Synthesis of Syndiotactic Polystyrene Macromonomers End Capped with Bromine Atoms: a Tool for a New Investigation of Styrene Polymerization Mechanism Catalyzed by Monocyclopentadienyl Titanium Compounds†

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ABSTRACT: Syndiotactic polystyrene samples end capped with bromine atoms in benzylic position have been synthesized by terminating the syndiospecific styrene polymerization catalyzed by Cp*$TiBn_3$/$B(C_6F_5)_3$/Al-Oct_3 (Cp* = η^5-$C_5(CH_3)_5$; Bn = CH_2Ph, Oct = $(CH_2)_7CH_3$) with *N*-bromosuccinimide (NBS) and 2-bromo-2-phenylethylisocyanate (BPEI). The chemical structure of the different polymer end groups was assessed by mono and bidimensional NMR techniques. The evaluation of the relative concentrations of the end groups permitted to give new insights into the bromination reaction and syndiospecific styrene polymerization mechanism. Aspecific bromination of the methine carbon of the growing polymer chain bound to the titanium catalyst was observed when NBS was used as terminating agent. The formation of Ti(III) hydrido complexes in the activation reaction was proved as well as the role of these species as active catalyst in syndiospecific styrene polymerization.

Introduction

Nanostructured polymeric materials are becoming of increasing interest in recent years for their peculiar physical and chemical properties and the potential applications in nanotechnology. The morphological control was successfully obtained both in solution and solid state by self-assembly of, e.g., diblock copolymers which can form, under appropriate conditions (solvent, temperature, concentration) micelles, vesicles, or layered materials.[1]

Recently we have been interested in the synthesis of multiblock and diblock copolymers comprising polymer segments of syndiotactic polystyrene.[2] The interest for this thermoplastic polymer arises from the high melting melting point of 273 °C, and the good resistance to the chemical attack of strong Lewis basic/acidic compounds and oxidating agents.[3] In addition syndiotactic polystyrene shows in solid state a peculiar polymorphic behavior. One of the crystalline forms, the so-called δ form, is nanoporous[4] and a variety of guest molecules can be hosted in the nanocavities (120−160 A^3) of the crystalline phase producing reversible clathrate and intercalate compounds under specific conditions.[5] Thus nanostructured materials containing domains of syndiotactic polystyrene can lead to the formation of ordered nanopatterns of guest molecules suitable for several practical applications.

Tailored amphiphilic diblock copolymers of syndiotactic polystyrene are particularly suitable to this purpose. The synthesis of these copolymers is a challenging task because of the incompatibility of polar monomers with Ziegler−Natta or early transition metal based olefin polymerization catalysts suitable for stereospecific olefin polymerization. A possible synthetic approach to this target requires a two steps polymerization: in the first step the styrene polymerization has to be carried out under living conditions and terminated with a specific reagent to introduce a functional end group; in the second step the end capped macromonomer is used as macroinitiator in the ATRP polymerization of polar monomers.[6]

Chung et al. synthesized syndiotactic polystyrene-*b*-polyacrylates using a similar approach. The syndiospecific polymerization of styrene was terminated with 9-borabicyclo[3.3.1]nonane (9-BBN)[7] and the resulting end group was later oxidized with molecular oxygen to produce the B−O−O−C end groups which in turn can act as initiator in the free radical polymerization of methylmetacrylate or *n*-butylmethacrylate. It noteworthy that the work up of the polymer product resulting from the first step was carried out under anaerobic condition to prevent the decomposition of the borane end capped polymer.

As a preliminary part of this research project herein we report on the use of brominating agent as *N*-bromosuccinimide or the properly designed terminating agent 2-bromo-2-phenylethylisocyanate (BPEI) to introduce a bromine atom end capping a syndiotactic polystyrene chain in benzylic position. This end group is air stable and highly and specifically reactive in ATRP of a large variety of polar monomers to yield selectively linear diblock copolymers. Moreover the functionalization reaction can be carried out *in situ* and the resulting polymer isolated without further reactions or reacted in situ in a single batch process.

This study gave us also the opportunity of reinvestigating the syndiospecific styrene polymerization mechanism allowing a closer inspection of the initiation and termination reactions.

Results and Discussion

Synthesis and Characterization of Syndiotactic Polystyrene Macromonomers End Capped with Bromine Atoms. Polymerization of styrene was performed using the Cp*$TiBn_3$/$B(C_6F_5)_3$/Al-Oct_3 (Cp* = η^5-$C_5(CH_3)_5$; Bn = $-CH_2Ph$, Oct = $-(CH_2)_7CH_3$) catalyst at 0 and 20 °C. The polymerization runs were terminated with Br_2, NBS and BPEI: the main results are summarized in Table 1.

Al-Oct_3 was used as scavenger to reduce the chain transfer reaction during polymerization:[8] living polymerization of styrene and butadiene was indeed reported with the Cp*$Ti(CH_3)_3$/$B(C_6F_5)_3$/Al-Oct_3 catalyst at −20 °C or lower temperature.[9] In the present study the benzyl complex Cp*$TiBn_3$ was preferred to the corresponding methyl complex because it furnishes a better control of the polymer yields and of the average molecular weight.[10]

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† Dedicated to Prof. Adolfo Zambelli on the occasion of his 75th birthday.

