Complex Macromolecular Architectures Based on *n*-Hexyl Isocyanate and ϵ-Caprolactone Using Titanium-Mediated Coordination Polymerization

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ABSTRACT: Well-defined diblock copolymers {PS-*b*-P(ϵ-CL)} and triblock terpolymers {PS-*b*-PI-*b*-P(ϵ-CL), PI-*b*-PS-*b*-P(ϵ-CL)} of polystyrene, PS, poly(ϵ-caprolactone), P(ϵ-CL), and polyisoprene, PI, were synthesized using $CpTiCl_2(OP)$ (P = PS, PS-*b*-PI, or PI-*b*-PS) as macroinitiator. Graft copolymers having polybutadiene, PBd, backbone and poly(*n*-hexyl isocyanate), PHIC, or P(ϵ-CL) branches {PBd-*g*-PHIC and PBd-*g*-P(ϵ-CL)} as well as block−graft terpolymers {PS-*b*-(PI-*g*-PHIC), PS-*b*-[PI-*g*-P(ϵ-CL)]} were also synthesized by performing hydroboration/oxidation reactions on the polydiene backbone and by transforming the introduced hydroxyl groups to initiation sites by reaction with $CpTiCl_3$. Finally, $PS(PHIC)_2$ and $PS[P(\epsilon\text{-CL})]_2$ 3-miktoarm star copolymers were synthesized using a heterofunctional initiator bearing one initiation site for atom transfer radical polymerization and two for titanium-mediated coordination polymerization. All intermediates and final products were characterized by size exclusion chromatography, equipped with refractive index and light scattering detectors, membrane osmometry, and ^1H NMR spectroscopy.

Introduction

Titanium complexes have been widely used in the field of polymer chemistry since the discovery of the Ziegler–Natta catalytic systems for the synthesis of polyolefins with controlled stereochemistry.[1] More recently, half-titanocenes, titanocenes, and other titanium complexes in combination with suitable cocatalysts have been employed for the polymerization of a wide variety of nonpolar and polar monomers.[2] For example, $Me_2Si(C_5Me_4)(NtBu)TiCl_2$ with methylaluminoxane, MAO, as the cocatalyst and $TiMe_2[2,6\text{-}iPr_2\text{-}C_6H_3N(CH_2)_3N\text{-}2,6\text{-}iPr_2C_6H_3]$ with $B(C_6F_5)_3$ or MAO[3,4] have been used for the polymerization of higher α-olefins (1-hexene, 1-octene, and 1-decene). Propylene and 1-butene have been successfully polymerized by $[N(CH_3)_2][Si(CH_3)_3N(NC_5H_5)]TiCl_2$,[5] whereas random copolymers of ethylene and 1-butene as well as of 1-hexene and 1-octene have been prepared using $CpTiCl_2(O\text{-}2,6\text{-}iPrC_6H_3)$ as the catalyst.[6] Half-titanocenes, such as $CpTiCl_3$ with MAO, have been used for the polymerization of dienes (1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, etc.) and styrene.[7]

Methyl methacrylate, MMA, was initially polymerized with $Cp_2TiCl[OC(OMe)=CMe_2]$[8] and more recently with titanocenes in the presence of aryl fluoroborates {e.g. $[Ph_3C]^+[B(C_6F_5)_4]^-$} as the cocatalyst.[9] *Ansa*-titanocenes, such as $[Me_2Si(Me_4C_5)(t\text{-}BuN)]TiMe^+MeB(C_6F_5)_3^-$, have also been employed for the polymerization of methacrylates.[10]

In that study, half-titanocenes were employed in the synthesis of complex macromolecular architectures based on *n*-hexyl isocyanate, HIC, and ϵ-caprolactone, ϵ-CL. PHIC is a rodlike polymer adopting a helical conformation either in solution or in bulk,[11] making the PHIC-based materials candidates for optical switches, recognition devices, etc.[12] On the other hand, P(ϵ-CL) is a biodegradable/biocompatible polymer and therefore suitable for medical applications and the production of environmentally friendly materials.[13]

For many years there were several limitations to the synthesis of PHIC by anionic polymerization.[14] Recent advances have succeeded in creating the necessary conditions for the living anionic polymerization of HIC,[15] although the polymerization has to take place at very low temperatures (−98 °C) using demanding experimental techniques. The ring-opening polymerization (ROP) of lactones has been achieved by a variety of initiators, such as neat alkaline metals and alkyls/alkoxides of alkaline metals or other less drastic alkoxides, such as Al compounds.[16] Moreover, new catalytic systems, such as ruthenium derivatives, zinc and magnesium alkoxides with sterically hindered multidentate N-donor ligands, ferric alkoxides, e.g. iron ethoxide, $Fe(OEt)_3$, and calcium, zirconium, and organolanthanide(III) complexes have been utilized for the polymerization of lactones.[17]

Alkoxytitanium initiators have been employed in the controlled polymerization of different polar monomers only in the past 15 years. Novak was the first to study the polymerization of HIC using complexes such as $TiCl_3(OCH_2CF_3)$ and $TiCl_3(OCH_2CF_3)(THF)_2$, with satisfactory results over the control of the molecular weight and the molecular weight distribution ($M_w/M_n = 1.1\text{–}1.2$).[18] In another study by the same group, semititanocene complexes were applied in the polymerization of HIC.[19] These complexes, due to their increased steric hindrance, offered better control over the polymerization procedure, leading to improved products. Moreover, Novak et al.[20] as well as other scientists have reported the use of semititanocene complexes for the synthesis of HIC-based polymers with complex macromolecular architectures. Hadjichristidis et al.[21] reported the synthesis of diblock copolymers and triblock terpolymers using macroinitiators of the formula $CpTiCl_2(OR)$, where R stands for a macromolecular chain. Recently, a bifunctional initiator containing an atom transfer radical polymerization and a semititanocene initiation site was utilized for the synthesis of block copolymers of PHIC with polystyrene, PS, and poly(methyl methacrylate), PMMA.[22]

To our knowledge, only Okuda et al.[23] used mono(cyclopentadienyl)titanium complexes of the general formula $Ti(\eta^5\text{-}C_5R_5)Cl_2(OCH_3)$ for the controlled polymerization of ϵ-CL. The results indicated that there was linear correlation between molecular weight and monomer conversion and that the molecular weight distribution remained narrow, at least at small conversions. However, at higher conversions, the formation of

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Table 1. Molecular Characteristics of the End-Functionalized Polymers

sample	$(M_n)_{PS} \times 10^{-3}$ [a]	$(M_w/M_n)_{PS}$ [b]	$(M_n)_{PS\text{-}b\text{-}PI} \times 10^{-3}$ [a]	$(M_w/M_n)_{PS\text{-}b\text{-}PI}$ [b]	wt % PS[c]
PS-OH #1	1.2	1.09			
PS-OH #2	2.5	1.07			
PS-OH #3	6.3	1.04			
PS-OH #4	12.0	1.05			
PS-*b*-PI-OH #1	2.9	1.09	5.5	1.07	66.1
PS-*b*-PI-OH #2	4.5	1.08	10.0	1.04	53.6
PI-*b*-PS-OH #1	4.3[d]	1.04	10.0	1.04	62.4
PI-*b*-PS-OH #2	5.7[d]	1.07	13.7	1.08	68.8

[a] By SEC-TALLS in THF at 35 °C. [b] By SEC in THF at 40 °C. [c] By ^{1}H NMR in $CDCl_3$ at 25 °C. [d] M_n of the PI block.

Table 2. Molecular Characteristics of the PS-*b*-P(ϵ-CL) Block Copolymers[a]

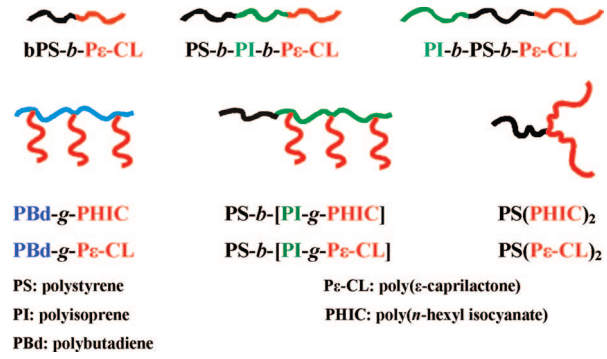
$CpTiCl_2$(OPS), mg	$(M_n)_{PS\text{-}b\text{-}P(\epsilon\text{-}CL)} \times 10^{-3}$ [f]	$(M_w/M_n)_{PS\text{-}b\text{-}P(\epsilon\text{-}CL)}$ [g]	$(M_n)_{stoichiom} \times 10^{-3}$	wt % PS[h]	conversion, %
35[b]	38	1.18	38	3.3	>95
55[b]	20	1.11	24	5.8	>95
70[b]	15	1.18	19	8.3	>95
90[b]	11	1.19	13	10.0	90
120[b]	8	1.17	8.5	14.3	85
35[c]	55	1.11	67	4.9	>95
50[c]	35	1.10	48	7.4	>95
75[c]	25	1.12	31	10.0	>95
100[c]	18	1.10	23	12.5	95
120[c]	12	1.06	19	21.3	95
35[d]	180	1.16	185	4.1	>95
45[d]	120	1.15	145	6.6	>95
60[d]	95	1.08	110	8.3	>95
90[d]	45	1.05	57	12.5	90
115[d]	27	1.06	40	21.3	85
135[d]	15	1.05	30	39.9	80
60[e]	110	1.06	162	11.0	90 (15)[i]
85[e]	60	1.12	90	18.9	80 (20)[i]
135[e]	27	1.06	39	44.3	65 (25)[i]
160[e]	22	1.06	19	53.6	50 (40)[i]

[a] Reaction conditions: solvent toluene 4 mL; [ϵ-CL] = 2.25 M; temperature 110 °C. [b] $CpTiCl_2$(OPS) from precursor PS-OH #1. [c] $CpTiCl_2$(OPS) from precursor PS-OH #2. [d] $CpTiCl_2$(OPS) from precursor PS-OH #3. [e] $CpTiCl_2$(OPS) from precursor PS-OH #4. [f] By SEC-TALLS in THF at 35 °C. [g] By SEC in THF at 40 °C. [h] By ^{1}H NMR in $CDCl_3$ at 25 °C. [i] Unreacted $CpTiCl_2$(OPS).

cyclic oligomers, due to the presence of "backbiting" side reactions, as well as transesterification reactions, resulted in a broadening of the molecular weight distribution.

