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A New Route to Model (A_2B) and Regular Graft Copolymers[†]

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ABSTRACT: We describe a new and easy route to model graft copolymers A_2B as the simplest model and regular graft copolymer in which the grafting points are regularly spaced and the grafts have strictly the same size. This route is based on a double addition−elimination reaction of polystyryl Li or K on a specific 1,1-diphenylethylene derivative. The resulting well-defined A_2B structures include $(PS)_2$PtBuMA, $(PS)_2$PMMA, $(PS)_2$PEO, $(PS)_2$PϵCL, $(PS)_2$PLLA, and regular graft copolymers with PS backbone and PEO or PtBuMA grafts.

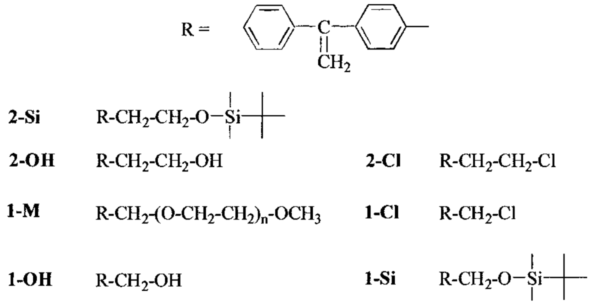
Introduction

While working in the field of ABC triarm star block copolymers (also called heteroarm or miktoarm[1]), we have encountered an unexpected reaction on a diphenylethylene derivative that opens an easy route to model graft copolymers, in which A_2B is the simplest model, and regular graft copolymers with perfectly and regularly spaced grafting points (of the A sequence) and B grafts of strictly the same size. Synthesis of an A_2B copolymer was first described by Teyssié et al.[2] PS $(PEO)_2$ was obtained by end-capping a living polystyryl carbanion by a naphthalene derivative followed by polymerization of ethylene oxide using naphthalene sodium radical ion as the initiator. A similar route using a symmetrical reinitiation on an ω,ω'-difunctionalized macroinitiator was described recently.[3] Other routes to A_2B copolymers involve coupling reactions on chlorosilane derivatives[4,5,6] or a nonhomopolymerizable linking agent.[7,8] Regular graft copolymers are synthesized either by polymerization of macromonomer, by using a polymer analogous reaction on a suitable backbone,[9] or by a step polymerization strategy.[10]

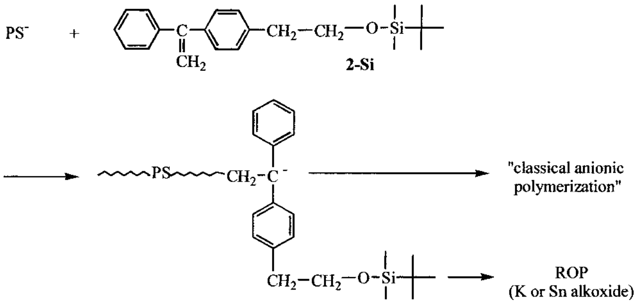
Until now, three different procedures have been used to synthesize ABC star block copolymers. The first one uses the selective, step-by-step substitution of the chlorine atoms in trichloromethylsilane with anionic living polymer chains to form the star copolymer.[11] The second is based on a macromonomer technique, in which non homopolymerizable macromonomers bearing a 1,4-bis(1-phenylethenyl)benzene (PDDPE) or a 1,1-diphenylethylene (DPE) group at one chain end are incorporated at the block junction of a diblock copolymer.[7,8,12,13] We recently developed a third method, which is based on two successive initiation steps on a "bifunctional macroinitiator".[14,15]

"Bifunctional initiators" are initiators bearing two chemically different functional groups able to independently initiate two polymerizations. Well-defined diblock copolymers have recently been obtained using this strategy either with successive[16,17,18] or with simultaneous[19] polymerizations of two monomers. To distinguish this type of initiator from the "classical" multifunctional initiators in which all the functional groups are identical, we suggest using the term heteromultifunctional initiator.

Scheme 1. Formula of Some DPE Derivatives



Scheme 2. Synthesis of ABC Star Block Copolymers Using a Heterobifunctional Macroinitiator



In the synthesis of ABC stars, the heterobifunctional macroinitiator was obtained by end-capping a polystyryl K (or Li) by the 1,1-diphenylethylene derivative **2-Si** (Schemes 1 and 2). The resulting carbanion initiates the "classical" anionic polymerization of methacrylic monomers [methyl (MMA) and tBu (tBuMA)] or ethylene oxide (EO). After deprotection, the hydroxy function was used to initiate the ring-opening polymerization (ROP) of EO and ϵ-caprolactone (ϵCL) via a potassium alkoxide or of L-lactide (LLA) via a tin alkoxide.

This leads to well-defined triarm star block copolymers of high molecular weight (up to 260 000, pdi ∼ 1.2) without contamination by any measurable amounts of homopolymers or diblock copolymers. Synthesis, characterization,[14,15] and some properties[20,21] of PS-arm-PEO-arm-PϵCL, PS-arm-PMMA-arm-PEO and PS-arm-PEO-arm-PLLA have already been described.

