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A common route to A_2B and A_3B multiarm star block copolymers

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Abstract

We have previously described a new route to A_2B star block copolymers by a double addition–elimination reaction of a polystyryl carbanion with a particular 1,1-diphenylethylene derivative. By using the same reagent, we are now able to prepare A_2 or A_3 homopolymers by changing the solvent, i.e. tetrahydrofuran or toluene/tetrahydrofuran, respectively. We propose a mechanism involving nucleophilic substitution reactions to explain this peculiar result and use this opportunity to prepare A_2B or A_3B star block copolymers based on styrene and ethylene oxide or *tert*-butyl methacrylate. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Star block copolymer; 1,1-Diphenylethylene chemistry; Nucleophilic substitution

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1. Introduction

At present, the only strategy leading to A_2B and A_3B type star block copolymers is the selective step-by-step coupling reaction on trichlorosilane or tetrachlorosilane. A_2B [1–4] and A_3B [5] were so obtained. Besides these coupling reactions, the other main access to star block copolymers with complex and well-defined architectures uses the chemistry of 1,1-diphenylethylene derivatives [6–8]. Recently, we have reported an unexpected reaction on a 1,1-diphenylethylene derivative, which opens an easy way to A_2B star block copolymers [9]. This reaction (Scheme 1a) occurs in a polar medium such as THF with potassium or lithium as counterion. A mechanism of double addition–elimination was proposed for the reaction of polystyryl carbanion on the 1,1-diphenylethylene derivative **1**-Si. After the first expected addition of polystyryl carbanion on the double bond of **1**-Si, a 1,6 elimination occurs, followed by a second addition on the intermediary to form a 1,1-diphenylethynyl carbanion bearing two PS chains. This carbanion is able to initiate the polymerization of a second monomer leading to A_2B star block copolymer.

In this paper, we described the influence of the medium composition on this previous reaction and consequently, the ability to obtain with the same reagent either A_2B or A_3B star block copolymers.

2. Experimental part

2.1. Measurements

Size exclusion chromatography was carried out using a Waters 2690 liquid chromatograph equipped with 3 Waters Styragel 5 μm columns, 10^4, 500 and 100 Å (columns, injection and refractometer temperature: 35 °C; injection volume: 100 μl; solvent: THF at 1 ml/min), a refractive index detector (Waters 410) coupled with a UV/vis photodiode array detector and a three angle laser light scattering detector with a laser source operating at 633 nm (Minidawn, Wyatt technology). Size exclusion chromatography was calibrated with PS standards.

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

2.2. Materials

Styrene (99.5%, Fluka 85959) and ethylene oxide (>99.8%, Fluka 03904) were stirred over sodium, *n*-butyllithium (1.6 M in hexane, pract., Fluka 20160), respectively, and then distilled under reduced pressure just before polymerization. *tert*-Butyl methacrylate (98%, Aldrich 46,335-3) was stirred over calcium hydride, distilled, treated by a solution of triethylaluminium (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 then over

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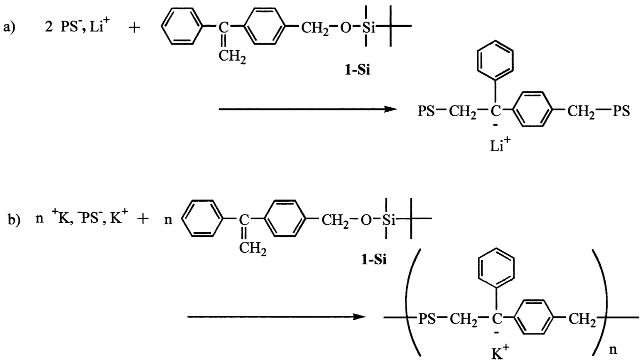
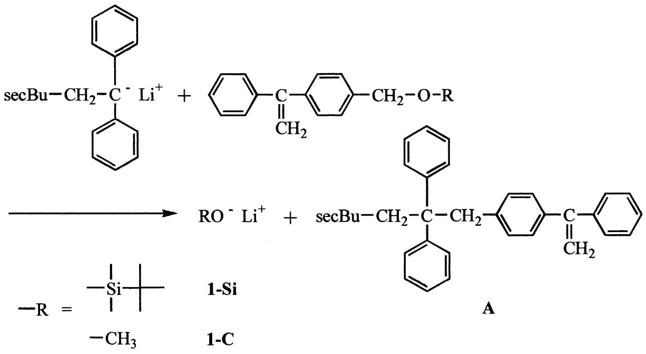


Scheme 1. Reactions of polystyryl carbanion with **1**-Si in THF medium.