In this work, a combination of titanium-mediated coordination polymerization with other polymerization techniques, such as anionic and ATRP, along with suitable postpolymerization reactions were employed for the synthesis of complex macromolecular architectures based on HIC and ϵ-CL. Diblock copolymers, triblock terpolymers, graft copolymers, block−graft terpolymers, and 3-miktoarm stars were obtained by this methodology (Chart 1). The synthesis of these polymers was monitored by several characterization techniques, such as size exclusion chromatography, SEC, equipped with different detectors, nuclear magnetic resonance, ^{1}H NMR, and membrane osmometry.

Chart 1



Experimental Section

Materials. HIC (Acros, 97%) was dried over calcium hydride (CaH_2) overnight, distilled in vacuo into ampoules, and stored at −20 °C. Before use, the monomer was dried once more over trioctylaluminum for at least 12 h. ϵ-CL (Aldrich) was dried over CaH_2 for 3 days and $CaCl_2$ for 1 more day. The purification of styrene (Aldrich, 99%), isoprene (Aldrich, 99%), butadiene (Aldrich, 99%), and the solvents (Aldrich; toluene, THF, and benzene) was performed using standard high-vacuum techniques reported elsewhere.[24] Triethylamine was dried over sodium and distilled just before use. 2-Ethyl-2-(hydroxymethyl)propane-1,3-diol (Aldrich, 99%) was purified by recrystallization from ethyl acetate. Trichlorocyclopentadienyltitanium(IV), 9-borabicyclo[3.3.1]nonane (Aldrich; 0.5 M THF solution), 2-bromoisobutyryl bromide (98%), 2,2′-bipyridyl (Fluka, >98%,), copper(I) bromide (Aldrich, 98%), pentaerythritol (Aldrich, 99%), and all other chemicals were used without further purification.

Synthesis of PBd, PS-OH, PS-*b*-PI-OH, and PI-*b*-PS-OH. Linear PBd was prepared by standard high-vacuum anionic polymerization procedures. End-functionalized PS and PS-*b*-PI chains with hydroxyl end groups PS-OH, PS-*b*-PI-OH, and PI-*b*-PS-OH were also prepared by anionic polymerization high-vacuum techniques and deactivation of the living chains with an excess of ethylene oxide, according to well-established synthetic routes.[25]

Selective Hydroboration of PBd[26]. High-vacuum techniques were used for the selective hydroboration of PBd. For this purpose 3.4 g of PBd (M_n = 19 000, I = 1.05, 9.3% 1,2 microstructure) were introduced into an appropriate apparatus, attached to the vacuum, and left to dry for 3 days. Purified THF (100 mL) was subsequently distilled into the apparatus. The resulting solution was cooled to −15 °C, and 8.2 mL (3.4 mmol) of 9-BBN (9-borabicyclo[3.3.1]nonane) was introduced. The solution was then stirred for 24 h at room temperature and was cooled to −25 °C, before the addition of 1 mL of anhydrous methanol. The solution was stirred for 20 min followed by the addition of 0.75 mL of NaOH (6 M). After 15 min, 1.5 mL of H_2O_2 (30% w/v) was added,

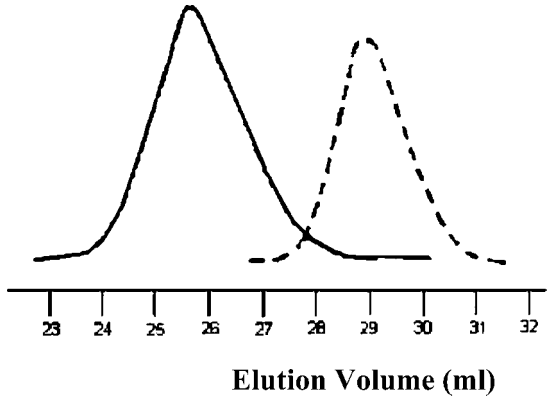


Figure 1. SEC profile of samples: PS-OH #3 (M_n = 6500, dashed line) and PS-*b*-P(ϵ-CL) (M_n = 45 000, solid line) produced by the macroinitiator $CpTiCl_2$(OPS) coming from PS-OH #3.

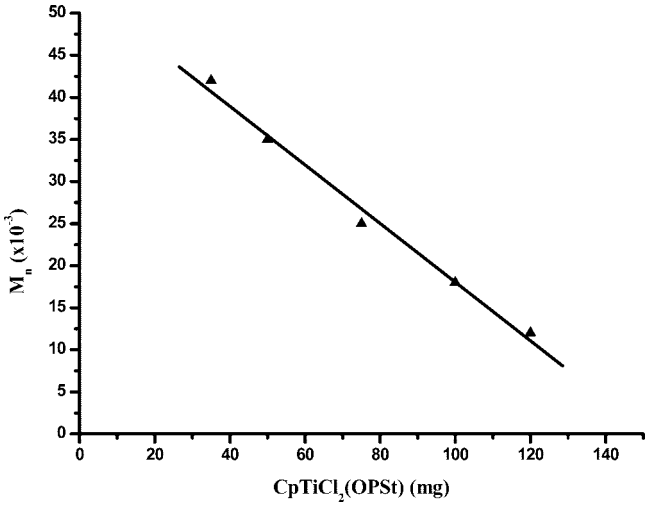


Figure 2. M_n vs the quantity of the macroinitiator $CpTiCl_2$(OPSt) produced from the PS precursor having M_n = 2500.

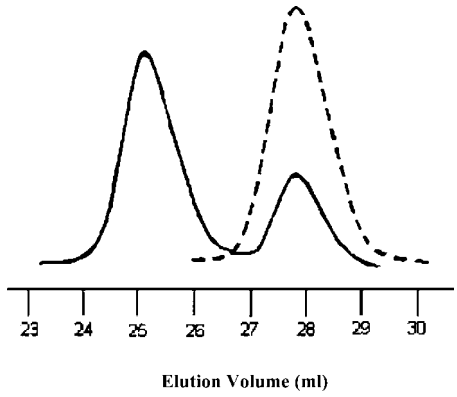


Figure 3. SEC profile of samples: (a) PS-OH #4 (M_n = 12 000, dashed line) and (b) PS-*b*-P(ϵ-CL) (M_n = 60 000, solid line) produced by the macroinitiator $CpTiCl_2$(OPSt) coming from PS-OH #4.

and the solution was left at room temperature (RT) under intense stirring (~2 h) and then the temperature was slowly raised to 55 °C, where it was heated for 1 h. The solution was then cooled to −78 °C, the apparatus was opened to the atmosphere, and the solution was slowly poured into 1000 mL of an aqueous 0.25 M NaOH solution. The precipitated polymer was filtered and redissolved in THF, followed by reprecipitation in the aqueous NaOH solution, where it was left under stirring overnight. The next day the polymer was precipitated, washed with copious amount of water, and vaccuum-dried.

Synthesis of (5-Ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol (2)[27]. (5-Ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol (**2**) was obtained from the reaction of 10 g (74.6 mmol) of (2-ethyl-2-(hydroxymethyl)propane-1,3-diol (**1**) with an excess of dry acetone, in the presence of Amberlyst 15 and magnesium sulfate. After filtration and evaporation of the excess acetone, **2** was isolated by distillation under vacuum. Yield: 70%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.80–0.85 (t, 3H, CH_3CH_2); 1.17–1.40 (m, 8H, $2CH_3$, CH_3CH_2), 3.55–3.70 (m, 6H, 3C H_2O).

Synthesis of (5-Ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methyl 2-Bromo-2-methylpropanoate (3)[28]. To a round-bottom flask, immersed in an ice bath, 5 g of **2** (28.7 mmol), 8.0 mL of triethylamine (57.4 mmol), and 80 mL of dry THF were added. 2-Bromoisobutyryl bromide (13.1 g, 57.4 mmol) was added dropwise to the solution, with continuous stirring under argon atmosphere, over a period of 1 h. The reaction was allowed to take place at RT for 48 h. The resulting insoluble amine salt was removed by filtration, and most of the THF was removed by a rotary evaporator, followed by extraction with dichloromethane and a 10^{-2} M solution of K_2CO_3. The solution was dried using magnesium sulfate, and the solvent was removed under vacuum. The crude product was purified by column chromatography (v/v: 8/2 petroleum ether/ethyl acetate).Yield: 80%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.80–0.85 (s, 3H, $-CH_3$), 1.95 (s, 6 *H*, $(C(CH_3)_2Br)$, 3.60–3.62 (d, 4 *H*, $CH-OH$), 4.25 (s, 2 *H*, $-CH_2O$).

ATRP of Styrene with the Use of 3 as Initiator. As an example, the synthesis of $PS(OR)_2$ #5 (Table 10) is given. All polymerization procedures took place under vacuum. Initially, copper(I) bromide (0.05 g, 0.35 mmol), 2,2-dipyridyl (0.17 g, 1.1 mmol), and 0.11 g (0.34 mmol) of **3** were added to the polymerization apparatus, which was degassed, before the addition of 6 mL of purified THF by distillation. The reaction medium was stirred for half an hour at RT, 6 mL of styrene was then introduced, and the solution was degassed and placed in an oil bath thermostatted at 110 °C for 16 h under rigorous stirring. The polymerization was terminated upon opening the apparatus to the atmosphere. The product (**4**) was subsequently dissolved in toluene and then passed through a column of silica gel to remove the copper salts. After evaporation of most of the solvent in a rotary evaporator, the polymer was precipitated in methanol, filtered, washed, and dried under vacuum resulting in a colorless powder. Yield: 55%. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.3–2.2 ppm (m, aliphatic main chain), 3.3–3.8 ppm (broad, 6H, initiator), 6.3–7.3 ppm (m, 5H, aromatic).

Deprotection of the Polystyrene Hydroxyl End Groups[29]. $PS(OR)_2$ (3.0 g) was dissolved in 300 mL of $CHCl_3$/100 mL of 80% acetic acid and was left, under stirring, at RT overnight. The next day an additional 200 mL of 80% acetic acid was added followed by refluxing at 85 °C in an oil bath for 3 h. The product (**5**) was recovered by evaporation of the volatile components in the vacuum line, then washed with water, and was finally dried at RT under vacuum. Yield: 100% deprotection. ^{1}H NMR ($CDCl_3$, δ, ppm): ^{1}H NMR ($CDCl_3$, δ, ppm): 1.3–2.2 ppm (m, aliphatic main chain), 3.2–3.9 ppm (broad, 6H, initiator), 6.3–7.3 ppm (m, 5H, aromatic).

Preparation of the Macromolecular Catalysts. All procedures were carried out with standard high-vacuum, Schlenk, or glovebox techniques. Representative examples from the synthetic routes are provided below.

