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Communications to the Editor

Ethylene as Catalyst Reactivator in the Propene−Styrene Copolymerization

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Some evidence has been reported in the literature suggesting that insertion of styrene in the ethylene−styrene copolymerization occurs in secondary fashion with metallocene-[1] and monocyclopentadienyl-based[2] catalysts. Such a hypothesis arises from the observation that the ^{13}C NMR analysis of the chain ends of copolymers obtained in the presence of $^{13}CH_3$-enriched catalysts shows the preference for the secondary insertion in the first insertion steps. On the other hand, on the basis of analogous experiments[3] and of other evidence,[4] the primary insertion of propene in the stereospecific polymerization with the *ansa*-metallocene-based catalysts is generally accepted. These regiochemical observations could explain the absence in the literature, to the best of our knowledge, of clear evidence about the propene−styrene random or alternating copolymerization while the ethylene−styrene copolymerization with homogeneous Ziegler−Natta catalysts is widely reported.[1,2,5] Actually a reasonable hypothesis is that steric hindrance prevents the primary propene insertion into the metal−polymer bond when the last inserted unit is secondary styrene while it is known that the styrene−styrene sequences are forbidden.[1,2,5a,b] As a consequence, in the propene−styrene copolymerization a growing polymer chain should become inactive as soon as styrene insertion turns up. However the goal of introducing some styrene units into the isotactic polypropylene deserves to be pursued because the presence of aromatic rings should confer some new interesting chemical and physical features to the polymeric material.[6] Our approach to gain this goal was to add to the comonomers mixture a small amount of ethylene with the idea that traces of this third comonomer could reactivate the catalytic site after secondary styrene insertion.

The copolymerizations have been performed by bubbling the gaseous monomers (propene−ethylene 20/1) at atmospheric pressure into a flask containing a styrene solution of the prototypical *ansa*-zirconocene complex *rac*-(ethylene)bis(1-indenyl)zirconium dichloride[7] activated by methylalumoxane. In Figure 1 is reported the aliphatic region of the ^{13}C NMR spectrum of the copolymer[8] obtained at −25 °C ([E]/[P]/[S] = 1/135/207 in the liquid phase[9] sample 1 of Table 1). One can observe, in addition to the peaks of the isotactic PP sequences at 21.5−20.4, 27.7, and 45.4 ppm, few signals and the lack of peaks related to the sequences PEP (expected around 24.4, 30.1, and 36.9 ppm). The assignment of the resonances not previously reported has been made on the basis of the rules of additivity of the chemical shifts and is reported in Table 1. Accordingly the structure of this copolymer can be supposed to be composed of isotactic polypropylene sequences jointed by the segments A or B, the segment A being slightly more frequent.

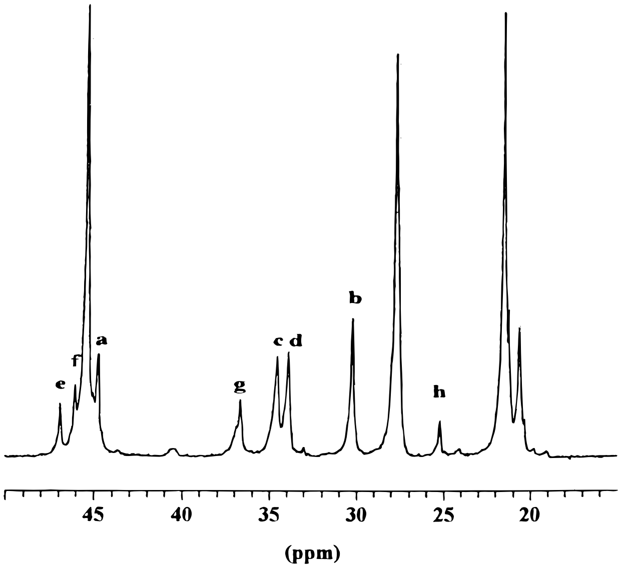

Figure 1. ^{13}C NMR spectrum of sample 1 (aliphatic region). TMS scale.