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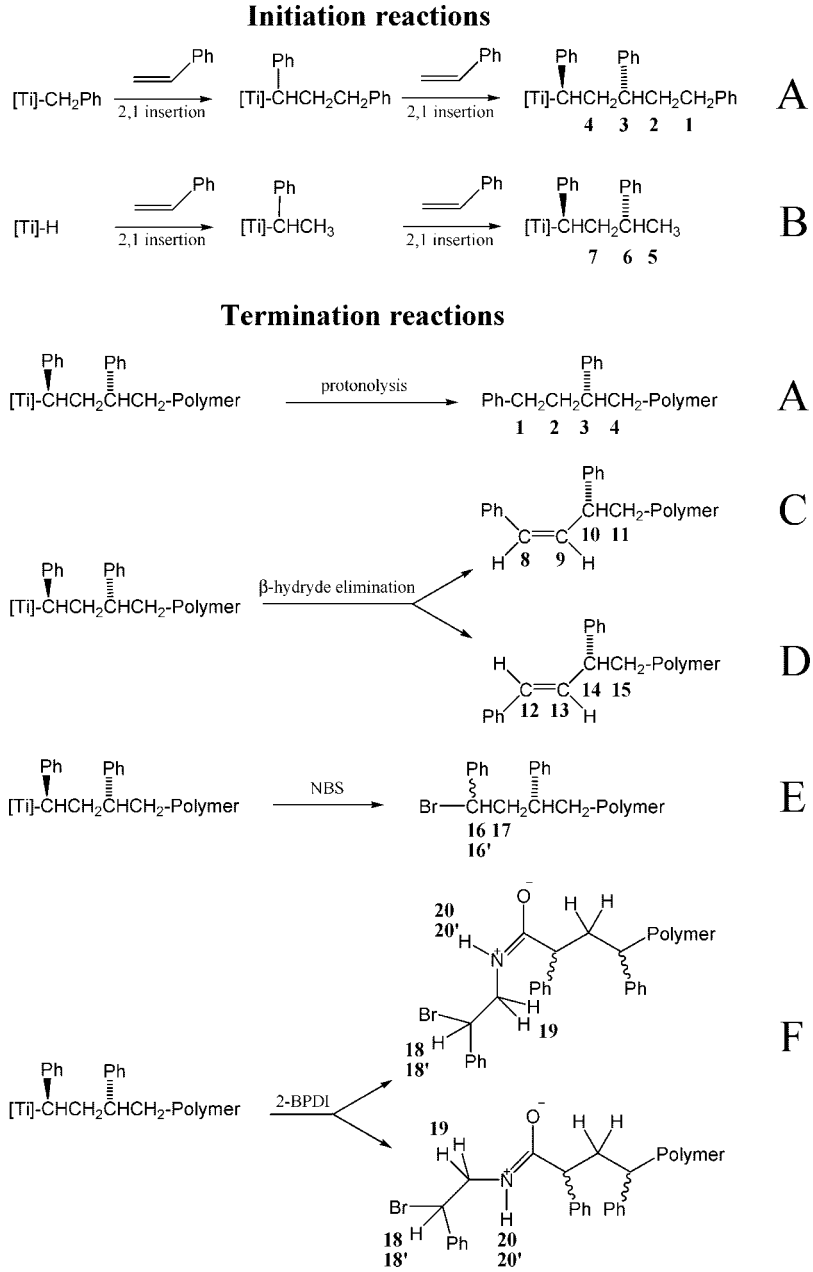
Table 1. Styrene Polymerization Catalyzed by Cp*TiBn$_3$/B(C$_6$F$_6$)$_3$/Al-Oct$_3$ and Terminated with Different End Capping Agents

run[a]	end capping agent	T (°C)	t (min)	conversion (%)	M_n (× 10^3)	M_w/M_n	% end capping efficiency[c]
1	Br_2	20	5	10	12	1.5	n.d.[d]
2	Br_2	0	30	79	22	1.4	n.d.[d]
3	NBS	20	5	50	9.0	1.8	70
4[b]	NBS	0	30	70	20	1.4	80
5	BPEI	20	5	25	16	1.6	32
6	BPEI	0	30	63	23	1.3	70
7		60	10	60	3.0	1.8	

[a] Styrene/Cp*TiBn$_3$/B(C$_6$F$_6$)$_3$/Al(Oct)$_3$ molar ratio = 100/1/1/1. Styrene (1 mL, 8.8 mmol), Cp*TiBn$_3$ (40 mg, 88 μmol), B(C$_6$F$_6$)$_3$ (45 mg, 88 μmol), Al(Oct)$_3$ (32 mg, 88 μmol) in 38 mL of toluene; end capping agent (4.4 mmol). [b] Styrene/Cp*TiBn$_3$/B(C$_6$F$_6$)$_3$/Al-Oct$_3$ molar ratio = 100/1/1/1. Styrene (5 mL, 44 mmol), Cp*TiBn$_3$ (200 mg, 0.44 mmol), B(C$_6$F$_6$)$_3$ (224 mg, 0.44 mmol), Al-Oct$_3$ (160 mg, 0.44 μmol) in 200 mL of toluene. [c] The end capping efficiency factor is the mole fraction of the brominated chain ending over the sum of the unsaturated end groups and brominated end groups, determined by integration of the corresponding ^{1}H NMR signals. [d] Not detected by ^{1}H NMR analysis.

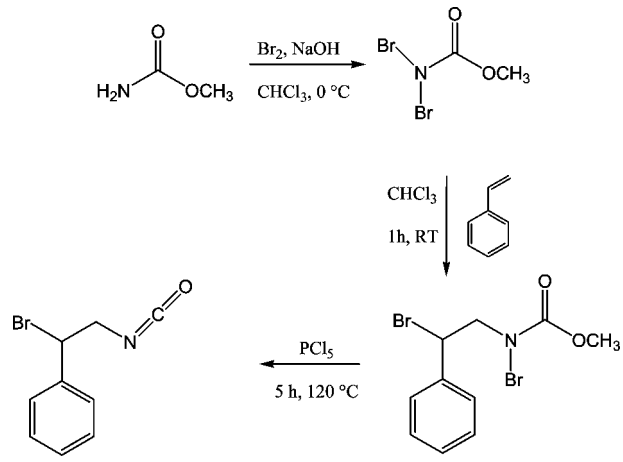
Scheme 1



The styrene concentration in the feed and polymerization time were properly calibrated in order to obtain low molecular weight polymers suitable for the NMR structural characterization of the chain end groups.

