

Copolymerization of ethene with styrene using CGC catalysts: the effect of the cyclopentadienyl ligand substitution on the catalyst activity and copolymer structure

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Dedicated to Professor Józef Ziółkowski on the occasion of his 70th birthday

Abstract

The ethene–styrene copolymerization has been investigated using the dimethylsilylene-bridged (amidocyclopentadienyl)dichlorotitanium(IV) complexes $[\text{TiCl}_2\{\eta^5\text{-}1\text{-}(\text{SiMe}_2\text{N}t\text{-Bu-}\kappa\text{N})\text{-}2,3,4\text{-Me}_3\text{-}5\text{-R-C}_5\}]$, where R = Me (**1**), H (**2**), Bu (**3**), Ph (**4**), 4-fluorophenyl (**5**), and but-2-en-2-yl (**6**) in combination with methylalumoxane (MAO) as catalysts. The nature of the substituent R strongly influenced the catalyst activity and selectivity and the copolymer microstructure and molecular weight. The catalysts derived from **1** to **3** were by about one order more active than those derived from **4** to **6**. At the optimum Al/Ti molar ratio of 900, the highly active catalysts produced a pseudo-random copolymer (95–97 wt.%) containing up to 47.8 mol% of incorporated styrene. The low-active catalysts gave mixtures of a pseudo-random copolymer (76–85 wt.%) with polyethene (10 wt.%) and polystyrene sequences (3–7 wt.%). The X-ray diffraction crystal structures of **2** and **4** were determined. Comparison of crystal structures of **1** and **2** versus **4** and **5** revealed a slightly shorter distances Ti–Cg (Cg – centroid of the cyclopentadienyl ring) and slightly larger Cl–Ti–Cl angles in **1** and **2**, indicating a higher electron density at the titanium atom. An electron attracting effect of phenyl or alkenyl substituents as well as their steric hindrance can account for a low catalytic performance of **4–6**/MAO catalysts.

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1. Introduction

A new class of highly active catalysts for polyalkene production emerged with the synthesis of (*tert*-butylamido)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane which affords the $\eta^5:\eta^1(N)$ -dianionic ligand [1] and, subsequently, *ansa*- $\{\eta^5:\eta^1(N)\text{-}1\text{-}[(\textit{tert}\text{-butylamido)dimethylsilyl}]\text{-}2,3,4,5\text{-tetramethylcyclopentadienyl}\}$ dichlorotitanium

(IV) (**1**) [2]. These catalysts, called “constrained geometry catalysts” (CGC), arise from mixing of the *ansa*-amidodicyclopentadienyl-titanium or -zirconium dichlorides with excess methylalumoxane (MAO) [3]. Compared to titanocene or zirconocene-based single-site catalysts they provide more acidic and less sterically encumbered cationic centres [4] and, consequently, display very high activities in the polymerization of ethene, propene and in copolymerizations of ethene with terminal alkenes, cycloalkenes and styrene [5]. In attempts to tune the polymerization properties the parent CGC complex

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1 was modified by replacing the cyclopentadienyl ligand by indenyl or fluorenyl ligands [6], and their rings [7] as well as the amide groups were variously substituted [8]. Recently, an effective route to CGC complexes substituted on otherwise fully methyl-substituted cyclopentadienyl ring in vicinal position to the *ansa*-bridge was developed affording a series of racemic complexes $[\text{TiCl}_2\{\eta^5\text{-}\eta^1(N)\text{-C}_5(1\text{-SiMe}_2\text{N}t\text{-Bu-2,3,4-Me}_3\text{-5-R})\}]$, where R = H (**2**), Bu (**3**), Ph (**4**), 4-fluorophenyl (**5**), and but-2-en-2-yl (**6**) [9,10]. The substituent R has been shown to considerably modify the activity of CGC catalysts in the polymerization of ethene [11] and propene [10], and to modify molecular weights of the polymers. Polydispersities of both the polymers were close to 2, indicating a single-site character of these catalysts. NMR analyses of these polymers revealed a low branching in polyethene [11] and a low content of syndiotactic attachments in largely atactic polypropene [10].

