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Ethylene−Styrene Copolymers by *ansa*-Zirconocene- and *half*-Titanocene-Based Catalysts: Composition, Stereoregularity, and Crystallinity

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Introduction

Copolymerization of ethylene with styrene has been recently achieved using a variety of homogeneous Ziegler−Natta catalysts.[1] The presence of a tertiary carbon atom in the styrene units of these copolymers makes stereoregularity possible, but in most of those copolymers previously described the stereoregularity, if present, was not satisfactorily defined. Kakugo et al.[1b] and, more recently, some of us[2] reported the synthesis of stereoregular, possibly isotactic, ethylene−styrene copolymers. At high styrene content these macromolecules show an alternating structure, due to the absence of styrene-styrene sequences.[2] The X-ray spectra of these high styrene content, crystalline copolymers exhibit patterns which are different from those of polyethylene and polystyrene.[1b,2] In this paper ethylene−styrene copolymers obtained with stereospecific and nonstereospecific catalysts are compared with respect to their crystallization behavior.

Results and Discussion

A series of atactic ethylene−styrene (E−S) copolymers have been synthesized with cyclopentadienyltitanium trichloride ($CpTiCl_3$) activated with methylalumoxane (MAO). The E−S copolymer was isolated from the reaction products by extraction with boiling benzene.[1a,h]

Alternatively, E−S copolymers with stereoregular alternating sequences have been prepared using the *rac*-(ethylene)bis(1-indenyl)zirconium dichloride (*rac*-EBI-$ZrCl_2$)/MAO catalyst system;[2] with this catalyst, the copolymer is the only reaction product.

All the E−S copolymers samples have been analyzed by ^{13}C NMR. The spectra of copolymers obtained in the presence of the stereospecific and nonstereospecific catalysts are reported in Figure 1. In the samples obtained with the zirconocene-based catalyst (Figure 1a), the signals assigned to the $S_{\beta\beta}$ carbon (around 23,5 ppm) are not split, which suggests the presence of stereoregular alternating sequences in accordance to refs 1b,g and 3. However, in the spectra of the copolymers obtained with $CpTiCl_3$ (Figure 1b) the $S_{\beta\beta}$ carbon resonance is split.

From the relative intensity of the resonances, the composition of the copolymers and the average length of the methylene sequences can be determined using previously reported relationships.[4] The results of these calculations are reported in Table 1. The styrene content ranges from 12 to 44%; however, one must keep in mind that with these catalysts styrene−styrene insertion is forbidden, and as a consequence, the theoretical upper limit for the styrene content is 50%.

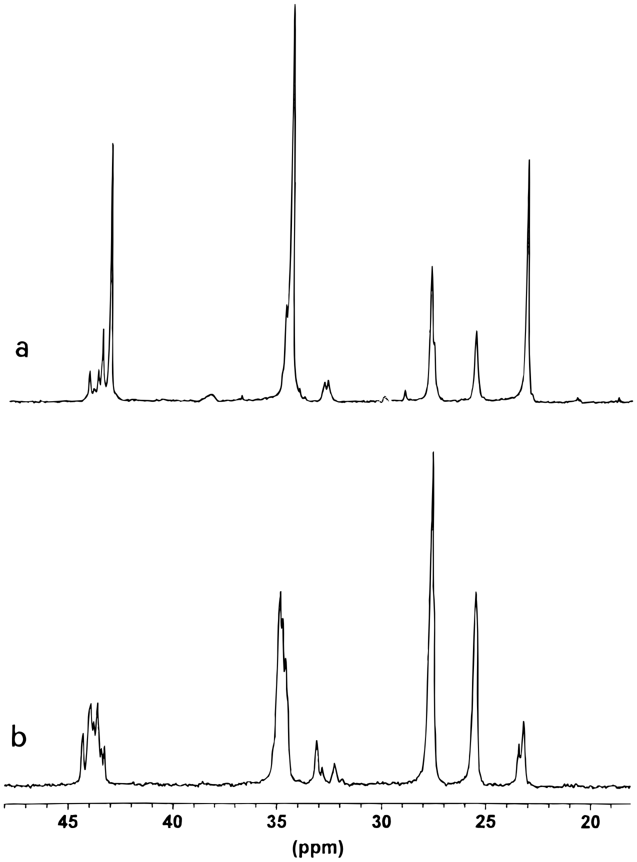

Figure 1. ^{13}C NMR spectra of the aliphatic region: (a) stereoregular E−S sample with 44% styrene molar content (HMDS scale); (b) nonstereoregular E−S sample with 34% styrene molar content.