Nevertheless, there are some limitations. The main limitation was observed when we wanted to use tBuMA (known as being easily hydrolyzable) in order to introduce a second hydrophilic block in star block copoly-

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[†] A part of this work was presented at the 1999 Prague meeting on macromolecules.

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mers. According to the route summarized in Scheme 2, the tBuMA polymerization is initiated by the heterobifunctional macroinitiator with Li as a counterion. After deprotection, the hydroxy function is able to initiate ROP of ethylene oxide, leading to the ABC star copolymer. A side reaction (intramolecular transesterification) on the poly tBuMA block during initiation of the ethylene oxide ROP[22] leads to a mixture of the expected star and of the intermediate PS-*b*-PtBuMA diblock copolymer.

Since this route is not suitable for the synthesis of stars containing simultaneously PEO and PtBuMA blocks, we have used an ethylene oxide macromonomer to polymerize tBuMA last and therefore avoid transesterification of the ester groups. For the macromonomer synthesis, we used a new 1,1-diphenyl derivative, which caused an unexpected reaction that opened an easy route to model graft copolymers.

Experimental Part

Measurements. Size exclusion chromatography was carried out using a Waters 2690 liquid chromatograph equipped with three columns, Waters Styragel 5 μm, 10^4, 500 and 100 Å (columns, injection, and refractometer temperature, 35 °C; injection volume, 100 μL; solvent, THF at 1 mL/min), and a refractive index detector (Waters 410) coupled with a UV/vis photodiode array detector. Size exclusion chromatography was calibrated with PS and PEO standards.

^{1}H NMR spectra were recorded on a 250 MHz spectrometer (Bruker AC 250) using $CDCl_3$ as a solvent.

Gas chromatography was carried out using a Hewlett-Packard 5890 Series II gas chromatograph (fused silica capillary BPX5 (25 m × 150 μm); carrier gas, helium N55; constant flow pressure, 18.0 psi; injector temperature, 240 °C; temperature program, 80 °C (3 min) to 310 °C (30 min) at 3.5 °C/min) coupled with a Hewlett-Packard MSD 5971 mass spectrometer (ionization energy, 70 eV; mass range, 40−500 uma; injected volume, 1 μL; solvent cut, 5 min).

Materials. Styrene (99.5%, Fluka 85959), ethylene oxide (>99.8%, Fluka 03904), and ϵ-caprolactone (99%, Aldrich 24 129-6) were stirred over sodium, *n*-butyllithium (1.6 M in hexane, pract., Fluka 20160), and calcium hydride, respectively, and then distilled under reduced pressure just before polymerization. *tert*-Butylmethacrylate (98%, Aldrich 46 335-3) was stirred over calcium hydride, distilled, treated by a solution of triethylaluminum (0.9 M in hexane, purum, Fluka 90320), and distilled under reduced pressure just before polymerization. Tetrahydrofuran (99.5%, SDS 0700248) and toluene (>99.5%, Fluka 89681) were distilled over CuCl/NaOH, and over sodium. They were stored over sodium and benzophenone leading to violet and red colors, respectively. They were cryodistilled into the polymerization reactors just before use. L-Lactide (98%, Aldrich 36 704-4), PEO macromonomers, and functionalized "double-PS" were dried before use by dissolution in dry toluene followed by an azeotropic distillation. The last impurities in the PEO macromonomer solution in THF were neutralized by addition of *sec*-BuLi (1.3M in cyclohexane, pract., Fluka 20185) until a deep red color appears. Naphthalene (>98%, Fluka 70210), potassium (>98%, Fluka 60030), diphenylmethane (>99%, Fluka 43100), and carbon dioxide (99.8%, Aldrich 29 510-8) were used without purification. Lithium chloride (>99%, Fluka 62478), stannous octoate (95%, Sigma S-3252), and potassium tertiobutoxide (95%, Aldrich 15 667-1) were dried before use.

Syntheses. 1-(4-Hydroxymethyl)phenyl-1-phenylethylene, 1-OH. The **1-OH** derivative was synthesized in the same way as the **2-OH** derivative.[23] The only discrepancy was the use of paraformaldehyde instead of ethylene oxide. First, 1-(4-bromo)phenyl-1-phenylethylene (DPEBr, 67.2 g, 0.259 mol) was converted at 64 °C in THF (200 mL) into the Grignard derivative by reaction with magnesium turnings (6.9 g, 0.284 mol). It was reacted at 40 °C for 5 h with paraformaldehyde (15.6 g, 0.520 mol). The medium was neutralized with hydrochloric acid. The organic phase was separated, dried over magnesium sulfate, filtered, and evaporated. The **1-OH** derivative was purified by column chromatography over silica gel using cyclohexane/ethyl acetate (80/20 in volume) as an eluant. The yield after purification was 10.9 g (21%) according to DPEBr.