Scheme 2. Nucleophilic substitution run with 1,1-diphenylhexyllithium on 1,1-diphenylethylene derivative.

sodium. They were stored over sodium and benzophenone and cryodistilled into the polymerization reactors just before use. Naphthalene (>98%, Fluka 70210), potassium (>98%, Fluka 60030), *sec*-BuLi (1.3 M in cyclohexane, Fluka 20185), phosphazene base *t*BuP$_4$ (1 M in hexane, Fluka 79421), 4-bromobenzyl alcohol (99%, Acros 18177), DMSO (99.5%, SDS 0350221), KHSO$_4$ (98%, Fluka 60363), KOH (85%, Fluka 60375) and CH$_3$I (99%, Aldrich I-850-7) were used without purification. Lithium chloride (>99%, Fluka 62478), DPE (~97%, Fluka 42740) and DPE derivatives (**1**-Si and **1**-C) were dried under reduced pressure just before use. Acetophenone (98%, Fluka 00800) was distilled under vacuum and stored on molecular sieves (4 Å). Magnesium (99.8%, Fluka 63035) was dried under vacuum at 60 °C during 2 h.

2.3. Synthesis

2.3.1. 1-(4-tert-Butyldimethylsiloxymethyl)phenyl-1-phenylethylene, 1-Si

1-Si was synthesized according to the procedure described earlier [9].

2.3.2. 1-(4-Methoxymethyl)phenyl-1-phenylethylene, 1-C

The synthesis of **1**-C was realized in the same way as **1**-Si. In the first step, 4-bromobenzyl alcohol (11 g, 59 mmol) was converted into 1-bromo-4-(methoxymethyl)benzene by reaction with CH$_3$I (16.7 g, 117 mmol) and KOH (13.2 g, 235 mmol) in DMSO (100 ml) at 25 °C during 3 h. The product was poured in water, extracted with CH$_2$Cl$_2$, dried over MgSO$_4$ and evaporated. After addition of Mg (1.4 g, 58.5 mmol) in THF (50 ml), this product (10.7 g, 53.2 mmol) was reacted slowly with acetophenone (5.8 ml, 49.5 mmol) in dry THF (50 ml) during 2 h. The solution was neutralized with HCl, extracted with diethyl ether, dried over MgSO$_4$ then under vacuum. The dehydration was realized at 160 °C during 2 h in presence of KHSO$_4$ (0.64 g, 4.7 mmol). After purification by flash chromatography (petroleum ether/toluene 95/5; $R_f = 0.3$), 6.69 g (29.8 mmol) of viscous and pale yellow liquid was obtained.

^{1}H NMR (CDCl$_3$ at 25 °C), δ (ppm): 7.42–7.25 (m, 9H, aromatic protons), 5.47 (s, 2H, =CH$_2$), 4.48 (s, 2H, –CH$_2$O–), 3.42 (s, 3H, –OCH$_3$).

2.3.3. Model reactions for nucleophilic substitution

1,1-Diphenylethylene (0.1 ml, 0.57 mmol) was dissolved in toluene (54 ml) at −50 °C. A few drops of *sec*-BuLi was first added until a slightly red color persisted. After the addition of *sec*-BuLi (0.44 ml, 0.57 mmol), the medium turned to dark red and **1**-Si (166 mg, 0.51 mmol) in THF (6 ml) was introduced. After 1 h, the medium was treated with methanol and evaporated. The crude products were separated by flash chromatography (CH$_2$Cl$_2$/diethyl ether 9/1; $R_f = 0.4$ and 0.1). The main fraction was analyzed by ^{1}H NMR and corresponded to the expected substitution product (Scheme 2).

