

# Syndiotactic-enriched propylene–styrene copolymers using fluorenyl-based half-titanocene catalysts

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## Abstract

The constrained geometry complexes  $\{3,6\text{-}^t\text{Bu}_2\text{C}_{13}\text{H}_6\text{SiMe}_2\text{N}^t\text{Bu}\}\text{TiCl}_2$  ( $X = \text{Cl}$ , **1**;  $\text{Me}$ , **2**), in combination with MAO or borane activators, have been investigated in the copolymerization of propylene with styrene at 25–60 °C, 1–5 atm. Both systems were found to give styrene–propylene (PP–PS) copolymers with up to 24 mol% of styrene incorporated and moderate molecular weights ( $M_w = 14,000\text{--}88,000$ ;  $M_w/M_n = 1.58\text{--}2.32$ ). Addition of some ethylene to the styrene–propylene feed improves the catalytic polymerization activity. The PP–PS copolymers feature a syndiotactic-enriched polypropylene microstructure ( $r > 92\%$ ), with randomly distributed single styrene and/or short polystyrene units.  
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**Keywords:** Constrained geometry catalyst; Polymerization; Propylene; Styrene; Titanium

## 1. Introduction

Copolymerization of  $\alpha$ -olefins with Group 4 metals catalysts has emerged as a powerful tool for the preparation of a broad variety of polymeric materials with controlled microstructure and predetermined physico-chemical properties [1]. In particular, polypropylene-based thermoplastic elastomers are widely accepted in many sectors of industrial activity and remain highly technology driven [2].

Styrene–propylene copolymers (PS–PP) could be of great practical value, considering the potential availability of stereoblock, alternating or random microstructures and valuable mechanical properties derived therefrom. However, it is well-known that propylene and styrene feature generally opposite insertion regiospecificities (1,2-insertion for propylene versus 2,1-insertion for styrene) and their reactivity ratios ( $r_P$  and  $r_S$ ) were reported to differ by several orders of magnitude, suggesting a basic incompatibility of these monomers [3]. Actually, there are few examples described in the literature of effective styrene–propylene copolymerization. Early reports deal with

random styrene–propylene copolymers having predominantly isotactic short polystyrene sequences, which were obtained using heterogeneous catalyst systems  $\text{TiCl}_3/\text{AlR}_3$  [3]. Effective alternating styrene–propylene copolymerization with  $C_2$  and  $C_S$ -symmetric metallocene catalysts was further achieved by introduction of a small amount ethylene, a third comonomer which can re-activate the catalytic site after secondary styrene insertion [4]. Also, a diblock *atactic*-polypropylene–*syndiotactic*-polystyrene copolymer was obtained recently by sequential copolymerization of propylene and styrene using  $\text{Cp}^*\text{Ti}(\text{OBz})/\text{MAO}$  system [5].

In this study, we strove to achieve efficient copolymerization of propylene with styrene using the half-sandwich fluorenyl-amido dichlorotitanium precursor **1**, designed by AtoFina Co. for the production of syndiotactic polypropylene [6], and the dimethyl precursor **2** derived thereof (Chart 1).

## 2. Experimental

### 2.1. Materials

Toluene and cyclohexane were refluxed over Na/K alloy, distilled and degassed by two freeze–thaw–vacuum cycles prior to use.  $\{3,6\text{-}^t\text{Bu}_2\text{C}_{13}\text{H}_6\text{SiMe}_2\text{N}^t\text{Bu}\}\text{TiCl}_2$  (**1**) was prepared using the published procedure [6]. Complex

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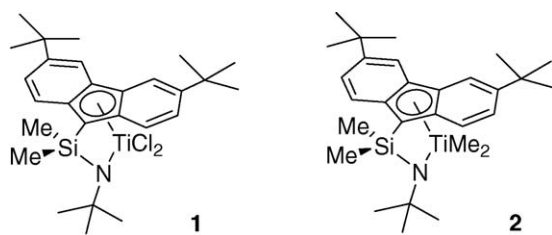


Chart 1.

