

# Synthesis and Properties of Ethylene/Styrene Copolymers Produced by Metallocene Catalysts

N. Haider,<sup>1</sup> M. T. Expósito,<sup>1</sup> A. Muñoz-Escalona,<sup>1</sup> J. Ramos,<sup>1</sup> J. F. Vega,<sup>1</sup>  
L. Méndez,<sup>2</sup> J. Martínez-Salazar<sup>1</sup>

<sup>1</sup>Departamento de Física Macromolecular, Instituto de Estructura de la Materia, CSIC, Serrano 113bis,  
28006 Madrid, Spain

<sup>2</sup>Repsol-YPF, Centro Tecnológico, Carretera de Móstoles km 18, 28931 Móstoles, Madrid, Spain

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**ABSTRACT:** Ethylene/styrene copolymers were synthesized under constant polymerization conditions using six different metallocene catalysts activated with methylaluminoxane. For all the catalysts used, the activity and molecular weight of the copolymers produced decreased with the amount of styrene in the reactor feed, but the styrene content of the copolymers increased. Catalysts with carbon bridges and bulky ligands gave rise to copolymers with higher styrene content. As a result of the increased styrene content of the copolymer, the melting temperature decreased. This effect was ascribed to a decrease in the crystallinity of the copolymers. It was also found that lamellar thickness could be significantly diminished by the

incorporation of comonomers. The copolymers showed a broad spectrum of mechanical properties as a function of the comonomer ratio. At low styrene contents, they behaved like typical semicrystalline thermoplastics, and at higher styrene contents, they exhibited the properties typical of elastomers. Of the catalysts tested, [rac-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride emerged as the most promising for the production of ethylene/styrene copolymers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3420–3429, 2006

**Key words:** copolymerization; metallocene catalysts; mechanical properties; thermal properties

## INTRODUCTION

The discovery of metallocene-based catalysts for the polymerization of  $\alpha$ -olefins has allowed the synthesis of new materials while effectively controlling stereoregularity, molecular weight, and molecular weight distribution, as well as the amount of comonomer in the final product. Copolymers synthesized in this way show improved or even entirely new properties compared to those produced by conventional Ziegler–Natta catalysts.<sup>1,2</sup>

Recent research in the field of polyolefin polymerization has focused on developing relationships between microstructure and desired end-use physical/mechanical properties. Since the advent of metallocene catalysts, there have been claims of polymers produced with tailored microstructural and controlled physical/mechanical properties.<sup>3</sup>

The affinity of metallocene compounds to nonpolar monomers such as ethylene and styrene allows the synthesis of ethylene/styrene copolymers (E/St copolymers) with controlled chain microstructure and stereoregularity, narrow-molecular-weight distribution, low density, and other physical and mechanical properties. In contrast, conventional Ziegler–Natta catalysts generate a mixture of homopolymers and some amount of copolymer with a very low styrene comonomer content.<sup>4</sup> Metallocene-based E/St copolymers are generating interest in the industry because both rigid and flexible polymers can be obtained, which enables the rigid and plasticized PVCs to be replaced with more environmentally friendly materials.<sup>5–7</sup> The copolymers that have been produced have a broad range of styrene contents—from 0 to 50 mol %—and have “pseudorandom” structures because the polymer segments show no head-to-tail styrene–styrene enchainment.<sup>5</sup>

Over the past decade, several constrained geometry (CGC) and metallocene catalysts activated with MAO or borates as cocatalysts have been successfully employed in the synthesis of a wide range of E/St copolymers.<sup>8–23</sup> Depending on catalyst structure and the polymerization conditions (i.e., the ethylene–styrene concentration ratio in the reactor feed), a broad variety of copolymers with different styrene compositions, structures, and properties can be obtained. Low styrene comonomer content generates polymers with

Correspondence to: J. F. Vega (imtv477@iem.cfmac.csic.es).  
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properties typical of ductile crystalline thermoplastics, whereas high comonomer content gives rise to elastomeric-type materials.<sup>7</sup>

A review of the literature<sup>8–23</sup> showed that mainly CGCs have been proposed as the catalysts for the synthesis of E/St copolymers are, with few reports of the use of metallocene-type catalysts. It was also very difficult to compare catalytic performance in copolymerization across different studies, even for the same catalyst, because polymerization was conducted under different reaction conditions. Arai et al.<sup>16</sup> and Albers et al.<sup>22</sup> published a systematic work on E/St copolymerization using different metallocene catalysts in an attempt to correlate catalyst structure with catalytic activity and the microstructure and thermal properties of the resulting copolymers. However, there have been certain discrepancies in the performance of metallocene catalysts according to several authors. For example, Ren et al.<sup>9</sup> obtained a copolymer with a styrene content of 10 mol % and an average molecular weight of about 100 kg/mol using 12 mL of styrene in 200 mL of toluene in the reactor and isopropylidene (cyclopentadienyl)(9-fluorenyl)zirconium dichloride as the catalyst. However, when Albers et al.<sup>22</sup> used the same catalyst to investigate the incorporation of styrene according to the styrene fraction of the monomer feed, they obtained higher-molecular-weight copolymers (around 300–200 kg/mol) than those generated by Ren et al. and styrene incorporation in the range of 3–32 mol % for feed compositions of 4–98 mol % styrene. The *rac*-(ethylene)bis(1-indenyl)zirconium dichloride catalyst activated with methylaluminoxane (MAO)<sup>13,16,17</sup> has been claimed to yield E/St copolymers with a styrene content of 13–44 mol % depending on the reactor feed and polymerization temperatures. The highest incorporation of styrene was observed at low temperatures (below 0°C).<sup>13</sup> However, when Arai et al.<sup>16</sup> used a higher temperature (50°C) and had styrene as a very large fraction of the feed, they found the copolymer had a lower styrene content (below 10 mol %) and low molecular weight (around 50 kg/mol). Instead of using *rac*-(ethylene)bis(1-indenyl)zirconium dichloride as the catalyst, we used *rac*-(ethylene)bis-(tetrahydroindenyl)zirconium dichloride, which is more stable than its indenyl ligand counterpart because decomposition by ring-slippage reactions cannot take place. To the best of our knowledge, only one previous study describing E/St copolymerization used this catalyst.<sup>23</sup> The result of one of the E/St copolymerization experiments in the present work was a copolymer containing 20 mol % styrene for 80 mol % styrene in the reactor feed.