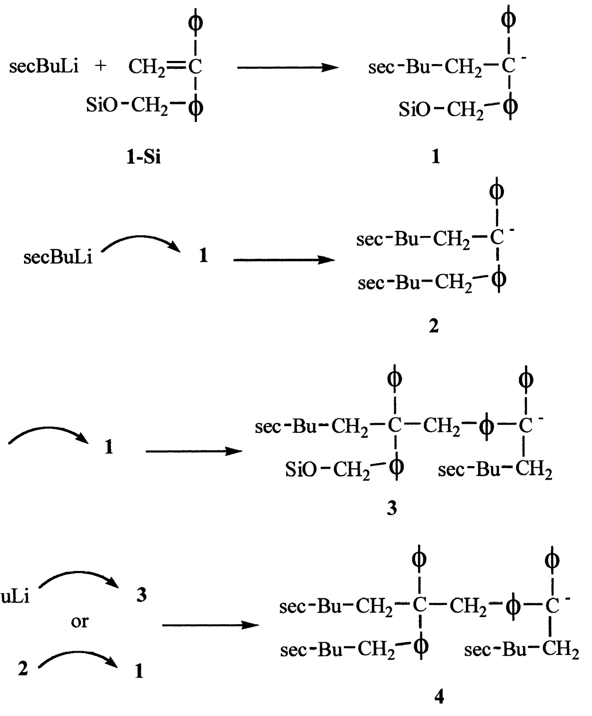
^{1}H NMR (CDCl$_3$ at 25 °C), δ (ppm): 7.30–7.17 (m, 15H, aromatic protons), 7.01 (d, $J = 7.3$ Hz, 2H, aromatic protons), 6.45 (d, $J = 8.2$ Hz, 2H, aromatic protons), 5.38 (d, $J = 14.3$ Hz, 2H, =CH$_2$), 3.47 (s, 2H, C$_6$H$_4$–CH_2–C), 1.98 (dd, $J = 14.0$, 4.3 Hz, 1H, CH–CH_2–C), 1.81 (dd, $J = 14.0$, 6.0 Hz, 1H, CH–CH_2–C), 1.54 (m, 1H, CH), 0.89 (m, 2H, CH_3–CH$_2$–CH), 0.69 (t, $J = 7.3$ Hz, 3H, CH_3–CH$_2$), 0.46 (d, $J = 6.7$ Hz, 3H, CH_3–CH).

The second fraction (a few %) corresponded to the slight excess of 1,1-diphenylhexyllithium. The yield of substitution reaction was about 100%.

The reactions with **1**-C and ϕCH$_2$OCH$_3$ were based on the same procedure (Scheme 2).

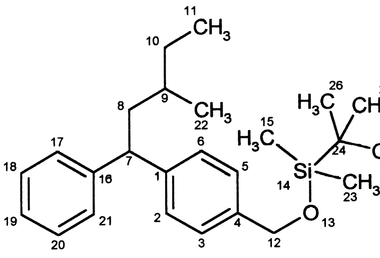
2.3.4. Reaction between sec-butyllithium and 1-Si

sec-BuLi (0.70 ml, 0.90 mmol) was first added to toluene (55 ml) at −50 °C. **1**-Si (195 mg, 0.60 mmol) in THF (7.50 ml) was then introduced (Scheme 3). The medium turned to red and the reaction was stopped after 4 min with methanol. The crude products were separated by flash chromatography (petroleum ether/toluene 95/5; $R_f = 0.8$ and 0.45). We obtained two fractions, each containing two products.



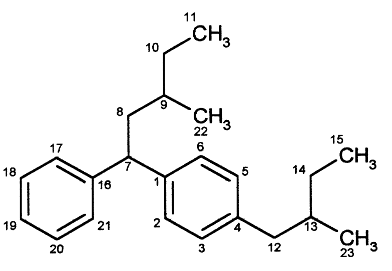
Scheme 3. Mechanism of reaction of *sec*-BuLi with **1**-Si in toluene/THF medium.