{3,6-*t*Bu<sub>2</sub>C<sub>13</sub>H<sub>6</sub>SiMe<sub>2</sub>N<sup>*t*</sup>Bu}TiMe<sub>2</sub> (**2**) was prepared by the treatment of **1** with 2 equiv of MeLi in toluene and its consistency was established by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and an X-ray diffraction analysis [7]. Activators [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and MAO (20 wt% solution in toluene) were generously provided by AtoFina, and used as received. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was purchased from Strem and sublimed twice before use. Polymerization grade ethylene and propylene were purchased from Air Liquide Company and used without further purification. Styrene (Acros) was dried over CaH<sub>2</sub> and vacuum distilled prior to use.

Gel Permeation Chromatography (GPC) was performed in Atofina research center on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10 μm Mixed-B or Mixed-B LS columns was used. Samples were prepared at 160 °C. Polymer molecular weights were determined versus polystyrene standards. DSC measurements were performed on a TA Instruments DSC 2920 differential scanning calorimeter. DMA was carried out on a T.A. Instruments DMA 2980 apparatus, at a heating rate of 3 °C min<sup>-1</sup> in the tension film mode with a deformation amplitude of 10 μm and 1 Hz frequency. Quantitative <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy of polymers was performed in C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub> solvent at 125 °C in 10 mm tubes on a AM-500 Bruker spectrometer operating at 125 MHz with the following parameters: pulse angle 90°, delay 30 s, acquisition time 1.18 s, TD 64 K and SW 27,777.77 Hz.

## 2.2. Typical (co)polymerization procedure

A 300 mL Top-Industrie glass high-pressure reactor was charged under argon with 50 mL of freshly distilled solvent. The reactor was loaded with the appropriate monomer(s) at

atmospheric pressure and a solution of catalyst (i.e. pre-catalyst + activator) in 5 mL of toluene was injected by syringe. Mechanical stirring (Pelton turbine, 1000 rpm) was started immediately and the gas pressure in the reactor was maintained constant throughout the experiment. After a given time period, the reactor was depressurized and the reaction was quenched by adding 5 mL of a 10% solution of HCl in methanol. The polymer formed was precipitated by adding of 500 mL of methanol, washed and dried in vacuo overnight at room temperature.

## 3. Results and discussion

For comparison purposes, the abilities of catalyst systems based on complexes **1** and **2** were first assessed in the homopolymerization of ethylene, propylene, 1-hexene and styrene. Representative results are summarized in Tables 1 and 2. Ethylene is polymerized with a high activity of 3775 kg PE/(mol(Ti) h) using the 1/MAO (1:500) system. Both precursors **1** and **2**, when activated with MAO (Ti/Al = 1:500) or borane (Ti/B = 1:3), show very high performances in the polymerization of propylene at room temperature under 5 atm (entries 2–4), which are comparable to the values for **2** independently reported quite recently by another group [7,8]. On the other hand, 1-hexene polymerization catalyzed by 1/MAO proceeded at room temperature or at 50 °C with significantly lower activities (entries 5 and 6), giving oily oligomers with syndiotactic-enriched microstructure as judged by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.

Complexes **1** and **2**, when activated by MAO or molecular activators, were found to exhibit poor activity for styrene polymerization (Table 2). This is especially the case when molecular activators were used (entries 10–12). All styrene polymerizations were conducted at a high monomer-to-catalyst ratio over a 12 h period, without addition of a scavenger. However, we checked that CpTiCl<sub>3</sub> (**3**) provides a very active catalyst under similar conditions (entry 13). Since it is generally admitted that syndiospecific polymerization of styrene is catalyzed by Ti(III) species generated in situ from Ti(IV) precursors [9], the modest catalytic activity observed from **1** and **2** can be tentatively attributed to the enhanced stability of these fluorenyl-amido titanium species (or their cationic derivatives) towards reduction. The PS polymers isolated are not soluble in organic solvents at room temperature, consistent with a stereoregular syndiotactic nature. The latter microstructure was independently confirmed

Table 1  
Homopolymerization of α-olefins catalyzed by binary systems based on **1** and **2**<sup>a</sup>

Entry	Catalyst	Activator	Monomer	<i>T</i> (°C)	Time (min)	Yield (g)	Activity <sup>b</sup>	<i>T</i> <sub>m</sub> (°C) <sup>c</sup>
1	<b>1</b>	MAO	Ethylene	25	5	6.0	3775	135
2	<b>1</b>	MAO	Propylene	25	15	6.5	1950	132
3	<b>2</b>	[PhNHMe <sub>2</sub> ][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	Propylene	25	15	4.33	1393	147
4	<b>2</b>	MAO	Propylene	25	60	19.2	1164	136
5 <sup>d</sup>	<b>1</b>	MAO	1-Hexene	25	720	1.0	21	Oily
6 <sup>d</sup>	<b>1</b>	MAO	1-Hexene	50	720	0.8	10	Oily

<sup>a</sup> Polymerization conditions unless otherwise stated: toluene = 50 mL, [Ti] = 380 μmol/L, [MAO]/[Ti] = 500 or [B]/[Ti] = 3 with [Al(*i*Bu)<sub>3</sub>]/[Ti] = 1000, *P* = 5 atm.