We report the synthesis of several E/St copolymers using different types of metallocene catalysts while keeping the polymerization conditions (temperature, catalyst concentration, Al/M ratio) and styrene/ethylene molar ratios constant in the reaction

feed. This enabled us to establish relationships between the type of metallocene catalyst and its polymerization activity with the molecular weight, microstructure, and thermal and mechanical properties of the resulting copolymers.

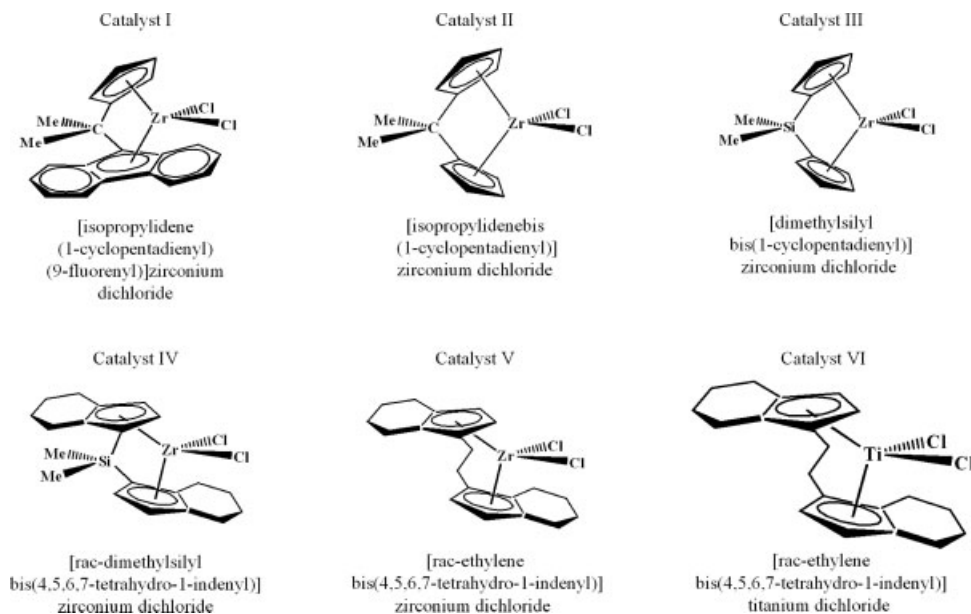
## EXPERIMENTAL

### Materials and sample preparation

A series of E/St copolymers of different comonomer concentration ratios was synthesized using six different metallocene catalysts with different ligand structures and bridge types, as shown in Scheme 1.

All the catalysts were supplied by Boulder Scientific, Co (Mead, CO) and used without further purification. The six catalysts were selected according to the following criteria: catalysts I and II have a carbon-based bridge, but different ligands, CpFlu and (Cp)<sub>2</sub>, respectively; catalyst III has a similar ligand, (Cp)<sub>2</sub>, to catalyst II, but its carbon-based bridge is replaced by a silicon-based bridge; catalyst IV has the same silicon-based bridge as that in catalyst III, but its ligand, THIn (tetrahydroindenyl), is bulkier; catalyst V has a ligand (THIn) similar to that in catalyst IV, but its silicon-based bridge is replaced by an Et carbon-based bridge. All the catalysts have a Zr metal center except catalyst VI, whose center is based on Ti. This catalyst was selected because a Ti-metal-based CGC catalyst has been successfully used for E/St copolymerization.

The polymerization conditions for copolymer preparation were the same for all the catalysts. The polymerization reactions were performed in a 1-L glass autoclave (Büchi). The reactor was filled with toluene (400 mL), styrene (at molar styrene/ethylene ratios of 1, 2 and 3), and some of the required methylaluminoxane (MAO) in a nitrogen atmosphere. In some cases, a small amount of triisobutyl-aluminum (TIBA) was added as a scavenger before the addition of MAO. After thermostating the reactor at the polymerization temperature, nitrogen was removed under vacuum, and the reaction mixture was saturated with ethylene. The rest of the MAO was added, and the reactor was pressurized with ethylene during the polymerization. Finally, the metallocene catalyst in a toluene solution was injected into the reactor. During polymerization, ethylene pressure was kept constant, and ethylene consumption was measured by a mass flow controller (Brooks Instrument B. V., Veenendaal, The Netherlands). The polymerization conditions used for all the experiments were: [cat] = 20 μmol/L, Al : Ti = 2000, ethylene pressure = 3 bar, and polymerization temperature = 35°C. Copolymerization was stopped by degassing the reactor to the atmosphere and adding a solution of 20 mL of acidic methanol (containing 5% HCl). Finally, the reaction products were washed in



Scheme 1

plenty of acidic methanol and acetone, filtered, and dried at 60°C under vacuum to a constant weight.

The copolymers were stabilized using a mixture of 1 wt % Irganox 1010 and Irgafos 168 by mixing the copolymer and the antioxidants during compression molding. The copolymer was compression-molded into a 1-mm-thick plate at 150°C under a nominal pressure of 50 kg/cm<sup>2</sup>. The same cooling program was used for all the compression-molded samples so that they would have similar thermal histories. The polymer plates were sandwiched between metallic sheets, heated at 150°C, held for 3 min under a nominal pressure of 100 kg/cm<sup>2</sup>, and cooled in the press from 150°C to 30°C at a rate of 15°C/min.

### Polymer characterization

All the E/St copolymer samples were analyzed by <sup>13</sup>C-NMR. The spectra were recorded at 100°C on a Bruker DRX 500 spectrometer operating at 500 MHz (<sup>13</sup>C-NMR). The samples were dissolved in hot 1,2,4-trichlorobenzene (TCB) and d<sup>6</sup>-benzene. Carbon signals and styrene contents were assigned according to the literature.<sup>8</sup>

The molecular weights ( $M_w$  and  $M_n$ ) and molecular weight distributions were determined by size exclusion chromatography (SEC) using a refractive index, RI, and viscosity detectors in a Waters 150 CV Gel Permeation Chromatograph. The solvent used for the analysis was TCB, the flow rate was 1.0 mL/min, and the temperature was 145°C. The SEC viscosity system was calibrated using polystyrene standards.

