

# Articles

## Stereospecific Ethylene–Styrene Block Copolymerization with *ansa*-Zirconocene-Based Catalyst<sup>†</sup>

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**ABSTRACT:** *rac*-[Methylene(3-*tert*-butyl-1-indenyl)<sub>2</sub>]ZrCl<sub>2</sub> activated by MAO, employed as catalyst in the ethylene–styrene copolymerization, shows a peculiar behavior. Actually, it produces block copolymers, whereas the homogeneous catalytic systems known to copolymerize these monomers preferentially give rise to alternating sequences of ethylene and styrene. The polystyrene blocks are isotactic and show crystallinity, also when their average length is as short as 10 units. Some evidence suggests the primary styrene insertion into the metal–carbon bond of the growing chain: this unusual regiochemistry could account for the observed tendency to give homosequences.

### Introduction

Since 1990, several catalytic systems have been reported to be able to promote ethylene–styrene copolymerization through polyinsertion.<sup>1</sup> As a general rule, they show a tendency to monomers alternation due to the inability to give styrene–styrene sequences<sup>1a,b</sup> and to a penultimate unit effect.<sup>1g</sup> When the regular alternation of the monomer units joins the stereoregularity, the polymer chains can arrange themselves into a crystalline lattice.<sup>1c,d,f–1</sup> In these cases X-ray diffraction analysis<sup>2</sup> as well as NMR comparison between copolymers and purposely synthesized low molecular mass models<sup>3</sup> indicates the isotactic structure. The presence of occasional styrene–styrene sequences in substantially alternating copolymers has been reported by Arai et al.,<sup>1h</sup> who used the [isopropylidenebis(1-indenyl)]zirconium dichloride-based catalyst. This system, because of the wide angle between the moieties of the ligand, is also able to homopolymerize the styrene.

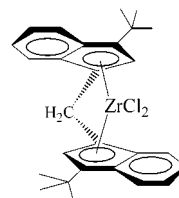
To rationalize the behavior of ethylene and styrene in copolymerization, it is necessary to point out that the styrene insertion with *ansa*-zirconocene-based catalysts generally occurs with formation of a Zr–benzylidene bond (secondary insertion).<sup>4</sup> Possibly this regiochemistry accounts for the observation that styrene is scarcely prone both to homopolymerize and to copolymerize with 1-alkenes, which on the contrary give primary insertion.<sup>5</sup>

The interest in copolymers containing polystyrene sequences arises mainly from the possible formation of phase separation of the styrene blocks into rigid microdomains, which works as reversible vulcanization. As a consequence, such a polymer material can show thermoelastomeric behavior and usually is obtained by backbone hydrogenation of poly(styrene-*block*-1,4-butadiene).<sup>6</sup> A few microstructural evidences of direct syn-

thesis of macromolecules with such a structure via ethylene–styrene copolymerization have been reported until now.<sup>1b</sup> On the other hand, the findings recently reported in the study on the behavior of a samarium-based catalyst toward these monomers indirectly indicate the formation of a block copolymer.<sup>7</sup>

### Results and Discussion

**Ethylene–Styrene Copolymerization.** The *ansa*-zirconocene complex *rac*-[methylene(3-*tert*-butyl-1-indenyl)<sub>2</sub>]ZrCl<sub>2</sub> activated by MAO has been reported to be highly regioselective with regard to the propene polymerization.<sup>8</sup>