The syndiospecific styrene polymerization mechanism catalyzed by monocyclopentadienyl titanium catalysts has been well assessed and the following features are commonly accepted: (i) the regiochemistry of styrene insertion in the initiation and propagation steps is secondary (e.g., 2,1-insertion);[11] (ii) the stereochemistry of styrene monomer insertion is controlled by the configuration of the benzylic carbon of the last monomer unit in the growing polymer chain (chain-end steric control);[12]

Scheme 2



(iii) the active catalysts is a Ti(III) species belonging from the Ti(IV) precatalyst;[10−13] (iv) termination reactions via β-hydrogen migration from the last monomer unit of the growing polymer chain to the metal is favored at high polymerization temperature.[14]

On the basis of this mechanism, one can expect to see the **A**−**F** chain-ends as a result of the initiation and termination steps (Scheme 1).

In the initiation reaction, the end groups **A** and **B** belong from secondary styrene insertion onto Ti-Bn or Ti−H bond, respectively. The benzyl group arises from the Cp*$TiBn_3$ precatalyst whereas the titanium hydrido species can be occasionally produced in the course of the polymerization reaction *via* β-hydride transfer from the last monomer unit of the growing polymer chain to the metal of the active species or by a secondary reaction pathway in the course of the formation of the active metal catalyst (*vide infra*).

When the polymerization run is terminated using Brønsted acidic compounds (e.g., HCl in aqueous methanol), end groups structurally similar to **A** are obtained. (see Scheme 1). Thermally activated termination reaction *via* β-hydride transfer to the metal gives the unsaturated end group **C** and **D,** which differ for the *cis* or *trans* configuration of the double bond, respectively. Previous studies on this subject showed that the stereoisomer **C** is prevalently formed at high temperature in styrene polymerization catalyzed by titanium compounds activated with MAO.[14] It was also demonstrated that the kinetic constant for the β-hydride transfer from the growing polymer chain to the monomer is negligible in comparison to the β-hydride transfer to the titanium when the Cp*$TiR_3/B(C_6F_5)_3$ catalysts are used.[10]

Termination of styrene polymerization with NBS and BPEI leads to the macromolecular chain endings **E** and **F** of Scheme 1. The use of NBS was previously described in the so-called Schwartz reaction in which the bromination of monoalkyl zirconocenes $Cp_2Zr(X)R$ yields $Cp_2Zr(X)Br$ and *n*-alkylbromide.[15] Recently Baird et al. applied this protocol for synthesizing polypropylene samples end capped with bromine atoms by terminating *ansa*-zirconocens catalyzed polymerization of propene with Br_2.[16]

BPEI can be used alternatively to NBS as an end capping agent: this compound has been properly synthesized using the modified literature procedure[17] sketched in Scheme 2.

BPEI includes two functionalities: a benzylic bromine atom suitable for initiating efficiently ATRP of polar monomers and the isocyanate group that is highly reactive in the insertion reaction onto titanium−carbon bond. It was previously shown that *tert*-butylisocyanate allows the fast and quantitative termination of *p*-methylstyrene polymerization catalyzed by Cp*$Ti(CH_3)_3/B(C_6F_5)_3$/Al-Oct_3:[9a] the formation of amido polymer end group (see Scheme 1) was used to confirm the living character of this polymerization by comparing the average molecular weight M_n determined by GPC and NMR methods.

The structural characterization of the polymer end groups **A**−**F** was carried out using mono and bidimensional ^1H and ^{13}C NMR techniques. The ^1H and ^{13}C NMR chemical shift values diagnostic of these end groups are given in Table 2.

In the case of the end group **A,** the corresponding ^1H signals are not resolved from those of the main chain whereas diagnostic ^{13}C signals are the methylene carbon atoms $\mathbf{C_1}$, $\mathbf{C_2}$, and $\mathbf{C_4}$ observed at 37.0, 31.8 and 42.4 ppm, respectively, and the methine carbon $\mathbf{C_3}$ at 39.2 ppm.

The ^{13}C NMR chemical shift of the carbon atoms of the polymer chain end **B** were previously assigned[14] and are given in Table 2 for a comparison. $^1H/^{13}C$ HMQC experiments permitted to attribute the ^1H doublet at 0.90 ppm to the methyl signal $\mathbf{H_5}$ whereas the partly overlapped multiplets at 2.27 ($\mathbf{H_6}$) and 1.2 ppm ($\mathbf{H_7}$) were assigned to the methine and methylene protons of the same end group.

The ^{13}C NMR signals of the olefinic carbon atoms diagnostic of the **C** end group were found at 127.4 ($\mathbf{C_8}$) and 132.8 ppm ($\mathbf{C_9}$).[14] The corresponding protons ($\mathbf{H_8}$, $\mathbf{H_9}$), identified by means a $^1H/^{13}C$ HMQC experiment, produce a broad pattern centered at 5.90 ppm. The small chemical shift difference between $\mathbf{H_8}$ and $\mathbf{H_9}$ protons confirms the *cis* configuration of the olefinic end group. In the ^1H NMR spectrum of samples **3**−**6** a doublet and a pseudo triplet at 6.1 and 5.5 ppm ($^{1,3}J = 11.4$ Hz) were additionally observed and attributed to the olefinic proton $\mathbf{H_{12}}$ and $\mathbf{H_{13}}$ of the end group **D**. The $\mathbf{H_{13}}$ proton exhibits further coupling with a methine proton at 3.5 ppm ($\mathbf{H_{14}}$) that is downfield shifted because of both the allylic nature and the position in α to the aryl group of the second styrene unit of the polymer chain.