Chemical composition distributions of the copolymers were determined by crystallization fractionation in a Polymer ChAR 200+ CRYSTAF/TREF instrument

(Valencia, Spain) equipped with five separate crystallization vessels for a simultaneous analysis of five samples. Samples of 21 mg were dissolved in 30 mL of TCB at a temperature of 160°C for 135 min. Then the solutions were allowed to reach thermal equilibrium at 95°C for another 45 min. Afterward, the solutions were cooled at a rate of 0.2°C/min to 35°C. The different solutions were sampled 30 times at temperature intervals between 95°C and 35°C, and the concentration of the remaining copolymer in the solutions was measured with a dual-wavelength infrared detector. The distribution curves were obtained from the cumulative curves as the simple first-derivative function.

For the DSC measurements, 5- to 10-mg round samples were punched out of the compression-molded polymer plates. The diameter of the samples (ca. 4 mm) was adjusted to that of flat-based DSC pans in order to achieve a constant geometry and good contact between the sample and the pan. All DSC measurements were performed on a Mettler Toledo DSC822<sup>e</sup> instrument. Temperature calibration was performed with indium. A heat capacity value of 28.45 J/g was used for temperature/area calibration. Crystallinity values were calculated from the heat of fusion using the peak area of the melting peak; a value of 288.4 J/g was used as the reference melting enthalpy for 100% crystalline polyethylene.<sup>24</sup> Melting and crystallization exotherms were recorded by heating the samples from -130°C to 160°C, followed by cooling from 160°C to -130°C at a heating/cooling rate of 10°C/min, and reheating again at 10°C/min. The melting points and crystallinity values were taken from the first heating scans. Melting thermograms were obtained for both the virgin and compression-molded samples.

The tensile stress–strain behavior of the metallocene-based E/St copolymers and polyethylene homopolymer were determined using an MTS universal testing machine. Compression-molded plates with a thickness of about 1 mm were cut into dumbbell shapes, with the width in the center approximately 1 mm and the gauge length 12 mm. These samples were tested at constant displacement rates of 1 and 10 mm/min at room temperature, a humidity of 50%, and a grip separation of 12 mm. The sample yield and ultimate break strength values were determined from the force-versus-displacement curves during deformation of the samples.

## RESULTS AND DISCUSSION

### Synthesis of copolymers

Table I shows a summary of the products of the ethylene–styrene copolymerization conducted using the different catalysts and different monomer ratios of the feed. Our results indicate that catalyst VI, based on the transition metal Ti, was rather ineffective at

copolymerization, given that the products were only small amounts of ethylene homopolymers. A suitable explanation for this may be found in a computational study we performed using high-level hybrid DFT methods.<sup>25</sup>

In general, for all the catalysts, copolymerization activity and copolymer molecular weight decreased as the styrene content in the feed increased (see Figs. 1 and 2, respectively). However, by increasing the styrene in the reactor feed, more styrene comonomer incorporation took place (Fig. 3). Similar results were reported by Sernetz et al.<sup>14,15</sup> using CGC. Catalysts with a carbon-based bridge tended to incorporate the highest amounts of styrene comonomer, in accordance with the results reported by Arai et al.<sup>16</sup> and Alberts et al.<sup>22</sup> On the other hand, when comparing catalysts I and II, which had the same carbon-based bridge, the molecular weights of the resultant copolymers were lower for catalyst II, which had the smallest Cp ligand. Catalysts with silicon-based bridges tended to show the highest activity but were more inefficient at styrene incorporation (compare catalysts II and III, Table I). Catalysts with silicon-

**TABLE I**  
Copolymerization of Ethylene with Styrene by Different Catalysts and with Several Monomer Styrene/Ethylene Feed Ratios

Catalyst	St/E ratio in reactor feed (M/M)	Activity <sup>a</sup>	Styrene content of copolymer		$M_w$ (kg/mol)	$M_w/M_n$
			mol %	wt %		
Catalyst I	0.0	1273	0.0	0.0	538	3.2
	1.0	622	2.4	8.4	363	2.5
	2.0	176	2.6	9.0	423	2.5
	3.0	245	6.6	20.8	324	2.2
Catalyst II*	0.0	3147	0.0	0.0	11	2.2
	2.2	400	0.9	3.3	10	1.6
	3.2	170	2.8	9.7	9	1.7
Catalyst III*	0.0	8483	0.0	0.0	213	5.2
	1.5	2360	0.2	0.7	164	7.2
	2.0	3333	0.3	1.1	75	3.5
	3.1	1081	0.3	1.1	82	2.4
Catalyst IV	0.0	16,397	0.0	0.0	767	2.6
	1.0	4648	0.3	1.1	449	2.3
SHZ	2.0	2651	0.4	1.5	436	2.2
	2.9	2008	0.4	1.5	359	1.9
Catalyst V	0.0	15,109	0.0	0.0	452	2.6
	1.0	4359	0.3	1.1	386	2.0
	3.0	1907	0.6	2.2	267	2.0
EHZ	5.6	754	0.7	2.6	184	2.1
	3.0 <sup>b</sup>	838	0.4	1.5	225	1.9
	5.6 <sup>b</sup>	690	0.9	3.3	129	2.4
	7.4 <sup>b</sup>	205	1.3	4.7	112	1.9
Catalyst VI	3.0	63	n.d. <sup>c</sup>	n.d. <sup>c</sup>	n.d. <sup>c</sup>	n.d. <sup>c</sup>
	7.4	16	n.d. <sup>c</sup>	n.d. <sup>c</sup>	n.d. <sup>c</sup>	n.d. <sup>c</sup>

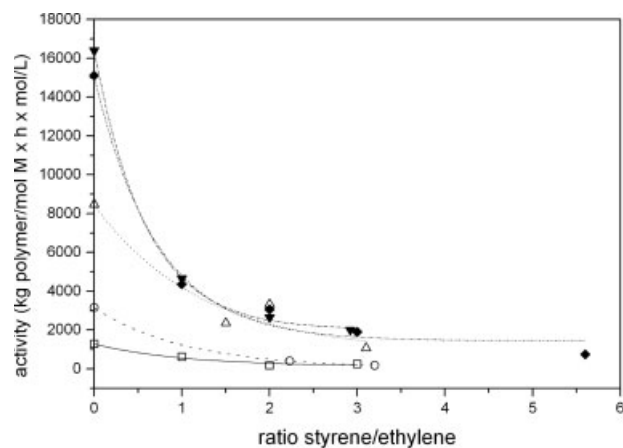
<sup>a</sup> Calculated by: kg polymer/(mol  $M \times h \times$  mol/l).