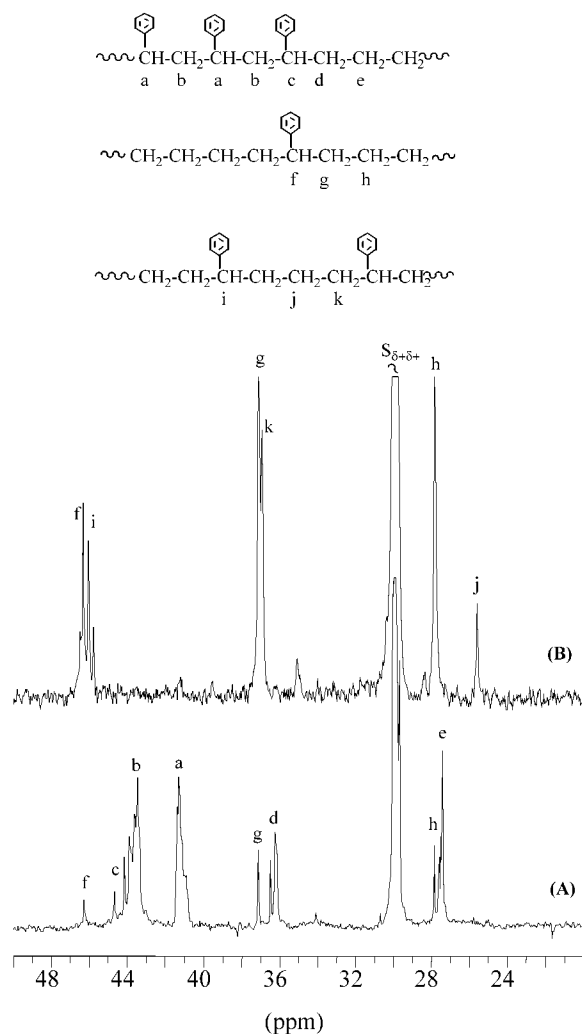
*rac*-[CH<sub>2</sub>(3-*t*-Bu-1-Ind)<sub>2</sub>]ZrCl<sub>2</sub>

Possibly such a regioselectivity must be related to the presence of the *tert*-butyl substituents in C(3) of the ligand that prevents the secondary propene insertion (regioerror). We have used this catalytic system in the ethylene–styrene copolymerization. The copolymerization products insoluble in boiling acetone and soluble in boiling THF were analyzed by NMR, GPC, and DSC techniques. In Figure 1A is reported the <sup>13</sup>C NMR spectrum of the copolymer we have obtained at 20 °C with a comonomer feed composition 0.011 M in ethylene and 7 M in styrene (run 4 of Table 1).

One can observe intense signals at 41.3 and 43.6 ppm due to the polystyrene sequences, at 29.9 ppm of the polyethylene sequences, and in addition peaks at 27.4, 36.2, and 43.7 ppm (*S*<sub>βδ<sup>+</sup></sub>, *S*<sub>αδ<sup>+</sup></sub>, and *T*<sub>βδ<sup>+</sup></sub>, respectively) of the sequence SSSEEE and weak peaks at 27.8, 37.1,

<sup>†</sup> In memory of Prof. Umberto Giannini.

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**Figure 1.** Aliphatic region of  $^{13}\text{C}$  NMR spectra and chemical shift assignments of the ethylene–styrene copolymers obtained in the presence of (A)  $\text{rac-CH}_2(3\text{-}t\text{-Bu-1-Ind})_2\text{ZrCl}_2$  (run 4 of Table 2) and (B)  $\text{rac-ethylene(Ind)}_2\text{ZrCl}_2$  based catalyst (15% styrene molar content).

**Table 1.** Assignment of the Observed Chemical Shifts in the  $^{13}\text{C}$  NMR Spectra of the Ethylene–Styrene Copolymers (Aliphatic Region)

carbon atom	$\delta$ (ppm)	carbon atom	$\delta$ (ppm)
a	41.3	g	37.1
b	43.6	h	27.8
c	43.7	i	45.6–46.6
d	36.2	j	25.5
e	27.4	k	36.6–37.2
f	46.2		

and 46.2 ppm ( $S_{\beta\delta^+}$ ,  $S_{\alpha\delta^+}$ , and  $T_{\delta^+\delta^+}$ , respectively) of the sequence EESEE (Table 1). From the relative intensities of the signals of the junctions with respect to those of the homosequences, an average length of 19 units can be calculated for the ethylene sequences and of 7 for the styrene sequences by using the equations

$$L_E = \{A_{29.9} + 0.5(A_{37.1} + A_{36.2}) + A_{27.8} + A_{27.4}\} / (A_{37.1} + A_{36.2})$$

$$L_S = \{0.5(A_{37.1} + A_{36.2}) + A_{43.7}\} / 0.5(A_{37.1} + A_{36.2})$$

The styrene molar content is 28% (see Experimental Part); previously described copolymers with similar or