$CpTiCl_2$(OPS): PS-OH was dried on the vacuum line for at least a day to remove volatile impurities. To a 50 mL Schlenk flask, $CpTiCl_3$ (0.461 g) was added and was dissolved in 30 mL of toluene. Subsequently, PS-OH (0.71 g) and triethylamine (0.255 mL) were added dropwise via a pressure-equalizing addition funnel. A white precipitate of $EtNH^+Cl^-$ was formed. The solution was stirred overnight and then filtered. The solvent was removed under vacuum, and the product was stored at 0 °C.

$CpTiCl_2$[O(PI-b-PS)]: 0.21 g of $CpTiCl_3$, 6.3 g of PS-*b*-PI-OH, 50 mL of toluene, and 0.15 mL of triethylamine were used.

$CpTiCl_2$[O(PS-b-PI)]: 0.13 g of $CpTiCl_3$, 3.5 g of PI-*b*-PS-OH, 50 mL of toluene, and 0.1 mL of triethylamine were used.

Table 3. Molecular Characteristics of the PS-*b*-PI-*b*-P(ϵ-CL) Block Copolymers[a]

$CpTiCl_2$(OPI-*b*-PS), mg	$(M_n)_{triblock} \times 10^{-3}$ [d]	$(M_w/M_n)_{triblock}$ [f]	$(M_n)_{stoichiom} \times 10^{-3}$	wt % ϵ-CL[g]	conversion, %
40[b]	100[e]	1.08	122	93.6	90
60[b]	65[e]	1.05	65.5	91.5	85
80[b]	45	1.08	44	89.3	80
100[b]	35	1.06	35	85.4	80
150[b]	28	1.09	22.5	81.3	75
70[c]	85[e]	1.04	102	89.5	85
100[c]	65[e]	1.04	64	86.9	80
130[c]	45	1.05	38.5	83.8	70
200[c]	25	1.06	18	39.2	60

[a] Reaction conditions: solvent toluene 4 mL; [ϵ-CL] = 2.25 M; temperature 110 °C. [b] $CpTiCl_2$(OPI-*b*-PS) from precursor PS-*b*-PI-OH #1. [c] $CpTiCl_2$(OPI-*b*-PS) from precursor PS-*b*-PI-OH #2. [d] By SEC-TALLS in THF at 35 °C. [e] By membrane osmometry in toluene at 37 °C. [f] By SEC in THF at 40 °C. [g] By ^{1}H NMR in $CDCl_3$ at 25 °C.

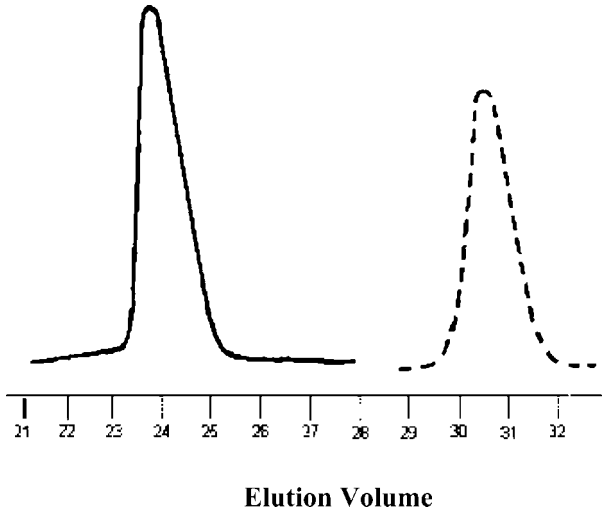


Figure 4. SEC profile of samples: PS-*b*-PI-OH #1 (M_n = 5500, dashed line) and PS-*b*-PI-*b*-P(ϵ-CL) (M_n = 100 000, solid line) produced by the macroinitiator $CpTiCl_2$(OPI-*b*-PSt) coming from PS-*b*-PI-OH #1.

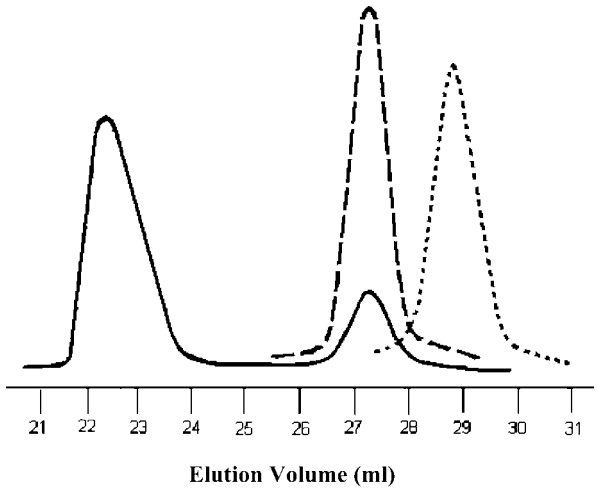


Figure 5. SEC profile of samples: (a) PS block of PI-*b*-PS-OH #1 (dotted line), (b) PI-*b*-PS-OH #1 (M_n = 10 000, dashed line), and (c) PI-*b*-PS-*b*-P(ϵ-CL) (M_n = 120 000, solid line) produced by the macroinitiator $CpTiCl_2$(OPS-*b*-PI) coming from PI-*b*-PS-OH #1.

PBd-(OCpTiCl$_2$)$_{11}$: The above procedure was employed: 0.59 g of $CpTiCl_3$, 3.4 g of PBd-$(OH)_{11}$ (soluble in toluene), 40 mL of toluene, and 0.4 mL of triethylamine were used.

PS-b-[PI-(OCpTiCl$_2$)$_9$]: 0.19 g of $CpTiCl_3$, 3.2 g of PS-*b*-[PI-$(OH)_9$], 60 mL of toluene, and 0.15 mL of triethylamine were used.

PS(OCpTiCl$_2$)$_2$: 0.14 g of $CpTiCl_3$, 3 g of PS$(OH)_2$, 40 mL of toluene, and 0.1 mL of triethylamine were used.

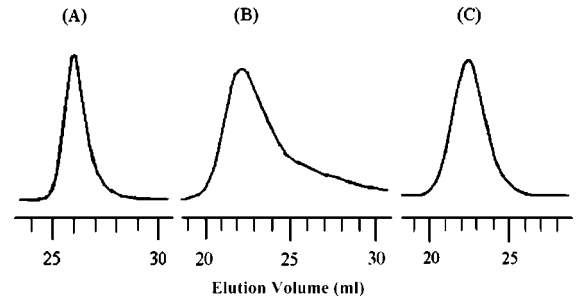


Figure 6. SEC profile of PBd-g-PHIC #2: the precursor PBd(OH) #2 (A), the final product before (B), and after fractionation (C).

Polymerization of HIC. As an example, the synthesis of sample PS$(PHIC)_2$ #5 (Table 11) is given. To a 50 mL Schlenk flask, the macromolecular catalyst (1.3 g) was added, followed by addition of toluene (4 mL) and stirring until homogeneity. HIC (6 g) was then introduced, and the reaction was allowed to proceed at RT, under rigorous stirring. After ∼24 h the viscosity of the solution had been significantly increased. Termination was achieved by the addition of a 5% solution (10 mL) of MeOH in THF. THF was added to dissolve the polymer because in some cases the solution was solidified. The polymer was precipitated in MeOH and was redissolved in THF. This procedure was repeated three times to remove traces of the unreacted macromoleculear catalyst. Finally, the polymer was filtered to afford a colorless powder and dried under vacuum. In a few cases, the unreacted macrocatalyst was removed by fractionation using toluene as the solvent and methanol as the nonsolvent.

Polymerization of ϵ-CL. A typical procedure for the polymerization of ϵ-CL is given below. The macromolecular catalyst $CpTiCl_2$(OPS) (50 mg) was added to a 100 mL Schlenk flask and was dissolved in 4 mL of toluene. ϵ-CL (1 mL, 9 mmol) was then introduced, and the flask was placed in an oil bath at 100 °C. The polymerization was allowed to continue for 24 h and was terminated by pouring the polymer solution into methanol. The polymer was rinsed with methanol and dried in a vacuum oven.

Characterization Methods. Size exclusion chromatography (SEC) experiments were conducted at 40 °C with a modular instrument consisting of a Waters model 510 pump, a U6K sample injector, a 401 refractometer, a 486 UV spectrometer, and a set of four μ-Styragel columns with a continuous porosity range of 10^6-10^3 Å. The columns were housed in an oven thermostatted at 40 °C. THF was the carrier solvent at a flow rate of 1 mL/min. The system was calibrated with seven PS standards having molecular weights between 2000 and 1 000 000.