The catalytic copolymerization of ethene and styrene which is only poorly catalyzed by titanocene-based catalysts [12] has been successfully conducted by CGC catalysts achieving a high styrene incorporation (up to 37%) [3,13]. Particularly, the copolymerization using the parent **1**/MAO catalyst was investigated in detail and the copolymers were fully characterized [14]. The **1**/MAO catalyst appeared to be more active than the catalysts based on indenyl, fluorenyl or benzylamido derivatives presumably due to a higher electron density induced by fully methyl-substituted cyclopentadienyl ligand in **1** [15].

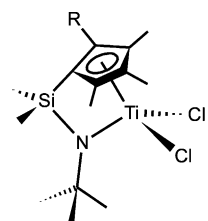
Here we report the catalytic copolymerization of ethene and styrene as depending on the substituent R in the series of catalysts **1–6**/MAO under optimized conditions.

2. Results and discussion

2.1. Ethene–styrene copolymerization

The *ansa*-amidocyclopentadienyltitanium dichlorides **1–6** (Scheme 1) were activated by MAO at molar ratios Al/Ti = 800, 900, and 1000 in the presence of ethene (E) and styrene (S) (molar ratio S/E = 10) in toluene solution, at temperatures 40–70 °C, and the overall concentration of the CGC catalyst (0.05–0.28 μmol/ml).

The polymerization run was started by adding the toluene solution of the respective CGC complex, and the time of polymerization was varied (30–120 min) in order to optimize the



R = Me (**1**), H (**2**), Bu (**3**), Ph (**4**), 4-fluorophenyl (**5**), but-2-en-2-yl (**6**)

Scheme 1.

Table 1
The dependence of catalyst activity on molar Al/Ti ratio^a

Catalyst	[Al]/[Ti]	Yield (g)	Activity (kg/mol _{Ti} h)
1 /MAO	800	7.421	192.4
	900	8.423	218.4
	1000	8.174	211.9
2 /MAO	800	7.919	213.4
	900	9.318	251.1
	1000	9.012	242.9
3 /MAO	800	7.231	194.9
	900	9.150	246.6
	1000	8.113	218.6
4 /MAO	2000	5.794	150.2
	800	1.076	23.9
	900	1.116	24.8
5 /MAO	1000	0.745	16.5
	800	0.926	19.7
	900	1.041	22.1
6 /MAO	1000	0.998	21.2
	800	0.598	12.7
	900	0.631	13.4
	1000	0.596	12.7

^a Polymerization conditions: toluene = 16 ml, styrene = 10 ml, constant pressure of ethene 140 kPa, temperature = 50 °C, [Ti] = 0.167 μmol/ml, time 60 min.

polymerization conditions. Series of polymerization experiments showed that the Al/Ti ratio equal to 900 afforded the highest yields of the copolymers for all the catalysts (Table 1). The polymerization temperature was found optimum at 50 °C except for the **2**/MAO and **5**/MAO catalysts where the optimum temperature was 60 °C (Table 2).

The polymerizations with varying concentrations of the catalysts revealed that the polymer yields were increasing with increasing catalyst concentration, however, the

Table 2
Temperature dependence of the catalysts activity^a

Catalyst	[Ti] (μmol/ml)	Time (min)	Temperature (°C)	Yield (g)	Activity (kg/mol _{Ti} h)
1 /MAO	0.11	60	40	4.585	180.1
			50	6.322	248.4
			60	4.803	188.7
2 /MAO	0.11	60	40	6.099	249.1
			50	7.598	310.3
			60	8.558	349.5
3 /MAO	0.11	60	70	6.943	283.5
			40	5.725	233.8
			50	7.066	288.5
4 /MAO	0.11	60	60	4.933	201.4
			40	0.588	19.8
			50	0.783	26.3
5 /MAO	0.11	60	60	0.552	18.6
			40	0.495	16.0
			50	0.521	16.8
6 /MAO	0.11	60	60	0.740	23.8
			40	0.619	19.9
			50	0.299	9.6
			50	0.462	14.9
			60	0.279	8.97

^a Polymerization conditions: toluene = 16 ml, styrene = 10 ml, constant pressure of ethene 140 kPa, [Al]/[Ti] = 900.

