ethene insertion. Both kinds of backbiting chains (**1(B)**) and (**1(C))** could give rise to cyclization reactions leading to formation of cyclopropane (**1(D)**) and cyclopentane (**1(E)**) rings, respectively, through intramolecular insertion of the coordinated double bond into the σ metal−alkyl bond.[8]

Scheme 1



(*E*)-1,1- and (*E*)-1,3-constitutional units from butadiene[9] could arise from both mechanism **a** or **b** shown in Scheme 2. Mechanism **a** presents a γ-H migration from C1 to C4 and the simultaneous breaking of the C2−C3 bond (**2a(G)**) of the (**2a(D)**) reaction intermediate (already sketched in Scheme 1 as (**1(D)**). The obtained allyl coordination intermediate would lead to 1,1- (**2a(I)**) or 1,3-units (**2a(L)**) after an ethene insertion. In fact, as already reported in ref 8, the lifetime of (**1(D)**) would be long enough to rearrange to other species at low concentrations of ethene. Mechanism **a** arises from an η^2 primary butadiene insertion described in Scheme 1.

Alternatively, the formation of (*E*)-1,1- and (*E*)-1,3-butadiene units could be justified hypothesizing a reaction pathway (**b**) that involves a secondary coordination (**2b(A)**) and insertion of butadiene (**2b(B)**). This plausible pathway involves β-H elimination to afford a diene species (**2b(C)**)/(**2b(D)**), followed by 1,4-reinsertion of the diene into the metal−H bond to form the syn η^3-allyl species (**2b(E)**).

Both mechanisms **a** and **b** present a syn allyl intermediate ((**2a(H))** and (**2b(E)**)), coordinated to metallocene that, as reported in a previous paper, presents lowest energy with respect to all possible disubstituted allyl intermediates.[8,10] In fact, the insertion of ethene into the external allyl carbons, which are bound to the growing chain or to the methyl substituent, would

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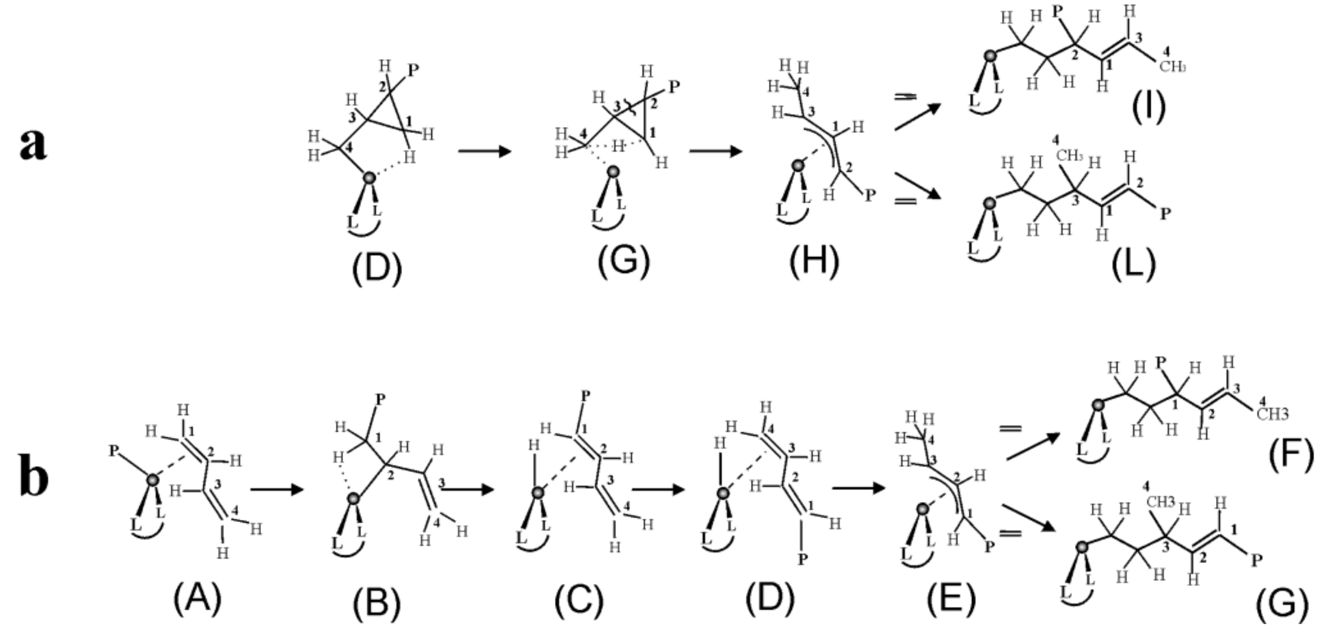
Scheme 2



produce 1,1- and 1,3-constitutional units, respectively, both with (*E*) configuration of the double bond.