^{1}H NMR ($CDCl_3$ at 25 °C), δ/ppm: 7.33 (m, 9H, aromatic protons), 5.46 (s, 2H, $CH_2{=}CRR'$), 4.72 (s, 2H, $-CH_2-O-$).

1-(4-*tert*-Butyldimethylsiloxymethyl)phenyl-1-phenylethylene, 1-Si. According to the procedure described in the litterature,[23] **1-OH** (5.3 g, 0.025 mol) was reacted in *N*,*N*-DMF (100 mL) at 45 °C for 4 h with *tert*-butyldimethylsilyl chloride (4.5 g, 0.03 mol) in the presence of imidazole (5.1 g, 0.075 mol) to give **1-Si**. The crude product was washed with an aqueous solution of sodium hydrogenocarbonate and extracted with heptane. Then **1-Si** was purified by column chromatography over silica gel using diethyl ether/cyclohexane (20/80 in volume) as an eluant. The yield after purification was 6.7 g (80%) according to **1-OH**.

^{1}H NMR ($CDCl_3$ at 25 °C), δ/ppm: 7.32 (m, 9H, aromatic protons), 5.45 (d, J = 1.25 Hz, 1H, $CH_2{=}CRR'$), 5.43 (d, J = 1.25 Hz, 1H, $CH_2{=}CRR'$), 4.76 (s, 2H, $-CH_2-O-$), 0.95 (s, 9H, $(CH_3)_3C-$), 0.11 (s, 6H, $-Si(CH_3)_2-R$).

1-(4-Chloromethyl)phenyl-1-phenylethylene. 1-Cl. The synthesis of **1-Cl** was realized in the same way as the chlorination of 5-hydroxymethylbicyclo[2.2.1]hept-2-ene[24] Triphenylphosphine (131 g,0.05 mol) in CCl_4 (200 mL) was added over 1 h under nitrogen atmosphere to **1-OH** (5.3 g, 0.025 mol). The medium was reacted at 60 °C for 24 h. The solution was filtered, extracted with petroleum ether, dried over magnesium sulfate, filtered, and evaporated. Then **1-Cl** was purified by column chromatography over silica gel using diethyl ether as an eluant. The yield after purification was 5.42 g (95%) according to **1-OH**.

^{1}H NMR ($CDCl_3$ at 25 °C), δ/ppm: 7.33 (m, 9H, aromatic protons), 5.48 (s, 2H, $CH_2{=}CRR'$), 4.62 (s, 2H, $-CH_2-O-$).

Polymerizations. Synthesis of a A_2B Star: $(PS)_2$-PtBuMA. A typical anionic polymerization was carried out in a flamed glass reactor under nitrogen atmosphere. Styrene (20 g, 0.19 mol) was first cryodistilled into a vial. A few drops of the *sec*-BuLi initiator solution was added to cryodistilled THF (200 mL) at −70 °C until a slightly yellow color persisted. After the addition of the calculated amount of the initiator solution (0.96 mL, 1.25 mmol), styrene was added dropwise over a period of 15 min leading to an orange to red color due to the polystyryl formation. The solution was kept at −70 °C for 1 h. The **1-Si** derivative (210 mg, 0.625 mmol) dissolved in THF (10 mL) was added and the mixture was allowed to react for 1 h at −60 °C. Then tBuMA (2.75 g, 19 mmol) was added into the reactor at 10 °C in the presence of LiCl (265 mg, 6.25 mmol)). After 20 min, the polymerization was terminated by addition of methanol (10 mL) and the copolymer was concentrated to 50 mL and precipitated into methanol (400 mL). Precursor: $M_n = 16.2 \times 10^3$, and pdi = 1.13. Double PS: $M_n = 32.8 \times 10^3$, and pdi = 1.17. Copolymer: $M_n(\mathrm{NMR}) = 36.8 \times 10^3$, pdi = 1.2, and yield = 90%.

Macromonomer Technique. Ethylene oxide (10 g, 227 mmol) was polymerized in THF (100 mL) at 35 °C during 48 h, using potassium *tert*-butoxide (tBuOK, 20 mg, 1.79 mmol) as an initiator. The polymer was then reacted with 1.5-fold excess of **1-Cl** (0.6 g, 2.6 mmol) under reflux for 1 h, concentrated to 50 mL and precipitated in diethyl ether (300 mL). $M_n = 5.7 \times 10^3$ (PEO standard), pdi = 1.2, yield = 92%. A part of this **1-M** macromonomer (5 g, 0.87 mmol) was dried by azeotropic distillation from a toluene solution and dissolved in THF (30 mL) at room temperature. It was added at −60 °C to a solution of polystyryllithium (0.87 mmol in 200 mL) prepared as previously described (8 g of styrene, $M_n = 9.2 \times 10^3$, and pdi = 1.14). The medium was allowed to react for 1 h at −60 °C and 30 min at 10 °C. Polymerization of tBuMA (13 g, 91 mmol in order to obtain $M_{n\,\mathrm{tBuMA}} = 15\,000$) was then realized according to the procedure described in previous section. After 20 min, the polymerization was terminated by addition of methanol and the copolymer was precipitated into