Table 3
The dependence of the catalyst activity on Ti concentration^a

Catalyst	[Ti] ($\mu\text{mol/ml}$)	Time (min)	Yield (g)	Activity (kg/molTi h)
1/MAO	0.05	60	1.022	88.4
	0.11		6.322	248.3
	0.167		8.423	218.4
	0.28		10.077	155.5
2/MAO	0.05	60	1.101	98.9
	0.11		7.598	310.2
	0.167		9.318	251.1
	0.28		11.614	186.3
3/MAO	0.05	60	1.088	97.7
	0.11		7.066	288.5
	0.167		9.150	246.6
	0.28		10.701	171.7
4/MAO	0.11	60	0.783	26.3
	0.167		1.116	24.8
	0.28		1.698	22.4
5/MAO	0.11	60	0.521	16.8
	0.167		1.041	22.1
	0.28		1.430	18.1
6/MAO	0.11	60	0.462	14.9
	0.167		0.631	13.4
	0.28		0.876	11.1

^a Polymerization conditions: toluene = 16 ml, styrene = 10 ml, constant pressure of ethene 140 kPa, temperature = 50 °C, [Al]/[Ti] = 900.

catalyst activity after reaching the optimum concentration was decreasing with increasing catalyst concentration. The optimum concentration of 0.11 $\mu\text{mol/ml}$ was found for all the catalysts except 5/MAO showing the optimum concentration at 0.167 $\mu\text{mol/ml}$ (Table 3). A large drop in the catalyst activity for the lowest catalyst concentration of 0.05 $\mu\text{mol/ml}$ was apparently due to the catalyst deactivation by the presence of impurities in the system.

A comparison of polymer yields, the catalyst activity, molecular weights M_w and M_n , and the distribution of molecular weight M_w/M_n for the whole series of the catalysts under standard conditions revealed that the catalysts prepared from CGC complexes 1 to 3 were by about one order more active than those prepared from 4 to 6 while the molecular weight characteristics varied considerably (Table 4).

The GPC analysis showed that the most active catalyst 2/MAO produced the polymer with the lowest molecular

Table 4
The E/S (S – styrene, E – ethene) copolymerizations under standard conditions^a

Catalyst	Yield (g)	Activity (kg/molTi h)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
1/MAO	8.4235	218.4	17287	46708	2.7
2/MAO	9.3181	251.1	10949	26746	2.4
3/MAO	9.1503	246.6	17543	41917	2.4
4/MAO	1.1160	24.8	41656	148052	3.5
5/MAO	1.0408	22.1	18197	53715	2.9
6/MAO	0.6306	13.4	19548	104099	5.3

^a Standard polymerization conditions: toluene = 16 ml, styrene = 10 ml, constant pressure of ethene 140 kPa, temperature = 50 °C, [Al]/[Ti] = 900, [Ti] = 0.167 $\mu\text{mol/ml}$, time 60 min.

Table 5
¹³C NMR resonances characterizing links between monomer units (S – styrene, E – ethene) in copolymers obtained using complexes 1–6; their presence is denoted (\times)^a

Chemical shift (ppm)	Carbon type	Sequence	1	2	3	4	5	6
25.6	S $\beta\beta$	SES	\times	\times	\times	\times	\times	\times
27.7	S $\beta\delta$ (S $\beta\delta+$)	SEE	\times	\times	\times	\times	\times	\times
29.9	S $\gamma\delta$, S $\delta\delta$ (S $\gamma\delta+$)	EEE	\times	\times	\times	\times	\times	\times
34.5–35.0	S $\alpha\beta$	SES or SS	\times	\times	\times	\times	\times	\times
37.0	S $\alpha\gamma$, S $\alpha\delta$ (S $\alpha\gamma+$)	SES, SEE	\times	\times	\times	\times	\times	\times
41.3	T $\beta\beta$	SSS				\times	\times	\times
43.4	T $\beta\delta$	ESS				\times	\times	
44.7	S $\alpha\alpha$	SS				\times	\times	\times
46.1	T $\delta\delta$ (T $\gamma\gamma+$)	ESE	\times	\times	\times	\times	\times	\times

^a Standard polymerization conditions see Table 4.

weight (M_w 26.7 $\times 10^3$) and the catalysts in the order of decreasing activity 3/MAO > 1/MAO \gg 5/MAO afforded polymers with moderately increasing molecular weights (M_w 41.9 $\times 10^3$ to 53.7 $\times 10^3$) while polydispersity of the polymers M_w/M_n was increasing from 2.4 to 2.9 (see Table 4). Surprisingly, the 4/MAO catalyst afforded the polymer with far the highest molecular weight (M_w 148.1 $\times 10^3$) whereas the M_w/M_n value further increased. The least active catalyst 6/MAO giving M_w 104.1 $\times 10^3$ afforded a polymer with far the highest value of M_w/M_n .