<sup>b</sup> kg polymer/(mol(Ti) h).

<sup>c</sup> Melting temperature determined by DSC.

<sup>d</sup> Bulk 1-hexene, total volume = 15 mL, [Ti] = 255 μmol/L.

Table 2  
Homopolymerization of styrene catalyzed by binary systems based on **1** and **2**<sup>a</sup>

Entry	Catalyst	Activator	<i>T</i> (°C)	Time (h)	Yield (%)	Activity <sup>b</sup>	<i>M<sub>w</sub></i> (10 <sup>3</sup> g/mol)	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>
7	<b>1</b>	MAO	40	12	11	192	30	1.59
8	<b>1</b>	MAO	60	12	20	350	30	2.27
9 <sup>c</sup>	<b>1</b>	MAO	60	12	17	297	nd	nd
10	<b>2</b>	[PhNHMe <sub>2</sub> ][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	25	12	3	52	66	2.74
11	<b>2</b>	[Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	25	12	5	87	nd	nd
12	<b>2</b>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	25	12	Traces	nd	nd	nd
13 <sup>d</sup>	<b>3</b>	MAO	25	2 min	76	102600	163	2.15

<sup>a</sup> Polymerization conditions unless otherwise stated: total volume = 10 mL, [Styrene] = 8.6 M (bulk), [Ti] = 410 μmol/L; [Styrene]/[Ti] = 21,000; [MAO]/[Ti] = 500 or [B]/[Ti] = 3 without scavenger.

<sup>b</sup> kg PS/(mol(Ti) h).

<sup>c</sup> Hexanes = 10 mL, [Styrene] = 4.3 M.

<sup>d</sup> [Styrene]/[Ti] = 4500; [Al]/[Ti] = 1000.

by the melting temperature of ca. 260–270 °C [10] and the presence in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the characteristic resonance at δ 145.5 ppm for the *ipso*-carbon atom of syndiotactic sequences [11].

Propylene/styrene copolymerizations were next performed using combinations of **1** and **2** with MAO or molecular activators. Representative results are summarized in Table 3. The copolymerization of propylene with styrene in toluene using the **1**/MAO system proceeds in a sluggish manner with poor reproducibility, as judged by the variable polymer yields (entries 14 and 15). Typically, these experiments gave PP–PS copolymers that have low molecular weight and relatively narrow polydispersity (Fig. 1, entry 14), and of which only a minor fraction is soluble in CHCl<sub>3</sub> and THF at room temperature. Both the soluble fraction at room temperature in CDCl<sub>3</sub> and the whole copolymer at 125 °C in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> show a low incorporation (4–5 mol%) of styrene, as determined by <sup>1</sup>H and/or <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. No distinct melting temperature was detected for these PP–PS copolymers by DSC analysis, contrary to the corresponding homopolymers (i.e. 132–147 °C for sPP and 260–265 °C for

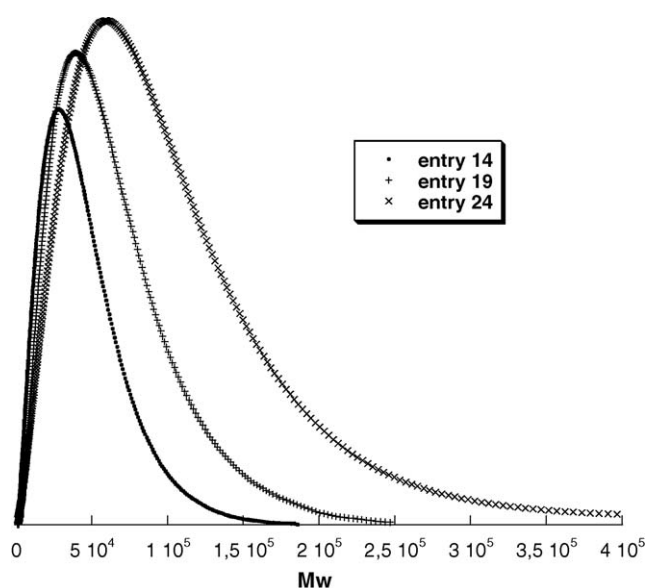


Fig. 1. GPC traces of PS–PP copolymers.