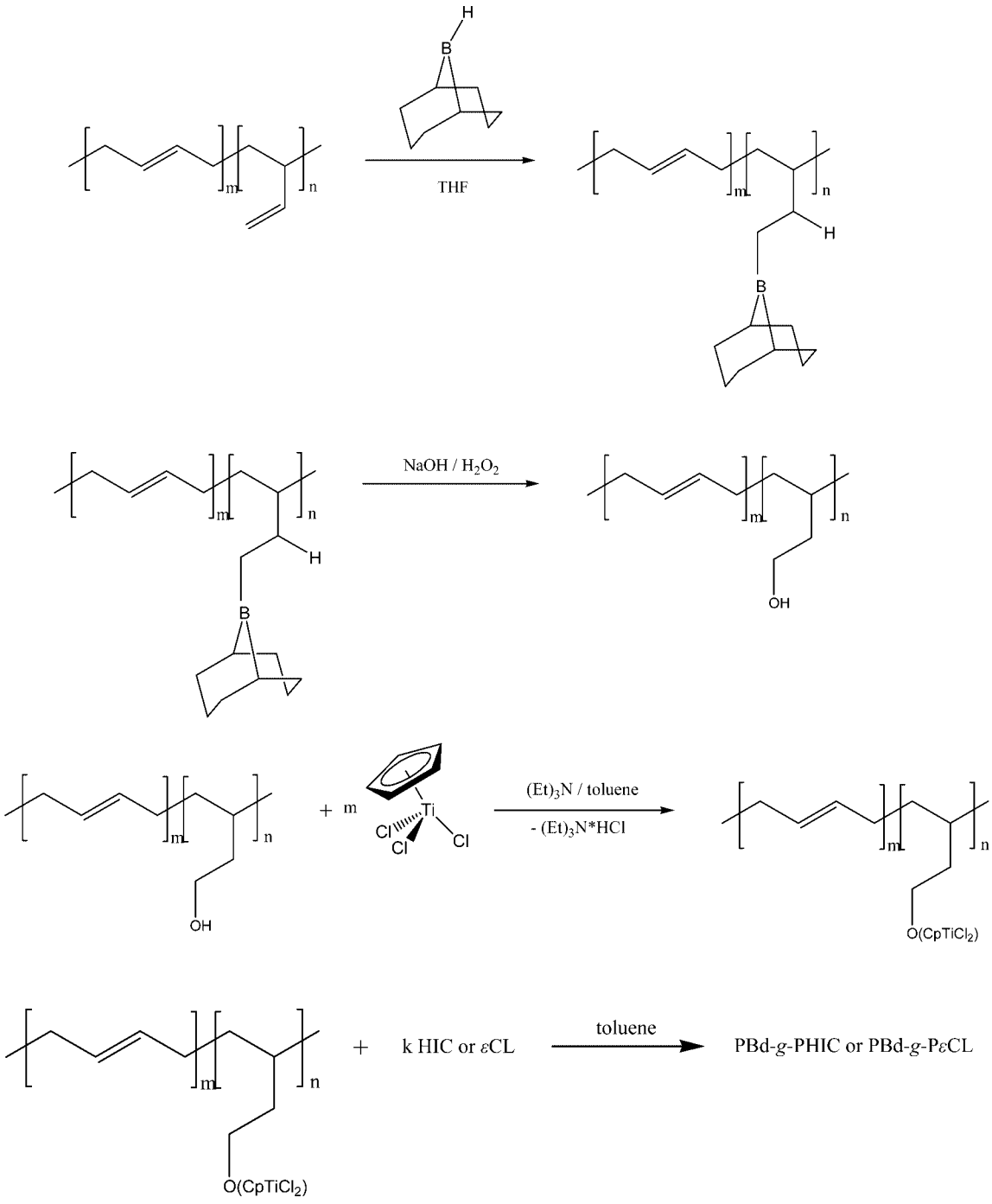
Multidetector SEC analysis [refractive index and two angle laser light scattering detectors (SEC-TALLS)], with a Waters 1525 high-pressure liquid chromatography pump, Waters Ultrastyragel columns (HR-2, HR-4, HR-5E, and HR-6E), a Waters 2410 differential

Table 4. Molecular Characteristics of the PI-*b*-PS-*b*-P(ϵ-CL) Block Copolymers[a]

$CpTiCl_2$(OPS-*b*-PI), mg	$(M_n)_{triblock} \times 10^{-3}$ [d]	$(M_w/M_n)_{triblock}$ [f]	$(M_n)_{stoichiom} \times 10^{-3}$	wt % ϵ-CL[g]	conversion, %
40[b]	120[e]	1.10	202.5	87.2	90
70[b]	75	1.06	102	79.3	85
130[b]	45	1.07	43	69.1	75
270[b]	25	1.08	18	61.1	60
35[c]	110	1.11	280.5	87.3	85
55[c]	70	1.07	142.5	79.5	75
100[c]	45	1.09	49	69.0	60
120[c]	25	1.10	27.5	46.4	50

[a] Reaction conditions: solvent toluene 4 mL; [ϵ-CL] = 2.25 M; temperature 110 °C. [b] $CpTiCl_2$(OPS-*b*-PI) from precursor PI-*b*-PS-OH #1. [c] $CpTiCl_2$(OPS-*b*-PI) from precursor PI-*b*-PS-OH #2. [d] By SEC-TALLS in THF at 35 °C. [e] By membrane osmometry in toluene at 37 °C. [f] By SEC in THF at 40 °C. [g] By ^{1}H NMR in $CDCl_3$ at 25 °C.

Scheme 1



refractometer detector, and a Precision 2020 two-angle (15° and 90°) light scattering detector, was also employed for the determination of the refractive index increments (d*n*/d*c*'s) and the weight weight-average molecular weights (M_w's) of the samples.

Table 5. Molecular Characteristics of the Hydroborated Polybutadienes

sample	$M_w \times 10^{-3}$ [a]	M_w/M_n [b]	% 1,2/1,4 [c] (before hydroboration)	number of OH per PBd chain [c]
PBd(OH) #1	6.2	1.03	10.8/89.2	6
PBd(OH) #2	20.0	1.05	12.8/87.2	11

[a] By SEC-TALLS in THF at 35 °C. [b] By SEC in THF at 40 °C. [c] By ^{1}H NMR in $CDCl_3$ at 25 °C.

Copolymer compositions were determined from ^{1}H NMR spectra, which were recorded in chloroform-*d* at 25 °C with a Varian Unity Plus 300/54 NMR spectrometer.

Fourier transform infrared (FTIR) spectroscopy was used for the determination of the structure of the hydroborated polydienes. A Perkin-Elmer Spectrun One model was used.

Results and Discussion

Synthesis of PS-*b*-P(ϵ-CL) Diblock Copolymers and PS-*b*-PI-*b*-P(ϵ-CL)/PI-*b*-PS-*b*-P(ϵ-CL) Triblock Terpolymers. The synthesis of PS-*b*-P(ϵ-CL) block copolymers and PS-*b*-PI-*b*-P(ϵ-CL) and PI-*b*-PS-*b*-P(ϵ-CL) triblock terpolymers was accomplished via a method similar to that reported for the synthesis of the corresponding PHIC-containing block co- and terpolymers.[21] According to this procedure, $CpTiCl_3$ was reacted with hydroxyl-functionalized polymers, P-OH (P = PS, PS-*b*-PI, or PI-*b*-PS) to form the corresponding macromolecular

$$CpTiCl_3 + HO\text{-}P + Et_3N \longrightarrow CpTiCl_2(OP) + Et_3NH^+Cl^- \downarrow$$

$$CpTiCl_2(OP) + \varepsilon CL \longrightarrow P\text{-}b\text{-}P(\varepsilon\text{-}CL)$$

catalysts, $CpTiCl_2(OP)$. Polymerization of ϵ-CL with these catalytic systems led to the synthesis of diblock copolymers and triblock terpolymers, according to the scheme.

The molecular characteristics of the OH-functionalized precursors are given in Table 1. The samples were characterized by narrow molecular weight distributions and controlled molecular weights. The functionalization reaction was quantitative, as confirmed by ^{1}H NMR analysis, in agreement with previous reports.[25]

The macromolecular catalysts $CpTiCl_2(OP)$ were used successfully for the synthesis of linear diblock copolymers and triblock terpolymers, as evidenced by the data in Table 2. The reaction sequence was monitored by SEC. Characteristic chromatograms are given in Figure 1. The polymerization of ϵ-CL with $CpTiCl_2(OP)$ (P: PS, M_n = 1200 and 2500) was conducted at 25, 40, 60, 80, and 100 °C. Up to 60 °C the only observed product was the PS precursor, whereas at 80 °C the copolymerization yield was very low. Only at 100 °C were high yields and the desired copolymer structures obtained. Thereafter, all experiments were performed at this temperature.

The copolymerization results obtained using PS precursors with molecular weight up to 6500 were similar and unambiguously support the conclusion that the macromolecular catalyst $CpTiCl_2(OP)$ promotes the highly controlled polymerization of ϵ-CL. The molecular weight distributions were very narrow for all samples synthesized. Specifically, M_w/M_n values lower than 1.19 were obtained, and for several samples $M_w/M_n < 1.10$ were measured. Furthermore, the molecular weights of the P(ϵ-CL) blocks scale linearly with the amount of the macromolecular catalyst (Figure 2). Only in the case of the macromolecular catalyst derived from the PS precursor with molecular weight equal to 6500 did the molecular weight of the P(ϵ-CL) blocks deviate from linearity. This result can be attributed to the increased viscosity of the high molecular weight catalyst solution, which hinders the growth of the P(ϵ-CL) blocks, affording nonquantitative yields. It should be noted that in all cases complete consumption of the macromolecular catalyst was observed, indicating the controlled nature of the copolymerization. Further evidence for the well-controlled polymerization is provided by the method's capability to synthesize P(ϵ-CL) blocks with molecular weights as high as 180 000 (Table 2, entry 11). NMR spectroscopy also supports the successful synthesis of the desired products.

This behavior was no longer observed when the macromolecular catalyst bearing PS with M_n = 12 000 was employed. Even though the molecular weight distributions of the products were narrow (1.12) and high molecular weight P(ϵ-CL) blocks could be prepared (100 000), the consumption of the macromolecular catalyst was not quantitative, as evidenced by the bimodal molecular weight distributions of the SE chromatograms (Figure 3). The higher the amount of the catalyst, the higher was the unreacted amount. This effect can be attributed to the increased steric hindrance introduced by the rather high molecular weight PS chain and the high viscosity of the catalyst solution. Both factors prevent the complexation of the lactone units to the catalyst and hinder the polymerization. Similar behaviors were observed in the synthesis of PS-*b*-PHIC using $CpTiCl_2(OPS)$ macromolecular catalysts,[21] with the exception that the limits of the PS molecular weight are shifted downward (M_n = 3200), showing that the polymerization of ϵ-CL can be even better controlled than the polymerization of HIC.

Using the same methodology, PS-*b*-PI-*b*-P(ϵ-CL) triblock terpolymers were also prepared, starting from the corresponding PS-*b*-PI-OH functionalized block copolymers. The molecular characteristics of the precursors are listed in Table 1, whereas those of the final products in Table 3. It is clear that nearly monodisperse samples were synthesized from both precursors. The experimentally observed molecular weights were in close agreement with the stoichiometric values, and the macromolecular catalyst was quantitatively consumed, as revealed by SEC analysis (Figure 4). The synthesis of the desired products was further verified by NMR spectroscopy. High yields were obtained for all samples. However, by increasing the catalyst quantity, relatively lower yields were obtained in agreement with previous observations for the $CpTiCl_2(OPS)$.