Table 1. Characteristics of Copolymers Obtained from Reaction of PS Li on the PEO Macromonomer

	PS precursor			double PS	PtBuMA	$(PS)_2$PtBuMA	
expt	$M_n \times 10^{-3}$ [a]	$M_p \times 10^{-3}$ [b]	pdi	$M_p \times 10^{-3}$ [b]	block $M_n \times 10^{-3}$ [c]	$M_n \times 10^{-3}$ [c]	pdi
1	12.7	14.5	1.12	29	32.8	58.2	1.09
2	9.2	10.1	1.14	21.5	30	48.4	1.07
3	12.5	14.5	1.12	30	21.8	46.8	1.09
4	9.4	10.6	1.16	20.6	12.1	30.9	1.10

[a] Determined by SEC. [b] M peak. [c] Calculated using ^{1}H NMR analysis and M_n of the PS precursor block.

a mixture of methanol/water (80/20, v/v). Copolymer: M_n(NMR) = 48.4 × 10^3, and pdi = 1.07. PtBuMA block: $M_{n\ tBuMA}$ (NMR) = 30 × 10^3, and yield = 86%.

Functionalized "Double-PS" and Syntheses of $(PS)_2$-PLLA, $(PS)_2$PEO, and $(PS)_2$PϵCL. The double PS Li was obtained as already described from the polymerization of styrene (30 g, 0.29 mol) initiated by *sec*-BuLi (4.12 mL, 5.36 mmol) in THF (300 mL) followed by the addition of **1-Si** (0.89 g, 2.68 mmol). The medium was allowed to react for 1 h at −60 °C and divided in two parts (approximately $^1/_3$ and $^2/_3$). The first part was treated at −60 °C for 2 h with a large excess of CO_2 (2 g, 45 mmol), reacted with methanol and the polymer **3** was recovered by precipitation into a mixture of methanol/water (80/20 v/v). A large excess of EO (4 g, 90 mmol) was introduced in the second part, and the medium was kept at 30 °C for 24 h. After reaction with methanol, the functionalized polymer **4** was precipitated into a mixture of methanol/water (80/20 v/v).). Precursor: M_n = 5.6 × 10^3, and pdi = 1.15. Functionalized double PS: M_n = 12.8 × 10^3, pdi = 1.2, and total yield = 85%.

Functionalized double PS **4** (5 g, 0.45 mmol) was previously dried by azeotropic distillation from a toluene solution and dissolved in toluene (150 mL) containing stannous octoate (20 mg, 0.05 mmol). L-Lactide (10.5 g, 73 mmol) was then added ([LL]/[Sn] about 1500) ,and the polymerization was realized at 100 °C during 3 days. To eliminate the small amount of homopolylactide, the crude copolymer was redissolved in chloroform and precipitated into methanol. M_n = 28 × 10^3, pdi = 1.19, and yield = 65%.

Naphthalene (8.45 g, 66 mmol) was sublimed over potassium (2.5 g, 64 mmol) and THF (200 mL) was cryodistilled. A dark-green color rapidly developed, and the solution was reacted under nitrogen atmosphere for 24 h until complete conversion of potassium. Fifty milliliters of this initiator solution were separated into another flask in which diphenylmethane (2.7 g, 16 mmol) was added. The solution was reacted under nitrogen atmosphere for 24 h leading to a rust color. Dry functionalized polymer **4** (5 g, 0.45 mmol) was dissolved in THF (100 mL) and diphenylmethyl potassium solution (1.4 mL, 0.45 mmol) was added to generate the potassium alkoxide group. Ethylene oxide (6 g, 136 mmol) was then introduced in the medium and polymerized at 30 °C during 48 h. The copolymer was recovered by precipitation into a mixture of methanol/water (80/20 v/v). M_n = 23.3 × 10^3, pdi = 1.19, and yield = 88%.

In the same manner, ϵCL (5.5 g, 48 mmol) was added to a similar solution of active functionalized polymer **4** (5 g, 0.45 mmol). The polymerization of ϵCL was realized at room temperature and stopped short in order to avoid oligomer formation by backbiting reactions. The copolymer was precipitated into methanol. M_n = 21.8 × 10^3, pdi = 1.22, and yield = 81%.

Regular Graft Copolymer. Styrene (5 g, 48 mmol) was polymerized at −70 °C in THF (300 mL) for 1 h, using naphthalene potassium (9.4 mL, 3 mmol) as an initiator. The **1-Si** derivative (0.5 g, 1.5 mmol, [**1-Si**]/[polymer chain] = 1) was added, and this mixture was allowed to react at −60 °C for 3 h. Ethylene oxide (50 g, 1.14 mmol) was introduced into the reactor and polymerized during 3 days at 30 °C. The copolymer was precipitated into diethyl ether. Precursor: M_n = 3.3 × 10^3, and pdi = 1.11. Multi PS: M_n = 19 × 10^3, and pdi = 1.9. Graft copolymer: M_n = 190 × 10^3, pdi = 1.97, and yield = 85%.