<sup>b</sup> Experiments where triisobutylaluminum (TIBA) was used as a scavenger.

<sup>c</sup> Not determined.

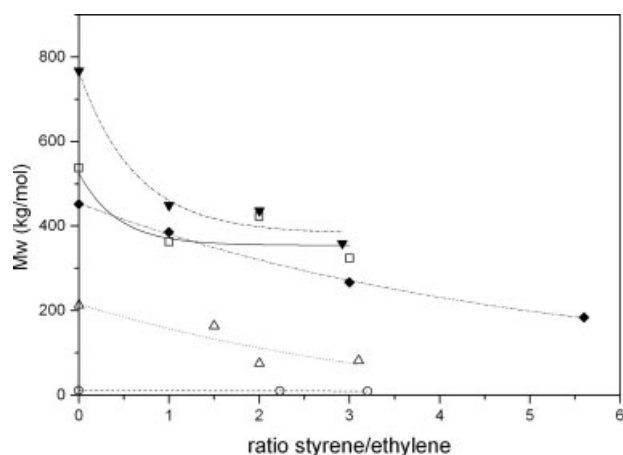
\* Catalysts II and III yielded E/St copolymers with 1-butene units and long chain branching as revealed by <sup>13</sup>C-NMR analysis (see text).



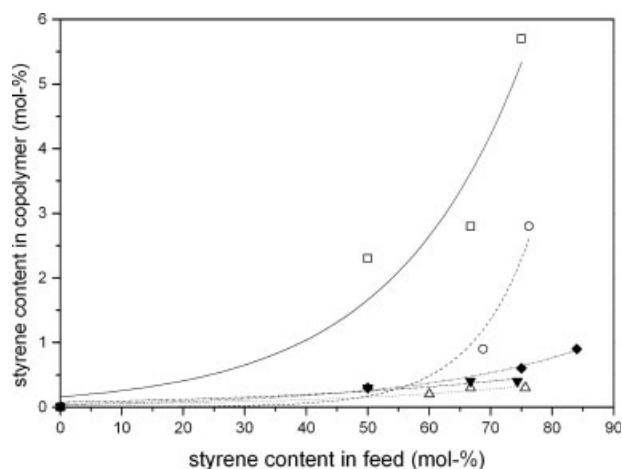


**Figure 1** Polymerization activity as a function of the styrene/ethylene molar ratio in the feed for different catalysts (experimental data are listed in Table I): (□) catalyst I, (○) catalyst II, (△) catalyst III, (▼) catalyst IV, and (◆) catalyst V.

based bridges yielded copolymers of higher molecular weight than those with the same ligands but with a carbon-based bridge (compare catalysts II vs. III and IV vs. V, Table I). Catalyst IV, which had a much bulkier ligand, gave rise to copolymers of higher molecular weight than those from catalyst III. This tendency of a catalyst with a bulkier ligand to yield higher-molecular-weight copolymers has also been reported for ethylene homopolymerization.<sup>26</sup> The molecular weights of the copolymers prepared using catalyst II were very low. All the polymers produced using metallocene catalysts and under similar polymerization conditions showed a uniform narrow-molecular-weight distribution with a polydispersity index (PI) of about 2, except for the polymers produced by catalyst III, whose PI values were in the range of 2.4–7.2. In addition, catalysts II and



**Figure 2** Weight-average molar mass of poly(ethylene-co-styrene) produced by different catalysts as a function of styrene/ethylene molar ratio in the feed (experimental data are listed in Table I). Symbols are the same as those in Figure 1.



**Figure 3** Styrene content of poly(ethylene-co-styrene) produced by different catalysts as a function of styrene content in the feed (experimental data are listed in Table I). Symbols are the same as those in Figures 1 and 2.

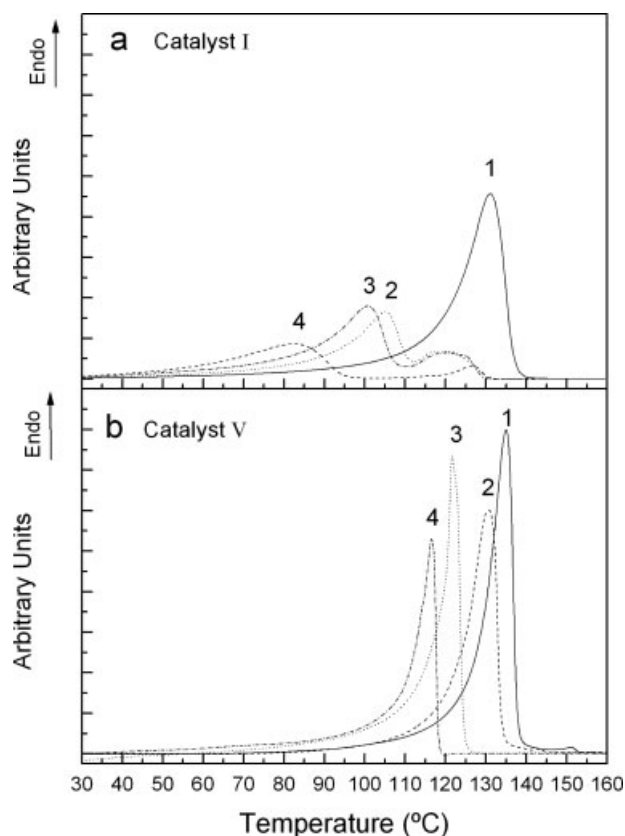
III yielded materials with 1-butene units and side branches longer than 6 carbon atoms (0.4–0.7 mol %), as revealed in the <sup>13</sup>C-NMR analysis. The spectra for these samples showed the characteristic 39.6 and 26.6 ppm signals of the methine and 2B<sub>2</sub><sup>+</sup> carbon resonances for the 1-butene units and the characteristic 32.2 and 22.2 ppm signals attributed to 3B<sub>6</sub> and 2B<sub>6</sub> carbon resonances in branches longer than 6.<sup>27,28</sup> The incorporation of these side branches probably was a result of a β-hydrogen transfer and elimination reactions to the metal or to the monomer during polymerization.