The large chemical shift difference between the olefinic protons suggests in this case a *trans* configuration of the carbon−carbon double bond; the corresponding $\mathbf{C_{12}}$ and $\mathbf{C_{13}}$ have been identified as two ^{13}C signals at 134.4 and 125.6 ppm, respectively. The relative concentration of the **C** and **D** signals depends on the polymerization temperature: the stereoisomer **C** is favored at 25 °C but reaches the 1:1 molar ratio with **D** at 60 °C. These chain end groups can result from β-hydride transfer to the metal from two different conformations accessible to the growing polymer chain. The relatively low polymerization temperature needed for reaching the equimolar concentration of **C** and **D** suggests a high conformational flexibility of the polymer segment bound to the metal catalyst, in agreement with a chain-end controlled polymerization mechanism.

The most interesting results come from the study of the stereochemistry of the end groups **E** and **F** resulting from the reaction with NBS and BPEI.

The search of ^1H NMR signals diagnostic of the **E** end group was systematically performed in ATRP polymerization of styrene to confirm that the polymerization mechanism operates *via* the halide exchange between the metal complex and the growing polytstyrenyl chain. Typically a broad featureless ^1H NMR signal at about 4.3 ppm was attributed to the brominated benzylic methine of the end group in the polystyrene chain.[18]

In the ^1H NMR spectrum of the sample **3** terminated with NBS, two doublets of doublets centered at 4.41 (1H; $J = 4.5$; 9.8 Hz) and 4.49 ppm (1H; $J = 6.3$; 9.0 Hz) have been found in 1:1 intensity ratio and attributed to the two diastereotopic methine protons $\mathbf{H_{16}}$ and $\mathbf{H_{16'}}$ of the brominated end groups **F.** The main structural difference between these two protons is the relative configuration, namely *erythro* and *threo*, of the ultimate and penultimate styrene units of the polymer chain.

Table 2. ^{1}H and^{13}C NMR Chemical Shifts Diagnostic of the A-F end groups[a]

chain end group	^{1}H NMR (δ in ppm)	^{13}C NMR (δ in ppm)
A[b]	1.5(**H$_1$**); 2.2 (**H$_2$**); 1.7 (**H$_3$**); 1.2 (**H$_4$**)	37.0 (**C$_1$**); 31.8 (**C$_2$**); 39.2 (**C$_3$**) 42.4(**C$_4$**)
B[b]	0.9 (**H$_5$**); 2.3 (**H$_6$**); 1.2 (**H$_7$**)	21.0 (**C$_5$**); 35.8 (**C$_6$**); 43.9 (**C$_7$**)
C[b,c]	5.9 (**H$_8$-H$_9$**); 3.1 (**H$_{10}$**) 1.7 (**H$_{11}$**)	127.4 (**C$_8$**); 132.8 (**C$_9$**) 44.1 (**C$_{10}$**)
D[c]	6.1 (**H$_{12}$**) 5.5 (**H$_{13}$**) 3.5 (**H$_{14}$**)	134.4(**C$_{12}$**) 125.6(**C$_{13}$**) 39.3 (**C$_{14}$**) 43.7 (**C$_{15}$**)
E[c]	4.4, 4.5 (**H$_{16}$**, **H$_{16'}$**); 2.1 (**H$_{17}$**)	51.0, 52.7 (**C$_{16}$**, **C$_{16'}$**) 41.4 (**C$_{17}$**)
F[c]	4.1, 4.2 (**H$_{18}$**, **H$_{18'}$**); 3.50 (**H$_{19}$**); 2.8, 3.1 (**H$_{20}$**, **H$_{20'}$**)	

[a] The numbering of the proton and carbon atoms are given with reference to Scheme 1. [b] Chemical shift values from literature (see ref 13). [c] Chemical shift values determined in this work (HMDS scale).

Table 3. Integral Values of the ^{1}H signals Diagnostic of the A-E End Groups in Samples 3 and 4

chain end group	^{1}H NMR signal	no. of protons	^{1}H area (sample **3**)	^{1}H area (sample **4**)
A (initiation)	**2**	2H	0.9 (0.3)[a]	2.9 (1.2)[a]
B (initiation)	**5**	3H	0.6	1.5
C (termination)	**8**−**9**	2H	0.5	0.5
D (termination)	**12**	1H	0.1	0.1
E (termination)	**16**	1H	0.4	1.4
main chain (CH)		1H	184	645

[a] Area value of the **A** end group attributed to the termination reaction via protonolysis. To get the molar fraction of the A end groups produced in the initiation reaction the value in parenthesis should be subtracted from the total value reported in the row.