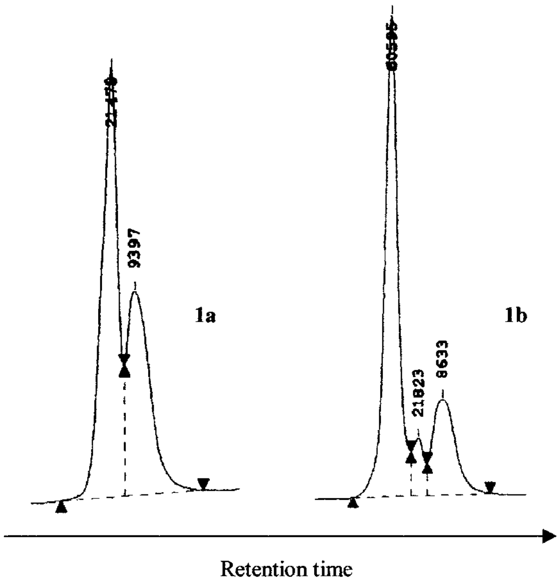


Figure 1. Size exclusion chromatography traces using the macromonomer strategy: (a) result of the reaction of a polystyryllithium on a PEO macromonomer; (b) the above followed by tBuMA polymerization. RI signals and retention time are in arbitrary units.

A similar experiment was realized using as reactants styrene (5 g; 48 mmol), naphthalene potassium (2 mL, 0.63 mmol), and **1-Si** (103 mg, 0.31 mmol), and was terminated by reaction with methanol in order to obtain the **5-H** compound. The product was precipitated into methanol, dried by azeotropic distillation, and reacted with *sec*-BuLi (0.24 mL, 0.312 mmol) in THF (100 mL) at −60 °C. Polymerization of tBuMA (2.9 g, 20.4 mmol) was then realized according to the previously described procedure. Precursor: M_n = 15.9 × 10^3, and pdi = 1.15. Multi PS: M_n = 85.2 × 10^3, and pdi = 1.93. Graft copolymer: M_n = 123 × 10^3, pdi = 2.10, and yield = 82%.

Results and Discussion

(a) Macromonomer Strategy. PEO macromonomers can be obtained by initiation by an alkoxide of a 1,1-diphenylethylene derivative or, more easily, by endcapping living PEO with a 1,1-diphenylethylene chloro derivative. Since the reaction between **2-Cl** (the chloro derivative of **2-Si**) and a living PEO mainly leads to HCl elimination instead of the expected macromonomer,[25] we synthesized a new chloro derivative **1-Cl**. As expected, the reaction between the living PEO and **1-Cl** leads to a PEO macromonomer **1-M**, with molecular weights M_n = 5700 (SEC, PEO standard) and 9200 (SEC, PS standard) and pdi = 1.2. Functionalization of the macromonomer was verified by the similar molecular weights determined by SEC and ^{1}H NMR.

The macromonomer strategy consists of 2 successive steps: (i) reaction of polystyryllithium with macromonomer **1-M** in THF at −60 °C, which is conveyed by the immediate change of the orange color of the polystyryl anion into the deep red color of a diphenylethylenyl anion; (ii) addition of tBuMA, which is conveyed by the immediate change of the deep red color into the yellow-green color of a polymethacrylate anion.

Instead of the expected PS-arm-PEO-arm-PtBuMA star, we obtained a mixture of a PS and PtBuMA based copolymer and a PEO homopolymer. The PEO block's molecular weight remained unchanged after the first step whereas that of polystyrene doubled (Table 1).

Scheme 3. Double Addition−Elimination Model Reaction

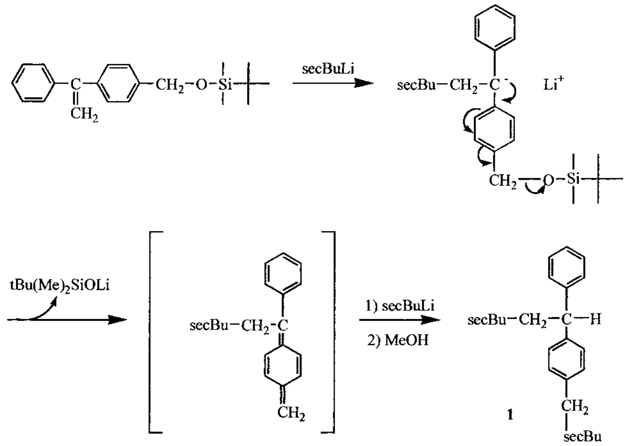


Figure 1 reports the SEC traces (RI detector) corresponding to experiment 2. Starting from a living polystyrene of M_n = 9200 (pdi = 1.14, M_p = 10 100) we obtained, after reaction with the PEO macromonomer, two peaks, one at M_p = 21 500 corresponding to the double PS and the second at M_p = 9400 (PS standard) corresponding to the PEO (Figure 1a). This agrees with the comparison between UV and RI detections. Only peak molecular weights are reported since the peaks overlap. After the second step (ii), the molecular weight increased (Figure 1b) from 21 500 to 60 500 (standard PS), corresponding to the polymerization of tBuMA to form a block copolymer as verified by ^{1}H NMR. A small amount (~7%) of double PS and the original PEO remained.