The microstructure of the above polymer samples was determined by ¹³C NMR and DSC analyses. The ¹³C NMR spectra resolved different types of attachments of styrene and ethylene units (see Table 5) and the quantitative evaluation of ¹³C NMR resonances allowed us to determine the composition of the copolymers (Table 6). The molar fraction of styrene in the copolymer chain X_S was calculated from areas of the methylene resonances according to published procedure [16,17]. The average length of methylene sequences L_{CH_2} was calculated according to Ref. [16]. The EE, ES and SS symbols represent the weight percentage of the corresponding diads calculated as described elsewhere [18]. The data from both tables show that catalysts 1–3/MAO produced mainly alternating copolymers containing only few percents of ethylene–ethylene links. The low-active 4–6/MAO catalysts produced less regular copolymers containing in addition

Table 6
Characterization of E/S copolymers obtained under standard conditions^a by means of the ¹³C NMR and DSC

Catalytic system	X_S^b (mol%)	$L_{CH_2}^c$	EE (wt.%)	ES (wt.%)	SS (wt.%)	T_g (°C)
1/MAO	46.4	3.3	3.2	96.8	0	25
2/MAO	41.7	3.8	4.8	95.2	0	18
3/MAO	47.7	3.2	3.2	96.8	0	30
4/MAO	39.5	4.1	11.9	84.4	3.7	22
5/MAO	40.8	3.9	10.8	85.1	4.1	26
6/MAO	31.2	5.4	16.9	76.0	7.1	–

^a Standard polymerization conditions see Table 4.

^b Molar fraction of styrene.

^c Average number of mutually linked CH₂ groups.

to an increased number of ethylene–ethylene links a certain content of incorporated styrene sequences.

The ethane–styrene copolymers produced by all the above CGC catalysts except **6**/MAO were amorphous since the DSC analysis did not show any endothermic peak attributable to crystalline phase melting. Glass transition temperatures (T_g) for these copolymers are listed in Table 6. At variance with Sernetz et al. [14], the T_g values were not clearly related to the styrene content in the copolymers, apparently due to the differences in molecular weights of the copolymers. The absence of glass transition for the copolymer produced by **6**/MAO on one hand and the occurrence of an endothermic peak at 126.8 °C on the other hand imply the presence of long polyethylene sequences, that is in line with the results of ^{13}C NMR analysis.

The kinetics of the E/S polymerization was investigated using the **2**/MAO catalyst by termination of polymer runs after the period of 20–90 min. The data given in Fig. 1 show that the initial high catalyst activity after 30 min is decreasing to about one half in the run terminated after 90 min.

One can suggest that the catalyst selectivity toward formation of the alternating copolymer is not much affected by the polymerization time because high contents of the E/S copolymer were obtained after standard 60 min reaction time (cf. Table 6).

Compared with the fundamental work by Sernetz et al. [14] on the ethene/styrene copolymerization catalyzed by **1**/MAO system it is remarkable that a considerably higher incorporation of styrene was achieved with the same or very similar CGC complexes **1**–**3**. To throw light on the reason of this discrepancy we carried out the copolymerization experiment using the **3**/MAO system with the same molar Al/Ti ratio equal to 2000 as used for **1**/MAO in Ref. [14] under otherwise the standard conditions (see Table 1). In addition to a drop in the catalyst activity (see Table 1 for **3**/MAO) we obtained the copolymer containing only 35.4 mol% of incorporated styrene, the content close to 34.6 mol% obtained by Sernetz et al. [14].