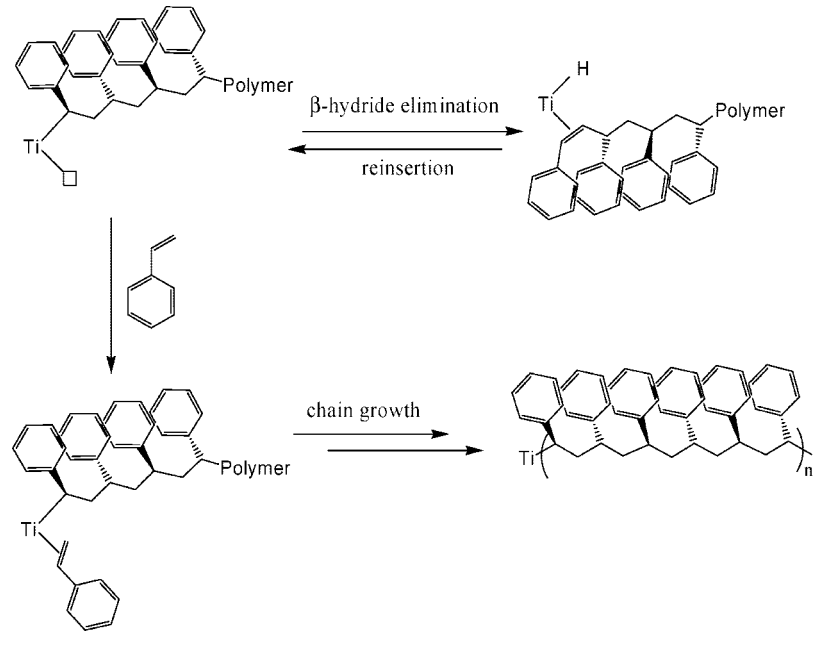
In the ^{1}H/^{1}H-COSY experiment these ^{1}H signals show a correlation peak with a benzylic methine proton which appears as a broad multiplet at 2.10 ppm (**H$_{17}$**). Correlation peaks in the ^{1}H/^{13}C HMQC spectrum between the two doublet of doublets and two equally intense methine carbons at 51.0 (**C$_{16}$**) and 52.7 ppm (**C$_{16'}$**) permitted one to assign the latter two ^{13}C signals to the brominated carbon atoms.

On the basis of this result one can argue that the termination reaction is not stereoselective. This is quite unexpected if one considers the chiral configuration of the methine carbon bound to the metal catalyst and the *erythro* steric relationship between the two aryl groups of the two last monomer units of the growing polymer chain.

Schwartz et al.[15] showed that the reaction of NBS or Br_2 with alkyl zirconocenes proceeds in stereospecific way and the cleavage of the zirconium−carbon bond proceeds through an electrophilic substitution with retention of configuration of the carbon atom in α position to the metal. This was attributed to the sole valence metal orbital accessible to the brominating agent that is forced to attack the Zr−C from the inner coordination sphere, namely in the cone space delimited by ZrCl(R) angle. The increased accessibility to the metal center in monocyclopentadienyl titanium compounds would make possible, for steric and electronic motifs, the metal−carbon cleavage *via* the electrophilic attack from both sides of Ti−C bond determining the racemization of the methine of the last monomer unit in the polymer chain.

Cp*TiBn$_3$ and NBS were treated in NMR tube at room temperature in chloroform-d_1 solution to model the bromination reaction (Ti/NBS molar ratio 2/1). The quick formation of benzylbromide and Cp*TiBr$_3$ and the decomposition of the catalyst precursor was actually observed under this condition. Elemental bromine is considered a brominating agent with properties similar to that of NBS and both have been successfully employed in Schwartz reaction or for the termination of olefin polymerization catalyzed by zirconocenes. In syndiospecific styrene polymerization catalyzed by Cp*TiBn$_3$/B(C$_6$F$_5$)$_3$ catalyst, Br_2 was found to be less efficient than NBS. We attributed this result to the rapid addition of elemental bromine to not reacted styrene at the end of polymerization run. However when bromine was added in large excess compared to the not reacted monomer (5

Scheme 3



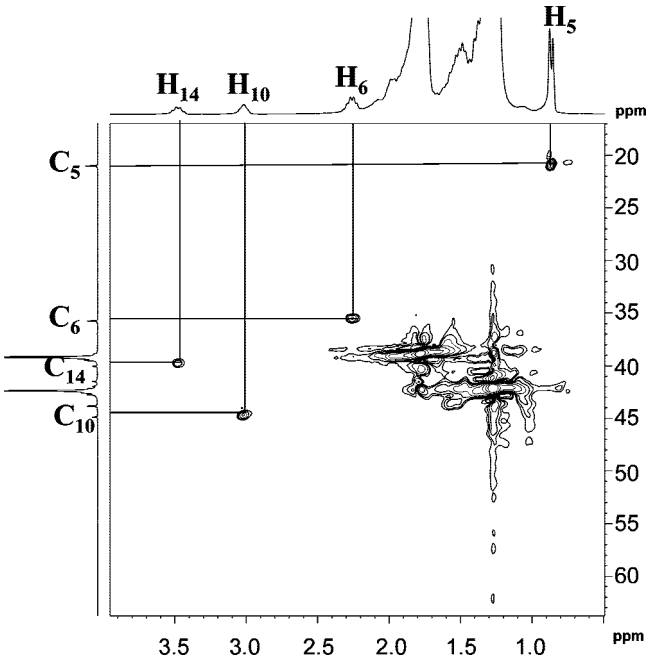


Figure 1. $^{1}H/^{13}C$ HMQC spectrum of the sample **7** (aliphatic region).

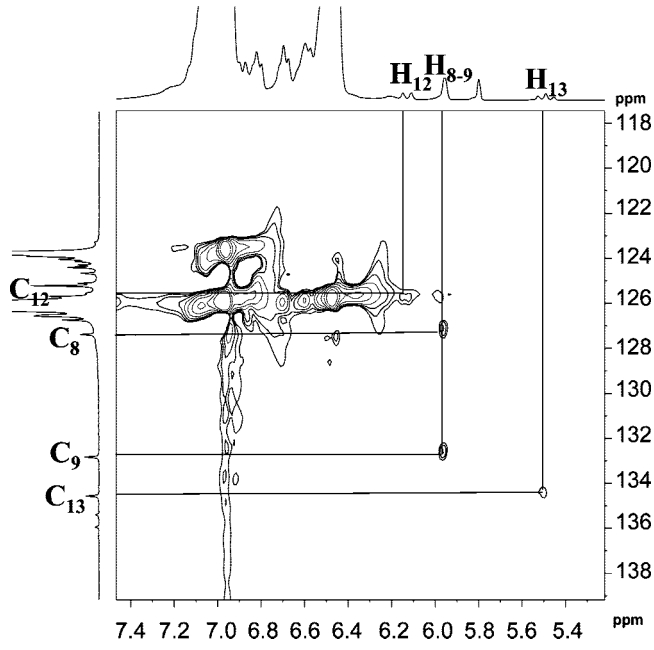


Figure 2. $^{1}H/^{13}C$ HMQC spectrum of the sample **7** (olefinic and aromatic region).