To check whether the order of the blocks influences the synthetic procedure, the functionalized copolymers PI-*b*-PS-OH were prepared by anionic sequential copolymerization and subsequently were treated with $CpTiCl_3$ to provide the corresponding macromolecular catalyst $CpTiCl_2$(O-PS-*b*-PI). Using these compounds, the synthesis of the triblock terpolymers PI-*b*-PS-*b*-P(ϵ-CL) was attempted. It should be mentioned that rather high molecular weight precursors were employed, as shown in Table 1 (M_n values equal to 10 000 and 13 700). SEC analysis revealed that bimodal distributions were obtained in both cases, corresponding to the desired PI-*b*-PS-*b*-P(ϵ-CL) triblock terpolymer and the PI-*b*-PS-OH precursor. The amount of unreacted precursor was increased with its increased quantity in the reaction mixture. Characteristic SEC traces are given in Figure 6. This behavior can be attributed both to the increased steric hindrance from the rather high molecular weight PI-*b*-PS chain attached to the catalyst and to the high viscosity of the catalyst solution, as in the case of the PS-*b*-P(ϵ-CL). Comparing these results with those obtained for the corresponding PS-*b*-PI-OH precursors of similar molecular weights, it seems that the higher flexibility of the PI chains, compared to that of PS, next to the catalytic site facilitates the polymerization of ϵ-CL. This result justifies the presence of a small peak in the SEC trace (Figure 5) corresponding to the unreacted PI-*b*-PS-catalyst. Despite this drawback, the triblock terpolymers were characterized by very narrow molecular weight distributions (Table 4).

Okuda and Rushkin[23] reported the polymerization of ϵ-CL using $CpTiCl_2(OCH_3)$ as the catalyst. Both this catalyst and our

Table 6. Molecular Characteristics of the PBd-*g*-PHIC Graft Copolymers[a]

sample	$(M_w)_{PBd} \times 10^3$ [d]	$(M_w)_{graft} \times 10^3$ [d]	M_w/M_n [e]	HIC (% w/w)[f]	conversion, %	number of branches	$M_w \times 10^3$ [g] (branch)
PBd-*g*-PHIC #1[b]	6.2	28.1	1.30	80.0	36	6	3.7
PBd-*g*-PHIC #2[c]	20	66.6	1.20	71.2	40	11	4.2
PBd-*g*-PHIC #3[c]	20	46.0	1.23	55.7	34	11	2.4
PBd-*g*-PHIC #4[c]	20	95.6	1.28	76.9	52	11	6.9
PBd-*g*-PHIC #5[c]	20	75.1	1.31	72.3	58	11	5.0

[a] Solvent: toluene; room temperature; polymerization time: 24 h. [b] Catalyst: PBd-$(OCpTiCl_2)_9$ produced from PBd(OH) #1. [c] Catalyst: PBd-$(OCpTiCl_2)_{11}$ produced from PBd(OH) #2. [d] By SEC-TALLS in THF at 35 °C. [e] By SEC in THF at 40 °C. [f] By ^{1}H NMR spectroscopy in $CDCl_3$ at 25 °C. [g] Calculated by the molecular weights of the graft copolymer and the PBd backbone taking into account that all the initiating sites have been efficiently employed for the polymerization of HIC.

Table 7. Molecular Characteristics of the PBd-*g*-P(ϵ-CL) Graft Copolymers[a]

sample	$(M_w)_{PBd} \times 10^{-3}$ [c]	$(M_n)_{graft} \times 10^{-3}$ [d]	M_w/M_n [e]	ϵ-CL (% w/w)[f]	conversion, %	number of branches	$M_w \times 10^3$ [g] (branch)
PBd-*g*-P(ϵ-CL) #1[b]	20	300	1.06	96.5	>95	11	27.1
PBd-*g*-P(ϵ-CL) #2[b]	20	220	1.10	96.0	>95	11	20.2
PBd-*g*-P(ϵ-CL) #3[b]	20	140	1.10	90.0	>95	11	12.2

[a] Reaction conditions: solvent toluene 4 mL; [ϵ-CL] = 2.25 M; temperature 110 °C. [b] Catalyst: PBd-$(OCpTiCl_2)_{11}$ produced from PBd(OH) #2. [c] By SEC-TALLS in THF at 35 °C. [d] By membrane osmometry in toluene at 37 °C. [e] By SEC in THF at 40 °C. [f] By ^{1}H NMR spectroscopy in $CDCl_3$ at 25 °C. [g] Calculated by the molecular weights of the graft copolymer and the PBd backbone taking into account that all the initiating sites have been efficiently employed for the polymerization of ϵ-CL.

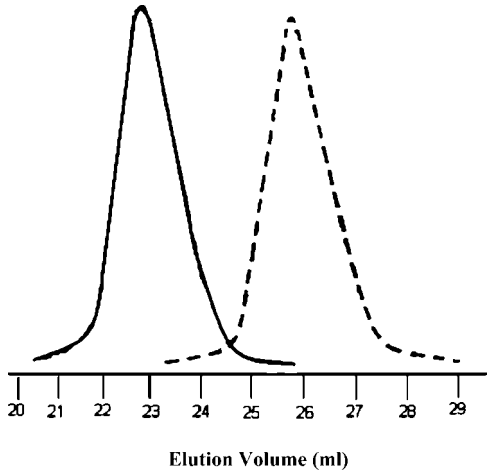


Figure 7. SEC profile of PBd-*g*-PϵCL #1: the precursor PBd(OH) #2 (dashed line); the final product (solid line).

macromolecular catalysts reported here offer a good control over the molecular weights, showing a linear relationship between the molecular weights and the quantity of the catalyst. However, in the Okuda and Rushkin[23] study the molecular weight distributions were found to increase upon increasing the conversion, since cyclic oligomers were formed, due to "backbiting" and transesterification side reactions. In our study, the side reactions were substantially suppressed, even when quantitative conversions were observed, thanks to the protective role of the polymer chains.

The same synthetic procedure was employed for the synthesis of PHIC-based copolymers, PS-*b*-PHIC, PS-*b*-PI-*b*-PHIC and PI-*b*-PS-*b*-PHIC.[21] It was concluded that the polymerization of ϵ-CL is much better controlled than that of HIC and is free of side reactions.

Synthesis of PBd-*g*-PHIC and PBd-*g*-P(ϵ-CL) Graft Copolymers. The synthesis of graft copolymers can be accomplished by three different methods:[30] the grafting "onto", the grafting "from", and the grafting "through" or macromonomer method. The literature is very extended regarding the synthesis of graft copolymers containing P(ϵ-CL) branches. The grafting "from" technique has been used primarily.[31] However, the other two methods have been applied as well.[32,33] The polymerization of ϵ-CL takes place by classic ROP methods, leading to products with rather broad molecular weight distributions. On the contrary, a very limited number of studies concerning the synthesis of graft copolymers with PHIC branches have been reported. In these cases the grafting "through" or macromonomer methodology was employed. PHIC macromonomers with styryl or methacrylate end groups were prepared by titanium coordination polymerization, using functionalized catalysts or suitable termination reactions in order to introduce the polymerizable end group.[34] The macromonomers were subsequently subjected to free radical polymerization to provide graft copolymers with few PHIC branches due to their low polymerizability.

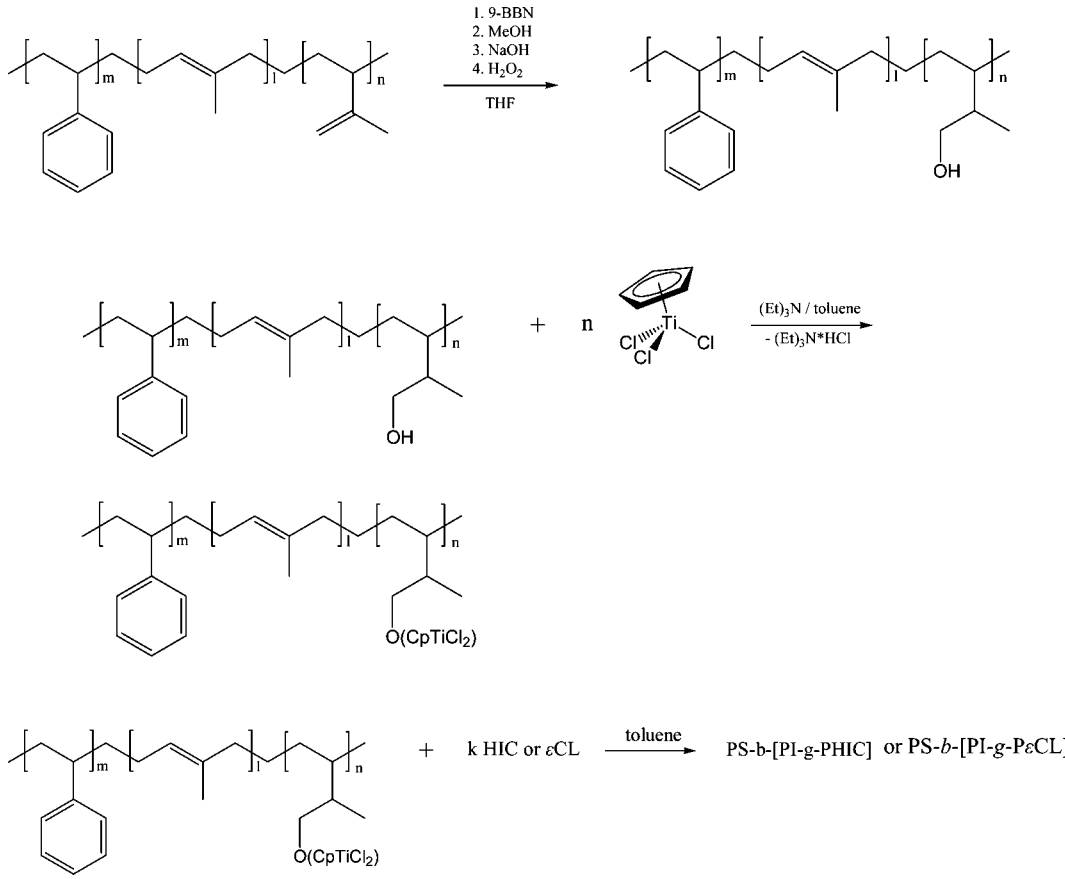
In the present study graft copolymers PBd-*g*-PHIC and PBd-*g*-P(ϵ-CL) were synthesized using the grafting "from" methodology. Anionic polymerization was employed for the synthesis of linear PBd chains, which were then subjected to hydroboration/oxidation reaction in order to incorporate functional hydroxyl groups along the backbone. The hydroxyl groups were reacted with a suitable amount of $CpTiCl_3$ to introduce coordination sites for the polymerization of HIC or ϵ-CL. The reaction sequence is displayed in Scheme 1.