### Thermal properties

The melting behavior of copolymers of different styrene contents obtained using metallocene catalysts has still not been systematically studied.

The melting and crystallization thermograms of the copolymers produced using catalysts I and V are shown in Figures 4 and 5, respectively. The thermograms of the copolymers produced with catalysts II, III, and IV are almost identical to those obtained using catalyst V and are therefore not shown. It can be seen that the shapes of the melting and crystallization thermograms were influenced by the amount of styrene comonomer.

Figures 4 and 5 show that both the melting and crystallization thermograms for copolymers obtained using catalyst I were nonhomogeneous, indicating the copolymers were a mixture of E/St copolymers and polyethylene homopolymer or of two E/St copolymers with different styrene contents. In addition, the most intense peak corresponded to the E/St copolymer with the highest styrene content, indicating this was the main component of the blends. This thermal and crystallization behavior of E/St copoly-



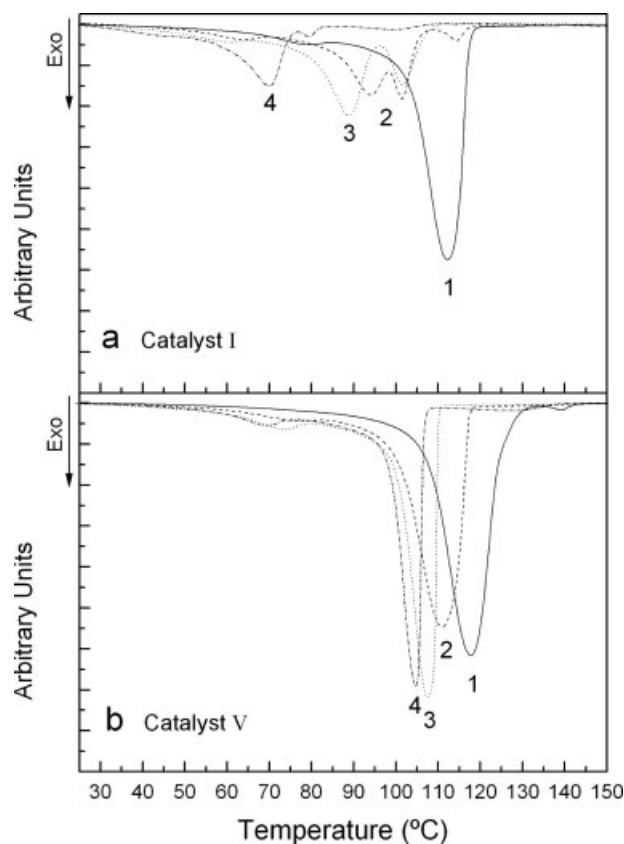
**Figure 4** DSC melting thermograms of poly(ethylene-*co*-styrene) with different styrene contents produced by different catalysts: (a) thermogram 1 corresponding to 0.0 mol % styrene content of the copolymer, thermogram 2 to 2.4 mol %, thermogram 3 to 2.6 mol %, and thermogram 4 to 6.6 mol %; (b) thermogram 1 corresponding to 0.0 mol % styrene content of the copolymer, thermogram 2 to 0.3 mol %, thermogram 3 to 0.7 mol %, and thermogram 4 to 1.3 mol %.

mers prepared using catalyst I has not been previously reported. Thus, Ren et al.<sup>9</sup> and Albers et al.<sup>22</sup> reported only one melting temperature for E/St copolymers obtained via the same catalyst.

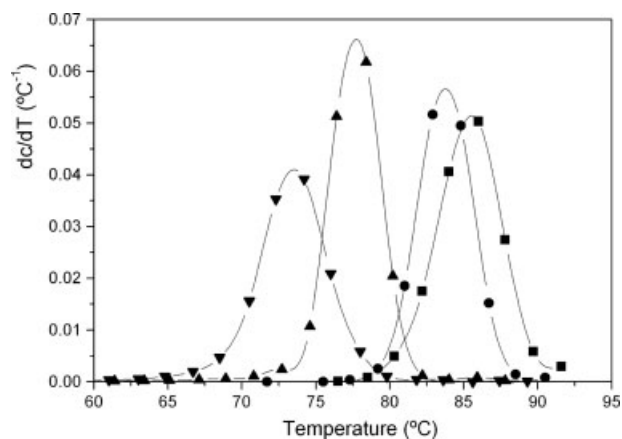
Arai et al.<sup>16</sup> and Venditto et al.<sup>17</sup> also examined E/St copolymers prepared using a metallocene catalyst, [rac-ethylenebis(indenyl)]zirconium dichloride, which can be considered similar to catalyst V used in the present study. Venditto et al.<sup>17</sup> reported two melting points at 85°C–125°C for a copolymer containing 13 mol % styrene, whereas Arai et al.<sup>16</sup> obtained a homogeneous copolymer with only one melting point in the thermogram, at 112°C, for a copolymer with a styrene content of 9 mol %. In comparison, we found that the copolymer produced using our catalyst V was also homogeneous with a single melting peak of 117°C for a copolymer containing 1.0 mol % incorporated styrene. Hence, a small difference in structure between the catalysts led to a significant difference in the melting temperature of the product, because although the copolymers had much lower styrene contents, their melting points were close. Chung et al.<sup>27</sup> explored the thermal proper-

ties of the ethylene-*p*-methylstyrene copolymers produced using the [rac-ethylenebis(indenyl)]zirconium dichloride catalyst, similar to catalyst V. These authors reported a melting point of 115°C for a methylstyrene content of 1.1 mol % in the copolymer, compared to our melting point of 117°C for 1.0 mol % of styrene. This indicates the similarity of the results obtained despite the differences in the chemical structure of both catalysts.