First fraction: Product 1



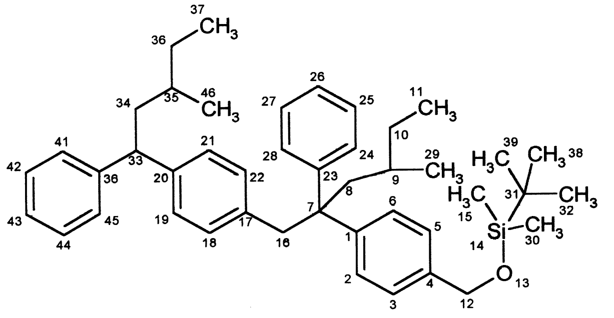
^{1}H NMR (CDCl$_3$ at 25 °C), δ (ppm): 7.34–7.26 (m, 5H, **17**–**21**), 7.18 (d, $J = 7.9$ Hz, 2H, **6**, **2**), 7.08 (d, $J = 7.9$ Hz, 2H, **5**, **3**), 4.79 (s, 2H, **12**), 4.04 (t, $J = 7.6$ Hz, 1H, **7**), 2.20–2.05 and 1.71–1.87 (m, 2H, **8**), 1.42–1.12 (m, 3H, **9** and **10**), 0.99–0.85 (m, 15H, **11**, **22**, **25**–**27**), 0.15 (s, 6H, **15**, **23**).

First fraction: Product 2



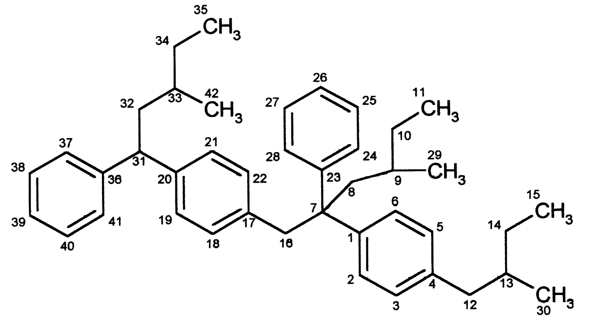
^{1}H NMR (CDCl$_3$ at 25 °C), δ (ppm): 7.34–7.26 (m, 5H, **17**–**21**), 7.18 (d, $J = 7.9$ Hz, 2H, **6**, **2**), 7.08 (d, $J = 7.9$ Hz, 2H, **5**, **3**), 4.04 (t, $J = 7.6$ Hz, 1H, **7**), 2.64–2.56 and 2.38–2.30 (m, 2H, **12**), 2.20–2.05 and 1.71–1.87 (m, 2H, **8**), 1.68–1.52 (m, 1H, **13**), 1.42–1.12 (m, 5H, **9**, **10**, **14**), 0.99–0.85 (m, 12H, **11**, **15**, **22**, **23**).

Second fraction: Product 3



^{1}H NMR (CDCl$_3$ at 25 °C), δ (ppm): 7.35–7.18 (m, 10H, **24**–**28**, **41**–**45**), 7.02–6.94 (m, 4H, **2**, **3**, **5**, **6**), 6.87 (d, $J = 7.9$ Hz, 2H, **19**, **21**), 6.41 (d, $J = 7.9$ Hz, 2H, **18**, **22**), 4.76 (s, 2H, **12**), 3.91 (t, $J = 7.0$ Hz, 1H, **33**), 3.36 (s, 2H, **16**), 2.02–1.55 (m, 4H, **8**, **34**), 1.50–1.06 (m, 6H, **9**, **10**, **35**, **36**), 0.92–0.79 (m, 15H, **32**, **37**–**39**, **46**), 0.67 (t, $J = 6.7$ Hz, 3H, **11**), 0.46 (t, $J = 6.7$ Hz, 3H, **29**), 0.11 (s, 6H, **15**, **30**).

Second fraction: Product 4



^{1}H NMR (CDCl$_3$ at 25 °C), δ (ppm): 7.35–7.18 (m, 10H, **24**–**28**, **37**–**41**), 7.02–6.94 (m, 4H, **2**, **3**, **5**, **6**), 6.87 (d, $J = 7.9$ Hz, 2H, **19**, **21**), 6.41 (d, $J = 7.9$ Hz, 2H, **18**, **22**), 3.91 (t, $J = 7$ Hz, 1H, **31**), 3.36 (s, 2H, **16**), 2.62–2.51 and 2.39–2.26 (m, 2H, **12**), 2.03–1.03 (m, 11H, **8**–**10**, **13**, **14**, **32**–**34**), 0.92–0.79 (m, 12H, **15**, **30**, **35**, **42**), 0.67 (t, $J = 6.5$ Hz, 3H, **11**), 0.46 (t, $J = 6.7$ Hz, 3H, **29**).