even lower styrene content show very different monomer units distribution with the relevant presence of SES sequences.<sup>1g</sup> On the contrary, such a sequence is not detected in the present copolymer where less than 2% of the overall styrene units are present as isolated units ( $^{13}\text{C}$  NMR resonances at 27.8 and 37.1 ppm). For comparison purposes in Figure 1B is reported the aliphatic region of the  $^{13}\text{C}$  NMR spectrum of an E–S copolymer obtained with the known alternating catalyst  $\text{rac-[ethylene(1-indenyl)}_2\text{]ZrCl}_2/\text{MAO}$ .<sup>1g</sup> In this copolymer the 15% styrene units content gives sequences SES ( $S_{\beta\beta}$  at 25.5 ppm) in addition to the SEE sequences, whereas the SS sequences are not detected (peaks expected around 41 and 43 ppm).

With regard to the physical properties of the block copolymer, the calorimetric analysis (DSC) shows a very broad endothermic peak around 100 °C. On the other hand, in the X-ray powder diffraction spectrum reported in Figure 2 can be detected the patterns of both crystallinity of polyethylene (peaks at  $2\theta = 21.5^\circ$  and  $23.9^\circ$ ) and isotactic polystyrene (peaks at  $2\theta = 8.21^\circ$ ,  $14.2^\circ$ ,  $16.3^\circ$ ,  $18.3^\circ$ , and  $36.1^\circ$ ).<sup>9</sup> One can conclude that, despite their shortness, the homosequences are able to arrange themselves into two distinct crystalline lattices.

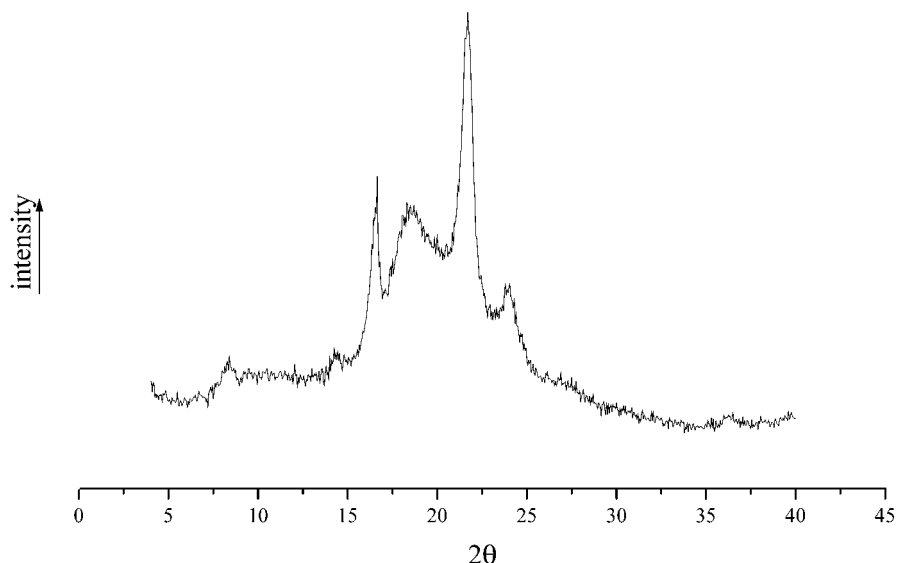
The GPC analysis shows low molecular mass ( $M_w = 7700$  Da) and polydispersity index 1.8. This latter result supports the clues arising from NMR analysis: actually, the macromolecular chains are grown in a single catalytic site.

A series of ethylene–styrene copolymerization runs carried out at two compositions of monomer feed and at different temperatures are reported in Table 2. The produced copolymers are blockwise as well, with different composition and styrene block length. It is worth noting the absence of an increase of the styrene relative reactivity with decreasing the temperature. Such a behavior also makes different this catalytic system with respect to the previously reported zirconocenes.<sup>1g</sup>

The product of the reactivity ratios, calculated on the basis of the diads content (see Experimental Part), is greater than unity, as expected for the block copolymerization. It is worth stressing that the rate of ethylene incorporation is higher than that of styrene incorporation, and balanced comonomer units composition is possible only by using styrene-rich feed composition.