Table 3  
Propylene–styrene copolymerization catalyzed by binary systems based on **1** and **2**<sup>a</sup>

Entry	Catalyst	[Styrene] (M)	<i>T</i> (°C)	<i>P</i> (atm)	C <sub>2</sub> H <sub>4</sub> added	Time (min)	Yield (g)	<i>M<sub>w</sub></i> (10 <sup>3</sup> g/mol)	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>	Styrene (mol%) <sup>b</sup>
14	<b>1</b>	4.3	25	5	–	50	2.5	30	2.01	5.0
15	<b>1</b>	4.3	25	5	–	50	0.7	40	1.58	nd
16	<b>1</b>	5.2	60	3	–	140	0.5	nd	nd	nd
17	<b>1</b>	8.6	60	5	–	180	1.0	54	21.1	nd
18 <sup>c,d</sup>	<b>2</b>	4.3	50	5	–	65	0.3	nd	nd	nd
19	<b>2</b>	4.3	25	5	–	150	2.0	43	1.81	7.4
20	<b>2</b>	4.3	60	5	–	240	1.2	14	1.63	24
21	<b>2</b>	0.9	25	5	–	160	8.7	40	2.07	1.2
22 <sup>d,e</sup>	<b>1</b>	4.3	50	1 <sup>e</sup>	Only <sup>e</sup>	60	1.2	36	1.81	60
23 <sup>d</sup>	<b>2</b>	8.6	25	5	+	180	3.2	88	1.53	20
24 <sup>d</sup>	<b>2</b>	4.3	25	5	+	180	8.7	65	2.32	4.4
25 <sup>d</sup>	<b>2</b>	2.2	25	5	+	180	26.1	25	2.16	2.5

<sup>a</sup> General conditions unless otherwise stated: solvent = cyclohexane (except for bulk experiments, i.e. [styrene] = 8.6 M), total volume = 50 mL, [Ti] = 380 μmol/L, [MAO]/[Ti] = 500.

<sup>b</sup> Amount of styrene incorporated in the copolymer, as determined by <sup>1</sup>H and/or <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.

<sup>c</sup> [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] used as activator with [B]/[Ti] = 3 and [Al(<sup>*i*</sup>Bu)<sub>3</sub>]/[Ti] = 50.

<sup>d</sup> Toluene used as solvent.

<sup>e</sup> No propylene introduced.

sPS, *vide supra*). This indicates minimal (if any) contamination of the PP–PS copolymers by homopolymers, in line with the monomodal, relatively narrow molecular weight distributions (Fig. 1). Rising of the polymerization temperature and increase of the styrene feed had deleterious effect on the activity (entries 16 and 17); significant amounts of copolymer were obtained only over a longer period of time, apparently, accompanied by gradual decomposition of catalyst as suggested by the broadening of polydispersity (entry 17).

The 2/MAO system was examined under similar conditions as for 1/MAO. This combination was selected for investigation because of the enhanced thermal stability of the dialkyl precursor 2 as compared to that of the dichloro derivative 1 [12], which may in turn minimize the formation of decomposition Ti products whose impact on catalysis is not obvious to address. However, as in the case of 1/MAO, increase of the polymerization temperature from 25 to 60 °C affected negatively the activity (compare entries 19 and 20). As a general trend, we observed that high concentrations of styrene inhibited the polymerization and did not result in increased styrene content in the copolymers. On the other hand, a copolymerization experiment using a lower styrene feed showed significantly higher activity, though the styrene content in the copolymer was low (entry 21). All the isolated copolymers feature only poor solubility in CDCl<sub>3</sub> and THF at room temperature and have moderate molecular weights with quite narrow monomodal distributions (Fig. 1, entries 19 and 24). Most copolymers did not show distinct melting temperature in DSC analysis, with the noticeable exception of the propylene-rich (98.8 mol%) copolymer for which a  $T_m$  of 123.6 °C was determined. This value lies on the low range of melting temperatures 124–150 °C usually observed for sPP samples with *rrrr* content of 80–95% [13].