Table 1. Styrene Content, Average Length of Methylene Sequences and DSC Endothermic Peaks of the E−S Copolymers

sample	catalyst	% styrene (mol)	$\bar{L}_{CH_2}$	mp, °C
1	$CpTiCl_3$	12	16.5	122
2	$CpTiCl_3$	15	11.7	110
3	$CpTiCl_3$	33	5.1	*a*
4	$CpTiCl_3$	34	5.3	*a*
5	$Et(Ind)_2ZrCl_2$	13	16.2	85−125[b]
6	$Et(Ind)_2ZrCl_2$	13	14.4	80−125[b]
7	$Et(Ind)_2ZrCl_2$	15	12.0	75−125[b]
8	$Et(Ind)_2ZrCl_2$	18	10.4	45−130[b]
9	$Et(Ind)_2ZrCl_2$	28	6.1	40−80[b]
10	$Et(Ind)_2ZrCl_2$	32	5.9	60−100[b]
11	$Et(Ind)_2ZrCl_2$	37	5.1	128
12	$Et(Ind)_2ZrCl_2$	37	4.6	128
13	$Et(Ind)_2ZrCl_2$	44	3.7	145

[a] No DSC peaks. [b] Wide transition range, probably due to the contemporary presence of the crystalline polyethylene homosequences and of the alternating sequences.

All the copolymers have been also analyzed by wide-angle X-ray scattering. A series of diffractograms of E−S copolymers with increasing styrene content are reported in Figure 2, and for comparison, the diffractogram of a sample of high-density polyethylene (HDPE) is also included.

At low styrene content (Figure 2b,c) the diffraction patterns, irrespective of the catalyst stereospecificity, are very similar to that of the HDPE (Figure 2a) in accordance with the findings of Kressler et al.[5]

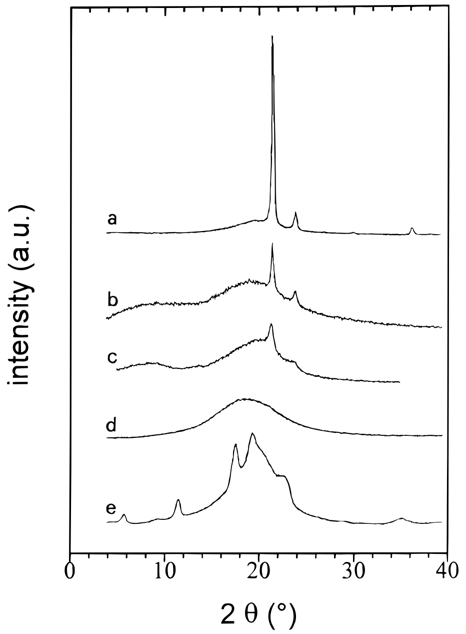

Figure 2. Wide-angle X-ray spectra: (a) HDPE sample; (b–e) E–S copolymers at increasing styrene content, samples 2, 5, 3, and 12, respectively.

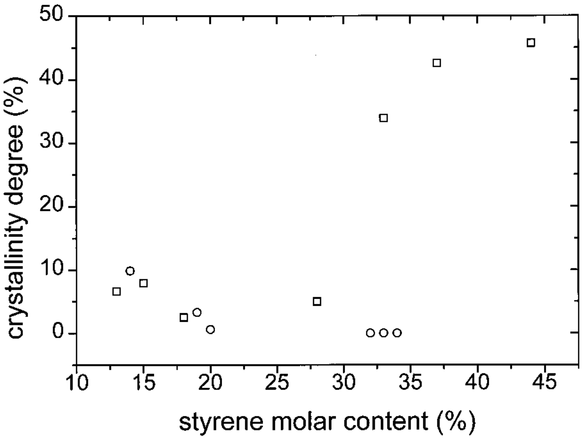

Figure 3. Crystallinity degree of E–S copolymers vs styrene molar content: (□) copolymers obtained with *ansa*-zirconocene catalyst; (○) copolymers obtained with *half*-titanocene catalyst.

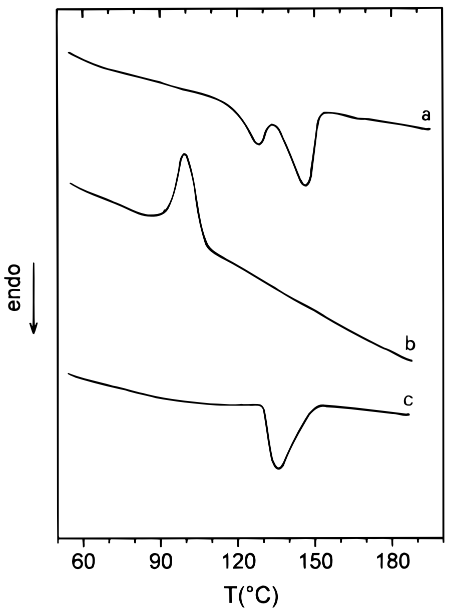

Figure 4. DSC curves of stereoregular alternating E–S copolymers with the highest styrene molar content (sample 12): (a) heating; (b) cooling; (c) heating of the sample annealed at T = 130 °C.