This implies that polystyryllithium added twice to the 1,1-diphenylethylene derivative **1-M**, with elimination of the PEO block followed by the tBuMA polymerization leading to a PS-*b*-PtBuMA copolymer. This unexpected reaction was probably linked to the presence of only one CH_2 between the phenyl ring and the oxygen since no reaction occurred between polystyryllithium and PEO macromonomers derived from DPE with spacers of three CH_2 [8] and two CH_2 [25] between the phenyl and the oxygen.

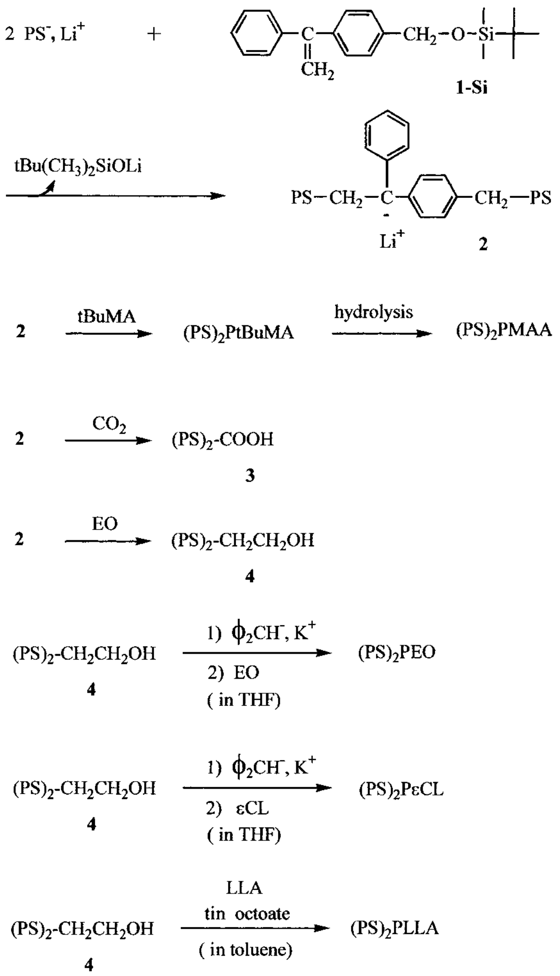
To establish the mechanism of these reactions and the structure of the final copolymer, the reaction between *sec*-BuLi and a model of the macromonomer was studied.

(b) Reaction between *sec*-BuLi and 1-Si. Silyl derivative **1-Si** is a model of the macromonomer. An excess of *sec*-BuLi was reacted with **1-Si** in THF at −60 °C leading to **1** (Scheme 3). ^{1}H NMR and gas chromatography data (four peaks of equal surface area partially resolved as **1** is a mixture of stereoisomers) coupled with a mass spectrometer (same fragmentation and maximum peak m/e = 308) were in agreement.

A mechanism of this double addition−elimination reaction was proposed (Scheme 3). After the first expected addition of *sec*-BuLi, there was a 1,6-elimination followed by a second addition on the reactional intermediate. A similar 1,6-elimination has already been reported for some para-styrene derivatives.[26] If this reaction was run with a molar ratio *sec*-BuLi/**1-Si** equal to 1, we obtained only **1** and unreacted **1-Si**, showing that only the double addition−elimination reaction has occurred.

This was only observed with para substituted derivatives containing one CH_2 between the phenyl ring and the oxygen linked to either a carbon or a silicon atom. No side reaction was reported on para-substituted 1,1-diphenylethylene derivatives with functional groups like $-(CH_2)_3-O-C$,[8] $-(CH_2)_2-O-Si$,[14,15,23] $-(CH_2)_2-O-C$[25] and $-O-C$.[27]

Scheme 4. Synthesis of Some A$_2$B Model Graft Copolymers



(c) Reaction between Polystyryllithium and 1-Si. We used this addition−elimination reaction for the synthesis of new complex architectures (Scheme 4). The reaction between polystyryllithium and **1-Si** in THF at −60 °C produced the same macrocarbanion **2** as the one obtained previously by reaction of polystyryllithium on the macromonomer **1-M**. In contrast to the previous reaction on **1-M**, reaction of the living polymer with **1-Si** proceeded without termination. This macrocarbanion **2** was able to initiate the tBuMA polymerization leading to $(PS)_2$ P(tBuMA) model graft copolymers. Characteristics of these copolymers are reported in Table 2, experiments 1−3. Molecular weights of double PS (obtained by termination of **2**) are in good agreement with the expected values. We observed a small increase of pdi between precursor and double PS. Molecular weights of tBuMA blocks, calculated using ^{1}H NMR correspond to the expected values.