equiv.) the end capping of the polystyrene chain was unsatisfactory. Moreover the unsaturated polymer chain ends **C** and **D** were not detected probably for the addition of bromine to the terminal double bond followed by degradation of the resulting product.[16] This hypothesis was supported by the study of bromination of low molecular weight polystyrenes containing olefinic chain-endings.[19]

BPEI was used for terminating the syndiospecific styrene polymerization catalyzed by $Cp^*TiBn_3/B(C_6F_5)_3/Al\text{-}nOct_3$. Inspection of the ^{1}H NMR spectrum of the sample **5** reveals the presence of two doublet of doublets in 1:1 intensity ratio at 4.11 (1H; J =;3.4, 8.2 Hz) ($\mathbf{H_{18}}$) and 4.25 ppm (1H; J = 6.3, 7.7 Hz) ($\mathbf{H_{18'}}$) that were attributed to the benzylic protons of the brominated carbons in **F**.

The $^{1}H/^{1}H$-COSY shows correlation peaks between these two multiplets and two not equivalent methylene protons at 1.5 ($\mathbf{H_{19'}}$) and 1.8 ppm ($\mathbf{H_{19}}$) that in turn produce correlation peaks with two amido protons at 2.80 ($\mathbf{H_{20}}$) and 3.10 ppm ($\mathbf{H_{20'}}$). The explanation for the diastereotopicity of $\mathbf{H_{19'}}$ and $\mathbf{H_{19}}$ is in this case not clear. This could arise from two stereogenic centers: the amido protons that were found in slow exchange at 120 °C (the temperature in which the ^{1}H NMR spectrum has been recorded) and the steric configuration with the benzylic proton of the last styrene unit of the polymer chain.

From the intensity ratio of the ^{1}H signal diagnostic of the different end groups produced in the termination reactions, an efficiency parameter of the bromination reaction can be determined: the corresponding values are given in Table 1 with reference to the different brominating agents. Syndiotactic polystyrene samples with narrow PDI and elevated degree of bromination (70−80%) were obtained at 0 °C (runs 4 and 6). Increasing the polymerization temperature, the efficiency of the end capping reaction is lower as a result of competitive termination reactions, primary the thermally activated β-hydrogen elimination reaction. NBS was found to be more efficient than BPEI at both 25 and 0 °C: the σ bond metathesis reaction between NBS and the monocyclopentadienylalkyltitanium complexes is thus faster than coordination−insertion reaction of BPEI. Elemental bromine produces trace amount of brominated polystyrenes under the conditions we explored.

New Insights into the Syndiospecific Styrene Polymerization Mechanism. The molar amount of the end groups **A**−**E** was quantitatively determined for the sample **3** and **4** using the integral values of the ^{1}H signals. The corresponding values are given in Table 3.

The relative concentration of the **B**−**E** end groups was determined by integration of the ^{1}H signals. Since the ^{1}H signals of **A** are not well resolved, the concentration of this end group has been estimated from the integral ratio of the corresponding ^{13}C signals using the ^{13}C signals of **B** as internal standard.

The interpretation of the data in Table 3 for the sample **3** is not straightforward. The area value of the end group **B**, corresponding to the initiation reaction onto the Ti−H species, is comparable to that of the unsaturated end groups **C** and **D**; in addition the area value of the end group **A**, corresponding to the initiation reaction onto the Ti-benzyl group of the precatalyst, is greater than that of the brominated end group **E** suggesting a not quantitative termination reaction with NBS. The data given in Table 3 for the sample **4** give the key for the interpretation. In this case the intensity of the methyl signal of the end group **B** is significantly greater than the sum of the **C** and **D** signals. This is further confirmed by the inspection of the ^{1}H spectra of sample **5** and **6** in which the intensity of the methyl end groups **B** is still higher than that of the unsaturated end groups. This suggests that a fraction of the end group **B** does not result from hydrido titanium species produced in the β-hydrogen elimination reaction but likely from a different reaction pathway. Moreover the area of the end groups produced in the activation reaction must be equal to that of the end groups produced in the termination reaction. The area of the signals of **A** and **B** is greater than that of end groups **C-E**; thus a fraction of the benzyl group **A** comes from the protonolysis of the termination reaction because of a not quantitative reaction with NBS. If we assume an integral value of 1.2 for the benzyl end groups due to the protonolysis termination, the molar concentration of the end groups of both the termination and initiation reaction is equal, and the average molecular weight $M_{n(NMR)}$[20] is in fine agreement with the $M_{n(GPC)}$ value determined by GPC (gel permeation chromatography).