On the other hand, as the styrene content increases, the reflections related to the polyethylene crystal lattice are substituted by a large amorphous halo (Figure 2d) in the atactic copolymers. However, in the copolymers obtained with the *ansa*-zirconocene catalyst these reflections are substituted by new reflections which are related to the crystallinity of the alternating stereoregular sequences. The diffraction pattern of the alternating E–S copolymer (Figure 2e) is similar to that reported by Kakugo et al.[1k]

A plot of the degree of crystallinity, determined by X-ray diffraction, vs the styrene content is reported in Figure 3 for the two series of copolymers. One can observe a similar decrease in the degree of crystallinity for both series of samples with an increase in the styrene content up to 20%. At 20% styrene content, the diffraction spectra for all the copolymers exhibit only an amorphous halo (like Figure 2d). However, as the styrene content increases above 20%, a difference in the behavior of the two series of copolymers begins to appear. The degree of crystallinity of the copolymers obtained with the *ansa*-zirconocene catalyst increases abruptly, due to the organization of the longer stereoregular alternating sequences, as shown by the diffraction pattern of Figure 2e. On the contrary, even when the styrene content exceeds 20% the atactic copolymers are still amorphous, most likely because the alternating sequences are not able to crystallize due to the absence of stereochemical order.

DSC analysis of the copolymer samples from both series with styrene contents of less than 20% show a very similar behavior. Very broad endothermic peaks are present in the DSC heating curves in the range 45–125 °C with ΔH values between 5 and 35 J/g. These peaks also shift to lower temperatures and decrease in intensities with an increase in the styrene content. In this range of composition, all samples exhibit a polyethylene X-ray diffraction pattern, but the random distribution of styrene units, which constitutes defects in the polyethylene chains, probably favors the existence of crystallites of different size and perfection.

When the styrene content is greater than 30%, the behavior of the two series of copolymers becomes different. The atactic copolymers, which by X-ray analysis appear amorphous, do not exhibit any DSC peak; however, the copolymers obtained with the *ansa*-zirconocene catalyst, which by X-ray analysis appear crystalline, show broad endothermic peaks which shift from 100 to 145 °C as the styrene content increases. It is likely that in this range of compositions the length of the stereoregular alternating sequences increases as the styrene content increases. As a consequence, the crystalline quality (size and perfection) improves.

Parts a and b of Figure 4 show the DSC heating and cooling curves of the sample with highest styrene content (44%). The double endothermic peak observed in the heating curve of Figure 4a is due to a recrystallization phenomenon. The X-ray diffraction pattern of this sample does not change after being annealed at the intermediate temperature of $T = 130$ °C (Figure 2e), and the DSC heating curve of the annealed sample (Figure 4c) shows only one endothermic peak at $T = 135$ °C with $\Delta H = 30$ J/g.

Experimental Part

Materials. Polymerization grade ethylene was purchased from Società Ossigeno Napoli and used without further purification. Toluene was dried by refluxing over metallic sodium and distilled under nitrogen atmosphere. Styrene was purified by distilling it over CaH$_2$ under reduced pressure of nitrogen. MAO was purchased as a 30 wt % solution toluene from Witco. *rac*-EBIZrCl$_2$ and CpTiCl$_3$ were synthesized according to the published procedures.[7]

Copolymerizations. Samples 1−4. An evacuated and thermostated (20 °C) Buchi glass autoclave previously was filled with a solution containing 100 mL of anhydrous toluene, 50 mL of styrene, 10 mmol of MAO, and 0.01 mmol of CpTiCl$_3$. The ethylene was quickly introduced at a pressure ranging from 1.4 to 3.9 atm. That temperature, pressure, and stirring rate (1000 rpm) were kept constant for the duration of the run. After 180 min, the ethylene was vented and the mixture was discharged into 300 mL of methanol acidified with HCl. The copolymerization product was recovered by filtration, washed with fresh methanol, and dried under vacuum.

Samples 5−12. Copolymerizations were carried out at different temperatures and at a different styrene feed compositions. A 100 mL glass flask was charged under a nitrogen atmosphere sequentially with toluene, styrene, and 3 mL of a 30 wt % MAO solution in toluene. The mixture was magnetically stirred and the glass flask was thermostated at the desired temperature (20, 25, or 50 °C). The inert atmosphere was removed and replaced with ethylene at 1 atm. Then 6 mL of a toluene solution of the zirconocene compound (2.4 mM) was introduced. In all runs the total volume in the glass flask was kept constant at ca. 35 mL. The copolymerizations were stopped after 2 h and the reaction mixture was poured into 100 mL of acidified methanol. The product was recovered by filtration, washed with boiling acetone, and dried under vacuum.

Analysis. By exhaustive extraction with methyl ethyl ketone and benzene the E−S copolymers were isolated as the benzene soluble−methyl ethyl ketone insoluble fraction.

^{13}C NMR Analysis. The spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode at a temperature of 120 °C. The samples were prepared by introducing 30−40 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 internal reference.

X-ray Analysis. Wide-angle X-ray diffractograms were obtained with Cu Kα Ni-filtered radiation using a PW 1710 Philips powder diffractometer. All samples were crystallized at room temperature after compression molding. The crystallinity degree was determined by subtracting the amorphous halo from the X-ray diffraction pattern.

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