The melting and crystallization thermograms of the copolymers produced using catalysts II, III, IV, and V were homogeneous. Thus, there was a lack of polyethylene homopolymer, and an increase in the comonomer content always resulted in a decrease in the melting point of the copolymers. The chemical homogeneity of some of the copolymers obtained has been proven by CRYSTAF analysis, more specifically those obtained by catalyst systems IV and V. Only the results corresponding to copolymers obtained from catalyst V are shown in Figure 6 to avoid overcrowding. The narrow and symmetrical CRYSTAF profiles illustrated



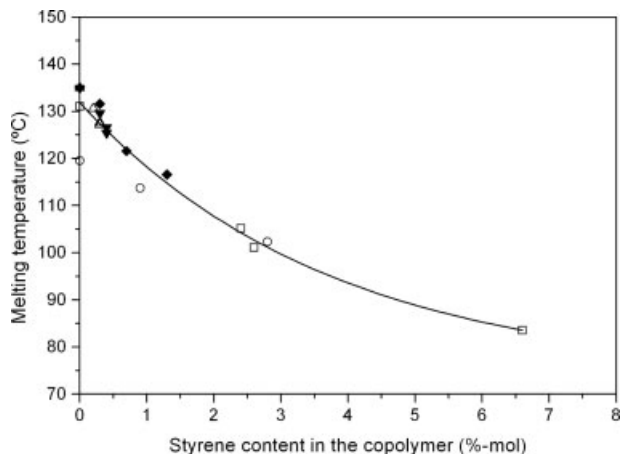
**Figure 5** DSC crystallization thermograms of poly(ethylene-*co*-styrene) with different styrene contents produced by different catalysts: (a) thermogram 1 corresponding to 0.0 mol % styrene content of the copolymer, thermogram 2 to 2.4 mol %, thermogram 3 to 2.6 mol %, and thermogram 4 to 6.6 mol %; (b) thermogram 1 corresponding to 0.0 mol % styrene content of the copolymer, thermogram 2 to 0.3 mol %, thermogram 3 to 0.7 mol %, and thermogram 4 to 1.3 mol %.



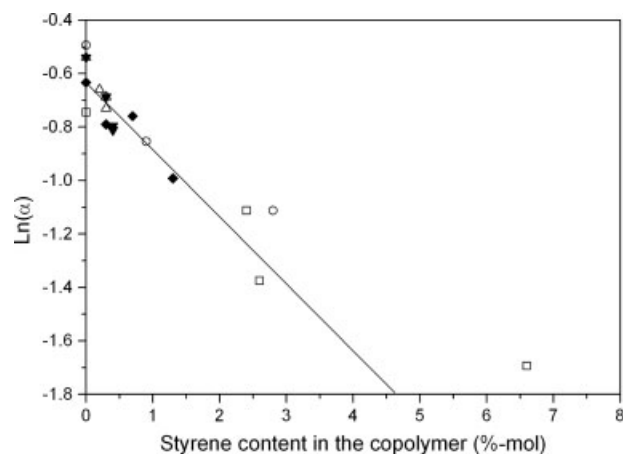
**Figure 6** CRYSTAF profiles of copolymer samples exhibiting a range of styrene incorporated into them obtained from catalyst V: (■) 0 mol %, (△) 0.3 mol %, (▲) 0.7 mol %, and (▼) 1.3 mol %.

in Figure 6 clearly indicate that no drift took place during the polymerization reactions regardless of styrene composition. This feature of the polymerization points to a remarkable homogeneity in the chemical composition of the copolymers obtained. In addition, it is worthwhile to note that the copolymers obtained with these catalyst systems have been shown to be the most homogeneous from both molecular (PI close to 2) and structural (only ethylene and styrene units) points of view, as is shown in Table I and discussed above.

The changes in melting temperature observed depending on comonomer content are shown in Figure 7. The reduced melting temperature with increased comonomer content was ascribed to a decrease in crystallinity. A systematic decrease was shown in the dependence of the melting temperature on comonomer content in the copolymers generated using all the catalysts. However, the lower melting temperatures of



**Figure 7** Melting temperature as a function of styrene content of the poly(ethylene-co-styrene) produced by different catalysts. Symbols are the same as those in Figures 1–3.



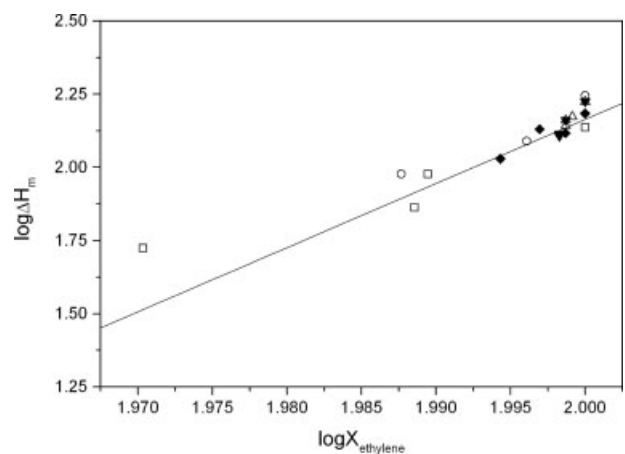
**Figure 8** Semilogarithmic plot of percent crystallinity from DSC as a function of styrene content of the poly(ethylene-co-styrene). Symbols are the same as those in Figures 1–3 and 7.

polymers produced by catalyst II could have been a result of their low molecular weight compared to that of the products yielded by the other catalysts.