In the light of these results, it is now possible similarly to understand the data for sample **3**. If we subtract, for the reason

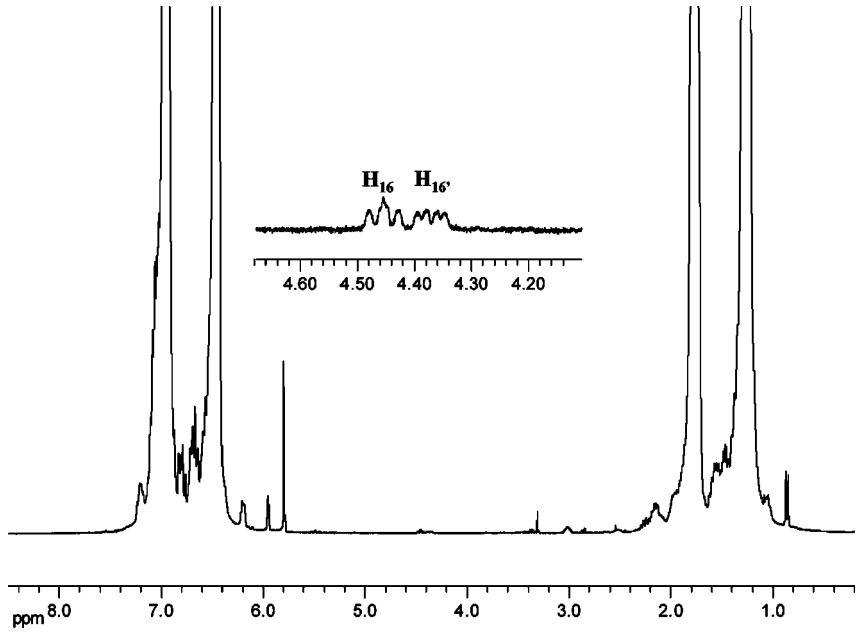


Figure 3. ^{1}H NMR spectrum of the sample **3**.

above-reported, an area value of 0.3 from A we get a total value for the end groups which furnishes a $M_{n(NMR)}$ value in good agreement with the $M_{n(GPC)}$. At 0 °C the termination reaction with NBS is favored in comparison to that via β-hydrogen elimination whereas at higher temperature, namely 20 °C, the opposite is true.

Previous studies based on ^{1}H NMR monitoring of the reaction of Cp*TiBn$_3$ with B(C$_6$F$_5$)$_3$ clearly showed the formation of the ion pair [Cp*TiBn$_2$][BnB(C$_6$F$_5$)$_3$] followed by a reductive reaction that leads to Ti(III) species without any evidence of formation of Ti(IV) hydrido species.[21] In the ESR spectrum of the same catalyst in toluene solution, a doublet was clearly detected in absence of styrene and this signal was attributed to Ti(III) hydrido species exhibiting hyperfine coupling of the d^1 electron with ^{1}H spin nucleus.[22] There was no conclusive assessment if these species are side products (inactive in styrene polymerization) or are active catalyst. Our results suggest that the Ti(III) hydrido species are active in syndiospecific styrene polymerization giving a further confirm that the oxidation state of the Titanium catalyst is +3. The chemical structure and the reaction pathway producing these species are still an open question.

The high concentration of the unsaturated end groups **D** and **E** seems incompatible with a living chain growth mechanism and narrow molecular weight distribution of the polystyrenes (Table 1). We tentatively suggest that the β-hydrogen reaction does not represent an irreversible termination reaction but the unsaturated polymer chain is a resting state in equilibrium with chain growth (see Scheme 3). This accounts for the large concentration of the unsaturated end groups and the controlled performances of the catalyst.

The synthesis of syndiotactic polystyrene-*b*-polymethylmetacrylate using the bromide end capped polystyrene macromonomers is in progress and will be the subject of forthcoming publications.

Conclusions

In situ termination with NBS of styrene polymerization catalyzed by Cp*TiBn$_3$/B(C$_6$F$_5$)$_3$/Al-Oct$_3$ provides a convenient and effective route for preparing syndiotactic polystyrene samples end capped with bromine atoms. Termination with elemental bromine or 2-bromo-2-phenylethylisocyanate resulted less effective.

The end groups of the polymer products were fully characterized by means of mono and bidimensional NMR experiments. The ^{1}H NMR pattern of the brominated end group obtained in presence of NBS was consistent with presence of the *meso* and *racemic* terminal diads indicating a racemization process of the last styrene units inserted in the polymer chain during the termination/bromination reaction.

Moreover the amount of the end group originated from the insertion of the styrene monomer on the Ti−H bond resulted higher than that expect on the basis of the olefinic end groups end capping the polymer chains. This indicates that a fraction of the methyl end group **B** results from the insertion of the styrene monomer onto Ti−H bond of hydrido species formed in the activation reaction. These results address an active role of the Ti(III) hydrido species formed in the decomposition/reduction of the ion pair [Cp*TiBn$_2$]$^+$[BnB(C$_6$F$_5$)$_3$]$^-$ precatalyst in styrene polymerization catalyzed by monocyclopentadienyltitanium derivatives.

Experimental Part

Materials. All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or a MBraun drybox. Commercial grade toluene (Carlo Erba) was dried over calcium chloride, refluxed 48 h over sodium, and distilled before use. Chloroform was dried by refluxing over calcium hydride and distilled prior to use. Styrene (Aldrich) was purified by distillation over calcium hydride under reduced pressure. The other chemicals were used as received. Cp*TiBn$_3$ was prepared according to the literature.[23] The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 300 or 400 FT-NMR spectrometers at 295 and 353 K in tetrachloroethane-d_2 (C$_2$D$_2$Cl$_4$). A relaxation delay of 3 s was used during the acquisition to yield quantitative ^{1}H NMR spectra. The chemical shifts were referenced to tetramethylsilane(TMS) at room temperature or hexamethyldisiloxane (HMDS) at high temperature using the residual protio-solvent (^{1}H) or the carbon (^{13}C) resonance of the deuterated solvents.