In contrast to mechanism **b**, mechanism **a** presents an isomerization of the carbon backbone.

To experimentally discriminate between the two proposed **a** and **b** mechanisms, we have copolymerized ethene in the presence of ^{13}C-labeled 1,3-butadiene by using specific reaction conditions (see Experimental Section) such as to obtain both cyclization reaction and 1,1- and 1,3-insertions of butadiene.

1,3-Butadiene enriched only on carbon 1 was synthesized and used in copolymerization with ethene. This clearly means that, 1,3-butadiene being a symmetric molecule, both carbon 1 and carbon 4 of the units generating from butadiene result ^{13}C enriched along the polymer chain. The ^{13}C NMR spectrum of the resulting polymer, obtained by using 4% ^{13}C-enriched 1,3-butadiene, was examined and compared with that of a copolymer sample obtained using the same reaction conditions and commercial monomers. This experiment clearly allowed us to check, without any doubt, whether the 1,1- and 1,3-butadiene constitutional units derive from a primary or secondary monomer insertion. In fact, a secondary insertion of butadiene would induce an enrichment in ^{13}C of the carbons of the methyl group and of the saturated methine of the 1,1-butadiene units (**2b(F)**) and of methyl group and of the unsaturated methine farther from the methyl group of the 1,3-butadiene units (**2b(G)**).

A primary insertion of butadiene would enrich in ^{13}C the carbons of the methyl group and of the unsaturated methine farther from the methyl group of the 1,1-butadiene units (**2a(I)**) and the carbons of the methyl group and of the methine closest to the methyl group of the 1,3 butadiene units (**2a(L)**).

The ^{13}C NMR spectra of a copolymer sample obtained by using ^{13}C-enriched butadiene (**a**) and of a copolymer sample obtained in the same reaction conditions by using commercial butadiene (**b**) are reported in Figure 1, where all the recognized units generated from butadiene are also shown.

The comparison between the intensities of the peaks related to the 1,1- and 1,3-butadiene constitutional units shows that those at 15.7_8 and 134.7_7 ppm (diagnostic of the carbons of the methyl group and of the unsaturated methine farther from the methyl group of the 1,1-butadiene units) and those at 18.8_5 and 134.6_2 ppm (diagnostic of the carbons of the methyl group and of the methine closest of the methyl group of the 1,3-butadiene units) are increased with respect to the peaks relative to the other carbons of such units.

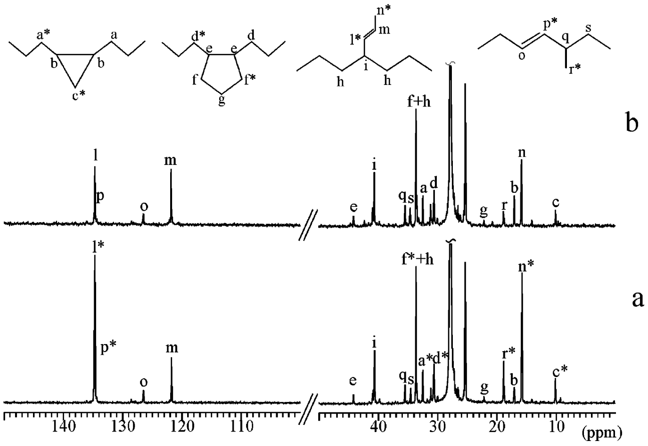


Figure 1. ^{13}C NMR spectra of a copolymer sample obtained by using ^{13}C-enriched butadiene (a) and of a copolymer sample obtained in the same reaction conditions by using commercial butadiene (b) (hexamethyldisiloxane scale).