**Styrene Homopolymerization.** To collect some information about the regiochemistry of the styrene insertion into the zirconium–carbon bond of the catalyst under investigation, a series of styrene polymerizations have been carried out at 50, 15, and  $-7$  °C.

Upon inspection of the  $^{13}\text{C}$  NMR spectra of the polystyrene obtained in each run, one can state that the polymerization is isospecific (signals at 41.3 and 43.6 ppm). In the polymer obtained at 15 °C are also detectable the resonances of the unsaturated chain end at 114.2 and 140.8 ppm and correspondingly in the  $^1\text{H}$  NMR the signals at 4.7 and 5.1 ppm (see Figure 3). The 2,4-diphenyl-1-alkenyl group (structure A) suggested by these NMR evidences can be related to the termination process via  $\beta$ -hydrogen abstraction from the growing polymer chain where the last inserted unit is bonded to the metal through the methylene carbon (primary insertion). Moreover, in the region of the aliphatic carbons can be observed signals at 33.3, 37.1, and 42.4 ppm assigned to carbons 1, 2, and 3, respectively, of 1,3-diphenylalkane (structure B). Such a structure is in accordance with the styrene primary insertion into the



**Figure 2.** Wide-angle X-ray spectrum of the ethylene–styrene block copolymer obtained in the presence of *rac*-CH<sub>2</sub>(3-*t*-Bu-1-Ind)<sub>2</sub>ZrCl<sub>2</sub> based catalyst (run 4 of Table 2). Cu K $\alpha$  Ni-filtered radiation.

zirconium–hydrogen bond in the polymerization initiation step. The peaks at 20.8, 36.6, 43.8, and 44.3 ppm account possibly either for the primary styrene insertion into the zirconium–methyl bond or for chain termination by hydrolysis of the chain growing with the same regiochemistry (*threo*-2,4-diphenylpentyl group) (structure **C**).<sup>10</sup> The presence of the same end group with the *erythro* configuration can be inferred from the less intense signal at 23.9 ppm. From the ratio of the intensities of this last signal and that of the *threo* configuration (at 20.8 ppm) can be deduced a measurement of the stereoselectivity. The value of this ratio is 1/10, indicating the isospecific insertion 10 times more likely than the syndiospecific one.<sup>10</sup>

The NMR spectra of the polystyrene obtained at 50 °C indicate the same structure of the previously described polystyrene prepared at 15 °C but for the more intense signals of the unsaturated chain ends. In addition, some secondary styrene insertion occasionally occurs in the polymerization carried out at 50 °C as suggested by weak signals of unsaturated chain end (see below) in the <sup>13</sup>C NMR spectrum at 131.3 and 130.9 ppm. At low temperature (–7 °C) the styrene polymer-

matter of fact, with this system ethylene and styrene are scarcely prone to give alternating sequences.

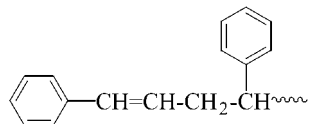
So by using a suitable comonomer feed composition, it is possible to synthesize ethylene–styrene copolymers with unprecedented structure. Actually, NMR evidences as well as physical characterization indicate that, in the macromolecules we have prepared, isotactic homosequences of styrene join homosequences of ethylene. Previously described catalysts, also when able to homopolymerize the styrene, produce copolymers with alternating or random structure.<sup>11</sup>

The peculiarity of the catalyst we used, in our opinion, should be related to the regiochemistry of the styrene insertion that is primary unlike the secondary insertion generally observed with the homogeneous catalysts. Possibly, the aromatic ring of the last inserted unit plays a role by interacting with the catalytic center and making less unfavorable the insertion of the styrene. This role should be similar to that played by the next to last unit when the insertion is secondary.<sup>1g</sup>

## Experimental Part

**Materials.** Ethylene was purchased from Società Ossigeno Napoli and used without further purification. Toluene was refluxed over metallic sodium and distilled under a nitrogen atmosphere. Styrene was stirred over CaH<sub>2</sub> and distilled under reduced pressure of nitrogen. Methylalumoxane (MAO) provided by Witco as a 30 wt % solution in toluene was dried before the use by removing in vacuo the solvent. *rac*-[Methylene(3-*tert*-butyl-1-indenyl)<sub>2</sub>ZrCl<sub>2</sub>] was synthesized according to the literature.<sup>8</sup>