The fact that styrene–propylene copolymerization reactions proceed with insufficient activities and poor incorporation of styrene is not surprising. It is in line with previous observations, which were explained, as aforementioned, by conflicting

regiospecificities of insertion of propylene and styrene [4]. Secondary insertion of styrene in metal–carbon bond results in steric hindrance at the metal center and, thereby, disfavors the following primary insertion of propylene. However, the stalled growing polymeric chain can be re-activated towards propylene by introduction of an ethylene molecule.

First, to corroborate the compatibility of ethylene and styrene for copolymerization with the present catalyst systems, a single run was conducted (entry 22). The PS–PE copolymer isolated featured indeed a high content of styrene incorporated. Next, copolymerization of styrene with propylene in the presence of small amounts of ethylene using the 2/MAO combination was investigated (Table 3, entries 23–25). For this purpose, the polymerization reactor was equipped with an extra reservoir of ethylene at 1 atm in order to get a ca. 100:1 propylene/ethylene mixture at the reactor inlet. The high yields of copolymers isolated demonstrate the obvious beneficial addition of some ethylene to the styrene/propylene mixture in terms of catalytic activity. Furthermore, the copolymers obtained featured from 2.5 to 20 mol% of styrene incorporated (determined by <sup>13</sup>C{<sup>1</sup>H} NMR, *vide infra*) (the amount of ethylene incorporated remained <1 mol%), as well as enhanced molecular weights and good polydispersities. Again, no distinct melting temperature for these PS–PP/PE terpolymers samples was detected by DSC. Glass-transition temperatures ( $T_g$ ) of 21–25 °C and Young modulus ( $E$ ) of 147–345 MPa (25 °C) were determined for these PS–PP/PE copolymers, which are to be compared with the respective characteristics  $T_g = -3$  °C and  $E = 325$ –330 MPa (25 °C) measured for a typical sPP sample ( $M_w = 160,000$  g/mol; *rrrr* = 83%) [14].

Considering that insertion of propylene in the Ti–C (growing polymer chain) proceeds in a 1,2-fashion and incorporation of styrene is secondary (2,1-), at least three limit PS–PP/PE terpolymer structures can be envisioned (Chart 2). The microstructure of PS–PP copolymers and PS–PP/PE terpolymers was determined by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy at 125 °C in tetrachloroethane-*D*<sub>2</sub>. Details of selected spectra and proposed assignments of

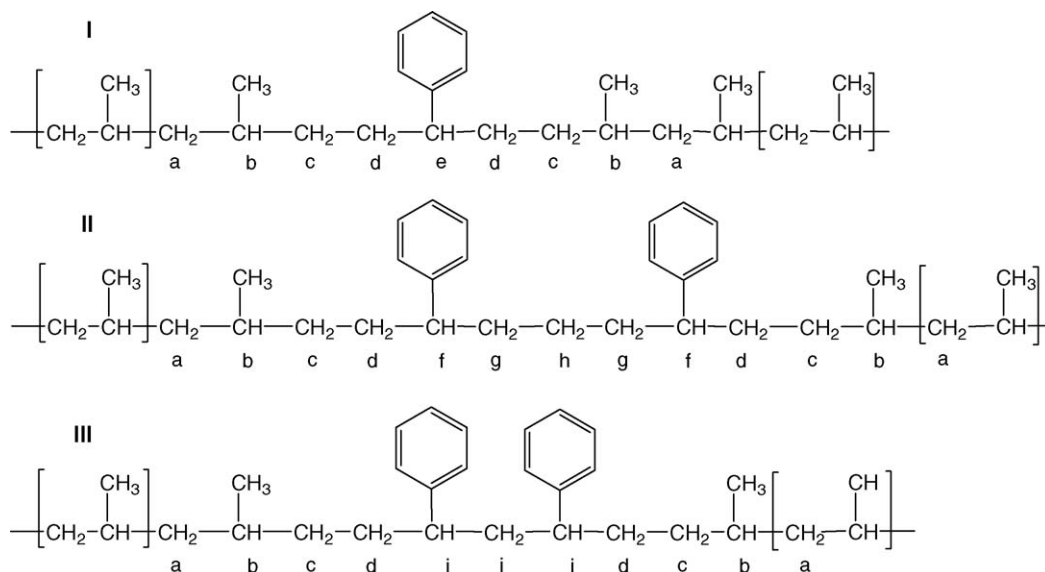


Chart 2. Some possible limit structures for PS–PP/PE terpolymers.