Comparison of plots of the styrene incorporated in copolymer versus the styrene content in the monomer feed for

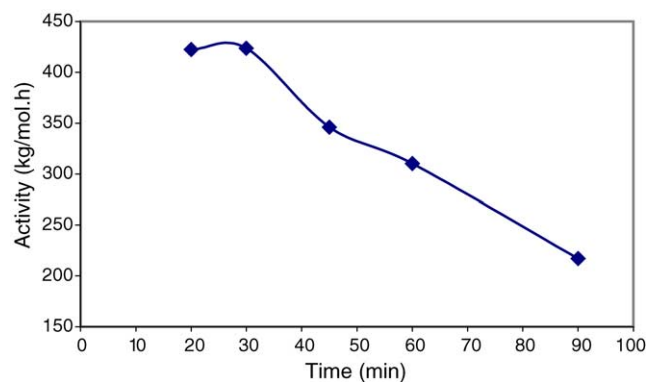


Fig. 1. The time dependence of activity of the **3**/MAO catalyst under standard conditions.

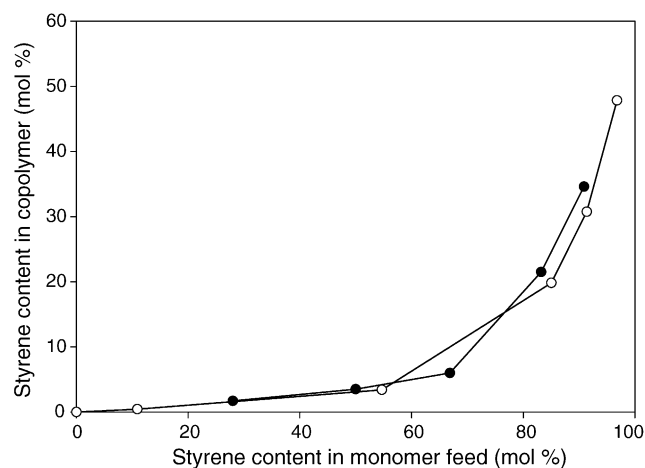


Fig. 2. Correlation between styrene content in the monomer feed and in copolymer for **1**/MAO, Al/Ti = 2000 [14] (—●—) and **3**/MAO, Al/Ti = 900 under otherwise standard conditions (—○—).

1/MAO (Al/Ti 2000) from Ref. [14] and the standard experiment with **3**/MAO (Al/Ti 900) catalyst (Fig. 2) shows that while in excellent agreement till about 70 mol% of styrene in the monomer feed the **1**/MAO (Al/Ti 2000) catalyst gave a slightly better incorporation of styrene at a higher styrene content in the monomer feed. However, at about 91 mol% of styrene in the monomer feed the catalyst activity dropped down and a higher styrene content in the monomer feed was not attempted [14]. In contrast, the **3**/MAO (Al/Ti 900) catalyst at the standard content of styrene in the monomer feed (96.6 mol%) showed the maximum activity with respect to the molar Al/Ti ratio (Table 1), and gave the copolymer containing as much as 47.8 mol% of styrene (Table 6). The low copolymerization activities of the **1**/MAO or **3**/MAO systems at large Al/Ti molar ratio (2000) compared to activities of the same systems at lower Al/Ti molar ratio (900) can be brought about by a deactivation action of excessive trimethylaluminium which is always present in toluene-soluble MAO.

2.2. Correlation of molecular parameters of compounds **1**, **2**, **4**, **5** and **6** with the copolymerization activity of the catalysts derived thereof

High-precious X-ray diffraction data were collected for single crystals of **2** and **4** allowing us to obtain molecular geometric parameters suitable for comparison with already known data for compounds **1**, **5** and **6** of the investigated series. The molecular structure of **4** is shown in Fig. 3, and important geometric parameters of **2** and **4** together with those of compounds **1**, **5** and **6** are gathered in Table 7.