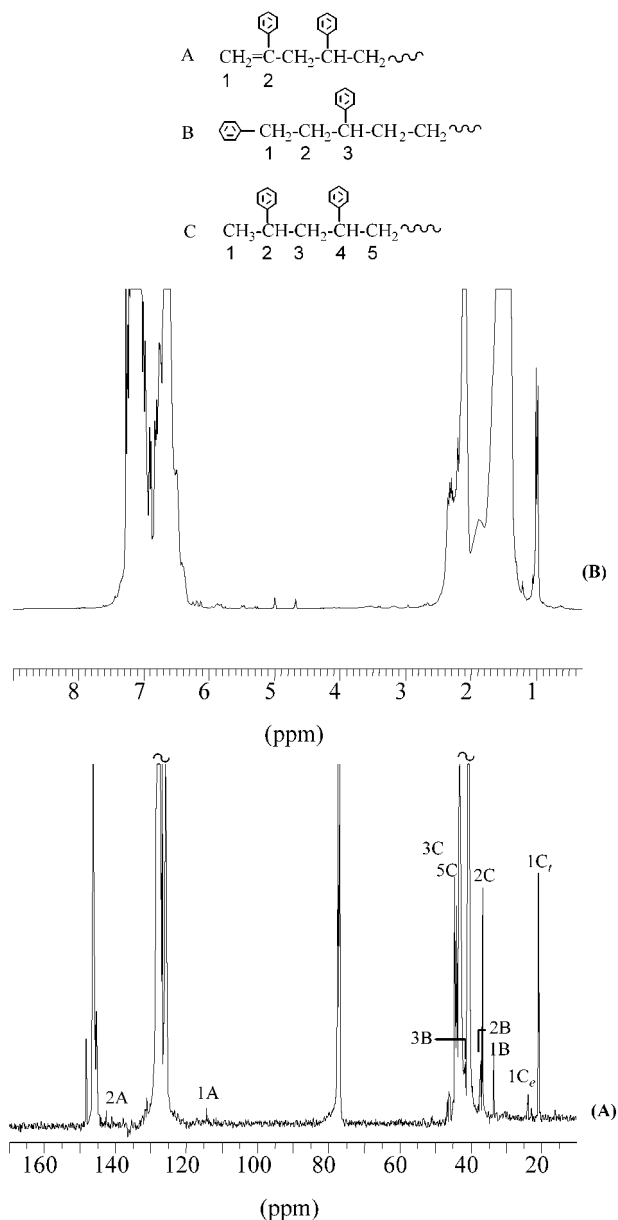
**Ethylene–Styrene Copolymerization.** Copolymerizations were carried out in a 100 mL glass flask charged under a nitrogen atmosphere sequentially with styrene (10 mL) and MAO (8 × 10<sup>–3</sup> mol). The mixture was magnetically stirred, and the glass flask was thermostated at the desired temperature. The inert atmosphere was removed and replaced with the ethylene feed, and then 3 mL of a toluene solution of the zirconocene compound (3.7 mM) was introduced (Al/Zr = 1000). The flask was fed with the gaseous monomer (neat ethylene or ethylene–argon mixture) over the polymerization time. The steadiness of gaseous mixture composition was monitored via GC. The copolymers were coagulated by pouring the reaction mixture into acidified methanol, filtered, washed with further methanol and then with boiling acetone, and dried in vacuo. The products were fully soluble in THF.



ization affords macromolecules with the only saturated chain ends because the  $\beta$ -hydrogen abstraction is practically absent. The main resonances of the chain ends are at 20.8, 36.6, 43.8, and 44.3 ppm (structure **C**). This result indicates primary insertion in the first step (into Zr–CH<sub>3</sub> bond) and in the last step (followed by hydrolysis) less intense peaks at 11.9 and 29.7 ppm can be assigned to the secondary insertion into the Zr–CH<sub>3</sub> bond.<sup>3</sup>

## Conclusions

The catalyst we have tested in the ethylene–styrene copolymerization shows a peculiar behavior with respect to the homogeneous catalysts previously reported to be active in the copolymerization of these monomers. As a



**Figure 3.**  $^{13}\text{C}$  NMR (A) and  $^1\text{H}$  NMR (B) spectrum of the polystyrene obtained at 15 °C in the presence of  $rac\text{-CH}_2(3\text{-}t\text{-Bu-1-Ind})_2\text{ZrCl}_2$ .