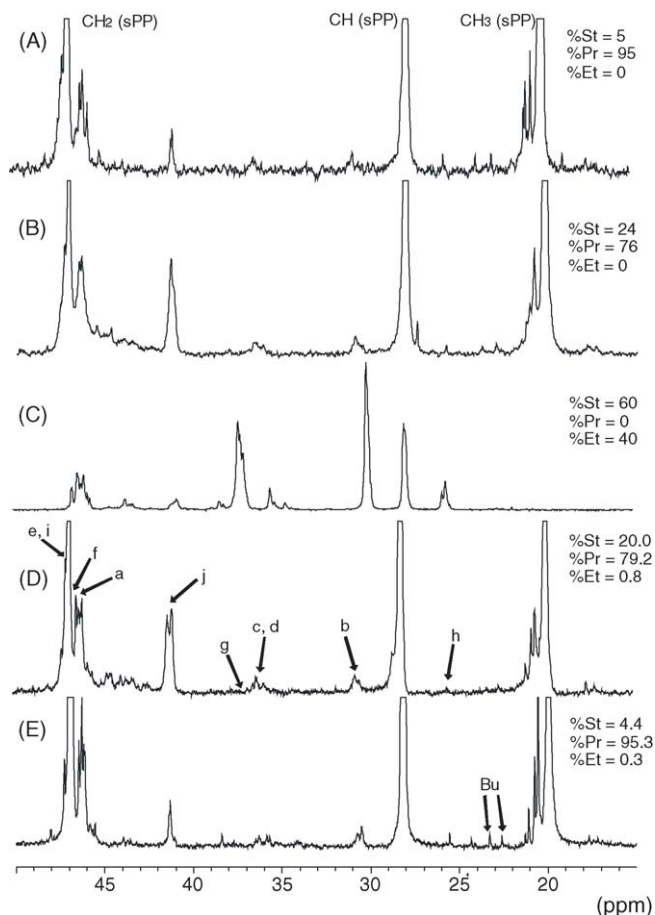


Fig. 2. Details of the aliphatic region of  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra ( $125^\circ\text{C}$ ,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 125 MHz) of: (A) PS–PP (entry 14); (B) PS–PP (entry 20); (C) PS–PE (entry 22); (D) PS–PP/PE (entry 23); (E) PS–PP/PE (entry 24). Descriptors a–j refer to C atoms as defined in Chart 2.

characteristic resonances [15] are shown in Fig. 2. The polymer chains are composed mostly by syndiotactic PP ( $r > 92\%$ ) sequences, which is indicated by the Me resonance at  $\delta$  20.3–20.9 ppm [16]. Single styrene units are randomly distributed along the polymer chain but enchaining of styrene units (S–S sequences, labeled i and j in Fig. 2) (Chart 2, III) is also operative. The presence of isobutyl resonances at  $\delta$  22.5–23.4 ppm is indicative of primary insertion of propylene in the initiation step [17]. The low intensity of SES sequences in terpolymer structures (labeled f, g and h in Chart 2) suggests that re-activation of the growing polymeric chain by insertion of an ethylene molecule is followed by incorporation of propylene (Chart 2, I) rather than styrene insertion (Chart 2, II).

#### 4. Conclusions

Constrained geometry titanocenes  $\{3,6\text{-}^t\text{Bu}_2\text{C}_{13}\text{H}_6\text{SiMe}_2\text{-N}^t\text{Bu}\}\text{TiX}_2$  ( $\text{X} = \text{Cl}$ , **1**;  $\text{Me}$ , **2**) are prominent catalyst precursors when activated by MAO for the polymerization of ethylene and syndiospecific polymerization of  $\alpha$ -olefins. However, these complexes were found to polymerize styrene in a rather sluggish manner. Copolymerization of propylene with styrene using the **2**/MAO combination yields random PS–PP copolymers with

prevailing syndiotactic polypropylene sequences. The polymerization activity can be significantly enhanced by introducing small amounts of ethylene as a comonomer, without significant impact on the molecular weight, molecular weight distribution and microstructure of the copolymers.

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