The hydroboration of PBd was performed in the presence of an appropriate monofunctional dialkylborane (9-borabicyclo[3.3.1]nonane) under vacuum to avoid gel formation. The subsequent oxidation reaction was conducted at low temperatures (−25 °C), using the stoichiometric amount of the oxidation reagent ($NaOH/H_2O_2$), in order to avoid oxidation of the residual PBd double bounds. Boric acid is one of the byproducts, which has to be removed quantitatively from the functionalized polymer, since it reacts slowly at room temperature with the pendent hydroxyl groups to form trialkoxyborane, gradually leading to cross-linking. The effective removal of boric acid was achieved using the procedure described by Chung et al.[26a]

It is well-known that, due to steric reasons, the hydroboration reaction preferentially takes place at the 1,2 vinyl groups of PBd. In the present study, the incorporation of only a small number of hydroxyl groups was planned. Stoichiometric quantities of the reagents for the selective reaction of the vinyl groups 1,2 of PBd were used. The hydroboration reaction was monitored by NMR spectroscopy. The results are displayed in Table 5. It is evident that the 1,4 microstructure remained unaffected by the hydroboration reaction, whereas the 1,2 content was drastically reduced. This was confirmed by the reduction of the signal at 5.00 ppm (CH_2) of the vinyl moieties and the appearance of a new signal at 3.65 ppm (CH_2−OH). It can be concluded that the hydroboration−oxidation reaction proceeds at a 75% yield.

FTIR spectroscopy is also suitable for drawing qualitative conclusions about the progress of the reaction. Comparing the

Scheme 2



IR spectra before and after the functionalization reaction, two absorption bands reflect the differences. The first band appears at 1050 cm^{-1} (hydroborated PBd) and is attributed to the vibrations of the ν(CO). The decrease of the intensity of the absorption band at 911 cm^{-1} of the spectrum of the final product is attributed to the vibrations of the vinyl groups. Both events indicate the success of the functionalization reaction. SEC analysis of the products revealed that neither the molecular weight nor the molecular weight distribution was changed, indicating that the polymers remain unaffected.

The functionalized polymers $PBd(OH)_n$ were then reacted with $CpTiCl_3$ to afford the macromolecular catalyst $PBd-(CpTiCl_2)_n$. The reaction took place in the presence of Et_3N for the removal of the HCl, which is produced during the reaction. To ensure the successful synthesis of the desired catalyst, a small excess of the functionalized polymer, up to 10%, was employed. The available catalytic sites were then used for the polymerization of HIC and therefore in the synthesis of the graft copolymers PBd-*g*-PHIC. The small excess of the functionalized polymer serves to prevent unreacted $CpTiCl_3$, which can initiate the polymerization of HIC and lead to PHIC homopolymer along with the block copolymer. On the contrary, $CpTiCl_3$ cannot efficiently polymerize ϵ-CL. Therefore, for the synthesis of the PBd-*g*-P(ϵ-CL) the macromolecular catalyst $PBd(CpTiCl_2)_n$ was prepared by a stoichiometric reaction between the −OH groups along the PBd backbone and $CpTiCl_3$ or with a very small excess of the titanium catalyst.

The molecular characteristics of the PBd-*g*-PHIC samples are reported in Table 6. The reaction sequence was monitored by SEC. A representative example is shown in Figure 6. In all cases, the analysis revealed the presence of a second peak corresponding to the $PBd(CpTiCl_2)_n$ macromolecular catalyst. This peak can be attributed to the excess of $PBd-(OH)_n$ used for the synthesis of the macromolecular catalyst or to graft copolymers with a lower number of PHIC branches. These byproducts were removed by fractionation with toluene/MeOH as the solvent/nonsolvent system. The synthesis of the desired structures was further confirmed by ^1H NMR spectroscopy.

Table 8. Molecular Characteristics of Hydroborated Copolymer PS-*b*-PI

sample	$M_w \times 10^{-3}$ [a]	M_w/M_n [b]	% w/w Is[c]	% 3,4 units of Is block[c]	number of OH groups per chain[c]
PS-*b*-PI-$(OH)_9$	25.0	1.04	36.7	6.5	9

[a] By SEC-TALLS in THF at 35 °C. [b] By SEC in THF at 40 °C. [c] By ^1H NMR spectroscopy in $CDCl_3$ at 25 °C.

Patten and Novak[18,19] reported the reversibility of the polymerization reaction of HIC with organotitanium(IV) catalysts. To avoid the depolymerization and to achieve high yields, the reaction should be conducted in bulk or at very high concentrations. However, in the present study, in order to facilitate the dissolution of the macromolecular catalysts and to avoid high-viscosity problems during the polymerization of HIC, the polymerization was conducted in adequately dilute toluene solution. Consequently, the conversions were not as high as those previously reported for the synthesis of PS-*b*-PHIC copolymers.[21] The solubility problems associated with the polymerization of HIC prevent the use of high molecular weight PBd samples as backbones.

The composition of the samples was determined by ^1H NMR spectroscopy and refractive index increment, d*n*/d*c*, measurements of the graft copolymers taking into account the d*n*/d*c* values of the PBd (0.136 in THF at 633 nm) and PHIC (0.088 in THF at 633 nm) homopolymers. Both methods gave similar results, indicating that polymers of high compositional homogeneity were prepared. For all samples there was good agreement between the stoichiometric and the experimentally observed molecular weights, taking into account the conversion

Table 9. Molecular Characteristics of PS-*b*-[PI-*g*-PHIC] and PS-*b*-[PI-*g*-P(ϵ-CL)] Block−Graft Copolymers[a]

sample	$M_w \times 10^3$ [c] (PS-*b*-PI backbone)	$M_n \times 10^3$ [d]	M_w/M_n [e]	HIC or ϵ-CL (% w/w)[f]	conversion, %	number of branches	$M_w \times 10^3$ (branch)[g]
PS-*b*-[PI-*g*-PHIC][b]	25.0	91.7[c]	1.33	79.0	58	9	10.8
PS-*b*-[PI-*g*-P(ϵ-CL)]#1[b]	25.0	110	1.06	71.7	>95	9	10.2
PS-*b*-[PI-*g*-P(ϵ-CL)]#2[b]	25.0	80	1.08	65.4	>95	9	6.8
PS-*b*-[PI-*g*-P(ϵ-CL)]#3[b]	25.0	54.9	1.05	56.7	>95	9	3.6
PS-*b*-[PI-*g*-P(ϵ-CL)]#4[b]	25.0	51.6	1.05	53.9	>95	9	3.2

[a] Reaction conditions for PS-*b*-[PI-*g*-PHIC]: solvent toluene; room temperature; polymerization time: 24 h; Reaction conditions for PS-*b*-[PI-*g*-P(ϵ-CL)]: solvent toluene 4 mL; [ϵ-CL]=2.25 M; temperature 110 °C. [b] Catalyst: PS-*b*-[PI-$(OCpTiCl_2)_9$]. [c] By SEC-TALLS in THF at 35 °C. [d] By membrane osmometry in toluene at 37 °C. [e] By SEC in THF at 40 °C. [f] By ^{1}H NMR spectroscopy in $CDCl_3$ at 25 °C. [g] Calculated by the molecular weights of the block-graft copolymer and the PS-*b*-PI backbone taking into account that all the initiating sites have been efficiently employed for the polymerization of HIC or ϵ-CL.

Table 10. Molecular Characteristics of Polystyrene Chains Having Two Protected Hydroxyl End Groups PS-$(OR)_2$[a]

sample	$M_w \times 10^3$ [b]	M_w/M_n [b]	conversion, %
PS$(OR)_2$ #1	12.7	1.19	60
PS$(OR)_2$ #2	31.6	1.15	62
PS$(OR)_2$ #3	44.3	1.16	58
PS$(OR)_2$ #4	5.80	1.15	88
PS$(OR)_2$ #5	5.40	1.15	55
PS$(OR)_2$ #6	10.6	1.14	53

[a] Solvent: toluene (samples 1–4), THF (sample 5); temperature: 110 °C; polymerization time: 16 h. [b] By SEC in THF at 40 °C.

of the polymerization. The molecular weight distributions were relatively narrow and symmetrical for all samples. These results strongly indicate that all the available initiating sites along the PBd backbone are effective in polymerizing HIC and produce uniform side chains (Figure 6).

A similar procedure was followed for the synthesis of the PBd-*g*-P(ϵ-CL). The molecular characteristics of the samples are displayed in Table 7. SEC analysis revealed that the macromolecular catalyst was quantitatively consumed during the grafting reaction. This result is attributed to the stoichiometric amounts of PB-$(OH)_n$ and $CpTiCl_3$ used for the synthesis of the macromolecular catalyst. The molecular weight distributions of the graft copolymers were very narrow and symmetrical, and the molecular weights, obtained by membrane osmometry, were in close agreement with the stoichiometric values. In addition, the conversions were near quantitative. These observations indicate that all the available initiating sites were equally active for the polymerization of ϵ-CL and led to well-defined products. Characteristic SEC chromatograms are given in Figure 7. The synthesis of the desired copolymers was also confirmed by NMR spectroscopy.

Synthesis of PS-*b*-[PI-*g*-PHIC] and PS-*b*-[PI-*g*-P(ϵ-CL)] Block−Graft Terpolymers. The same procedure was adopted for the synthesis of PS-*b*-[PI-*g*-PHIC] and PS-*b*-[PI-*g*- P(ϵ-CL)] block−graft terpolymers. The reaction sequence is given in Scheme 2. The PS-*b*-PI diblock was prepared by standard anionic polymerization high-vacuum techniques and sequential addition of the monomers. The molecular characteristics of the sample are given in Table 8. The hydroboration−oxidation procedure took place under the same conditions as previously described. Stoichiometric quantities of 9-BBN toward the vinyl 3,4 units were used. The functionalization takes place exclusively at the vinyl groups, since steric hindrance prevents the addition of the hydroxyl groups to the double bonds of the 1,4 units. This behavior was confirmed by NMR spectroscopy by the disappearance of the signals attributed to the two vinyl protons of the 3,4 microstructure. Using the aromatic protons of the polystyrene units as internal reference, it was concluded that the 1,4 units remained unaffected by this functionalization reaction.

The functionalized copolymer was further reacted with $CpTiCl_3$ to form the macromolecular catalyst, which was then employed for the polymerization of HIC or ϵ-CL to obtain the corresponding block−graft terpolymers. The molecular characteristics of the samples are displayed in Table 9. Characteristic chromatograms concerning the synthesis of the block−graft terpolymers are shown in Figures 8 and 9. The SEC trace of the sample PS-*b*-[PI-*g*-PHIC] showed a small peak at the lower molecular weight regime corresponding to the small excess of the PS-*b*-PI precursor, which was used to ensure the quantitative synthesis of the macromolecular catalyst. The pure product was then obtained by fractionation with toluene/MeOH as the solvent/non solvent system. On the other hand the PS-*b*-[PI-*g*-P(ϵ-CL)] crude products showed single SEC traces of very narrow molecular weight distribution. This is another manifestation of the better control achieved over the polymerization of ϵ-CL compared to the polymerization of HIC. The ^{1}H NMR spectra confirm the successful synthesis of the desired products.