2.4. Polymerizations

2.4.1. Synthesis of a multiPS, CD7

A typical anionic polymerization was carried out in a flamed glass reactor under nitrogen atmosphere. *sec*-BuLi (0.50 ml, 0.65 mmol) was first added to cryodistilled toluene (100 ml) at 0 °C. The addition of styrene (9.75 g, 93.8 mmol) led to an orange to red color of the medium. The reaction was run 30 min at 0 °C and 45 min at 30 °C. The **1**-Si derivative (104 mg, 0.32 mmol) in THF (20 ml) was added at − 50 °C and the mixture was allowed to react during 2 h. The polymerization was terminated by addition of methanol; the polymer was concentrated and precipitated into methanol. Precursor: $M_n = 13\ 300$, pdi = 1.07; multiPS: SEC—$M_p = 15\ 800$ and 44 000 (pdi = 1.1), LS—$M_n = 15\ 500$ and 46 100; yield = 90%.

2.4.2. Synthesis of a PS_3PEO, CE76

The previous procedure was used to polymerize styrene (5 g, 0.048 mol) in toluene (100 ml), using *sec*-BuLi (0.37 ml, 0.48 mmol) as an initiator. **1**-Si (104 mg, 0.32 mmol) in THF (10 ml) was added to the polystyryl carbanion. After 2 h, phosphazene base *t*BuP$_4$ (0.53 ml, 0.53 mmol) was introduced in the reactor just before ethylene oxide (25 g, 0.57 mol). Polymerization was run at 35 °C during 48 h and terminated by addition of methanol. Precursor: $M_n = 10\ 300$, pdi = 1.17; multiPS: SEC—$M_n = 33\ 400$, pdi = 1.2, LS—$M_n = 35\ 200$; copolymer: SEC—$M_n = 61\ 500$, pdi = 1.4, LS—$M_n = 200\ 000$; yield = 82%.

3. Results and discussion

3.1. Reaction of PSLi and **1**-Si in an apolar solvent

We re-examined the reaction of PSLi on **1**-Si in an apolar solvent such as toluene. In order to obtain a quick addition of 1,1-diphenylethylene derivative on the PSLi, we used a small amount of THF so that the toluene/THF ratio was between 10/1 and 5/1 (v/v). The reaction was run at − 50 °C with PSLi/**1**-Si = 2. We observed an instantaneous deep red color, characteristic of the 1,1-diphenylethylenyl carbanion. Results are given in Table 1 and SEC trace is reported in Fig. 1. Instead of the expected double addition, we observed a threefold increase of the molecular weight with a slight increase of pdi and the presence of a great amount of PS precursor. As the precursor and the multiPS are of same nature, we evaluated their weight percent: 20% and 80%, respectively. These results will be fulfilled with the later proposed mechanism which involves a stoichiometry PSLi/**1**-Si = 1.5. Starting from a ratio PSLi/**1**-Si = 2, this implies a PS residual amount of 25%.

Table 1
Reaction between PSLi and **1**-Si in toluene/THF (5/1, v/v) at − 50 °C

Experiment	PS precursor, SEC			MultiPS			
				SEC			LS, M_n
	M_n	M_p	pdi	M_p	%w	pdi	
CD7	13 300	14 200	1.07	15 800 44 000	~20 ~80	~1.1	15 500 46 100

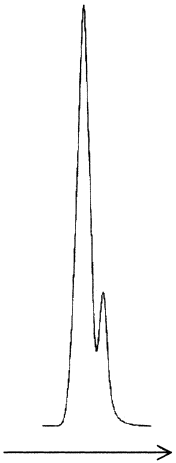


Fig. 1. SEC trace of multiPS obtained by reaction between PSLi and **1**-Si in toluene/THF medium. RI signals and retention time are in arbitrary units.