The data show that the substituents R have a negligible effect on most of the molecular parameters, however, distances Ti–Cg (Cg – centroid of the cyclopentadienyl ring) which are shorter by 0.01 Å in **1** and **2** compared to **4** and **5** and the Cl–Ti–Cl angles which are larger by about 3° in **1** and **2** indicate a higher electron density on the Ti atom. A discernible

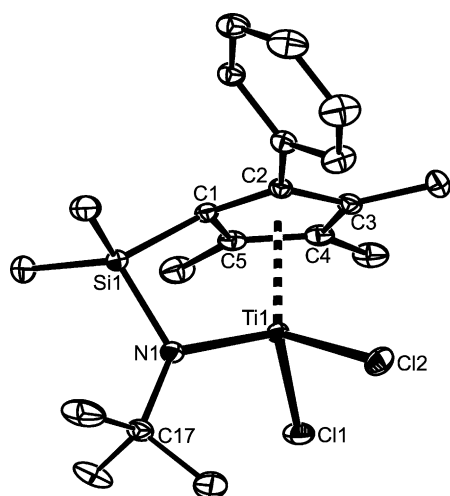


Fig. 3. The molecular structure of **4** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

difference in the first reduction potential of these complexes was also found by cyclic voltammetry with extreme values of E_p^{red} for **1** – 1.28(2) V and **4** – 1.12(2) V [11]. A lower electron density on the Ti atom in **4** and **5** is compatible with the presence of electron attracting phenyl and 4-fluorophenyl groups. On the other hand, the butyl substituent in **3** is expected to donate electron density although less effectively than the methyl

group in **1** but more effectively than but-2-en-2-yl group in **6** with the double bond in conjugation position toward the cyclopentadienyl ligand. The molecular geometry data (Ti–Cg and Cl–Ti–Cl) for **6** fall between the data for pairs **1/2** and **4/5**, and hence, the very low activity of the **6**/MAO catalyst points to a suggestion that also the steric effect of R influences the catalytic activity. The effective copolymerization of styrene apparently requires more coordination space at the titanium atom than, e.g., the homopolymerization of ethene (which is also much faster [3,5,11]), and the most active complex **2** bearing only hydrogen atom instead of R affords the largest space for coordination and polymerization at the titanium atom. The copolymer obtained from **2**/MAO had a significantly lower molecular weight than the polymers from **1**/MAO or **3**/MAO, probably as a result of easy chain transfer. This behaviour seems to be compatible with the poor activity and far the lowest molecular weight in the polymerization of propene where the order of decreasing activity was **1** > **3** > **4** > **6** > **5** > **2** but activities of **1** and **2** differed only four-times [10].

2.3. Conclusions

Combined electronic and steric effects of substituents on the cyclopentadienyl carbon atom vicinal to the *ansa*-bridge in CGC complexes **1–6** strongly affect the catalytic activity and selectivity of the **1–6**/MAO catalysts in the

Table 7
Selected bond lengths (Å) and angles (°) for complexes **2** and **4**, and literature data for **1**, **5** and **6**

	Atoms				
	2	4	1 ^a	5 ^a	6 ^b
Lengths					
Ti–C1	2.2689 (16)	2.2876 (16)	2.264 (4)	2.284 (4)	2.285 (2)
Ti–C2	2.3076 (17)	2.3724 (17)	2.329 (3)	2.373 (4)	2.355 (2)
Ti–C3	2.4470 (17)	2.4440 (17)	2.445 (3)	2.452 (4)	2.445 (2)
Ti–C4	2.4593 (17)	2.4306 (18)	2.445 (3)	2.425 (4)	2.432 (2)
Ti–C5	2.3451 (16)	2.3347 (17)	2.329 (3)	2.316 (4)	2.336 (2)
Ti–Cg ^c	2.0342 (8)	2.0405 (9)	2.033 (2)	2.040 (3)	2.037 (1)
Ti–(C1–C5) ^d	2.0232 (7)	2.0336 (8)	2.023 (2)	2.032 (3)	2.030 (1)
Ti–N	1.9130 (15)	1.9109 (15)	1.910 (4)	1.910 (3)	1.911 (1)
Si–N	1.7559 (15)	1.7579 (15)	1.745 (4)	1.744 (4)	1.763 (1)
Si–C1	1.8630 (17)	1.8722 (18)	1.866 (4)	1.875 (4)	1.872 (2)
Ti–Cl1	2.2806 (5)	2.2780 (6)	2.265 (1)	2.269 (2)	2.2718 (5)
Ti–Cl2	2.2751 (5)	2.2762 (6)	2.265 (1)	2.274 (2)	2.2859 (5)
Angles					
Cg–Ti–N	108.22 (5)	108.18 (6)	107.8 (2)	107.6 (2)	107.86 (5)
Cg–Ti–Cl1	112.58 (3)	114.39 (3)	114.55	115.94	115.89 (3)
Cg–Ti–Cl2	115.93 (3)	116.00 (3)	114.55	114.87	114.23 (3)
Cl1–Ti–Cl2	103.81 (2)	100.97 (2)	103.17 (8)	100.68 (6)	101.49 (2)
N–Si–C1	90.96 (7)	91.18 (7)	90.4 (2)	90.8 (2)	90.71 (6)
Si–N–Ti	104.58 (7)	104.89 (7)	105.3 (2)	105.6 (2)	104.98 (7)
τ_1 ^e	0.50 (9)	0.31 (8)	0	1.8 (2)	4.14 (7)
τ_2 ^f	177.2 (2)	175.3 (2)	180	179.2 (3)	174.1 (1)