The tBuMA block was hydrolyzed either by *p*-toluenesulfonic or trifluoroacetic acids, respectively, in toluene and chloroform. Quantitative hydrolysis was followed by IR analysis using the shift of the carbonyl band (1724 cm^{-1} for tBu ester to 1702 cm^{-1} for acid). The resulting $(PS)_2$PMMA star copolymers are amphiphilic and form micelles both in water and in

Table 2. Characteristics of A_2B Model Graft Copolymers

	PS precursor		double PS		B block	A_2B $(PS)_2PtBuMA$	
expt	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,b}$ PtBuMA	$M_n \times 10^{-3}$	pdi
1	16.2	1.13	32.8	1.17	4.4	36.8	1.20
2	15.8	1.13	32.1	1.18	59.9	91.5	1.10
3	5	1.20	11.4	1.23	7	17	1.19

	PS precursor		double PS		B block	A_2B $(PS)_2PMAA$	
expt	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,b}$ PMAA	$M_n \times 10^{-3}$	pdi
1 H	16.2	1.13	32.8	1.17	2.7^c	35.1^c	
3 H	5	1.20	11.4	1.23	4.2^c	14.2^c	

	PS precursor		double PS		B block	A_2B $(PS)_2PLLA$	
expt	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,b}$ PLLA	$M_n \times 10^{-3}$	pdi
4	5.6	1.15	12.8	1.20	16.8	28	1.19

	PS precursor		double PS		B block	A_2B $(PS)_2P\epsilon CL$	
expt	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,b}$ ϵCL	$M_n \times 10^{-3}$	pdi
5	5.6	1.15	12.8	1.20	10.6	21.8	1.22

	PS precursor		double PS		B block	A_2B $(PS)_2PEO$	
expt	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,a}$	pdi	$M_n \times 10^{-3\,b}$ PEO	$M_n \times 10^{-3}$	pdi
6	5.6	1.15	12.8	1.20	12.1	23.3	1.19

[a] Determined by SEC. [b] Calculated using ^1H NMR analysis and M_n of the PS precursor blocks. [c] Calculated values assuming a complete hydrolysis.

chloroform. Studies on their micellization behavior are in progress.

Functionalization of PS was achieved by reaction of **2** with CO_2 (THF at −60 °C) and ethylene oxide (THF at 30 °C) leading to carboxylic (**3**) or hydroxy (**4**) function located at the middle of the PS chain. To confirm the hydroxy functionalization, polymerizations of ethylene oxide and ϵ-caprolactone were initiated by the potassium alkoxide of **4** (Table 2, experiments 5 and 6). This is not the best route to synthesize $(PS)_2$ PEO and $(PS)_2$ PϵCL since the macrocarbanion **2** with potassium as counterion can initiate directly their polymerizations without the functionalization and activation steps. The intermediate functionalization can be used to synthesize a range of A_2B copolymers having exactly the same polyA blocks and in the polymerization of L-lactide initiated by a tin alkoxide, leading to $(PS)_2$ PLLA copolymers (Scheme 4 and Table 2, experiment 4).

(d) Reaction between Difunctional Polystyrylpotassium and 1-Si. This reaction of addition−elimination on **1-Si** does not depend on the nature of the counterion since it was also observed with potassium. As **1-Si** acts as difunctional compound, reaction with difunctional polystyrylpotassium can lead to a PS chain containing regularly spaced anions, giving access to regular graft copolymers. This strategy is summarized in Scheme 5.

Scheme 5. Synthesis of Regular Graft Copolymers

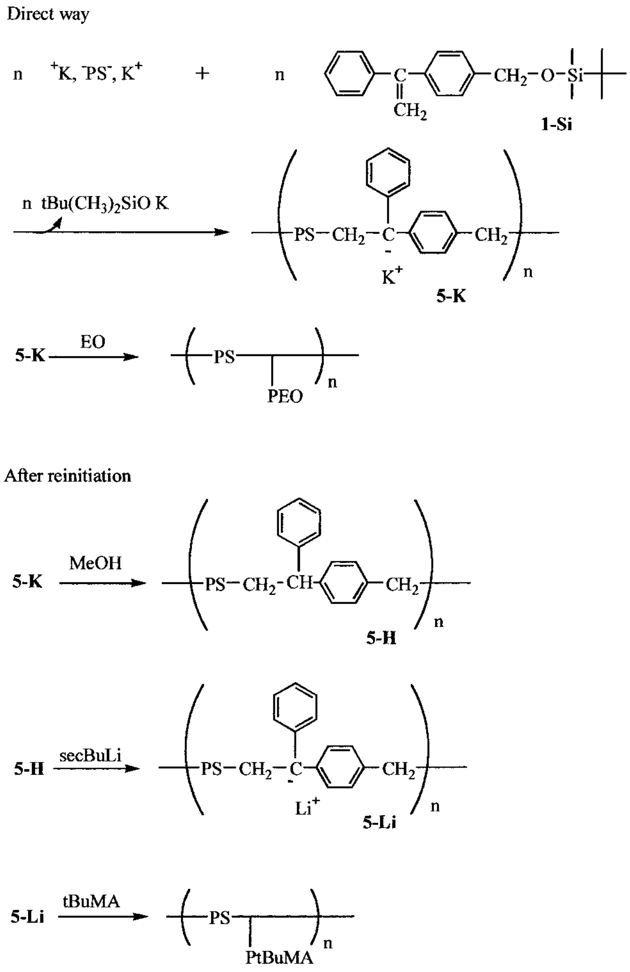


Table 3. Study of the Reaction between a Difunctional Polystyryl K and 1-Si

time (h)	$M_n \times 10^{-3\,a}$	pdi	color
0	15.9	1.15	orange
1.5	65	1.70	deep red
3.5	85.7	1.88	deep red
7	85.2	1.93	deep red