Table 1. Assignments for the Observed Chemical Shifts in the Aliphatic Region and Relative Areas of the Peaks

		area %		
carbon	δ^a (ppm)	sample 1	sample 2	sample 3
a	44.8	5.7	4.4	7.1
b	30.3	6.4	5.1	6.6
c	34.6	5.7	4.4	6.5
d	33.9	5.7	4.4	6.7
e	46.9	1.7	2.2	2.9
f	46.1	2.3	n.d.[b]	2.2
g	36.7	3.4	n.d.[b]	2.5
h	25.2	1.5	n.d.[b]	1.2
CH_2 (PPP)	45.4	18.8	24.0	14.7
CH (PPP)	27.7	20.5	25.3	20.3
CH_3	21.5−20.4	28.2	30.0	29.2

[a] From tetramethylsilane (TMS) used as internal chemical shift reference. The spectra were recorded in $CDCl_3$ at 293 K. [b] Not detected.

In structure A one tertiary carbon atom bearing the phenyl ring is surrounded in both sides by sequences of two methylene groups while in structure B the junction is characterized by the presence of two tertiary carbon atoms bearing the phenyl ring separated by

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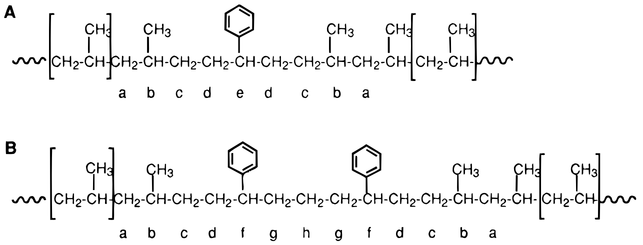

three methylene groups. It is worth noting in both cases the symmetry of the macromolecule due to the fact that the ethylene units "correct" the inversion of regiochemistry made by the styrene. Such a microstructure seems to strongly support the above-discussed regiochemistry of insertion of the two asymmetric monomers. It is reasonable to affirm that the insertion of the propene is primary and as a consequence that of the styrene is secondary, possibly for electronic reasons. In this case the information on the regiochemistry of insertion of a monomer (styrene) is obtained from the NMR analysis of the microstructure of the inner part of the polymer chain, while this information is generally inferred by analysis of the chain end, e.g., from the insertion in the initiation and in the termination steps.

From the areas of the ^{13}C NMR peaks a styrene molar content of 0.12 has been evaluated by using the following relationship:

$$x_S = (0.5A_{33.9} + A_{25.2})/\{2(0.5A_{33.9} + A_{25.2})+(A_{44.8}+ A_{45.4}+ 0.5A_{34.6})\}$$

The average length of the propene isotactic homosequences can be calculated from the equation $L_{\text{prop}} = 2(0.5A_{34.6} + A_{44.8} + A_{45.4})/A_{33.9}$ and is 10.

Despite the shortness of the stereoregular propene sequences, the copolymer shows some crystallinity with an endothermic melting peak in the DSC thermogram around 76 °C and $\Delta H = 10$ J/g. The thermal analysis shows also that the glass transition temperature of this copolymer is -7 °C. With respect to the T_g of the polypropylene (≈ -10 °C) there is possibly a balance between the increase of T_g which should be induced by the presence of styrene units and the decrease of T_g which should be induced by the presence of the ethylene units. From a technological point of view such a result is relevant to avoid the brittleness induced by higher values of glass transition temperature. The powder X-ray spectrum (Figure 2) is in accordance with a crystalline structure and shows the presence of a sharp reflection at $2\theta = 17°$ presumably due to isotactic polypropylene sequences packed in the γ crystalline form.[10]

By reducing the styrene content in the comonomer feed composition ([E]/[P]/[S] = 1/135/65 in the liquid phase) a copolymer (sample 2) with a 6% styrene units is obtained. The ^{13}C NMR analysis seems to indicate that the polypropylene sequences are separated by the only A type junctions. A melting temperature of 103 °C with $\Delta H = 3.5$ J/g is observed by DSC analysis.