^a Ref. [9].

^b Ref. [10].

^c Centroid of the C1–C5 cyclopentadienyl ring.

^d The perpendicular distance of the Ti atom from the least-squares plane of the cyclopentadienyl ring C1–C5.

^e Torsion angle Cl1, Si, N, Ti.

^f Torsion angle Cl1, Si, N, C17.

copolymerization of ethene and styrene. The catalysts **1**/MAO–**3**/MAO at relatively low Al/Ti molar ratio (900), S/E molar ratio 10:1, and at mild temperature of 50 °C produce pseudo-random E/S copolymers containing up to 47.8 mol% of incorporated styrene. The by one order less active **4**–**6**/MAO catalysts yield less regular copolymers with lower contents of incorporated styrene units (31–41 mol%) containing some percentage of styrene–styrene links and increased contents of ethane–ethene links. This difference in the catalytic behaviour can be related to a higher electron density at the central titanium atom induced by electron-donating alkyl substituents R combined with a low steric congestion in compounds **1**–**3**. The X-ray diffraction single crystal study of compounds **1**, **2**, and **4**–**6** found Ti–Cg distances to be shorter by 0.01 Å and Cl–Ti–Cl angles larger by about 3° in **1** and **2** compared **4** and **5**, in line with electron-donating and electron attracting effect of the respective substituents. Since auxiliary amidocyclopentadienyl ligands ligate to the central Ti atom in a catalytic cationic complex [19] the substituents R should modify the electronic and steric properties of the catalytic metal ion in a similar manner.

3. Experimental

3.1. Chemicals

Toluene was purified by treating with a solution of radical-anion formed in the sodium benzophenone/dibenzo-18-crown-6-ether system, and distilled in vacuum prior to use. Styrene (Kaučuk, a.s., Czech Republic) was dried over CaH₂ and then twice distilled in vacuum just before use. Ethene, polymerization grade (kindly donated by Chemopetrol, a.s., Czech Republic) was further purified by passing through columns with a Cu deoxygenation catalyst and molecular sieve 13X before use. Methylalumoxane (MAO) (10% solution in toluene) (Crompton, Germany) was used as received. Solid complexes **1**, **2**, **4**, **5** [9], **3**, and **6** [10] were dissolved in toluene under purified nitrogen to give 0.01 M solutions.

3.2. Polymerizations

Polymerization runs were carried out in a glass vessel (250 ml) connected to a high vacuum line and equipped with a magnetic stirring bar and thermostatted water jacket. All components in the order toluene, styrene, and MAO were dosed into the reactor using hypodermic syringes against stream of a high purity nitrogen. Before the reactor was closed, the nitrogen atmosphere was replaced by ethene, and the reactor was heated up to the reaction temperature (40–60 °C). When the required temperature and pressure were reached, the solution of the CGC complex in toluene (0.01 mmol/ml) was added through septum to initiate the polymerization. The polymerization was run for 20–90 min, and was terminated by adding a solution of 5% HCl in ethanol (20 ml). A precipitated polymer product was washed with

ethanol (20 ml), filtered, and dried in a vacuum oven at 55 °C to constant weight. In copolymerizations with lower styrene content in monomer feed styrene amounts 0.025, 0.25, 1.25 and 2.5 ml were dosed instead of standard 10 ml.