Synthesis of 2-Bromo-2-phenylethyl Isocyanate. *N,N-Dibromomethyl Carbamate.* Br$_2$ (13.6 mL, 0.266) was added dropwise to 100 mL of a chloroform solution of methylcarbamate (10 g, 0.133 mol) at 0 °C under stirring.. At the end of the addition 290 mL of

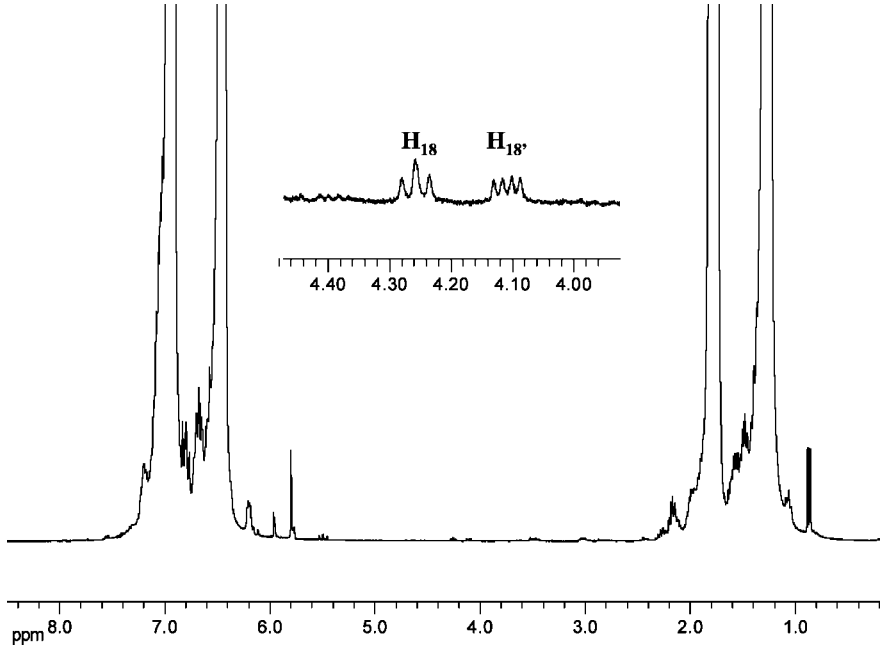


Figure 4. ^{1}H NMR spectrum of sample **5**.

an aqueous solution of NaOH (12.2 g; 4%w/w) was slowly introduced into the reactor at 0 °C. The reaction mixture was left to react for 2 h at 10 °C under vigorous stirring. The organic layer was isolated, washed twice with water and dried over $MgSO_4$. Distillation of the solvent in vacuo produces an oil that after cooling at 0 °C yields an orange solid. This solid was washed several times with cold hexane to remove the excess of bromine and dried in vacuo (13.8 g; yield = 45%). The product is enough pure to be used in the next step. Yield = 13.8 g (45%). ^{1}H NMR ($CDCl_3$, 25 °C, δ in ppm): 3.85 (s, 3H, OCH_3).

N-Bromo-N-(2-bromo-2-phenylethyl)methyl Carbamate. Three milliliters of a chloroform solution of *N,N*-dibromomethylcarbamate (3.0 g, 12.9 mmol) was dropwise added to a stirred solution of styrene (1.34 mL, 11.7 mmol) in chloroform (2 mL). The reaction is exothermic and fast. At the end of the addition, the solvent was removed *in vacuo* to give the product as a pale-yellow oil that was quickly used in the next step to avoid decomposition.

^{1}H NMR ($CDCl_3$, 25 °C, δ in ppm): 3.67 (s, 3H, OCH_3), 4.11 (dd, 1H, CH_2N, J = 7.7 Hz), 4.23 (dd, 1H, CH_2N, J = 7.3 Hz), 5.21 (t, 1H, CHBr, J = 7.5 Hz), 7.37 (m, 5H, ArH).

2-Bromo-2-phenylethyl Isocyanate. PCl_5 (2.7 g, 12.9 mmol) was added to *N*-bromo-*N*-(2-bromo-2-phenylethyl)methyl carbamate and the resulting mixture was kept at 120 °C for 5 h, permitting the gas to evolve from the reactor. The resulting brown oil was distilled in vacuum (84−86 °C, 0.05 Torr) to give the product as a colorless oil. Yield = 2.0 g (46% based on *N,N*-dibromomethyl carbamate).

^{1}H NMR ($CDCl_3$, 25 °C, δ in ppm): 3.7 (dd, 1H, CH_2N, J = 5.8 Hz), 3.8 (dd, 1H, CH_2N, J = 7.4 Hz), 5.0 (t, 1H, CHBr, J = 5.8 Hz), 7.4 (m, 5H, ArH). ^{13}C{^{1}H}NMR ($CDCl_3$, 25 °C, δ in ppm): 50.3 (CH_2N), 62.2 (CHBr), 124.5 (NCO), 127, 3, 128.9, 129.4, 137.8 (Ar). IR (film) [m/cm^{-1}]: 2258 (NCO).

Styrene Polymerization. The polymerization runs were carried out following a standard procedure. A 100 mL flask equipped with a magnetic bar was charged with Al-Oct$_3$ (88 μmol), styrene (1 mL, 8.8 mmol) and toluene (38 mL). After equilibration of the solution at the polymerization temperature, the reaction was started by the simultaneous injection of a toluene solution (1 mL) of Cp*TiBn$_3$ (40 mg, 88 μmol) and B(C_6F_5)$_3$ (45 mg, 88 μmol). The run was terminated after the prescribed time by introducing the proper terminating agent (NBS, Br_2, BPEI, 4.4 mmol) and keeping the mixture under stirring for 1 h at room temperature. The polymer was coagulated in methanol acidified with aqueous HCl, recovered by filtration, washed with an excess of CH_3CN, and dried *in vacuo* at 40 °C.

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Supporting Information Available: Text giving experimental details and figures showing selected ^{1}H, ^{1}H−^{1}H COSY, and ^{1}H/^{13}C HMQC NMR spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Determined from the area ratio of the ^{1}H signals of the methine of the main chain vs that of the end groups A′, C, D, and E [(or (A−A′) + B)].
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