**Table 2. Polymerization Conditions and Copolymers Composition**

run <sup>a</sup>	$f_E^b$ ( $\times 10^3$ )	$F_E^c$	$T$ (°C)	yield (mg/h)	$L_S$	$L_E$
1	0.79	0.4	60	240	25	14
2	1.16	1.0	60	330	12	12
3	0.79	1.2	20	80	12	15
4	1.16	2.6	20	80	7	19
5	0.79	1.1	0	50	9	11
6	1.16	4.9	0	50	5	21

<sup>a</sup> All the runs have been carried out in the presence of  $rac$ -[methylene(3-*tert*-butyl-1-indenyl) $_2$ ZrCl $_2$  ( $5 \times 10^{-6}$  mol in 3 mL of toluene), MAO ( $5 \times 10^{-3}$  mol), styrene (10 mL), and the ethylene pressure fit for producing the desired monomer feed composition.

<sup>b</sup> Mole ratio of ethylene to styrene in the feed. <sup>c</sup> Copolymer composition, molar ratio of ethylene to styrene units in the copolymer determined by  $^{13}\text{C}$  NMR.

The ethylene concentration in the liquid phase was calculated by using the Lewis and Luke's equation conjoined with the fugacity function chart of ethylene as reported in the literature.<sup>12</sup>

**Styrene Polymerizations.** Styrene polymerizations were carried out in a 100 mL glass flask charged under a nitrogen atmosphere sequentially with toluene (20 mL), styrene (10 mL), and MAO ( $8 \times 10^{-3}$  mol). The mixture was magnetically stirred, the glass flask was thermostated at the desired temperature, and then 2 mL of the solution 4 mM of the catalyst in toluene was injected. After 12 h the polymerization mixture was poured in methanol, and the polystyrene was recovered by filtration, washed with fresh methanol and then with boiling acetone, and finally dried in a vacuum. Yields: 5.5 g at 50 °C, 1.2 g at 15 °C, and 0.2 g at -7 °C.

**$^{13}\text{C}$  Analysis.** The spectra of the copolymers were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode and at a temperature of 365 K. The samples were prepared by dissolving 30 mg of polymer into 0.5 mL of tetrachloro-1,2-dideuterioethane. The chemical shifts are referred to the central peak of  $\text{C}_2\text{D}_2\text{Cl}_4$  used as internal reference at  $\delta = 74.26$  ppm.

The resonances of carbon atoms c, d, and e have been calculated by adding the contribution of the phenyl substituent to  $S_{\alpha\alpha}$  in a polystyrene sequence or to  $S_{\beta\gamma^+}$  in an ethylene–styrene copolymer.

Extensive  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift assignments on polystyrene have been carried out using a combination of mono- (DEPT) and two-dimensional (HMBC)<sup>13</sup> experiments. The spectra were recorded on an AV 400 Bruker operating at 100 MHz in the Fourier transform mode at room temperature. By using the areas of the peaks, the comonomer units composition can be evaluated by means of the following equation:

$$x_S = 0.5(A_{36.2} + A_{37.1}) + A_{43.6} / (0.75(A_{36.2} + A_{37.1}) + 0.5A_{29.9} + A_{43.6})$$

Likewise, the product of the reactivity ratios  $r_E = k_{EE}/k_{ES}$  and  $r_S = k_{SS}/k_{SE}$  was calculated on the basis of the diads content:

$$r_E r_S = ([EE][SS]) / [SE]^2 \text{ where } [EE] = (A_{29.9} + 0.5A_{27.4} + 0.5A_{27.8})/2$$

$$[SS] = (A_{43.6} + 0.5A_{36.2} + 0.5A_{37.1}) \text{ and } [SE] = 0.5(A_{36.2} + A_{37.1})$$

**X-ray Analysis.** Wide-angle X-ray diffractogram was obtained with Cu K $\alpha$  Ni-filtered radiation using a PW 1710 Philips powder diffractometer.