Synthesis of PS$(PHIC)_2$ and PS[P(ϵ-CL)]$_2$ 3-Miktoarm Star Copolymers. Miktoarm stars have evolved as a valuable class of polymeric materials due to their very interesting properties both in bulk and in solution.[30,35] The synthesis of miktoarm stars has been accomplished by a rich variety of methods and polymerization techniques.[36] Despite the extended work dedicated to this field of polymer science, there is only one report of the synthesis of $(PS)_n(PHIC)_n$ miktoarm stars[37] by anionic polymerization techniques and relatively few studies for P(ϵ-CL) miktoarm stars.[38] In the latter case the polylactone arms were synthesized exclusively by classic ring-opening polymerization, ROP, techniques ($SnOct_2$ or triethylaluminum as initiators), leading to products with relatively high molecular weight distributions.

Table 11. Molecular Characteristics of PS$(PHIC)_2$ Miktoarm Star Copolymers[a]

sample	$M_w \times 10^3$ [f] (PS arm)	$M_w \times 10^{-3}$ [g] (star)	M_w/M_n [f]	% w/w HIC[h]	conversion, %	$M_w \times 10^{-3}$ [i] (PHIC arm)
PS$(PHIC)_2$ #1[b]	12.7	35.0	1.19	70.7	38	11.2
PS$(PHIC)_2$ #2[c]	5.80	28.2	1.17	87.5	42	11.2
PS$(PHIC)_2$ #3[c]	5.80	29.7	1.18	83.0	51	12.0
PS$(PHIC)_2$ #4[d]	5.40	32.9	1.13	82.9	44	13.8
PS$(PHIC)_2$ #5[e]	10.6	36.4	1.13	79.6	42	12.9

[a] Solvent: toluene; room temperature; polymerization time: 24 h. [b] Catalyst: PS-$(OCpTiCl_2)_2$ #1. [c] Catalyst: PS-$(OCpTiCl_2)_2$ #4. [d] Catalyst: PS-$(OCpTiCl_2)_2$ #5. [e] Catalyst: PS-$(OCpTiCl_2)_2$ #6. [f] By SEC in THF at 40 °C. [g] M_w by SEC-TALLS in THF at 35 °C. [h] By ^{1}H NMR spectroscopy in $CDCl_3$ at 25 °C. [i] Calculated by the molecular weights of the miktoarm star copolymer and the PS arm taking into account that both initiating sites have been efficiently employed for the polymerization of HIC.

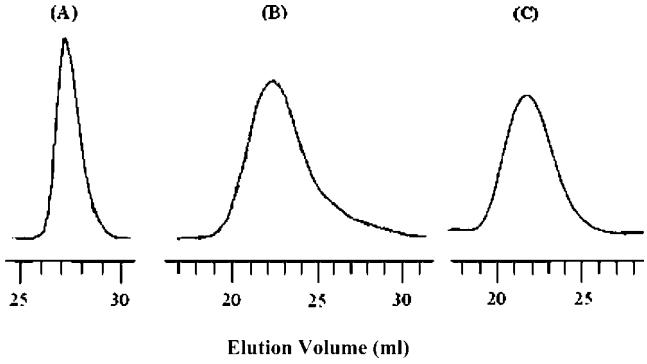


Figure 8. SEC profile of PS-*b*-[PI-*g*-PHIC]: PS-*b*-PI(OH)$_9$ precursor (A), final product before (B), and after fractionation (C).

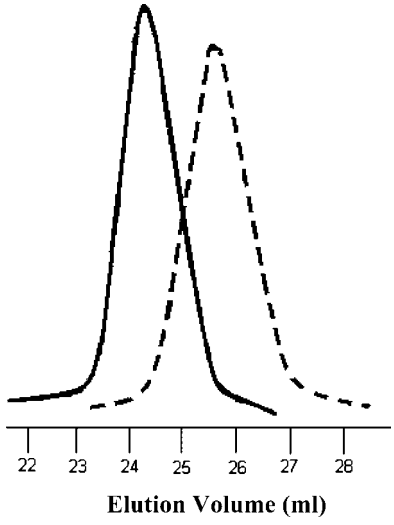


Figure 9. SEC profile of PS-*b*-[PI-*g*- Pϵ CL]: PS-*b*-PI(OH)$_9$ precursor (dashed line); final product (solid line).

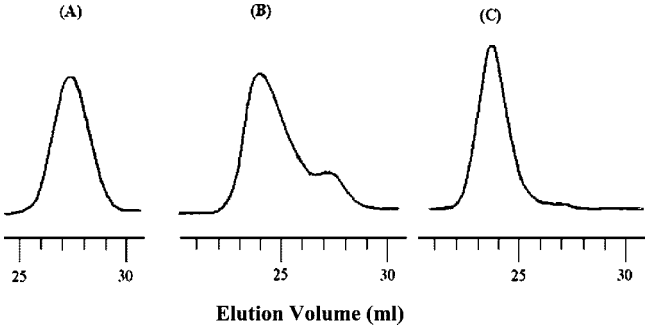


Figure 10. SEC profiles of PS(PHIC)$_2$ #5: PS arm (A), the final product before (B), and after fractionation (C).

In this study a heterofunctional initiator combining one active site for ATRP of styrene and two cyclopentadienyl titanium dichloride groups, for the polymerization of HIC or ϵ-CL, was synthesized to afford PS(PHIC)$_2$ and PS[P(ϵ-CL)]$_2$ 3-miktoarm star copolymers (Scheme 3). 2-Ethyl-2-(hydroxymethyl)propane-1,3-diol (**1**) was the starting material for the synthesis of the heterofunctional initiator. The two adjacent hydroxyl groups were protected by reaction with acetone, following literature procedures.[27] Amberlyst 15 was used as acid catalyst, while $MgSO_4$ was used to shift the equilibrium to the desired protected products (**2**), which is a high-viscosity liquid in contrast to the starting material, a crystalline solid of very high melting point. The final product was isolated by distillation under vacuum (∼60 °C), and its purity was confirmed by ^{1}H NMR spectroscopy and thin-layer chromatography. The second step of the synthetic

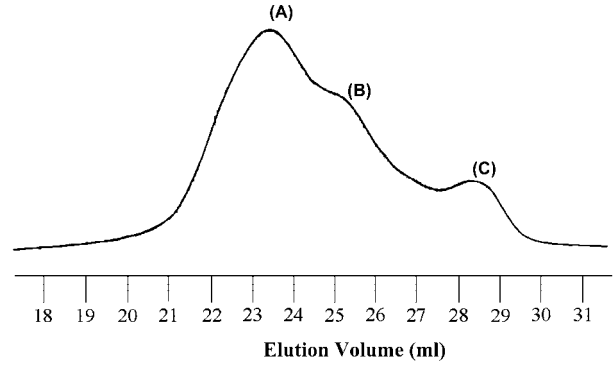


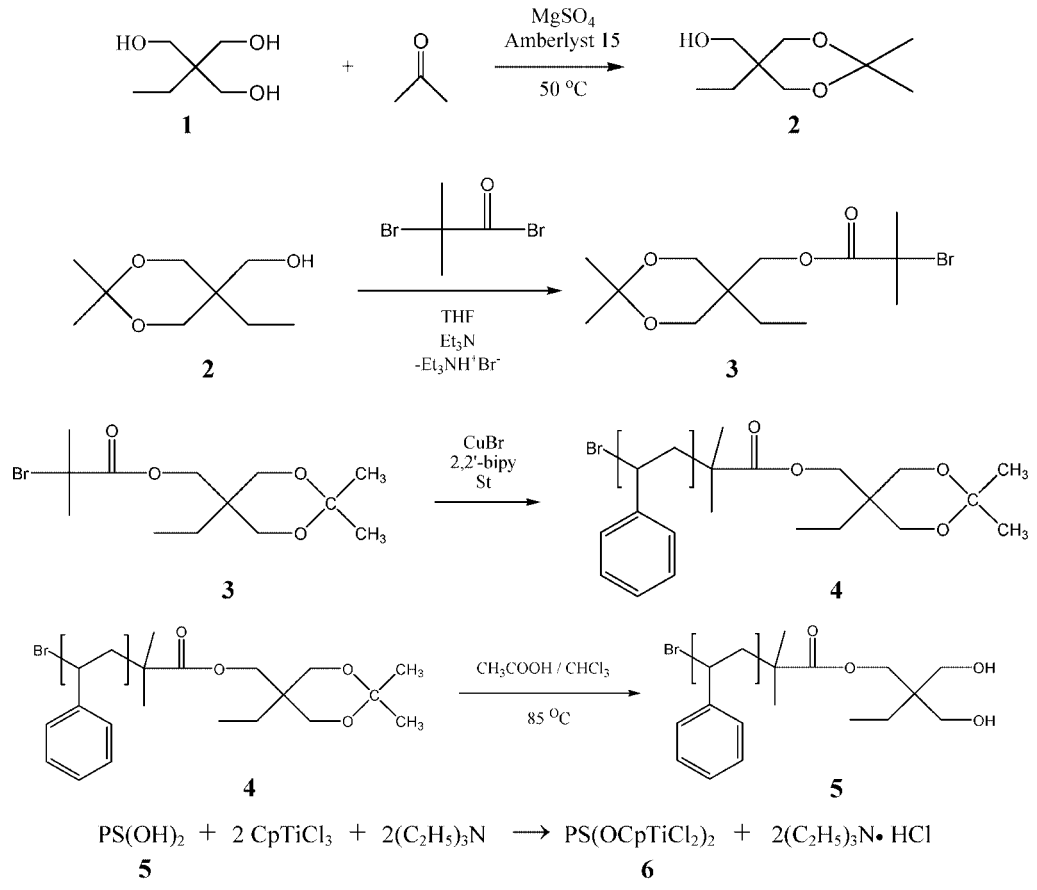
Figure 11. SEC profile of the crude product resulting from the reaction of a large excess of PS(OH)$_2$ with CpTiCl$_3$: PS(PHIC)$_2$ miktoarm star (A), PS-*b*-PHIC block copolymer with a hydroxyl group at the junction point (B), and excess PS(OH)$_2$ (C).

route involves the esterification of the remaining hydroxyl group with a small excess of 2-bromoisobutyryl bromide. The reaction takes place in the presence of triethylamine, shifting the equilibrium to the desired ester (**3**). The remaining 2-bromoisobutyryl bromide was easily removed by repeating extractions with K_2CO_3 aqueous solution, and the final product was purified by column chromatography (silica gel of diameter 0.040–0.063 nm) to give the heterofunctional initiator. ^{1}H NMR spectroscopy was employed to confirm the purity of the product.