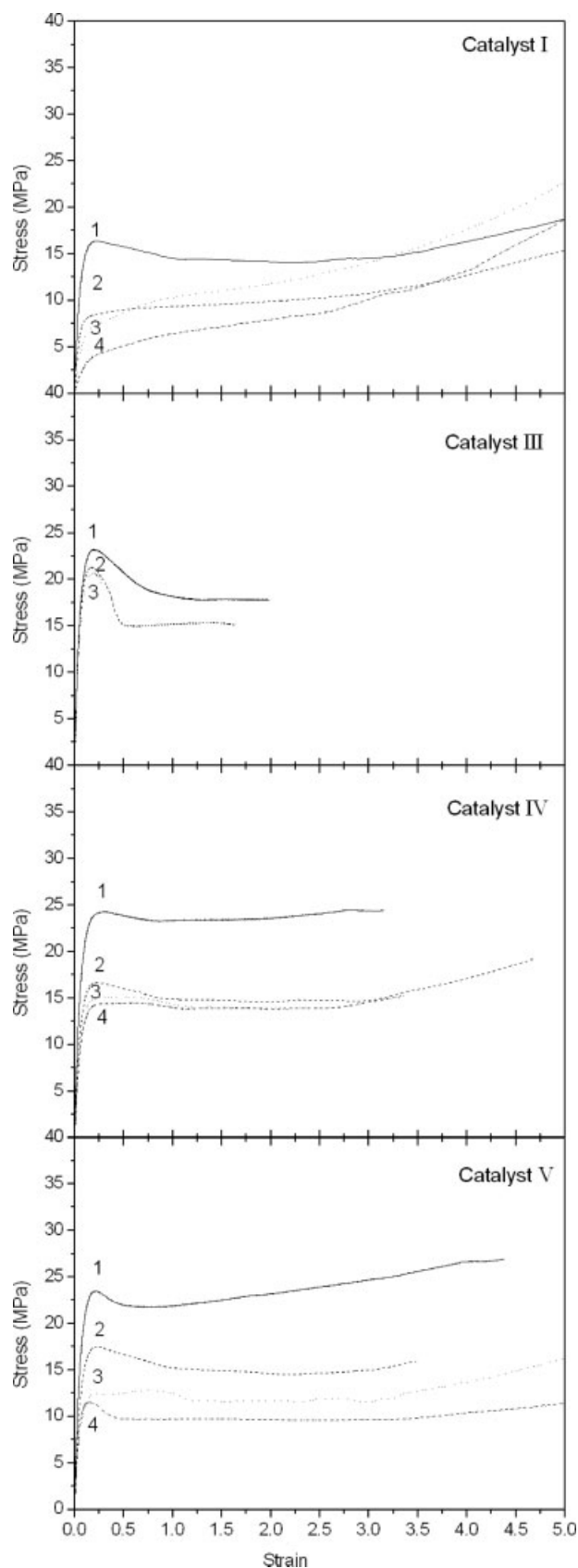
Figure 8 shows a semilogarithmic plot of percentage crystallinity against comonomer content, revealing a linear dependence. Thus, crystallinity ( $\alpha$ ) decreased exponentially with comonomer content ( $x_{st}$ ) according to the empirical equation  $\alpha = \alpha_0[\exp(-bx_{st})]$ , where the constants  $\alpha_0$  and  $b$  have values of 0.65 and 0.24, respectively. The copolymers obtained with catalysts I and II showed some difference in their dependence, probably because of the chemical heterogeneity, as revealed by  $^{13}\text{C}$ -NMR and DSC analyses.

Furthermore, it has been suggested that the enthalpy of melting ( $\Delta H_m$ ) is related to the ethylene mole fraction ( $X_e$ ) according to the Burfield equation [eq. (1)].<sup>30</sup>

$$\Delta H_m = k(X_e)^n \quad (1)$$



**Figure 9** Logarithmic plot of DSC heat of melting as a function of ethylene mole fraction of the poly(ethylene-co-styrene). Symbols are the same as those in Figures 1–3, 7, and 8.



where  $k$  is a constant related to the crystallinity of the homopolymer, and the exponent  $n$ ) is the minimum ethylene sequence length that can be crystallized. However, if it is assumed that the comonomer does not contribute to the crystallization then it is appropriate to correct the heat of melting as:

$$\Delta H'_m = \Delta H_m / W_E \quad (2)$$

where  $W_E$  is the weight fraction of ethylene in the copolymer. Thus, Figure 8 shows the logarithmic relationship between the melting enthalpy,  $\Delta H_m$ , and ethylene mole fraction,  $X_e$ , of the E/St copolymers. A linear relationship between  $\log \Delta H_m$  and  $\log X_e$  was observed for copolymers obtained from catalysts III, IV, and V. The best linear fit in Figure 9 shows a value of  $n = 21$ . Because eq. (2) was derived from probability arguments,  $n$  should depend on the ethylene sequence distribution, which in turn is determined by the catalyst system and the polymerization conditions.<sup>3,30</sup> However, the good correspondence between  $\Delta H'_m$  and  $X_e$  for synthesized copolymers with different catalysts suggests that at low styrene contents the comonomer distribution does not affect the length of the sequence of crystallizable material. Values of  $n$  previously reported for  $\alpha$ -olefin copolymers prepared by conventional heterogeneous multisite catalysts were in the range of 8–18. An  $n$  of 13 was obtained by Bensason et al. for ethylene-octene and ethylene-styrene copolymers.<sup>3,31</sup>

Given that in the extended PE chain, the length of the C—C bond was 1.53 Å and the bond angle was 112°, the minimum ethylene sequence length that could crystallize was obtained from eq. (1). Thus, the minimum crystallized PE chain length of 53.34 Å corresponded to a value of  $n = 21$ . This value obtained for the E/St copolymers is almost consistent with those cited in the literature using CGC. The small differences observed could be mainly a result of differences in the thermal history of the samples or in the polymerization conditions.<sup>3,6</sup>

**Figure 10** Engineering stress–strain curves at deformation rate of 1 mm/min for ethylene/estylene copolymers synthesized by different catalysts: (a) copolymer produced with catalyst I—curve 1 corresponds to 0.0 mol % styrene content of the copolymer, curve 2 to 2.4 mol %, curve 3 to 2.6 mol %, and curve 4 to 6.6 mol %; (b) copolymer produced with catalyst III—curve 1 corresponds to 0.0 mol % styrene content of the copolymer, curve 2 to 0.2 mol %, and curve 3 to 0.3 mol %; (c) copolymer produced with catalyst IV—curve 1 corresponds to 0.0 mol % styrene content of the copolymer, curve 2 to 0.3 mol %, curve 3 to 0.4 mol %, and curve 4 to 0.4 mol %; (d) copolymer produced with catalyst V—curve 1 corresponds to 0.0 mol % styrene content of the copolymer, curve 2 to 0.3 mol %, curve 3 to 0.7 mol %, and curve 4 to 1.3 mol %.