3.3. Characterization of ethene/styrene copolymers

The structure of the polymer was examined by ¹³C NMR spectroscopy using a 500 MHz Bruker DRX spectrometer operating at 125 MHz with 77° pulse, pulse interval 20 s, at temperature 100–105 °C, decoupling Waltz 17 with a minimum sample rotation and with an exponential constant LB = 1. The copolymer samples were prepared in sample tubes *d* = 10 mm by dissolving 210 mg of the polymer in 1.7 ml of 1,2,4-trichlorobenzene containing 0.4 ml of C₆D₆ and a trace of Irganox 1010 as a stabilizer. Hexamethyldisiloxane (HMDSO) was used as the internal chemical shift reference. Spectra were calibrated on the basis of TMS scale: the HMDSO signal δ 2.0 ppm. Relaxation times for quantitative analyses were optimized by using the method of “Fast inversion recovery” to meet the quantitative analysis conditions. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC 7 instrument. Thin film specimens weighing between 3 and 8 mg were treated as follows: heated from 30 to 180 °C at a rate of 10 °C/min (first heating), held at 180 °C for 10 min, cooled to 30 °C (10 °C/min),

Table 8
Crystallographic data, data collection and structure refinement for **2** and **4**

	Compound	
	2	4
Chemical formula	C ₁₄ C ₂₅ Cl ₂ NSiTi	C ₂₀ H ₂₉ Cl ₂ NSiTi
Molecular weight	354.24	430.33
Temperature (K)	150 (2)	150 (2)
Crystal description	Yellow prism	Yellow plate
Crystal size (mm ³)	0.60 × 0.30 × 0.25	0.70 × 0.25 × 0.125
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i> (no. 14)	<i>P'</i> (no. 2)
<i>a</i> (Å)	14.0000 (1)	8.2800 (2)
<i>b</i> (Å)	12.2630 (2)	10.1160 (3)
<i>c</i> (Å)	11.1000 (2)	17.3780 (5)
α (°)	90	84.6850 (18)
β (°)	113.1690 (9)	73.7730 (19)
γ (°)	90	71.2710 (18)
<i>V</i> (Å ³)	1764.49 (4)	1095.10 (6)
<i>Z</i>	4	2
<i>D</i> _c (g cm ⁻³)	1.333	1.305
μ(Mo Kα) (mm ⁻¹)	0.844	0.693
<i>F</i> (000)	744	452
θ Range (°)	2.29–27.46	2.95–27.50
Measured diffractions	29616	16778
Unique diffractions	4011	4961
Observed diffractions ^a	3635	4337
Parameters	184	249
<i>R</i> , w <i>R</i> obsd. diffractions	0.0332, 0.0898	0.0357, 0.0820
<i>R</i> , w <i>R</i> all data	0.0375, 0.0932	0.0434, 0.0867
<i>S</i>	1.037	1.034
Δρ (e Å ⁻³)	0.825, -0.474	0.419, -0.415

^a Diffractions with *I*₀ > 2σ(*I*₀).

and re-heated from 30 to 180 °C at a rate 10 °C/min (second heating).

Gel permeation chromatography (GPC) analyses were carried out on 0.2% (w/v) filtered samples on a Waters Discovery PL-GPC-220 equipped with a Styragel (HR4E+HR5E) column set and two detectors (RI 410 and PAD 996) at 35 °C in THF. Since differences in MW values obtained from the two detectors were very small the results obtained from the RI detector are reported.

3.4. X-ray crystallography

Yellow prism of complex **2** and yellow plate of **4** were inserted into Lindemann glass capillaries in a glovebox and sealed by a wax. Diffraction data were collected on a Nonius KappaCCD diffractometer. The structures were solved by direct methods (SIR-92 [20]) and refined by full-matrix least-squares on F^2 (SHELXL97 [21]). Relevant crystallographic data are given in Table 8. All non-hydrogen atoms were refined anisotropically. The hydrogen atom residing on carbon atom C(2) of the cyclopentadienyl ring in compound **2** was identified on difference electron density maps and refined with isotropic thermal motion parameters while all other hydrogen atoms of **2** and **4** were included in calculated positions.

4. Supplementary material

Crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (**2**: CCDC-232740, **4**: CCDC-232741). Copies of the data can be obtained free of charge upon application to CCDC (e-mail: deposit@ccdc.cam.ac.uk).

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