The product **3** was used for the ATRP of styrene, resulting in **4**. CuBr served as the catalyst for the polymerization and 2,2′-bipyridyl as the ligand in a 1:1:3 molar ratio of initiator, catalyst, and ligand. Initially, the polymerization of styrene was conducted in bulk, leading to high conversions (∼80%) but with rather broad molecular weight distributions. Consequently, all polymerizations were carried out in either THF or toluene, in high monomer concentrations (50–60% v/v). The molecular characteristics of the samples synthesized are displayed in Table 10. The less than quantitative conversions reflect the early polymerization termination effected in order to obtain narrow molecular weight distributions and control over the molecular weights. As revealed in Table 10, the polydispersities were lower than 1.20 for all samples, and there was a good agreement between the stoichiometric and the experimentally measured molecular weights. The samples were characterized by SEC analysis and ^{1}H NMR spectroscopy.

The deprotection of the hydroxyl groups was achieved by treatment with CH_3COOH leading to **5**, as evidenced by ^{1}H NMR spectroscopy. Subsequent reaction with CpTiCl$_3$ gave the macromolecular catalyst PS(OCpTiCl$_2$)$_2$ (**6**), which was further employed for the polymerization of HIC or ϵ-CL to obtain the corresponding miktoarm star copolymers. The molecular characteristics of the PS(PHIC)$_2$ samples are given in Table 11. A representative series of chromatograms for the synthesis of these miktoarm stars is shown in Figure 10. As mentioned above, the macromolecular catalyst for the synthesis of the PS(PHIC)$_2$ samples was obtained using a small excess of the functionalized precursor, PS(OH)$_2$. Therefore, in all cases the SEC trace of the crude product included an extra peak corresponding to the excess PS(OH)$_2$. The pure product was isolated by fractionation using toluene/MeOH as the solvent/nonsolvent system. All the samples showed narrow molecular weight distributions ($M_w/M_n < 1.2$), which is clear evidence for the successful synthesis of well-defined miktoarm star copolymers. The use of both initiation sites for the polymerization of HIC and the preparation of the desired structures was further explored by reacting a large excess of the functionalized precursor, PS(OH)$_2$ with CpTiCl$_3$. The product was expected to be a mixture of macromolecular catalysts with one and two reactive groups, PS(CpTiCl$_2$)(OH)

Scheme 3



$$PS(OH)_2 + 2\,CpTiCl_3 + 2(C_2H_5)_3N \longrightarrow PS(OCpTiCl_2)_2 + 2(C_2H_5)_3N\bullet HCl$$

5 **6**

$$PS(OCpTiCl_2)_2 + n\ HIC \text{ or } \varepsilon CL \longrightarrow PS(PHIC)_2 \text{ or } PS(P\ \varepsilon CL)_2$$

6

Table 12. Molecular Characteristics of PS[P(ϵ-CL)]$_2$ Miktoarm Star Copolymers[a]

sample	$M_w \times 10^{-3}$ [e] (PS arm)	$M_w \times 10^{-3}$ [f] (star)	M_w/M_n [e]	% w/w ϵ-CL[h]	conversion, %	$M_w \times 10^{-3}$ [i] [P(ϵ-CL) arm]
PS[P(ϵ-CL)]$_2$ #1[b]	5.40	58.0[g]	1.13	87.4	>95	30.1
PS[P(ϵ-CL)]$_2$ #2[b]	5.40	35.8	1.13	84.9	>95	15.2
PS[P(ϵ-CL)]$_2$ #3[b]	5.40	27.7	1.14	80.5	>95	11.2
PS[P(ϵ-CL)]$_2$ #4[c]	10.6	75.0[g]	1.12	87.4	>95	36.7
PS[P(ϵ-CL)]$_2$ #5[c]	10.6	62.7	1.14	83.1	>95	26.0
PS[P(ϵ-CL)]$_2$ #6[c]	10.6	34.9	1.16	69.6	>95	12.15
PS[P(ϵ-CL)]$_2$ #7[c]	10.6	30.2	1.15	64.9	>95	9.8
PS[P(ϵ-CL)]$_2$ #8[d]	12.7	27.1	1.13	53.2	70	7.2
PS[P(ϵ-CL)]$_2$ #9[d]	12.7	21.9	1.13	42.0	55	4.6
PS[P(ϵ-CL)]$_2$ #10[d]	12.7	17.9	1.14	29.1	50	2.6

[a] Reaction conditions: solvent toluene 4 mL; [ϵ-CL]=2.25 M; temperature 110 °C. [b] Catalyst: PS-(OCpTiCl$_2$)$_2$ #5. [c] Catalyst: PS-(OCpTiCl$_2$)$_2$ #6. [d] Catalyst: PS-(OCpTiCl$_2$)$_2$ #1. [e] By SEC in THF at 40 °C. [f] Calculated by the M_w of PS arm and the composition of the miktoarm star copolymer. [g] M_n by membrane osmometry in toluene at 37 °C. [h] By ^{1}H NMR spectroscopy in CDCl$_3$ at 25 °C. [i] Calculated by the molecular weights of the miktoarm star copolymer and the PS arm taking into account that both initiating sites have been efficiently employed for the polymerization of ϵ-CL.

and PS(CpTiCl$_2$)$_2$, respectively, and unreacted precursor, PS(OH)$_2$. The SEC trace of the crude product (Figure 11) after the polymerization of HIC using this mixture consisted of three peaks corresponding to the PS(PHIC)$_2$ miktoarm star, the PS-*b*-PHIC block copolymer with a hydroxyl group at the junction point, and the excess PS(OH)$_2$. This result is direct evidence that both initiation sites were reactive for the polymerization of HIC, and judging by the very low polydispersity of the final products, it seems that both polymerization sites have comparable rates of initiation.

For the synthesis of the PS[P(ϵ-CL)]$_2$ 3-miktoarm star copolymers the same macromolecular catalyst (**6**) was employed. However, for the preparation of **6** a small excess of CpTiCl$_3$ was used, as previously mentioned. Three different PS(OH)$_2$ precursors, with M_n values ranging from 5.0×10^3 to 10.7×10^3, were involved in the synthesis of three different series of miktoarm stars. The molecular characteristics of the samples are given in Table 12, whereas characteristic SEC traces of the reaction series are given in Figure 12. It is obvious that for all cases, even for the higher molecular weight PS precursor, the chromatogram of the crude product consisted of single and symmetric peaks with narrow molecular weight distribution ($M_w/M_n < 1.16$), indicating that the consumption of the macromolecular catalyst is complete. The conversion of the polymerization of ϵ-CL is very high, except when the higher molecular weight PS(OH)$_2$ precursor was used. In this case the conversions were lower than 70% and were decreased upon increasing the amount of the macromolecular catalyst. As was earlier discussed, this effect

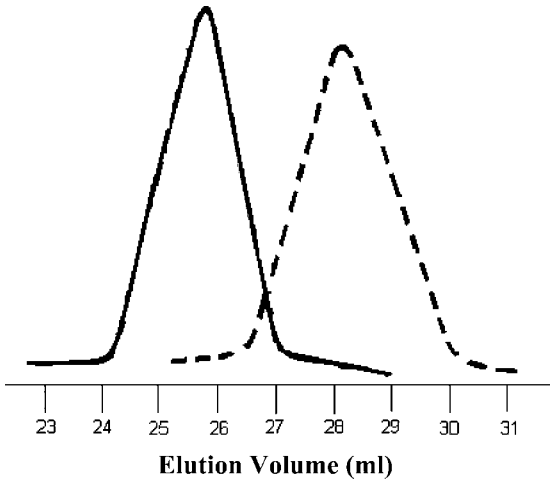


Figure 12. SEC profiles of PS(PϵCL)$_2$ #7: PS arm (dashed line); the final product (solid line).

can be attributed to the increased steric hindrance exercised by the rather high molecular weight PS chain and the high viscosity of the concentrated catalyst solution. ^{1}H NMR spectroscopy confirmed the synthesis of the desired products.

A few examples appear in the literature concerning the synthesis of similar miktoarm stars with ϵ-CL arms using classic ROP techniques. The advantage of our process is the better control obtained over the molecular weights and especially over the molecular weight distributions. In previous works the M_w/M_n values were higher than 1.3 but here were lower than 1.16. Furthermore, side reactions, observed during the classic ROP methodology, are avoided to a great extent.

Conclusions

$CpTiCl_2$(OP) (P = PS, PS-*b*-PI or PI-*b*-PS) was employed as macroinitiator for the polymerization of ϵ-CL leading to the synthesis of PS-*b*-P(ϵ-CL) block copolymers and PS-*b*-PI-*b*-Pϵ-CL and PI-*b*-PS-*b*-Pϵ-CL triblock terpolymers. Products of controlled molecular weights and narrow molecular weight distributions in high yields were obtained. When the molecular weight of the P precursor was higher than 10 000, the consumption of the macromolecular catalyst was not quantitative due to the increased steric hindrance and the high viscosity of the catalyst solution. Hydroboration/oxidation reactions were performed to incorporate hydroxyl groups along the polydiene chains. These groups were transformed into catalytic initiating sites after reaction with $CpTiCl_3$ and were subsequently used to polymerize HIC and ϵ-CL, leading to the formation of PBd-*g*-PHIC and PBd-*g*-P(ϵ-CL) graft copolymers as well as PS-*b*-(PI-*g*-PHIC) and PS-*b*-[PI-*g*-P(ϵ-CL)] block−graft terpolymers. Products with narrow molecular weight distributions and controlled number of branches were obtained. In the case of the graft copolymers having PHIC branches the polymerization yield was not very high, since the polymerizations were conducted in less concentrated solutions to avoid solubility problems. A heterofunctional initiator containing an atom transfer radical polymerization initiation site and two sites for titanium-mediated coordination polymerization was utilized for the synthesis of well-defined PS(PHIC)$_2$ and PS[P(ϵ-CL)]$_2$ 3-miktoarm star copolymers.

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Supporting Information Available: M_n vs the quantity of the macroinitiator $CpTiCl_2$(OPSt) plot (PS precursor having M_n = 6500), SEC traces, and NMR and IR spectra of intermediate and final products. This material is available free of charge via the Internet at http://pubs.acs.org.

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