### Mechanical properties

Because of their low molecular weight, the E/St copolymers prepared using catalyst II were extremely brittle, which prevented their mechanical testing. The stress–strain behavior of the polymers produced with other catalysts is shown in Figure 10. In general, PE homopolymers and copolymers with low styrene content exhibited a yield maximum in the stress–strain curve that coincided with the start of a well-defined neck during tensile testing at all the testing rates. This result differs from that obtained by Chang et al.,<sup>7</sup> who possibly used copolymers produced with CGC. These authors reported nonuniform deformation, seen as diffuse necking, for highly crystalline materials; increasing the comonomer content abolished the necking.

The homopolymers produced showed the highest elastic modulus and yield stress, which was related to their low level of branching and high crystallinity. Moreover, their deformation characteristics were similar to those of many semicrystalline thermoplastics with localized yielding, unlike copolymers with higher levels of branching for which a lower modulus and uniform deformation are more characteristic of elastomeric behavior. As the crystallinity and spherulitic structure decayed with increasing amounts of styrene, stress at yield decreased and elongation to yield increased until the material becomes so rubbery that there was no longer a yield point. The yielding region was found to broaden with reduced crystallinity or increased comonomer content. These results are in agreement with observations by Chang et al.<sup>7</sup> for E/St copolymers probably produced using a constrained geometry catalyst.

As the proportion of crystalline material increased, tensile strength at yield increased, which was closely related to the stiffness of the sample. The highest tensile strength at yield was found for the copolymers prepared using catalyst V, whereas the lowest tensile strength at yield was shown by copolymers obtained using catalyst I. The mechanical properties of the copolymers produced using catalyst III were poor, likely because of their low molecular weight.

The percent elongation of a material is a measure of its ability to deform and dissipate energy. A sample of low crystallinity has a large fraction of amorphous polymer and it is the slippage and disentanglement of the amorphous polymer that allows it to deform. In the literature, Jordens et al. observed that with decreasing crystalline density, percent elongation was higher.<sup>32</sup> Bensason et al. also observed an increase in percent elongation for low crystallinity poly(ethylene-*co*-1-octene) copolymers with increasing comonomer contents.<sup>33</sup> As can be seen in Figure 10, the samples prepared using catalyst V showed the highest percent elongation, whereas the lowest percent elongation was recorded for the samples produced with catalyst I. At

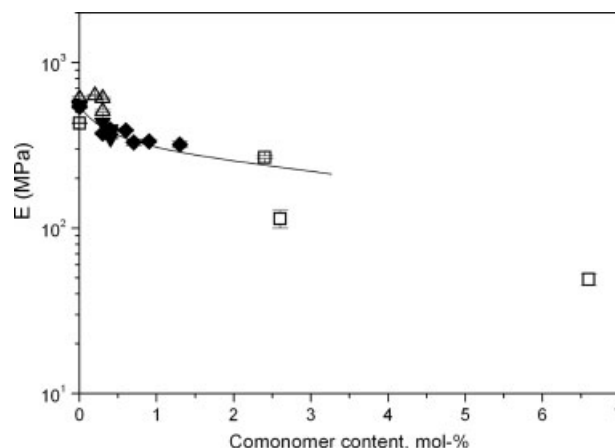
low strain, the crystallinity of a sample was the dominant factor during the deformation process, but at high strain the role of entanglements prevailed.<sup>33,34</sup> The balance between low- and high-crystalline material resulted in a blending of the tensile properties. From these results it was inferred that the samples prepared using catalyst V were the toughest because they showed the highest elongation percentages.

Finally, Figure 11 shows the dependence of the Young modulus on styrene molar content for all E/St copolymers, except those obtained with catalyst II. The modulus was observed to steeply decrease as crystallinity decreased and consequently with an increase in the comonomer content. However, no single correlation of modulus with comonomer dependence was obtained. Only samples polymerized with catalysts IV and V seemed to follow a unique trend. The materials obtained from catalysts I and III did not follow the described trend above, as a clear consequence of their chemical heterogeneity, as shown in the molecular and structural analyses.

### CONCLUSIONS

The copolymers synthesized showed a broad spectrum of thermal and mechanical properties according to their comonomer contents. Of the six catalytic systems tested, the [rac-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride catalyst (V) was found to be a good candidate for the production of E/St copolymers given its high activity, which would allow a high level of styrene incorporation. The result was the formation very homogeneous copolymers of high molecular weight and excellent thermal and mechanical properties.

Catalyst I also yielded interesting results because its end product was a mixture of ethylene homopoly-



**Figure 11** Young modulus as a function of molar styrene content of the copolymers synthesized by the different catalysts: catalyst I ( $\square$ ), catalyst III ( $\triangle$ ), catalyst IV ( $\blacktriangledown$ ), and catalyst V ( $\blacklozenge$ ). The solid line is drawn to guide the eye.

mer and E/St copolymer with good mechanical properties as compatibilized polyblends. Catalysts II, III, and IV generated E/St copolymers of either low molecular weight or low styrene content, and therefore, they seem to be inefficient at copolymerization.

Our findings indicate that the final balance of properties depended on the proportions of materials of high and low crystallinity such as that using a metallocene catalyst system; the structure and properties of an E/St copolymer can be tailored to the intended application of the polymer product. Indeed, establishing the relationship between the mechanical properties and microstructure of the final product and the nature of the catalyst is an important step toward controlling some of the properties of polymers.

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