We have also previously reported the reaction of **1**-Si with a difunctional polystyryl potassium in THF. Since **1**-Si acts globally as a difunctional compound, this reaction lead to a PS chain containing regularly spaced anions, and gave access to regular graft copolymers [9] (Scheme 1b). When the same reaction was run in toluene, we obtained a gel which was insoluble in PS solvents. As polystyryl potassium is always difunctional, it means that, in toluene, **1**-Si behaves at least as a trifunctional compound.

The threefold increase of molecular weight with a monofunctional carbanion and the gel formation with a difunctional carbanion clearly show that the mechanisms are different in toluene and in THF.

The reactions of three carbanions on a single **1**-Si molecule being impossible, two **1**-Si molecules must be implied in a series of reactions. The only hypothesis is a nucleophilic substitution (NS) on the benzylic CH$_2$ involving a 1,1-diphenylethylenyl carbanion. Such hypothesis was put forward by Hirao et al. [10] in order to explain the obtention of dimer, trimer and oligomers in the end capping of PSLi by a 1,1-diphenylethylene derivative bearing two CH_2OCH_3 groups in *meta* position.

To our knowledge, such NS on a benzylic ether or siloxy derivative was never described, so that we checked this hypothesis by running the reaction between **1**-Si and a 1,1-diphenylethylenyl carbanion.

3.2. Model reactions for nucleophilic substitution

Two 1,1 diphenylethylene derivatives (**1**-Si and **1**-C) were used. 1,1-Diphenylhexyllithium was chosen in order to avoid addition reaction on the double bond of these products. Reactions were run at − 50 °C during 1 h. After desactivation, the purified products were analyzed by ^{1}H NMR. The results reported in Table 2 showed that the reactions with **1**-Si and **1**-C in toluene/THF mixture led to the total disappearance of siloxy

Table 2
Nucleophilic substitution run with 1,1-diphenylhexyllithium

Compound	Solvent	Yield for NS (%)[a]
1-Si	Toluene/THF (10/1)	100
1-C	Toluene/THF (10/1)	100
	THF	85
ϕCH_2OCH_3	Toluene/THF (10/1)	0

[a] Determined by ^1H NMR.

and methoxy groups and the quantitative obtention of the same compound A (Scheme 2). The reaction with **1**-C was more slow in THF than in toluene/THF mixture. The nucleophilic substitution of the siloxy and the methoxy groups occurred, probably due to the delocalization of π electrons between the phenyl groups and the double bond, since no reaction has taken place with ϕCH_2OCH_3 in the same conditions.

In order to propose a mechanism for reaction of PSLi on **1**-Si in an apolar medium, we have run a second series of model reactions.

3.3. Reaction between sec-butyllithium and **1**-Si

Reaction was run in the same toluene/THF mixture at −50 °C during 4 min in order to obtain all the intermediate products. After desactivation and fractionation, the ^1H NMR analysis showed four compounds which were clearly identified (Scheme 3).

The absence of compound with the double bond and siloxy group indicated that the addition reaction of *sec*-BuLi was faster than the nucleophilic substitution. The series of reaction starts with the addition of *sec*-BuLi on the double bond (compound **1**). The NS of a second *sec*-BuLi on the siloxy group of **1** leads to compound **2**. Compound **3** is the reaction product of **1** with itself and compound **4** is obtained by the reaction of either **2** with **1** or *sec*-BuLi with **3**. Compounds **2** and **4**, which contain the 1,1-diphenylethylene derivative and two or three *sec*-Bu groups, respectively, are the models for multiPS of A_2 and A_3 type. More complex compounds obtained from **3** by NS are able to be formed, but were not detectable by ^1H NMR analysis.

The identification of the different signals of the ^1H NMR analysis was unambiguous but the quantification of the corresponding integration was difficult. Nevertheless, it appeared that **1** and **3** were present in very small amount (a few %) besides **2** and **4**. The similar amount of **2** and **4**, which are the models of double and triple addition of PS, was surprising since the triple molecular weight was preponderant in the SEC trace of experiment CD7 (Fig. 1). Very slight increase of pdi from 1.07 (PS precursor) to 1.1 (multiPS) indicated that double addition could be present but in a very small quantity.