A copolymer with substantially the same composition as sample 1 ($x_S = 0.13$) but characterized by the large prevalence of the A type junctions and a melting point of 83 °C ($\Delta H = 14$ J/g) was obtained in lower yield (sample 3) by bubbling propene-ethylene gaseous feed into a flask thermostated at 0 °C and containing the same catalyst in a toluene−styrene 2:1 solution ([E]/[P]/[S] = 1/106/142 in the liquid phase).

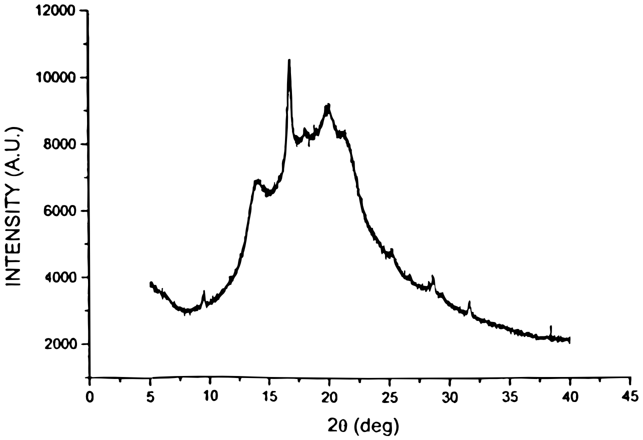

Figure 2. Wide-angle X-ray spectrum of sample 1. Cu Kα Ni-filtered radiation.

A change in the gaseous comonomer feed composition strongly effects the copolymer composition and in particular higher ethylene content in the feed produces an amorphous terpolymer characterized by a more complex ^{13}C NMR spectrum.

The results reported in this communication show that it is possible to introduce some styrene units in an isotactic polypropylene sequence by using a small amount of ethylene to reactivate the catalyst after the styrene insertion. Notwithstanding the presence of three different monomers in the feed, only two different repeating units can be detected in the copolymer chain. As a matter of fact the styrene−ethylene sequence can be incorporated into a repeating unit because, after the styrene insertion, the insertion of ethylene is necessary to relieve the steric congestion and make possible the chain growing while the ethylene insertion after the insertion of propene is highly infrequent due to the low ethylene content in the comonomers feed mixture. It is worth noting that because of the reactivity of the aromatic ring this copolymerization can be also considered an useful approach toward a functionalized polypropylene.

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Supporting Information Available: A table of ^{13}C NMR chemical shift assignments and text giving synthesis and characterization experimental details. This material is available free of charge via the Internet at http:/pubcs.acs.org.

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(8) Following a general procedure, a 100 mL glass flask thermostated at the desired temperature was charged under a nitrogen atmosphere with 30 mL of styrene (sample 1) or 30 mL of a 3 M toluene solution of styrene (samples 2 and 3) and MAO (8.2 mmol). A mixture of ethylene and propene was bubbled through the liquid phase at a flow rate of 0.21 L/min, and then *rac*-Et(Ind)$_2$ZrCl$_2$ (7.9 × 10^{-6} mol) dissolved in 2 mL of toluene was added. The copolymerization products were quenched after 4 h in acidified ethanol, filtered, washed with further ethanol and then with boiling acetone, and dried in vacuo. Yields: 122, 140, and 40 mg for samples 1, 2 and 3, respectively. The M_w values were 3 × 10^4 (sample 1), 4 × 10^4 (sample 2), and 7 × 10^4 (sample 3), with $M_w/M_n = 1.8$, 2.0, and 1.9, respectively.

(9) The comonomers composition in the liquid phase was calculated by Lewis and Luke's equation in conjuction with the fugacity function chart of ethylene and propene as reported in: Maxwell, J. B. *Data Book on Hydrocarbons*; Van Nostrad Co. Inc.: New York, 1950; pp 45, 46, 52, 53.

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