**DSC Analysis.** The thermal measurements were carried out on a Du Pont 2920 differential scanning calorimeter at heating rate of 10 °C/min on about 10 mg of sample. The instrument was calibrated by the measurement of the melting point of indium.

**GPC Analysis.** GPC of the copolymers was recorded on a Waters 150-C gel permeation chromatography with four polystyrene gel columns ( $10^4$  Å pore size) in dichlorobenzene at 120 °C by using standard polystyrene samples for calibration. All the samples show a polydispersity around 2 and  $M_w$  below 10 000 Da.

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## References and Notes

- (1) (a) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. (Dow Chemical Co.) Eur. Pat. Appl. EP 416,815, 1991; *Chem. Abstr.* **1991**, 115, 93163. (b) Longo, P.; Grassi, A.; Oliva, L. *Makromol. Chem.* **1990**, 191, 2387. (c) Kakugo, M.; Miyatake, T.;

- Mizunuma, K.; Yagi, V. (Sumitomo Chemical Co., Ltd., Japan), U.S. Patent US 5,043,408; 1991; *Chem. Abstr.* **1991**, 114, 229616. (d) Kakugo, M.; Miyatake, T.; Mizunuma, K. *Stud. Surf. Sci. Catal.* **1990**, 56, 517. (e) Pellecchia, C.; Pappalardo, D.; D'Arco, M.; Zambelli, A. *Macromolecules* **1996**, 29, 1158. (f) Oliva, L.; Izzo, L.; Longo, P. *Macromol. Rapid Commun.* **1996**, 17, 745. (g) Oliva, L.; Longo, P.; Izzo, L.; Di Serio, M. *Macromolecules* **1997**, 30, 5616. (h) Arai, T.; Ohtsu, T.; Suzuki, S. *Macromol. Rapid Commun.* **1998**, 19, 327. (i) Xu, G. *Macromolecules* **1998**, 31, 2395.
- (2) Oliva, L.; Immirzi, A.; Tedesco, C.; Venditto, V.; Proto, A. *Macromolecules* **1999**, 32, 2675.
- (3) Izzo, L.; Oliva, L.; Proto, A.; Trofa, M. *Macromol. Chem. Phys.* **1999**, 200, 1086.
- (4) (a) Oliva, L.; Caporaso, L.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1995**, 28, 4665. (b) Caporaso, L.; Izzo, L.; Oliva, L. *Macromolecules* **1999**, 32, 7329.
- (5) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, 20, 1015.
- (6) (a) Traugott, T. D. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. C., Menges, G., Eds.; Wiley-Interscience: New York, 1987; Vol. 16, p 77. (b) Grassi, A.; Caprio, M.; Zambelli, A.; Bowen, D. E. *Macromolecules* **2000**, 33, 8130.
- (7) Hou, Z.; Zhang, Y.; Tezuka, H.; Xie, P.; Tardif, O.; Koizumi, T.; Yamakazi, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2000**, 122, 10533.
- (8) Resconi, L.; Balboni, D.; Baruzzi, G.; Fiori, C.; Guidotti, S.; Mercandelli, P.; Sironi, A. *Organometallics* **2000**, 19, 420.
- (9) (a) Natta, G.; Corradini, P. *Nuovo Cimento Suppl.* **1960**, 15, 40. (b) Petraccone, V.; De Rosa, C.; Tuzi, A.; Fusco, R.; Oliva, L. *Eur. Polym. J.* **1988**, 24, 297.
- (10) Longo, P.; Grassi, A.; Oliva, L.; Ammendola, P. *Makromol. Chem.* **1990**, 191, 239.
- (11) Arai, T.; Otsu, T.; Suzuki, S. (Denki Kagaku Kogyo Kabushiki Kaisha) Eur. Pat. Appl. EP 876697; *Chem. Abstr.* **1998**, 129, 316697.
- (12) Maxwell, J. B. *Data Book on Hydrocarbons*; Van Nostrand Co.: New York, 1950; pp 45, 46, 52, 53.
- (13) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, 108, 2093.

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