Thus, the ^{13}C-enriched carbons of 1,1- and 1,3-butadiene units are those expected for a primary coordination, insertion, and cyclization of butadiene followed by cyclopropane breaking and consequent carbon skeleton isomerization (mechanism **a**). It is worth noting that η^2 primary butadiene insertion was already predicted by our previous molecular modeling calculations which clearly indicated that the insertion transition state energy relative to a η^2 primary coordinated butadiene is at least 4.5 kcal/mol lower than the energy of one involving a secondary monomer coordination.[10] Moreover, comparison of the intensities of the signals related to the 1,2-cyclopentane and cyclopropane units shows that the peaks at 10.0_8 and 32.4_5 ppm, related to the carbons of the methylene of the 1,2-

disubstituted cyclopropane ring and the methylene closest to the cyclopropane rings, and those at 33.9_1 and 30.5_4 ppm, related to the two methylenes closest to the methine of the cyclopentane units, increased with respect to the peaks relative to the other carbons of cyclic units. These results are also consistent with the pathway we already proposed for the butadiene cyclization reaction.

Conclusions

Novel polyolefins derived from common feedstocks can be obtained by using Ziegler−Natta catalytic systems. In particular, *rac*-(CH_2-(3-*tert*-butyl-1-indenyl)$_2$)$ZrCl_2$/MAO catalyzes the copolymerization of ethene and 1,3-butadiene leading to a polyethene presenting prevailingly cyclopropane, cyclopentane, or 1,1- and 1,3-units, depending on the reaction conditions. Copolymerizations conducted in the presence of ^{13}C-labeled 1,3-butadiene was able to clarify the polymerization mechanism leading to 1,1- and 1,3-units and to confirm the hypothesis, previously reported, relative to the mechanism leading to cyclopropane and cyclopentane units. In particular, all kinds of inserted butadiene units arise from an η^2 primary butadiene coordination and insertion. Evidently, the sterical hindrance of the catalytic system induces the η^2 primary butadiene coordination and insertion, instead of the more typical η^4-cis or η^2-trans coordination followed by formally secondary insertion.

Experimental Section

All of the operations were performed under a nitrogen atmosphere using conventional Schlenk-line techniques. Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. 1,3-Butadiene and ethylene were purchased from Società Ossigeno Napoli (SON) and used without further purification. Methylaluminoxane (MAO) was purchased by Witco and used as a solid after distillation of solvent.

rac-(CH_2-(3-*tert*-butyl-1-indenyl)$_2$)$ZrCl_2$ was prepared as reported in ref 6.

1,3-Butadiene-*1*-^{13}C was prepared according to the procedure reported in the literature[11] by reaction of acrolein (2.1 mL, 32.0 mmol) and ^{13}C-methylmagnesium iodide (32 mL of 1.0 M solution in ethyl ether, 25% enriched), followed by dehydration with H_3PO_4.[12] The product was purified by distillation over $Al(C_2H_5)_3$ obtaining 0.415 g of butadiene (yields 24%).

The copolymerizations were carried out at 50 °C in 10 mL of toluene feeding the diene as a liquid and pumping the ethene at 1 atm on the reaction mixture using 1.0×10^{-5} mol of catalyst and 1.0×10^{-2} mol of MAO (based on Al). Samples **a** and **b** were obtained by utilizing 0.13 g of 4% ^{13}C-enriched 1,3-butadiene and 0.13 g of commercial 1,3-butadiene, respectively. Polymerization time: 30 min. Yields: $a = 0.350$ g, $b = 0.300$ g.

Compositions of copolymer **a**: $X_E = 0.98\%$, $X_B = 0.02$; $f_{B\Delta} = 0.12$, $f_{\text{B⬠}} = 0.10$, $f_{B1,1} = 0.59$, $f_{B1,3} = 0.19$.

Compositions of copolymer **b**: $X_E = 0.98$, $X_B = 0.02\%$; $f_{B\Delta} = 0.14$, $f_{\text{B⬠}} = 0.08$, $f_{B1,1} = 0.55$, $f_{B1,3} = 0.23$.

The molar fractions of ethylene and butadiene (X_E and X_B) in the copolymers were calculated as reported in ref 7. $f_{B\Delta}$, $f_{\text{B⬠}}$, $f_{B1,1}$, and $f_{B1,3}$ are the fractions of butadiene leading to cyclopropane, cyclopentane, 1,1-inserted, and 1,3-inserted units.

NMR spectra were recorded on an Avance 300 Bruker spectrometer operating at 75.47 MHz at 373 K. The samples were prepared by dissolving 40 mg of polymer in 0.5 mL of tetrachlorodideuterioethane. Hexamethyldisiloxane was used as the internal chemical shift reference. The resonances were assigned on the basis of the data reported in the literature.[7,8]

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