Table 3
Structure of multiPS obtained with **1**-Si in different medium compositions at −50 °C

Experiment	THF/toluene (v/v)	MultiPS structure
CE76	10/90	Triple
CD7	20/80	Triple
CE74	30/70	Double
Ref. [9]	100/0	Double

3.4. Solvent effect

Different medium compositions have been used and the results are summarized in Table 3. It clearly appeared that the change in multiPS structure occurred in the range 20–30% of THF in the mixture. This can be homologous to the functionalization reaction of PSLi with CO_2 [11]. In this case, the content of THF in the medium must also be higher than 25% in order to obtain a single and clear functionalization reaction. As in our case, it appeared that the THF content was critical to obtain only one type of reaction.

In THF, organo Li compounds exist generally as ion pairs, tight or loose (also called solvent separated) and as free ions [12,13]. In aromatic or aliphatic solvent, PSLi compounds, present as associated ion pairs, are totally disassociated into tight ion pairs by adding a small amount of THF (THF/Li up to 20) [14]. Moreover, in benzene/THF medium, loose ion pairs (large increase of $k_{app\pm}$) appear at a THF molar content of about 20%, and free ions at a content $\geq 50\%$ [15]. As the change of multiPS structure occurred in our case between 25 and 40%, it seems that the nature of ion pairs influences directly this change.

As a consequence, tight ion pairs would lead to addition and NS, and loose ion pairs only to addition.

3.5. Mechanism

As previously seen, there was a discrepancy between the similar amounts of compounds **2** and **4** (models of A_2 and A_3) by using *sec*-BuLi and the only A_3 type observed in the case of polymers. The model using *sec*-BuLi is just a qualitative one for polymers. This limitation is probably due to the nucleophilic character of polystyryl carbanion which is higher than the *sec*-butyl one, and perhaps to the difference of steric hindrance of these carbanions.

The proposed mechanism for polymers in toluene/THF medium involves two intermediate products corresponding to addition and double addition with **1**-Si and the final structure of multiPS. Different products will be noted like $\mathbf{1}^{PS}$, for example, by analogy of **1** in case of *sec*-BuLi (Scheme 3). The first reaction involves the classical addition of polystyryl carbanion on the double bond of **1**-Si. To obtain final structure ($\mathbf{4}^{PS}$), two possibilities for the NS can

Table 4
Characteristics of star block copolymers

Experiment			CE58	CE76	CE60
Counterion			K[a]	Li[b]	Li[b]
Solvent (v/v)			THF	Toluene/THF (10/1)	Toluene/THF (10/1)
Second monomer			EO	EO[c]	tBuMA[d]
PS precursor	SEC	M_n	11 200	10 300	7600
		M_p	13 600	13 900	8800
		pdi	1.14	1.17	1.11
MultiPS	SEC	M_n	22 000	33 400	20 800
		M_p	27 400	39 100	21 400
		pdi	1.25	1.20	1.26
	LS	M_n	24 200	35 200	23 800
Structure			PS_2PEO	PS_3PEO	$PS_3PtBuMA$
Star block copolymers	SEC	M_n	40 200	61 500	52 100
		M_p	53 400	70 800	63 500
		pdi	1.28	1.40	1.34
	LS	M_n	70 200	200 000	–[e]
		M_n[f]	$(11\,200)_2$, (38 700)	$(10\,300)_3$, (141 000)	$(7600)_3$, (43 100)

[a] Initiator = phenyl isopropyl potassium.

[b] Initiator = *sec*-BuLi.

[c] Addition of tBuP$_4$ before EO polymerization (40 °C/48 h) with tBuP$_4$]/[carbanion] = 1.1.

[d] Addition of LiCl for tBuMA polymerization (0 °C/30 min) with [LiCl]/[carbanion] = 5.

[e] The results of d*n*/d*c* measurements cannot be correlated.

[f] Determined by both ^{1}H NMR and SEC analysis.

be considered:

(i) substitution of polystyryl carbanion on $\mathbf{1}^{PS}$ leading to $\mathbf{2}^{PS}$ as intermediate and substitution of $\mathbf{2}^{PS}$ on $\mathbf{1}^{PS}$;
(ii) substitution of $\mathbf{1}^{PS}$ on $\mathbf{1}^{PS}$ leading to $\mathbf{3}^{PS}$ as intermediate and substitution of polystyryl carbanion on $\mathbf{3}^{PS}$.