[a] Determined by SEC.

First, we studied this reaction in THF at −60 °C as a function of time (Table 3). After 3 h, the molecular weight seems to reach a plateau and the final pdi ~ 2, which is consistent with a step polymerization. Assuming a molecular weight of 16 000 (15 900 for PS block plus diphenylethylene) for the repeating unit, the degree of polymerization *n* is about 5.

This particular step polymerization leads to polystyryl end groups since the two reactive sites of **1-Si** always react through a concerted double addition, whatever the initial excess of **1-Si** or $K^{+-}PS^{-+}K$. As stoichiometry would not affect the nature of end groups, the low value of *n* mainly seems linked to termination of the living polystyrene.

In a second set of experiments, EO was added to the polyanion **5-K** after a 3 h reaction (in THF, at −60 °C) (Scheme 5) leading to the graft copolymer. The significant increase in the molecular weight (with practically the same pdi) and complete solubility in a mixture of methanol/water (80/20 v/v) showed that the copolymer is free of polystyrene homopolymer. Characteristics are given in Table 4. Assuming there is one graft per repeating unit of PS, this leads to a molecular weight about 30 000 for each PEO graft.

After termination of the polyanion **5-K** (Scheme 5), we obtained polystyrene **5-H** with 1,1-diphenylethylene

Table 4. Synthesis and Characteristics of Regular Graft Copolymers

	PS precursor		multi PS		graft copolymer				
expt	$M_n \times 10^{-3}$ [a]	pdi	$M_n \times 10^{-3}$ [a]	pdi	strategy[b]	counter ion	second monomer	$M_n \times 10^{-3}$ [c]	pdi[d]
1	3.3	1.11	19	1.90	direct	K^+	EO	190	1.97
2	15.9	1.15	85.2	1.93	reinitiation	Li^+	tBuMA	123	2.10

[a] Determined by SEC. [b] See Scheme 5. [c] Calculated using ^{1}H NMR analysis and M_n of the multi PS determined by SEC. [d] Estimated from SEC.

units regularly spaced along the main chain. Reaction between **5-H** and *sec*-BuLi (in THF at −60 °C, with a slight excess of **5-H** in order to avoid unreacted *sec*-BuLi) produced an instantaneous deep red color and **5-Li**. Derivative **5-Li** initiated the tBuMA polymerization, leading to a graft copolymer. Characteristics are given in Table 4. Using this strategy, we are not sure if all of the potential carbanions are generated to obtain one graft per unit. Assuming quantitative reinitiation, the molecular weight of each PtBuMA graft should be about 8000.

Conclusion

Mono- or difunctional polystyryl carbanion undergoes an unexpected and interesting double addition−elimination reaction on a new 1,1-diphenylethylenyl derivative **1-Si** (bearing one CH_2 between the phenyl ring and the oxygen). The proposed mechanism involves, after the first expected addition of PSLi on the double bond of the diphenylethylene derivative, a 1−6 elimination of the silanolate group allowing a second addition of PSLi. This reaction occurs with a polystyryl carbanion having either a lithium or a potassium counterion.

When a monofunctional polystyryl carbanion is used, this double addition−elimination reaction on **1-Si** leads, after polymerization of a second monomer, to A_2B model graft copolymers. This strategy allows easy and quantitative synthesis of well-defined A_2B copolymers such as $(PS)_2$ PtBuMA model graft copolymers.

An intermediate functionalization of the polymer (resulting from the double addition−elimination reaction) achieved by addition of ethylene oxide permits the ring-opening polymerization of EO, ϵ-caprolactone (with potassium alkoxide) or L-lactide (with tin alkoxide) leading to $(PS)_2$ PEO, $(PS)_2$ PϵCL, and $(PS)_2$ PLLA model graft copolymers.

When a difunctional polystyryl carbanion is used, this double addition−elimination reaction on **1-Si** leads to (A-*g*-B)$_n$ graft copolymers in which the grafting points (of the A sequence) are regularly spaced and the B grafts have presumably the same length. This is achieved by polymerizing the second monomer either directly on an intermediate polystyrene multianion (pdi ~ 2) produced by a step polymerization, or after reactivation of the grafting sites. (PS-*g*-PEO)$_n$ and (PS-*g*-PtBuMA)$_n$ were synthesized by this route.

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