(i) This possibility is not very probable because polystyryl carbanion would be regarded as more nucleophilic than diphenylethylenyl carbanion for NS. Moreover, the CD7 experiment with an excess of polystyryl carbanion should lead to a mixture of A_2 and A_3 structures, which was not the case.(ii) In this case, the nucleophilic character between polystyryl carbanion and diphenylethylenyl carbanion is respected. It seems also reasonable that the so formed compound $\mathbf{3}^{PS}$ cannot react on itself because of steric hindrance.

As a consequence, the (ii) possibility seems the more probable one.

The decrease of the NS rate, pointed out in THF, is not sufficient to explain the difference in results. Indeed, if the mechanism was independent of the medium, and as the substitution reaction was slower in THF than in mixtures, we should obtain two structures (A_2 and A_3). In THF, the proposed mechanism is not realistic and the reaction occurs, as previously described [9], according to an addition–elimination followed by an addition.

3.6. Synthesis of star block copolymers

In all cases, the final product was a 1,1 diphenylethylenyl carbanion, both in mixtures toluene/THF (A_3 carbanion) as well in THF (A_2 carbanion). By using **1**-Si and by changing the solvent, the active carbanion (bearing 2 or 3 PS chains) was able to initiate the polymerization of a second monomer (EO or tBuMA), leading to A_2B or A_3B star block copolymers.

Three experiments were realized. To avoid residual PS,

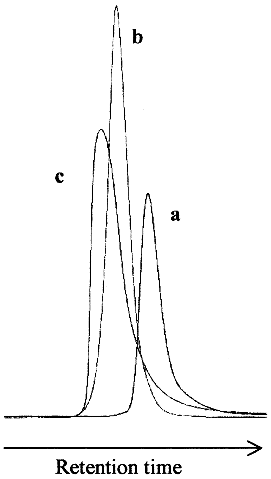


Fig. 2. SEC traces of polymers in the synthesis of PS_3PEO star block copolymer. (a) PS precursor; (b) triple PS; (c) PS_3PEO copolymer. RI signals and retention time are in arbitrary units.

CE58 experiment with EO in THF and K as counterion was run with carbanion/**1**-Si = 2/1; this ratio was 3/2 for CE76 and CE60 experiments, where EO and *t*BuMA were polymerized in toluene/THF with Li as counterion. For experiment CE76, phosphazene base *t*BuP_4 [16] was added just before EO to active its polymerization.

The results are summarized in Table 4. As expected, the structure of the multiPS was A_2 type in THF and A_3 type in mixture toluene/THF. The carbanion/**1**-Si being chosen from the proposed mechanism, the SEC traces (Fig. 2) effectively showed that the star block copolymers were free of precursor. The pdi increased slightly after the polymerization of the second monomer, probably due to the use of phosphazene for EO and LiCl for *t*BuMA. The molecular weight of PEO and PtBuMA sequences were determined by ^{1}H NMR analysis. The M_n values obtained by LS analysis were calculated by using the measured d*n*/d*c* of the copolymers. The hydrodynamic volume contraction was very important for the star block copolymers PS_nPEO.

4. Conclusion

The reaction between PSLi and 1,1-diphenylethylene derivative **1**-Si (bearing one CH_2 between the phenyl ring and the oxygen) has been studied in different solvents such as THF and toluene/THF mixtures. According to the nature of the medium, two different structures (A_2 and A_3 type) have been obtained from the same **1**-Si. We have run model reaction and identify the intermediate. We have pointed out that a nucleophilic substitution occurred on the benzylic group of **1**-Si. This reaction, which was not described in literature, was probably due to the delocalization of π electrons between the phenyl groups and the double bond. These results and considerations about the nature of the ion pairs in different media allowed us to propose a mechanism for PSLi. It involves, after the first expected addition of PSLi on the double bond of the diphenylethylene derivative, the nucleophilic substitution reactions of the siloxy groups by the carbanions present in the medium. These new and unexpected reactions have led to living 1,1-diphenylethylenyl carbanions bearing two or three PS chains. These carbanions have easily polymerized ethylene oxide and *tert*-butyl methacrylate in order to prepare well-defined A_2B and A_3B star block copolymers.

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